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**TERNARY OXIDE SEMICONDUCTOR
PHOTOANODES FOR
SOLAR ENERGY CONVERSION**

PhD Course in Chemistry

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Abstract

Collecting and storing solar energy into chemical bonds, mimicking nature in photosynthesis, is a highly desirable approach towards the development of a fossil fuel-free, sustainable energy society. Photoelectrochemical (PEC) water splitting is an established powerful technology to convert and store solar energy into clean H_2 from a renewable source. In this regard, dual-absorber tandem cells are a promising strategy to accomplish unassisted solar water splitting with high solar-to-hydrogen conversion efficiency.

The work conducted in the frame of this PhD thesis aimed at playing a part in the development of efficient oxide-based semiconductor photoanodes for water oxidation, which is the kinetic bottleneck of the overall PEC water splitting reaction. The attention has been focused on three different classes of promising ternary metal oxides, namely $BiVO_4$ (band gap 2.4 eV), $CuWO_4$ and its derivative $CuW_{0.5}Mo_{0.5}O_4$ (band gap 2.3 eV and 2.0 eV, respectively), and $ZnFe_2O_4$ (band gap 2.0 eV), which stand out for their relatively narrow band gap allowing efficient visible light harvesting, chemical stability and highly oxidative valence band edge. Efforts have been devoted to optimize their intrinsic properties as single photoabsorber flat films with high optical transparency, through a comprehensive photoelectrochemical study.

The present PhD thesis is organized as follows.

Chapter 1 provides a general overview on the actual global energy issue and consequent need for an imminent transition towards renewable energy sources, among which solar fuels emerge as most attractive alternative. Particular emphasis has been devoted to PEC water splitting as a promising candidate over other technologies to produce solar hydrogen from water.

In Chapter 2, after a general overview on the principles of PEC water splitting, the fundamentals of semiconductors, as main components of PEC devices, are discussed in detail. The description is reported of the main physico-chemical properties of the semiconductor/electrolyte interface under different conditions, *i.e.* both in the dark and under illumination, either without or under the application of an external bias. All the provided elements were finally employed in the discussion on the PEC water splitting mechanism carried out by two different architectures, namely the single photoabsorber approach and the dual-absorbing tandem cell configuration.

Chapter 3 provides an exhaustive survey on metal oxide semiconductors, as good candidate materials to fabricate photoanodes for water oxidation, and in particular on the recently emerged multinary (*e.g.* ternary and quaternary) oxides, which offer a large tunability of the electronic structure in addition to satisfying the key requirements for the fabrication of efficient photoanodes. Furthermore, a comprehensive discussion is also presented on the structural, optical and photoelectrochemical properties, as well as on the state-of-the-art for each of the multinary oxides of interest for this thesis.

Chapter 4 presents the experimental techniques, synthesis methods and set-ups employed in this PhD thesis to produce the investigated oxide photoanodes as well as their physical, PEC and electrochemical characterizations, accompanied by a theoretical background.

Chapters 5, 6 and 7 deal with an in depth investigation conducted onto BiVO₄-based photoanodes, as one of the most promising materials to perform solar water oxidation, either as a single component or in combination with the wide band gap TiO₂ semiconductor. The TiO₂/BiVO₄ heterojunction, presented in Chapter 5, aims at combining the desired properties of each component, namely the excellent visible light photoactivity of BiVO₄ and the more negative conduction band potential of TiO₂, for the production of highly reducing electrons under visible light irradiation. In Chapters 6 and 7, the intriguing role of Mo⁶⁺ incorporation into the bulk and the interfacial charge transfer properties of BiVO₄ photoanodes, in carrying out water oxidation both in the presence and in the absence of a suitable electron donor species, has been thoroughly investigated by means of a combined photoelectrochemical and electrochemical impedance spectroscopy study, with the dopant content being systematically changed in the two versatile synthetic approaches employed.

Chapters 8 and 9 have been focused on copper tungstate-based photoanodes as visible light-active and more stable derivative of wider band gap WO₃. In Chapter 8 the ultrafast relaxation dynamics of charge carriers photogenerated in CuWO₄ electrodes, responsible for their typically poor PEC performance, has been first investigated by means of transient absorption spectroscopy. An energy diagram model for the CuWO₄ band structure has been proposed, based on the results of the spectroscopic analyses in combination with those of electrochemical and photochromic studies. In Chapter 9, the novel quaternary CuW_{0.5}Mo_{0.5}O₄ material obtained upon 50% Mo for W substitution in CuWO₄, was investigated to ascertain the effective gain in visible light photoactivity compared to that of pure CuWO₄, based on the band gap narrowing induced by a conduction band edge shift to lower energy. The role of Mo substitution on the poor charge separation properties of CuWO₄ electrodes was also evidenced for the first time.

Chapter 10 and 11 present a systematic study aiming at improving the poor conductivity of ZnFe₂O₄ flat films, an emergent class of narrow band gap materials known for their remarkable stability. These flat films are ideal models to shed light onto the influence that several parameters, such as the annealing temperature, a post-synthesis reductive treatment and the film thickness, have on the overall PEC performance. Two different synthetic approaches were adopted to vary both the synthesis temperature (Chapter 10) and the film thickness (Chapter 11) over a wide range. From the comparison of the obtained results with those of a previous study on ZnFe₂O₄ films with a nanorod architecture, a crucial role of the film morphology was established in determining which one among the structural parameters, *i.e.* the film crystallinity and the cation disorder,

mainly governs the electronic properties of ZnFe_2O_4 and the resulting photoanode performance.

Finally, Chapter 12 provides an overview on the main results and perspectives of each of the here investigated materials for efficient photoanodes fabrication.

Chapter 1

World energy outlook and motivation

1.1 The global energy issues

In the last few decades, the global energy consumption has increased rapidly, driven by the up-growing population concomitant with the economic and industrial development. Despite the continuous rapid growth in renewable energy, fossil fuels, which have driven the development of our civilization since the industrialization of the 19th century, still represent about 80% of the World's total energy consumption nowadays^{1,2} (see Figure 1.1a).

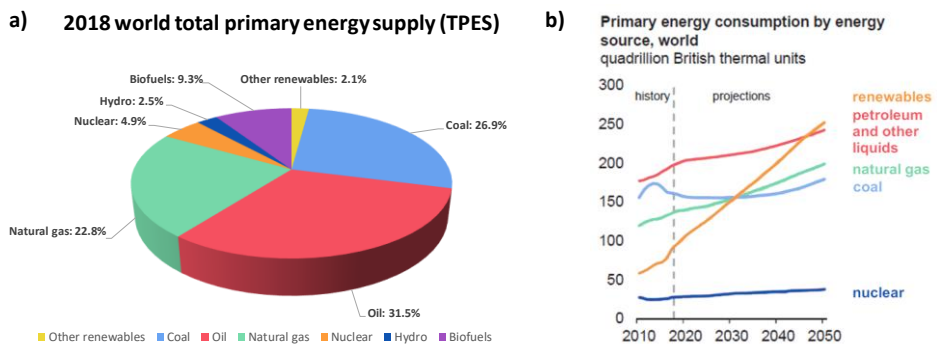


Figure 1.1 (a) World total primary energy supply (TPES) by source in 2018. Source: IEA, Total primary energy supply by fuel, 2018.² (b) World primary energy consumption trend by energy source, from 2010 up to 2050. Adapted from International Energy Outlook 2019 (EIA).³

Moreover, according to both the *BP Statistical Review of World Energy 2019* and the *International Energy Outlook 2019* from the U.S. Energy Information Administration (EIA), although renewable energy (including solar, wind, and hydroelectric power) exhibit the fastest growth over the years (see Figure 1.1b), fossil fuels will continue to meet much of the world's energy demand until 2050.^{3,4} This arises from the fact that fossil fuels, including coal, oil, and natural gas, present the advantages of possessing a very high energy density, in addition to be easily stored or transported, which contribute to the dramatic expansion in energy exploitation occurred over the past 150 years. However,

besides the rapid depletion of fossil fuels supplies with their increasing demand, side-effects of this phenomenon are the environmental pollution that threatens human health, the greenhouse gases associated with global warming and, ultimately, the geopolitical tensions linked to international conflicts. These harmful effects of the incessant use of fossil fuels are treated more in depth in the following.

With the ever-increasing world population from 8 billion people nowadays to the 10 billion people expected by 2050⁵ (Figure 1.2), as a consequence of the increase in global life expectancy thanks to the continuous improvement in healthcare worldwide, the actual world energy consumption of about 18.5 terawatt year (TWy) per year has been projected to grow by nearly 50% within the next 30 years.³ This tremendously fast growth in energy demand compared with our finite non-renewable fossil fuel resources, which will be increasingly depleted, is clearly on a collision course. In fact, according to the *International Energy Agency (IEA) SHC programme*⁶ the economically exploitable and finite reserves of fossil fuels amount at ca. 1570 TWy, meaning that they can sustain the increasing global energy demand for another 50 years only. Therefore, the need for sustainable and renewable energy sources comes first from the unsustainable nature of fossil resources itself.

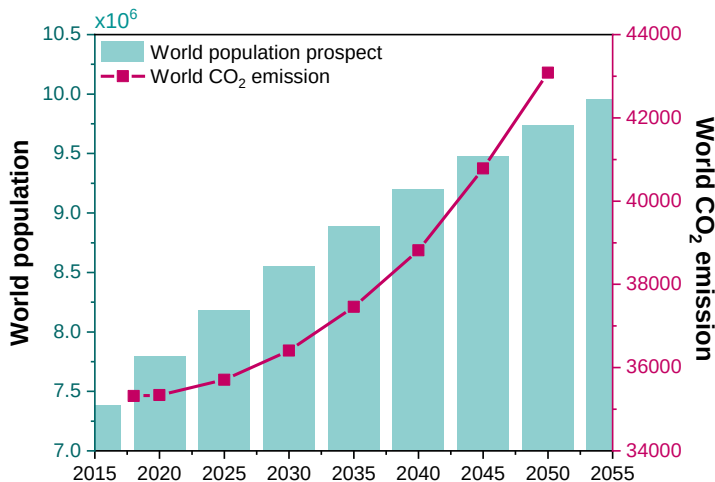


Figure 1.2 Forecast about the world population development (left axis) and world carbon dioxide emissions (right axis) in million metric tons of carbon dioxide. Data from World population prospect 2019⁵ and World Energy Projection System Plus 2019 (EIA),⁷ respectively.

A further concern in the use of fossil fuels lies in their uneven distribution around the Earth,⁴ which has indirectly contributed to establish disparities and inequities in human society. Deposits of fossil fuels depend on the climate and organisms that lived in that region millions of years ago, and the geological processes that have since taken place. In this way, almost half of the total primary energy supply is consumed by about 10% of the population living in rich countries, while the poorest 25% of mankind consumes less than 3% of global energy supply.⁸ This unequal production of energy has resulted into

geopolitical tensions and unfair distribution of wealth, well represented by the fact that about 1.3 billion people in the developing world have no access to electricity. In this context, the goal of a decentralized and sustainable energy systems is even more imperative in view of guarantying the stability of our society.⁹

In the end, the most critical issue regarding the rising consumption of fossil fuels is the acceleration in CO₂ emissions, which has represented the leading cause of the global climate change taken over by the Paris Agreement in 2016.¹⁰ Indeed, carbon dioxide, which is a product of the fossils combustion, represents one of the so-called greenhouse gases, whose increasing accumulation in the atmosphere over the past 150 years has triggered to an unprecedented rise of the planet temperature. According to the Intergovernmental Panel on Climate Change (IPCC) report of 2018, the original approximately 1.0 °C increase of the global surface temperature, caused by human activities with respect to pre-industrial levels, is likely to reach 1.5 °C between 2030 and 2052 if global warming increase will continue at the current rate.¹¹ This may result in other tremendous environmental changes such as the melting of the polar ice sheets, the concomitant rise of sea level, extreme weather events, etc. Therefore, awareness should be gained that the world is on an unsustainable path which is moving even further away from the accelerated transition envisaged by the Paris climate goals.⁴

To face this challenge, the global energy system will need to undergo a clean energy transition from fossil fuels as primary energy supply today towards an increasingly cleaner, more sustainable and decentralized energy mix. But, so far, what are these carbon-free energy sources?

1.2 Solar energy challenges

Among the potential fossil-free energy sources, nuclear energy from fission of radioactive uranium, although not producing significant amounts of carbon dioxide, does not represent a viable choice due to its non-renewable character, to radioactive byproducts contamination and to the relatively low power production of each power station (around 1 GW). Indeed, only 5.5 GW additional nuclear capacity was set in 2019, which is relatively low in comparison with the 15 GW required annually between 2020 and 2040 to reach the Sustainable Development Scenario program (SDS) level.¹² For these main reasons, the required global energy transition must ultimately aim to other alternative sources (see Figure 1.3).

According to the BP Statistical Review of World Energy 2019,⁴ the use of renewable energy, including hydropower, biomass, geothermal, ocean thermal energy conversion, waves, tides, wind, solar, *etc.*, continue to grow far more rapidly than any other form of energy (see Figure 1.1b), led by wind and solar power. Renewables made up indeed about 27.3% of global electricity generation by the end of 2019 and are expected keep increasing up to 70% by 2050.^{1,13}

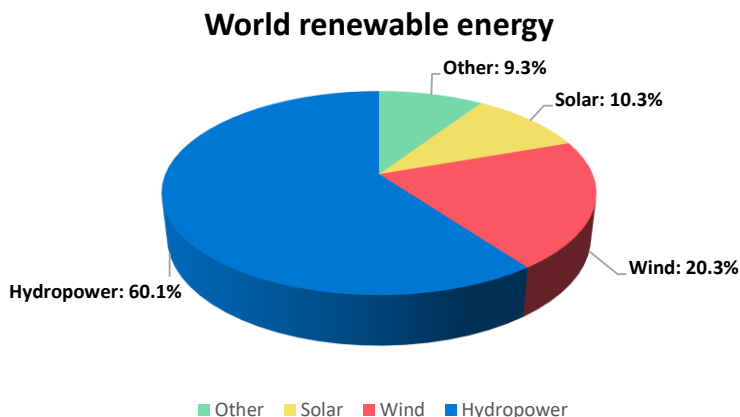


Figure 1.3 World renewable energy generation in 2019. Source: BP Statistical Review of World Energy.⁴ Note: 'Other renewables' refers to renewable energy sources including geothermal, biomass, waste, wave and tidal.

Among all renewable energies (see Figure 1.3), sunlight is a decentralized, inexhaustible and by far most abundant natural energy resource, capable of delivering to the Earth in 1 hour the amount of energy consumed by the world human population in a year.^{14,15} This is well depicted in Figure 1.4, where the estimated finite fossil and nuclear resources are compared with the yearly potential of the renewable planetary alternative energy reserves along with the world energy consumption in 2018 (18.5 TWy).⁶ Here, it is striking to note that all reported energy sources are far dwarfed in comparison with the astounding potential of the Sun, whose 23000 TWy of energy emitted, being more than three orders of magnitude larger than the annual global energy consumption, is far enough to potentially solve the energetic problem. In addition to its abundance and inexhaustibility on the human time scale, the increasing attractiveness of solar energy over the last few decades has been tied to the fact that it represents also a clean and a virtually cheap energy source.

Nevertheless, solar energy presents the great limitation that it cannot be directly utilized, but requires to be converted into heat or electricity. This is due, first, to its inhomogeneous distribution on the Earth's surface, since all regions on the planet are differently irradiated by sunlight. Moreover, the availability of solar energy is highly variable and intermittent, since it is subjected to weather conditions as well as to both the daily and seasonal variability. Finally, differently from fossil fuels that are concentrated sources of energy, sunlight has a diffusive character such that the photons emitted over the Earth have a modest power density, and they need to be concentrated first and then stored.¹⁶

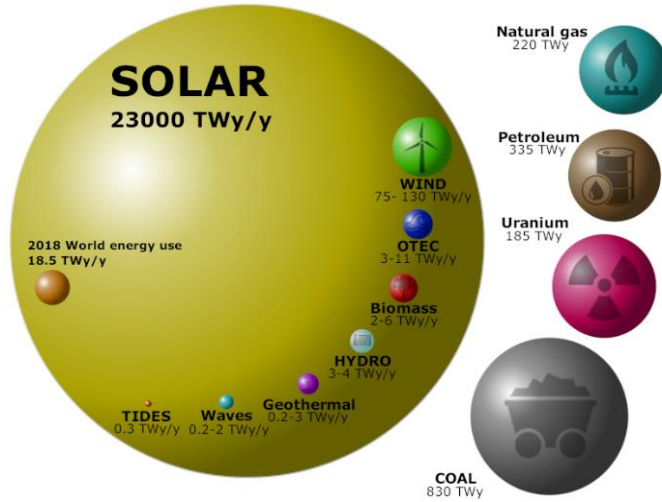


Figure 1.4 Estimated finite and renewable planetary energy reserves in Terawatt years (TWy) and Terawatt years per year (TWy/y), respectively, adapted from the IEA SHC program Solar Update 2015.⁶ The reported energy values are proportional to the volumes of the corresponding spheres.

Nowadays there are several strategies to convert solar energy, including i) *photovoltaics* (PV) for direct sunlight conversion into electricity through creation of charge carriers, ii) *solar thermal energy*¹⁷ technologies for concentrating the Sun's thermal power into heat that can be directly used or converted into electricity and, ultimately, iii) *artificial photosynthesis* allowing to convert and store sunlight into chemical fuels by mimicking the natural photosynthesis performed by green plants.

Photovoltaics is one of the most active research fields as well as the fastest growing technology in the last 50 years,¹⁸ with the silicon-based PV cells having been at the forefront of the technological deployment of solar conversion systems. The current efficiency record of silicon heterojunction solar cells (Si solar cells) has indeed reached 26.7%, which is almost comparable with their theoretical conversion efficiency limit of 29.1%.¹⁹ More recently, solid-state perovskite solar cells (PSC) with outstanding optoelectronic properties have emerged, reaching a certified record efficiency of 25.2% in 2019,¹⁸ which approaches that of the benchmark Si solar cells. However, the typical instability of the hybrid perovskite systems under ambient conditions sets serious limits to their scale-up and commercialization.

Overall, the output of PV technologies is strictly tied to the intermittence of sunlight, since direct conversion of solar energy into electricity is only possible during the day hours, while no electricity production is guaranteed during the night, when the energy demand reaches its maximum value. Moreover, another limit of the direct sunlight to electricity conversion via PV is the risk for grid overload, occurring when the energy drawn by the population is lower than that produced by a solar plant. The above discussion emphasizes the mismatch between the energy supply and demand, and points

out the need for the development of efficient and inexpensive solar energy technologies capable of storing the excess of energy produced by solar power plants during sunny days, in order to accelerate the deployment of PV devices into the energy market on a global scale.²⁰ Despite one current possible initialized energy storage system is represented by batteries, their widespread implementation is still prevented by their relatively small capacities which hamper the displacement of large quantities of energy, as well as by the short battery lifetime, which makes them suitable for daily storages only.

In this context, solar energy storage in the form of chemical bonds of high energy molecules, such as hydrogen (H_2), via artificial photosynthesis has proved to be an attractive route to undertake for pursuing the energy transition from fossil fuels to renewables. Compared to batteries, solar chemical fuels offer a more effective way of storing energy in the smallest possible configuration represented by the chemical bond, thus exhibiting a higher gravimetric energy density, besides the easy transportability and storage which allow their use on request.²¹ The need and possibility to achieve artificial photosynthesis was already predicted in a far-sighted way about one century ago by the Italian chemist Giacomo Ciamician:²²

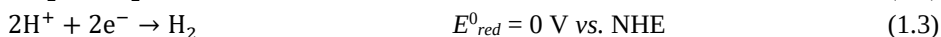
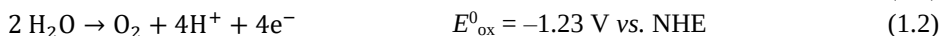
“And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the Sun shines! If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness”.

The idea of artificial photosynthesis was then reconsidered in concomitance of the energy crisis of the 1970s, but it was only with the recent awareness of the harmful risks of fossil fuels and of the intrinsic difficulties of nuclear energy, that it has become object of intensive investigation.⁸ In this prospect, photocatalysis and photoelectrochemistry²³ established by the pioneering work of Fujishima and Honda in the early 1970s,²⁴ have recently been the focus of many efforts as valuable strategies to directly capture and convert sunlight into chemical energy, thus potentially addressing the solar energy storage problem.

1.3 Solar hydrogen from PEC water splitting

Among the various solar fuels (such as methanol and formic acid) acting as energy vector of renewable sources, hydrogen from water photolysis is the most appealing output of artificial photosynthesis, given the abundance of water covering ~71% of the Earth's surface. Moreover, besides the easy transport and storage, hydrogen exhibits higher gravimetric energy density (141.9 MJ kg^{-1}) than most of the conventional fossil fuels (46.4 MJ kg^{-1} for regular gasoline),²⁵ and can be efficiently converted into electricity whenever necessary, either through direct combustion or in fuel cells, without emissions and only producing harmless water.^{26,27}

Solar energy conversion into hydrogen molecule via water photolysis is inspired to the first step of natural photosynthesis of green plants, which consists in breaking water under the energy input of sunlight, which is then stored into sugar via CO_2 conversion. Similarly, artificial photosynthesis makes use of a photoabsorber semiconductor material, playing the role of leaves in the corresponding natural process, *i.e.* of light harvester driving the overall up-hill water splitting reaction (Eq. 1.1) into H_2 and O_2 ,^{28–30} through the following oxidation and reduction half reactions (Eqs. 1.2 and 1.3, respectively), in acidic media:^{21,31}



where E° is the standard potential of the half-reaction, expressed with respect to the Normal Hydrogen Electrode (NHE). Overall, according to Eqs. 1.2 and 1.3, a 4-electron and 2-electron reactions are required for each evolved oxygen and hydrogen molecule, respectively. It follows that the overall water photolysis reaction is kinetically limited by the photooxidation step. Water splitting (Eq. 1.1) is an endergonic reaction requiring a standard free energy $\Delta G^0 = 237.2 \text{ kJ mol}^{-1}$, corresponding to an electrochemical potential of 1.23 V per electron according to the Nerst equation (Figure 1.5).

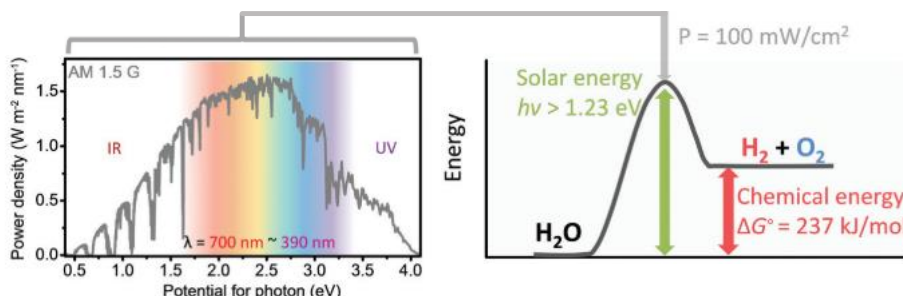


Figure 1.5 Solar spectrum AM 1.5 G (*i.e.* 1 sun condition, 100 mW cm^{-2} power density, left panel) and photoelectrolysis of water as an energetically uphill reaction (right panel).²⁵

According to this, even if a difference in potential energy between the photogenerated electrons and holes of 1.23 V should be in principle enough to split water, in practice the reaction occurs at a considerably higher voltage. Indeed, additional overpotentials are needed to overcome the main kinetic barrier of the process given by the largely sluggish water oxidation half-reaction, the activation energy of water reduction and the electrical resistivity of the system. Such energy input can be supplied by the sunlight to a suitable semiconductor material able to absorb and convert into charge carriers photons with energy higher than the thermodynamic water splitting voltage of 1.23 V plus the kinetic overpotentials of the system, amounting to *ca.* 1.6 V.³² Hence, a semiconductor band gap energy larger than 1.6 eV is required to generate photo-excited charge carriers having suitable energy to carry out the two redox semi-reactions.²⁵ In light of the foregoing and

for the sake of simplicity, throughout the text we will refer to 1.23 eV as the theoretical minimum photon energy required to perform overall water splitting using a single semiconductor photocatalyst, also known as one-step photoexcitation system. Indeed, the involved overpotentials should be strictly related to the selected operative system.

Therefore, photocatalytic water splitting in one-step photoexcitation (see Figure 1.6a) requires the employed semiconductor to be endowed with a band gap energy large enough to split water, as well as with suitable band edge positions straddling the reduction and oxidation potentials of water, *i.e.* the conduction band (CB) bottom of the semiconductor located at a more negative potential than the H^+/H_2 energy level (0 – 0.059 pH, V versus NHE), whereas the valence band (VB) top being more positive than the $\text{O}_2/\text{H}_2\text{O}$ energy level (1.23 – 0.059 pH, V versus NHE).³³ It is worth noting that, nevertheless, this thermodynamic requisite is in contrast with the need for a band gap as small as possible (typically smaller than 3 eV) for the material to absorb a large portion of the solar spectrum (Figure 1.5),³⁴ which mostly consists of visible light ($400 < \lambda < 800$ nm). In fact, metal oxides which have been extensively studied as photocatalysts for water splitting, possess VB usually consisting of O 2p orbitals, whose top is located at *ca.* 3 V vs. NHE, or at even higher potential. This means that, in order to have the bottom of the CB located at potentials more negative than the water reduction potential, the band gap energy should be inevitably larger than 3 eV, with a consequent inactivity of the material in the most useful visible-light region of the solar spectrum. Therefore, the extreme difficulty in finding photocatalytic systems able to meet both the above-described requirements makes overall water splitting carried out on a single semiconductor material the “Holy Grail” of chemistry.^{30,35}

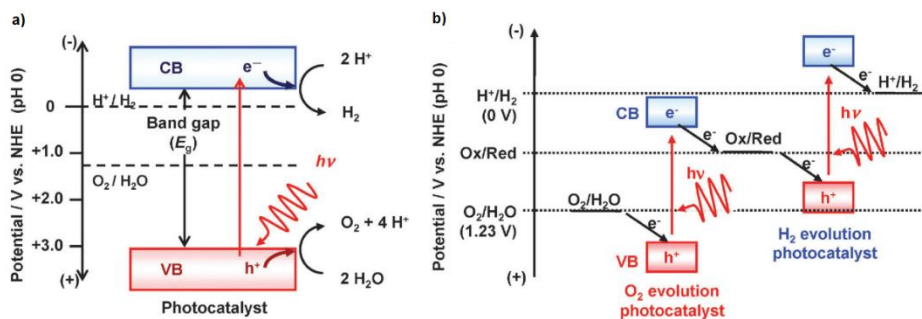


Figure 1.6 Band energy diagrams for photocatalytic water splitting based on (a) one-step excitation (or single photocatalyst) and (b) two-step excitation (Z-scheme).³⁶

One possible solution to this issue was introduced by Bard in 1979³⁷ and consists of a two-step photocatalytic system known as “Z-scheme”, inspired to natural photosynthesis in green plants conducted by the photosystem I (PS I) and photosystem II (PS II) harvesters, and such that two distinct photocatalysts with different band gap energy are combined using an appropriate shuttle redox mediator or via direct heterojunction in a monolithic device, in order to separately evolve H₂ and O₂ (Figure 1.6b).²⁵

Despite a double number of photons is involved in this two-step photoexcitation process compared to water splitting carried out with a single photocatalyst, the former allows visible light to be utilized in a more efficient way than in the conventional one-step photoexcitation system, because a reduced energy compared to the theoretical electromotive force of 1.23 eV is required to drive each of the two photocatalysts.^{35,38} Indeed, as shown in Figure 1.6b, in the Z-scheme each of the two semiconductors employed can be in principle deficient in terms of either the CB bottom level (*i.e.* the CB edge can be more positive than the H^+/H_2 potential) or the VB top level (that is, the VB edge can be more negative than the O_2/H_2O potential). In this way, a larger driving force for water splitting is likely to be available than in the case of a one-step photoexcitation system.³³ Therefore, the use of two separate photocatalysts opens the possibility to employ smaller band gap materials, active under a larger portion of the solar radiation, thus allowing, at the same time, photogenerated electrons/holes with stronger reduction/oxidation abilities to be accessible without the need of absorbing highly energetic photons.³⁸

Besides the above-described photocatalytic (PC) water splitting, which is performed using particulate semiconductor materials (as shown in Figure 1.7a) and appearing, conceptually, as the simplest approach to hydrogen production,³⁹ solar-assisted water splitting can be also carried out via photoelectrochemistry, by taking advantage of an applied bias to ensure band bending sufficient to prevent recombination between the photogenerated electron-hole couples.⁴⁰ As already mentioned, the first demonstration of photoelectrochemical (PEC) water splitting dates back to 1972 when a cell consisting of a single photoelectrode of TiO_2 connected to a Pt wire counterelectrode catalysing, under ultraviolet (UV) light irradiation, the O_2 and H_2 evolution semi-reactions, respectively, was first reported by Fujishima and Honda.²⁴ Since then, many efforts have been devoted to the development of more efficient PEC technologies and semiconductor photoelectrodes (described in detail in the next two chapters) to be mostly employed as photoanodes for the oxygen evolution reaction, as the main kinetically limiting step of the overall process.

Among these recent technologies, indirect PEC water splitting using hybrid system where a photovoltaic (PV) device is coupled to an electrolyser (PV-EC), also known as photovoltaic-assisted water electrolysis, is already commercially available with record efficiencies (Figure 1.7b).²⁵ However, the large-scale implementation of this architecture is limited by the availability and prices of the constituent materials, which result in a H_2 production not economically competitive with fossil fuels. Moreover, a major and general drawback of these devices comes from the variability of the number of solar cells required to generate sufficient potential voltage output on light intensity, which can result in a 50% energy loss, and challenges the viability of the PV + electrolysis approach.³¹ Finally, a further disadvantage of the PV-EC devices, strictly connected to their high efficiency, is the superior complexity in PV designs over PC and PEC technologies, which in turn

implies higher costs.²⁵ All these factors have moved research in the last decade towards the development of devices, based on earth-abundant materials, which can potentially avoid these drawbacks and convert solar energy at a price competitive with fossil sources.

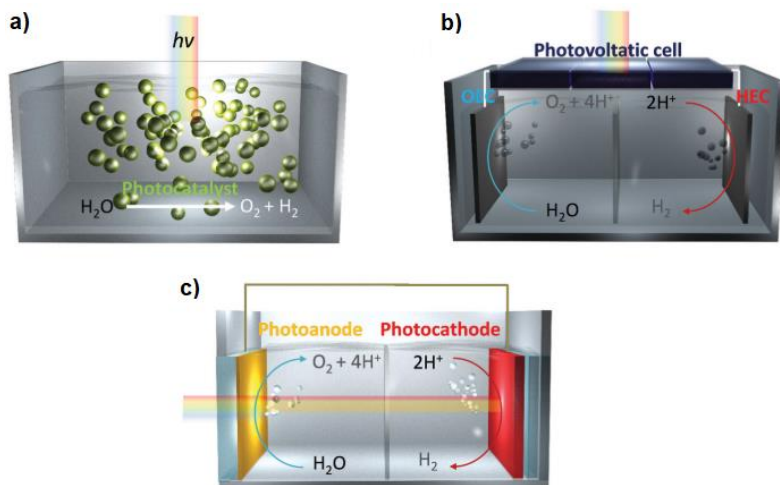


Figure 1.7 Representation of the three different photo-driven water splitting systems and their charge flows upon light absorption: (a) PC, (b) PV-EC and (c) PEC devices.²⁵

In this context, direct PEC water splitting – which will be thoroughly treated in the next chapter – is considered a promising technology which offers a much more compact design compared to the PV-EC system, since charge generation and electrochemical processes occur inside the same integrated unit, as well as a higher efficiency than particulate photocatalyst devices.³⁶ In more detail, the PEC water splitting configuration, where the semiconductor and the electrolyte are directly interfaced in a PEC cell, proved to be a more straightforward approach for light-induced chemical reactions than the PV-EC device, which results not only in a notably simplified system architecture, but also in a reduced number of potential loss channels, since fewer electron transfer steps are required.

PEC water splitting is accomplished by two electrodes plunged in aqueous solution and electrically connected to each other, where one or both are composed of semiconductor materials capable of generating free charge carriers upon light absorption. The so generated charge couples are directed, upon application of an external bias, towards the electrodes/electrolyte interface of the two different electrodes, thus allowing O_2 and H_2 gas evolution to occur at different sites, with a resulting facilitated products separation (Figure 1.7c).

The work presented in the frame of this PhD thesis has been devoted to the comprehensive development and optimization study of suitable semiconductor materials acting as photoanodes for water oxidation, thus contributing to the global efforts spent in the improvement of the efficiency of the overall PEC water splitting process.

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Chapter 2

Photoelectrochemical water splitting

2.1 General overview

The simplest configuration of a PEC cell involves a single photoabsorber semiconductor electrode, typically working as anode, able to split water by absorbing two photons in the so-called S2 scheme,¹ immersed into an electrolyte solution and connected to a metal counter electrode acting as cathode through an external circuit (Figure 2.1).

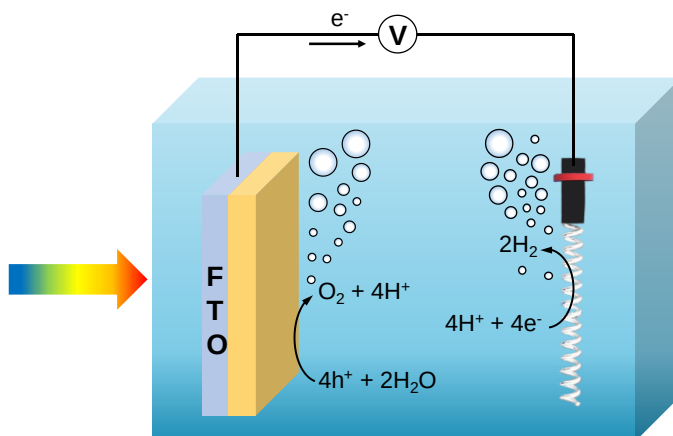


Figure 2.1 Schematic illustration of a typical PEC water splitting cell with a single absorber acting as photoanode.

Indeed, being water oxidation the much more challenging step of the overall water splitting process from both the thermodynamic and kinetic point of view, due to the involvement of four holes for one molecule of gaseous oxygen to evolve, research in this field has been mainly focused on the development of efficient semiconductor-based materials acting as photoanodes. More complicated but efficient architectures that involve two photoabsorber electrodes acting both as anode and cathode in the so called D4 or *tandem cell* configuration will be presented at the end of this chapter.

The main component of PEC water splitting is the semiconductor, which converts incident photons to electron-hole pairs. The first step is the generation of charge carriers

through absorption, from sunlight irradiation, of photons with energy equal to or higher than the band gap of the semiconductor, able to promote electrons from the VB into the CB, thus leaving behind holes in the VB. The so photogenerated electron-hole couples can either recombine or be separated by the built-in electric field inside the space charge region, generated at the semiconductor–liquid junction (SCLJ) after equilibration of the semiconductor Fermi level with the redox potential of the electrolyte. For this to occur, electron transfer between the two levels leading to electric neutrality is required, which also generates bending of the conduction and valence bands near the semiconductor/electrolyte interface that drives the separation of the photogenerated charge carrier couples. In this way, under the effect of the semiconductor built-in electric field inside the space charge region, holes are drift towards the semiconductor's surface to perform the oxygen evolution reaction, meanwhile electrons are transferred via an external circuit to the counter electrode where protons reduction can take place.

At this point, the thermodynamic requisite for water splitting to occur is that the top of the VB of a semiconductor must be more positive than the O_2 evolution potential of 1.23 V vs. NHE (pH = 0), whilst the bottom of the CB must be more negative than the H_2 evolution potential of 0 V vs. NHE (pH = 0).^{2,3} However, while a difference in bias of only 1.23 V should be sufficient to split water, due to the entropic energy loss in driving the electrons excitation process the externally available thermodynamic free energy developed for a single semiconductor upon light absorption ($\Delta\mu_{ex}$) is significantly less than its band gap.^{3,4} Moreover, the overpotentials required to overcome the kinetics of both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) must be considered^{1,5} which, together with the thermodynamic water splitting potential of 1.23 V, typically account for an overall potential larger than 1.6–1.9 V.^{6–9} In light of this, to afford (bias) unassisted simultaneous solar water oxidation and reduction with a single photoelectrode in the S2 scheme, semiconductor band gaps over 3.0 eV are typically necessary (such as TiO_2 and $SrTiO_3$), both to satisfy the thermodynamic requirement for water splitting and take into account the entropic loss and overpotentials.^{2,3,6} On the other hand, such a large band gap energy required to generate sufficient $\Delta\mu_{ex}$ and for the conduction and valence bands to straddle the H^+/H_2 and O_2/H_2O levels, precludes the harvesting of a significant fraction of the solar spectrum, composed for *ca.* 43% of visible light.²

To date, a single semiconductor material has not yet been identified that simultaneously offers enough photovoltage $\Delta\mu_{ex}$, substantial solar light harvesting and appropriate bands edge alignment with respect to the water reduction and oxidation potentials, to perform S2 water splitting with high solar-to-chemical energy conversion efficiency. To address this issue, the application of an external bias or tandem devices connecting two semiconductors acting as photoanode and photocathode in a Z-scheme (which will be dealt at the end of this chapter) can be resorted to provide the sufficient energy required to split water. In addition to compensate for an eventually insufficient

semiconductor photovoltage, the application of an external bias to a S2 system can also help to alleviate photogenerated charge recombination and to drive electrons and holes towards the appropriate direction, *i.e.* the counter electrode and the semiconductor/electrolyte interface, respectively, where water reduction and oxidation can take place.

Overall, efficient water splitting requires the following key criteria to be simultaneously met: (i) relatively narrow material band gaps for optimized sunlight utilization, which are concurrently capable of satisfying the thermodynamic requisite of appropriate band positions straddling the HER and OER potentials, and of providing enough photovoltage to carry out the overall reaction; (ii) efficient charge separation and mobility of charge carriers in the material bulk to allow them reaching the electrode's interfaces quantitatively; (iii) rapid consumption of photogenerated holes in water oxidation at the electrode surface with minimized overpotential; and (iv) excellent stability for practical applications.

All the above-listed requisites account for the fundamental role played by semiconductor materials acting as photoabsorbers in a PEC device, in light harvesting first and in subsequent solar-to-chemical energy conversion. Therefore, the following sections will be devoted to the illustration of the basic structure and energetics of semiconductor materials, followed by the description of the physico-chemical properties of the semiconductor/electrolyte interface, either in the dark or under illumination. After having provided the fundamental elements, the relevant processes occurring either in the S2 scheme under an external bias application or in carrying out bias-unassisted solar water splitting through the complete tandem PEC cell, will be treated.

2.2 Semiconductor fundamentals

2.2.1 The band model

In opposite to molecular systems, whose electrons are localized into discrete molecular orbitals of quantified energy, extended solid state materials develop the so called “band structure”, where atomic orbitals of several atoms combine together forming energetically closely sets of allowed states giving rise to relatively wide regions known as energy bands, which can be effectively considered a continuum of energy levels. In this way, two energy bands corresponding to the bonding and anti-bonding energy levels are formed, named as valence band (VB) and conduction band (CB), respectively, separated by a forbidden energy gap defined band gap (E_g) occurring between the top level of the VB and the bottom level of the CB. The material band gap is the main factor distinguishing semiconductors, where it usually ranges between 1 eV and 4 eV,¹⁰ from metals, whose bands are almost overlapped, and from insulators, characterized by far wider band gaps, as in case of SiO₂ exhibiting a band gap of *ca.* 8 eV (Figure 2.2). Since the bands associated with higher excited states normally overlap with the conduction band, the allowed electronic energy levels extend from the bottom of the CB to infinite

energy.¹¹ Moreover, only in the case of a perfect crystal there are no effectively allowed energy levels for electrons in the forbidden intra band gap region.

At 0 K temperature, the VB is filled with electrons, whereas the CB is mostly empty, thus corresponding to the highest-occupied and the lowest-unoccupied bands, respectively. Since for a solid state material to be conductive (*i.e.*, for electrons to move throughout the material) electrons must occupy partially filled bands, it follows that electrons that are effectively immobile in the VB (*i.e.* in the fundamental state) should be promoted into the CB to become mobile. In semiconductors, the energy required for electrons to be excited from the VB to the CB, corresponding to the band gap energy of the material, is not small enough to be supplied by room-temperature thermal activation, but can be provided by the energy of sunlight. This feature is a very special property of semiconductors which makes them very suitable for solar cells and PEC water splitting applications. Indeed, electrons excitation in the semiconductor upon absorption of electromagnetic radiation with associated energy equal or higher than the band gap, leads to the generation of a mobile charge carriers couple. This consists in an excited electron in the CB, which can move freely, thus being responsible for the material conductivity, and a hole in the VB (also considered as an empty level in the valence band), which can be treated as a mobile positive charge carrier as well, moving freely through the VB and contributing to the conduction. Therefore, the band gap energy is the most important characteristic of semiconductor solids as it influences all their important electronic properties.

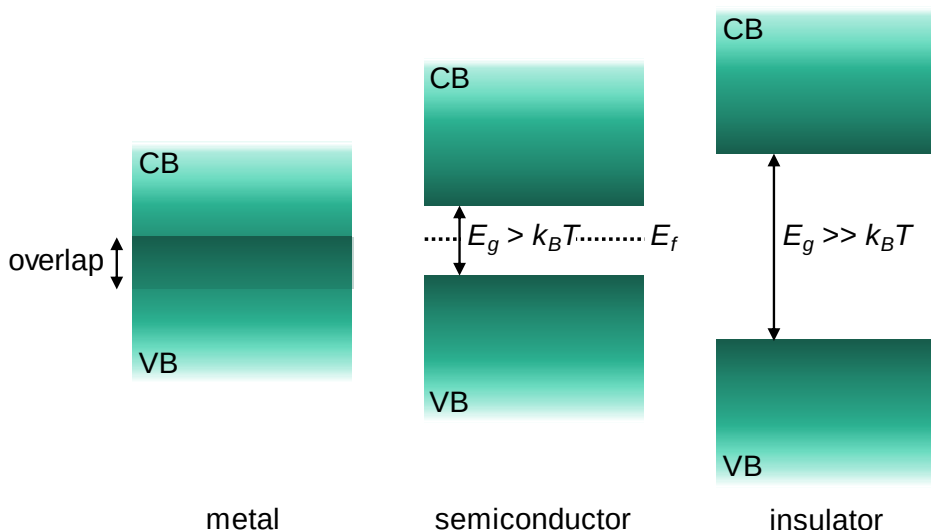


Figure 2.2 Energy diagram of a metal, a semiconductor and an insulator.

2.2.2 Intrinsic semiconductors

The occupation probability of electrons over the available energy levels in a solid is described by the Fermi–Dirac distribution function and the density of states in the conduction and valence band. The Fermi–Dirac distribution ($f(E)$) determines the probability of an energy level E to be occupied by an electron at a certain temperature T , according to the following equation:

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} \quad (2.1)$$

where E_F is the Fermi energy, k_B the Boltzmann constant and T the temperature (Kelvin). According to Eq. 2.1, the Fermi energy is defined as the energy level E at which the probability of occupancy by an electron is 1/2. This probability decreases and increases for levels E above and below E_F , respectively. The Fermi energy can also be viewed as the electrochemical potential of electrons in a solid.⁴ Ideally, at absolute zero temperature (0 K) where the VB of a semiconductor is filled with electrons, whereas the CB is completely empty, the E_F level is located at exactly halfway between the valence and the conduction bands. However, above 0 K, the chance for an electron to be thermally excited to the conduction band is larger than zero.

At room temperature, when a few electrons are thermally excited across the forbidden gap into the conduction band, leaving behind holes in the valence band, the concentration of electrons (n) and holes (p) can be expressed in terms of the Fermi–Dirac probability function for the presence (f) or absence ($1 - f$) of electrons, respectively:

$$n = \int_{E_{CB}}^{\infty} DOS_{CB}(E) f(E) dE \quad (2.2)$$

$$p = \int_{-\infty}^{E_{VB}} DOS_{VB}(E) (1 - f(E)) dE \quad (2.3)$$

where DOS_{CB} and DOS_{VB} are the density of state (DOS) distributions defining the number of available energy states at the conduction and valence bands, respectively, and E_{CB} and E_{VB} are the bottom and top energy levels of the CB and VB edges, respectively. The DOS distributions are given by the following equations:

$$DOS_{CB}(E) = \frac{m_e^* \sqrt{2m_e^* (E - E_{CB})}}{\pi^2 \hbar^3} \quad (2.4)$$

$$DOS_{VB}(E) = \frac{m_h^* \sqrt{2m_h^* (E_{VB} - E)}}{\pi^2 \hbar^3} \quad (2.5)$$

where m_e^* and m_h^* are the effective masses of electrons and holes, respectively; $\hbar = h/2\pi$ with h the Planck's constant. In this way, since the energy difference between the Fermi energy level and the conduction or valence band is such that that $(E - E_F) \gg k_B T$, Eq. 2.1 can be simplified to $\exp(-(E - E_F)/k_B T)$. Under this assumption and by combining the Fermi–Dirac distribution with the density of states, the solutions of Eq. 2.2 and 2.3 yield

the following expressions for the concentrations of electrons in the CB (n) and holes (p) in the VB, respectively:¹²

$$n = N_C \exp\left(-\frac{E_{CB} - E_F}{k_B T}\right) \text{ with } N_C = \frac{2(2\pi m_e^* k_B T)^{\frac{3}{2}}}{h^3} \quad (2.6)$$

$$p = N_V \exp\left(\frac{E_{VB} - E_F}{k_B T}\right) \text{ with } N_V = \frac{2(2\pi m_h^* k_B T)^{\frac{3}{2}}}{h^3} \quad (2.7)$$

where N_C and N_V are the effective DOS in the CB and VB, respectively. The general Eqs. 2.6 and 2.7 are valid for both undoped and doped semiconductors.⁶

In an intrinsic semiconductor, *i.e.* without any doping impurities, the concentrations of electrons (n) and holes (p) must be equal in order to preserve charge neutrality. The analytical expression of the Fermi level E_F for the semiconductor can then be calculated from Eqs. 2.6 and 2.7, as follows:

$$E_F = \frac{E_{CB} + E_{VB}}{2} + \frac{k_B T}{2} \ln\left(\frac{N_V}{N_C}\right) = \frac{E_{CB} + E_{VB}}{2} + \frac{3k_B T}{4} \ln\left(\frac{m_h^*}{m_e^*}\right) \quad (2.8)$$

Accordingly, in an intrinsic (undoped) semiconductor the Fermi level E_F is close to the middle of the energy gap, and for $m_e^* = m_h^*$ (or, analogously, for $N_C = N_V$) is exactly at the middle of the band gap, as shown in Figure 2.2. Moreover, the equilibrium concentrations of electrons and holes are related by the following mass balance equation, obtained by multiplying Eqs. 2.6 and 2.7:

$$np = n_i^2 = N_C N_V \exp\left(-\frac{E_g}{k_B T}\right) \quad (2.9)$$

which also provides the intrinsic carrier density (n_i) for an intrinsic semiconductor, where each electron inside the conduction band corresponds to a hole inside the valence band (*i.e.* $n = p$). From the exponential term in Eq. 2.9 it follows that the concentrations of electrons and holes in an intrinsic semiconductor rapidly increase with temperature.

2.2.3 Doped semiconductors

Intrinsic or pure semiconductors (Figure 2.3a) exhibit poor conductivity which is not desired for practical applications. To overcome this, extrinsic semiconductors doped with impurity atoms as either electron donors or acceptors, depending on their valency, are often employed.

The donor-doped semiconductors have impurity atoms with a greater number of valence electrons than the host atom (for example P or Ar into Si), resulting in an electron-rich (n -type) semiconductor, whilst the acceptor-doped semiconductors have impurity atoms with fewer valence electrons than the host atom (for example Al into Si), resulting in hole-rich semiconductors (p -type). As a result, in an n -type semiconductor the extra valence electrons supplied by the donor-type dopants introduce occupied energy levels into the band gap close to the bottom edge of the conduction band, from which electrons

can be easily promoted into the CB, thereby improving the conductivity of the semiconductor (Figure 2.3b).

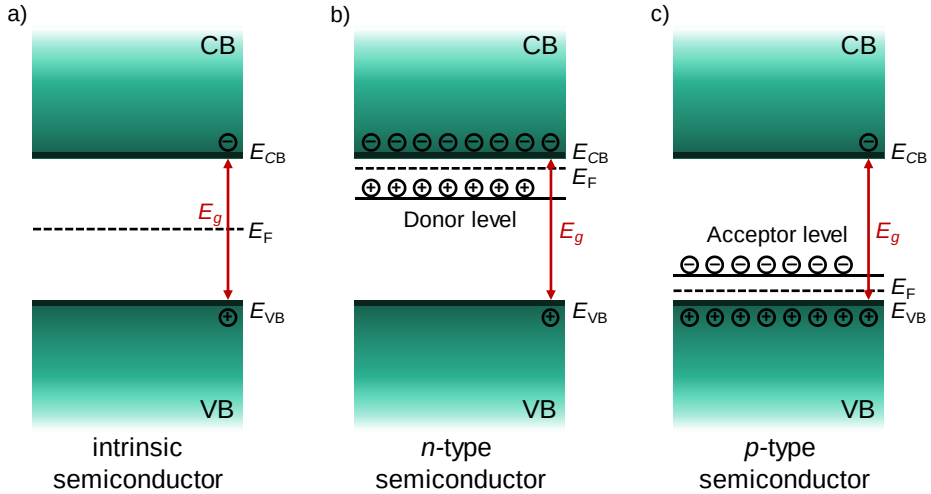


Figure 2.3 Simplified band diagram of (a) an intrinsic semiconductor and extrinsic semiconductors of (b) *n*-type and (c) *p*-type, under thermal equilibrium. In the *n*-type and *p*-type semiconductors, the presence of donor and acceptor levels, respectively, gives rise to majority and minority charge carriers population of the bands.

In contrast, in a *p*-type semiconductor the presence of acceptors induces vacant energy levels into the band gap close to the top edge of the VB, which can be occupied by electrons from the VB of the semiconductor, where holes are consequently produced (Figure 2.3c). It follows that, while the concentration of holes and electrons are equal in an intrinsic semiconductor, for *n*-type and *p*-type semiconductors one type of charge carrier among electrons and holes has a much higher concentration inside the bands, resulting in the existence of majority and minority carriers. Therefore, while in *n*-type semiconductors the dominant (or majority) charge carriers are electrons populating the CB, holes into the VB are the majority charge carriers in *p*-type semiconductors.

In the presence of impurities, the Fermi level is no longer in the middle of the band gap but must adjust itself to preserve charge neutrality. Consequently, in an *n*-type semiconductor, due to the large presence of electrons in the CB, the Fermi level lies just below the conduction band. Similarly, in a *p*-type semiconductor the Fermi level is located just above the VB, because of the existence of holes in the VB.^{4,12,13} The energy band diagrams in Figure 2.3 show the relative position of the E_F in an intrinsic, *n*-type and *p*-type semiconductor. The Fermi level of a doped semiconductor can be indeed expressed as:¹⁴

$$E_F = E_{Fi} - k_B T \ln\left(\frac{n}{n_i}\right) \quad \text{or} \quad E_F = E_{Fi} + k_B T \ln\left(\frac{p}{p_i}\right) \quad (2.10)$$

where E_{Fi} is the Fermi level position in the intrinsic semiconductor (*i.e.* when $n = n_i$ or $p = p_i$), and n_i and p_i represent the electrons and holes concentration of an intrinsic semiconductor, respectively. Therefore, Eq. 2.10 states that doping a semiconductor with donors will produce a more negative Fermi level because $n > n_i$, while the doping of a semiconductor with acceptors yields a more positive Fermi level, given that $p > p_i$.

It is often convenient to refer the Fermi level to reference levels that are closed to the band edge energies. If the CB of an n -type semiconductor is filled with electrons to a value equal to the effective density of states in the CB N_C , then the Fermi level would shift up to reach the exactly position of the bottom of the CB, E_{CB} . Similarly, in a p -type semiconductor the Fermi level position can be referred to the energy of the top of the VB, E_{VB} . In other words, the expression for the Fermi level for a doped semiconductor in Eq. 2.10 becomes:¹⁴

$$E_F = E_{CB} - k_B T \ln\left(\frac{n}{N_C}\right) \text{ or } E_F = E_{VB} + k_B T \ln\left(\frac{p}{N_V}\right) \quad (2.11)$$

The above discussed discrepancy between the two types of charge carriers in a doped semiconductor is essential not only to improve the electrical conductivity of intrinsic semiconductors, but also for the photoelectrochemistry of the semiconductor, starting from the charge flow that occurs when the doped semiconductor phase is brought into contact with an electroactive solution phase, which is the topic of the next section.

2.2.4 The semiconductor/electrolyte interface

When a semiconductor is placed in contact with an electrolyte solution, a charge transfer reaction across the junction occurs until electronic equilibrium is reached between the two phases, with consequent formation of a semiconductor–liquid junction (SCLJ). For the two phases to reach the equilibrium, their electrochemical potentials, *i.e.* the redox potential of the electrolyte solution, E_{redox} , and the Fermi level for the semiconductor phase, E_F , must be equal.¹⁴ Due to the typically larger density of majority charge carriers in the semiconductor than in the liquid phase, electrons flow from the semiconductor to the electrolyte solution, with a consequent variation in the position of the semiconductor E_F , until it equals the E_{redox} level of the solution. This leads to the formation of a Schottky junction (electric double layer) between the semiconductor and the electrolyte and of a space charge region of width W at the SCLJ, extending for 100–10000 Å inside the semiconductor, where majority carriers are depleted. This depletion region is therefore a zone where the charge distribution differs from the material bulk. As a result of the initial electrochemical potential difference between the semiconductor and the solution, the semiconductor phase experiences a potential drop in the space charge region, associated with an electric field with maximum strength at the semiconductor/electrolyte interface. This leads to bending of the conduction and valence bands, which are pinned at the semiconductor surface, across the space charge region.

In practice, for an *n*-type semiconductor electrode at open circuit, *i.e.* in equilibrium with a redox system, having an initial less negative potential than the semiconductor E_F (Figure 2.4a), electrons should have been transferred from the semiconductor into the solution leaving behind a positive excess charge formed by immobile ionized donor states, which results in the formation of a positively charged depletion layer, reflected by an upward bending of the band edges (Figure 2.4b). On the other hand, for a *p*-type semiconductor in which case E_F is generally more positive than the electrolyte redox potential, electron transfer from the solution to the electrode must occur to attain equilibrium, which generates a negatively charged depletion region and a consequent downward bending of the band edges.

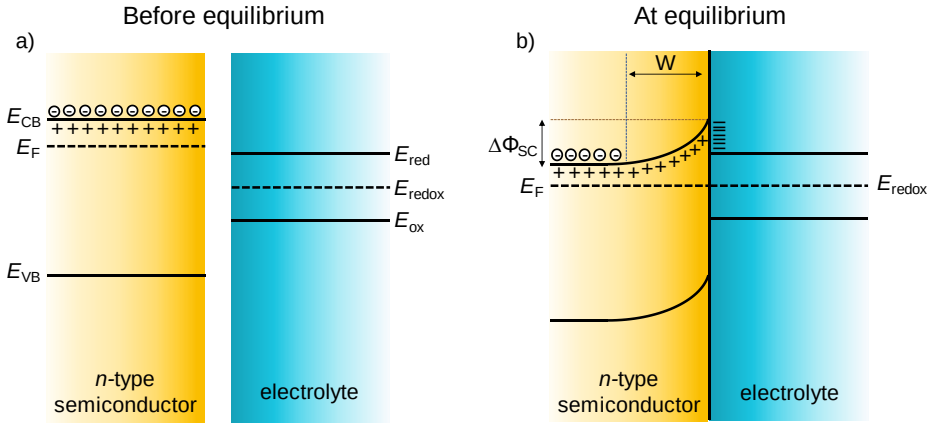


Figure 2.4 Formation of a semiconductor–liquid junction (SCLJ) between an *n*-type semiconductor and an electrolyte solution with a chemical potential E_{redox} . Representation of (a) the isolated band diagram of both semiconductor and electrolyte and (b) the band diagram at equilibrium.

The potential distribution in the space charge region can be obtained by integrating the Poisson's equation in one dimension, under the simplifying assumption that the charge due to electrons in the space charge region can be neglected (abrupt depletion approximation).⁴ The potential drop $\Delta\Phi_{\text{SC}}$ across the space charge region is therefore expressed by the following relationship:

$$\Delta\Phi_{\text{SC}} = \frac{qN_D W^2}{2\varepsilon_r \varepsilon_0} \quad (2.12)$$

where q is the elemental charge, ε_0 the permittivity of vacuum, ε_r the relative permittivity of the semiconductor material and N_D the concentration of ionized donors (commonly known as donor density). From this equation, it is possible to calculate the width of the space charge layer (W), extending between the semiconductor surface and the distance where the bands flatten (Figure 2.4b).

$$W = \sqrt{\frac{2\Delta\Phi_{\text{SC}} \varepsilon_r \varepsilon_0}{qN_D}} \quad (2.13)$$

This equation, which is valid for n -type semiconductors, can be also extended to p -type semiconductors after replacing N_D with the shallow acceptor density, N_A . It is worth noting that the potential drop $\Delta\Phi_{SC}$ is equal to $|E - E_{FB}|$ where E_{FB} is the flatband potential, that is the potential at which the space charge region, and consequently bands bending, vanish. The flatband condition is realized when using a redox electrolyte, or if applying an external voltage E (see the discussion below), such that E_{redox} or E is equal to the E_F of the semiconductor, so that no charge is removed from the semiconductor and no space charge region is formed.

The fixed space charge in the semiconductor is balanced by a net charge of opposite sign in the electrolyte that is due to a rearrangement of the mobile ions which form an electrical double layer, that is, the compact Helmholtz layer with an excess of negative (positive) charge in case of contact with an n -type (p -type) semiconductor, that spreads over the solution region closer to the electrode, followed by the diffuse Gouy-Chapman layer.¹⁵ In substance, the interfacial charge transfer leads to the formation of a capacitor with an excess of positive charges in the (n -type) semiconductor and an excess of negative charges in the solution. Since the charge stored in the depletion layer is proportional to the width of the space charge region W , the space charge capacitance per unit area can be obtained by differentiating it with respect to $\Delta\Phi_{SC}$:

$$C_{SC} = \frac{dQ_{SC}}{d\Delta\Phi_{SC}} \quad (2.14)$$

The exact solution gives the Mott-Schottky equation, written in the following for an n -type semiconductor:

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon_r \epsilon_0 A^2 e N_D} \left(\Delta\Phi_{SC} - \frac{kT}{e} \right) \quad (2.15)$$

where A is the surface area of the semiconductor material and $\Delta\Phi_{SC}$, the voltage drop in the space charge region, can be expressed as $\Delta\Phi_{SC} = |E - E_{FB}|$ when an external potential E is applied. This relationship is fundamental for the determination of the intrinsic properties of semiconductor materials, such as the donor density N_D and the flatband potential E_{FB} , which can be extrapolated from the slope and the intercept with the potential axis of the plot of $1/C_{SC}^2$ as a function of E , respectively.

2.2.5 Application of a potential bias

The band bending and the depletion width can be also influenced by the application of an external voltage to the semiconductor, as illustrated in Figure 2.5. Under the application of an external applied voltage, the semiconductor E_F is no longer in equilibrium with E_{redox} of the redox species of the electrolyte solution, but rather with the external applied bias E .

We have already seen that a semiconductor is at open circuit when its E_F is in equilibrium with the redox potential of the electrolyte. In case of an n -type semiconductor electrode in equilibrium with a redox system with an initial less negative Fermi energy,

this corresponds to upward bending of the semiconductor bands after equilibration of the levels, as shown in Figure 2.5a.⁴

The flatband potential of the semiconductor (E_{FB}) has been above referred as the potential value for which there is no excess charge in the semiconductor and therefore no band bending (the bands are flat). For this to occur, a redox electrolyte species with a potential that is equal to the Fermi level of the semiconductor should be employed or, alternatively, the photoelectrode should be polarized by a potentiostat at its E_{FB} , so that the conduction and valence bands are flat throughout the semiconductor (Figure 2.5b).⁴

When a potential is applied to the photoelectrode, the semiconductor Fermi level shifts relatively to the solution redox level and electron flow between the redox system and the semiconductor becomes thermodynamically possible. The shift of the semiconductor Fermi level along the vacuum (reference) level is followed by that of the band edges in the bulk of the semiconductor (*i.e.*, away from the depletion region), which varies with the applied bias in the same way as the E_F . Since, on the contrary, the energy of the band edges at the semiconductor/electrolyte interface is not affected by the change in the applied potential, while remaining pinned at the semiconductor surface, this causes the change of the depletion region width of the semiconductor, and consequently of the band bending, under variation of the external voltage (Figure 2.5c).¹³

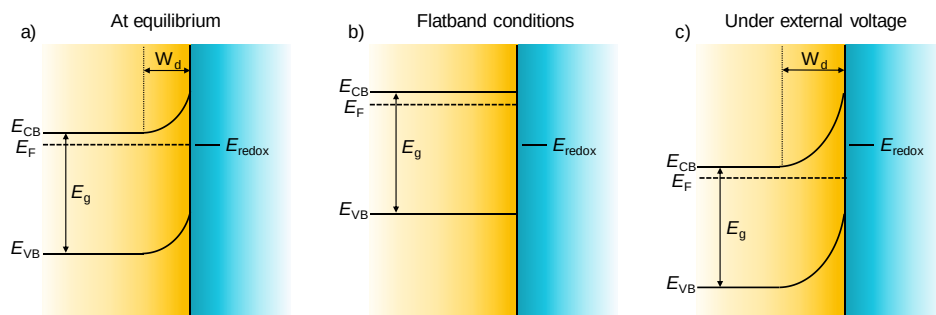


Figure 2.5 Semiconductor–liquid junction in the dark (a) at equilibrium with the redox electrolyte species, (b) under flatband conditions and (c) under an applied external voltage.

Moreover, according to the type of semiconductor (*n*-doped or *p*-doped) and the kind of polarization of the photoelectrode, we can have one of the following situations. As the E_F of an *n*-type (*p*-type) semiconductor is shifted from its equilibrium condition under application of a more positive (more negative) potential, the potential drop in the space charge region increases, thus resulting in a progressive extension of the space charge region in the semiconductor and, therefore, in the increase of the upward (downward) bending of the bands (Figure 2.5c), which drives photogenerated charge separation in PEC applications.

On the contrary, under application of a more negative (more positive) potential than the equilibrium potential for an *n*-type (*p*-type) semiconductor, the bands bending decreases. Beyond the flatband potential, there will be an excess of the majority charge

carrier in the space charge region, which can be referred to as an accumulation region in opposite to the above discussed depletion region. The excess of the majority charge carriers available for charge transfer, which is responsible for a downward (upward) bending of the conduction and valence bands towards the interface in case of an n -type (p -type) semiconductor, makes the behaviour of the semiconductor electrode similar to that of a metal electrode.

2.2.6 The semiconductor/electrolyte interface under illumination

Under illumination, the semiconductor absorbs photons with energy $h\nu \geq E_g$, leading to excitation of electrons across the forbidden gap, from the VB to the CB of the semiconductor. The electron–hole couples which are generated inside or next to the depletion region can take advantage of the electric field in this region to be separated, while those produced into the semiconductor bulk typically undergo easier recombination, together with the production of heat. The increase in electron and hole density due to light absorption perturbs the local concentrations of electrons and holes from their equilibrium values in the dark (Figure 2.6a), so that they cannot be longer described by the same electrochemical potential in terms of E_F .

For this reason, the concept of the splitting of the dark Fermi level E_F into two different quasi-Fermi levels (QFL) for electrons ($E_{F,n}$) and holes ($E_{F,p}$), near the semiconductor/electrolyte interface, should be introduced (Figure 2.6b).^{1,3,4,6} These QFL are related to the concentration of free carriers inside the depletion width before illumination described by Eqs. 2.6 and 2.7, plus the extra amounts due to light absorption, therefore:^{4,6}

$$n + \Delta n = N_c \exp\left(-\frac{E_{CB} - E_{F,n}}{k_B T}\right) \quad (2.16)$$

$$p + \Delta p = N_v \exp\left(\frac{E_{VB} - E_{F,p}}{k_B T}\right) \quad (2.17)$$

where Δn and Δp represent the additional photogenerated electrons and holes, respectively. It is worth noting that, since under illumination the majority carriers are repopulating the depletion region, bands bending decreases with respect to the dark condition consequently to the rise of $E_{F,n}$ with respect to E_F in the dark (compare Figure 2.6b with Figure 2.6a). Moreover, the change in majority carriers concentration induced by illumination is negligible with respect to the five orders of magnitude increase of the minority concentration, so that $(n + \Delta n \approx n)$ and $(p + \Delta p \approx \Delta p)$ in the case of an n -type semiconductor.¹ As a consequence, only the minority carriers QFL changes significantly under illumination respect to the equilibrium (dark) condition, whilst the QFL of the majority carriers is almost unchanged with respect to the E_F in the dark and stays constant across the space charge region. In the case of an n -type semiconductor this corresponds to a substantial shift of the hole QFL, in contrast to the insignificant change in the electron QFL. Conversely, a p -type semiconductor under illumination is subjected to a significant

shift in the electron QFL but just to a little hole QFL variation. It is worth noting that the QFL of minority carriers is an important concept in PEC water splitting, since it roughly corresponds to the oxidizing power of holes in a photoanode and to the reducing power of electrons in a photocathode.

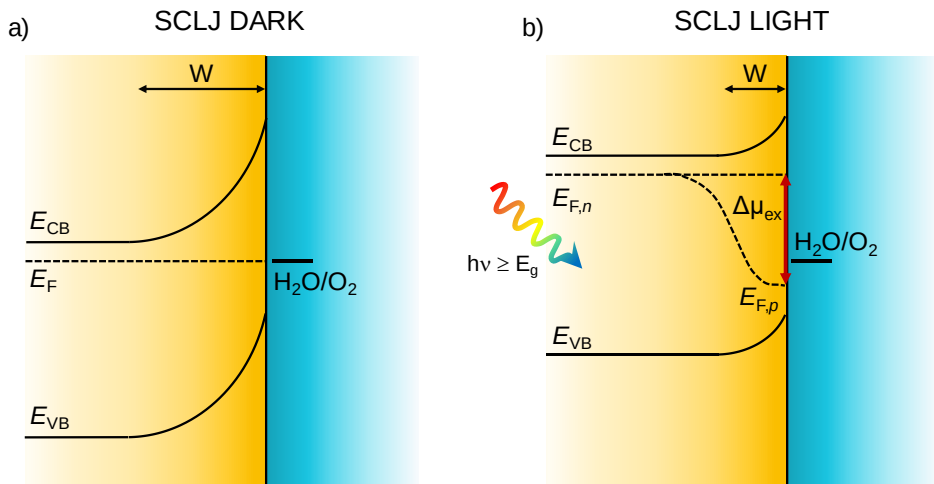


Figure 2.6 Schematic representation of an *n*-type semiconductor acting as photoanode in contact with an aqueous electrolyte solution (a) at equilibrium in the dark and (b) under illumination.

Importantly, some of the photogenerated charges will be successfully extracted in the water splitting process, while the remaining will recombine, losing energy as radiation or heat. Under the effect of the built-in electric field in the space charge region, while the minority carriers are spontaneously driven towards the SCLJ, the majority carriers are repelled. This means that an *n*-type semiconductor, where holes are driven towards the electrolyte interface to eventually carry out, with the appropriate energetics and kinetics, the OER oxidation reaction, behaves as a photoanode. At the same time, photoexcited electrons are driven towards the electrode's back-contact to be then transferred to the counter electrode where they can promote the HER. Conversely, a *p*-type semiconductor in contact with an electrolyte solution will act as a photocathode, where photogenerated electrons can reduce the redox species in the electrolyte.

It is worth mentioning the crucial role played by the QFL description of a photoelectrode under illumination (*i.e.* in non-equilibrium conditions), since the real energetics and useable photovoltage under light irradiation are dictated by the quasi-Fermi levels, and not by the band edges⁶ (as instead stated in the general description presented in Section 2.1 for the sake of simplicity).

In this description, the semiconductor photovoltage $\Delta\mu_{\text{ex}}$, which determines the useable energy for driving the reaction, is given by the quasi-Fermi levels separation in the semiconductor. Solar assisted water splitting, carried out without any additional external bias, requires $\Delta\mu_{\text{ex}}$ to exceed the thermodynamic 1.23 eV needed to split water

plus the electrochemical overpotentials required for the oxidation, η_{ox} , and reduction reactions, η_{red} , and the entropic losses. Moreover, as reported by Weber,¹⁶ the thermodynamic requisite for the overall water splitting reaction to occur requires the quasi-Fermi levels, and not the conduction and valence band edges, to straddle the water redox potentials. This corresponds to having an electron QFL sufficiently high to drive the water reduction half-reaction, including the η_{red} loss, and simultaneously a hole QFL sufficiently low to trigger water oxidation, including the η_{ox} loss (Figure 2.6b).

The main aim of any practical energy conversion device based on a photoabsorber semiconductor is to extract the largest possible fraction of the chemical energy stored into the $\Delta\mu_{\text{ex}}$. However, as discussed in Section 2.1, the semiconductor photovoltage is always less than the semiconductor band gap, meaning that large band gap materials are required to provide sufficient photovoltage for water splitting, although this precludes the harvesting of a large fraction of the solar spectrum.

In this context, the identification of a semiconductor material capable of performing alone unassisted water splitting at high solar-to-chemical conversion efficiencies, in the S2 configuration presented at the beginning of this chapter, is still a big challenge. For this reason, many efforts have been focused on the research on the dual-absorbing tandem cell dealt in Section 2.3.2, where two semiconductors with different band gap energies are wired together to harvest complementary portions of the solar spectrum.

2.2.7 Surface states and Fermi level pinning

The semiconductor interface may also be able to store electronic charge in energy levels that lie in the forbidden gap, arising from structural defects such as dangling bonds or vacancies, or chemisorbed species from an electrolyte solution. These surface states, which can act either as donors or acceptors, can therefore affect the processes occurring at the SCLJ, such as by promoting charge accumulation and surface recombination, or by mediating charge transfer towards the dominant redox species into the electrolyte solution. Surface states should be distinguished from bulk defects in the crystal lattice, usually acting as traps recombination centers between photogenerated charges, and thus mainly affecting the efficiency of charge separation. In practice, preparing semiconductors without a significant concentration of bulk or surface defects is very difficult. It is worth noting that the surface states distributed in the band gap, particularly those endowed with a high density of electron levels, strongly influence the properties of the interfacial electric double layer.

To understand how the presence of surface states can influence the SCLJ, we should consider the relative position of the semiconductor Fermi level at the SCLJ with respect to the surface state level, under polarization of a semiconductor electrode. Indeed, as long as E_F is far from the surface DOS, or in the absence of a significant surface states population, the charge in the surface state remains constant and the entire change of electrode potential due to anodic or cathodic polarization occurs in the space charge layer,

without producing hence any variation across the Helmholtz layer. This situation is known as *band edge level pinning* to indicate that the levels of the conduction and valence band edges are constant at the electrode interface, while they progressively bend across the space charge layer as a consequence of the linear variation of the potential drop $\Delta\Phi_{SC}$ in this region with the applied bias.

On the other hand, as the Fermi level of the electrode approaches the surface states level, equilibration of the semiconductor E_F with the energy of these states occurs. If a sufficiently high density of surface states is present, the semiconductor E_F at the interface stays pinned at the surface states level until these states, which behave as a capacitor, are fully charged or discharged by accepting or donating electrons. As long as this phenomenon, known as *Fermi level pinning*,¹⁷ occurs, any additional applied voltage results in the charging (or discharging) of the surface states, rather than in an increase of the band bending of the semiconductor. Indeed, in such condition of Fermi level pinning, the potential drop $\Delta\Phi_{SC}$ in the space charge layer remains constant and all the change in potential upon electrode polarization is distributed across the Helmholtz layer.¹⁸ The Fermi level pinning can occur also when E_F at the interface is polarized into either the conduction or the valence band of semiconductor electrodes.

It is worth remarking that the control of the electrode potential can be provided by either an external applied bias or a change of the dominant redox species which determines the potential of the electrolyte solution (E_{redox}). Therefore, the above described behaviour which has been referred to the change of the electrode potential upon polarization with an external bias, can also occur by varying the electrolyte redox species involved in the equilibrium with the semiconductor Fermi level. Indeed, if the density of surface states at the semiconductor–liquid junction is sufficiently high for Fermi level pinning to occur, the charges required for equilibration of the junction is extracted from the surface states rather than from the semiconductor, so that the equilibrium is reached without producing any variation in $\Delta\Phi_{SC}$.¹⁴

The effect of the presence of surface states on the equilibration of the semiconductor/electrolyte junction for an *n-type* semiconductor in contact with two different electrolyte redox species such that $E_{redox,1} \neq E_{redox,2}$ is represented in Figure 2.7. While in the absence of surface states the band bending in the dark and the photovoltage under illumination increases as the semiconductor equilibrates with a species having a more positive redox potential (Figure 2.7a), in the presence of a high density of surface states the Fermi level is pinned to their energy and E_{VB} and E_{CB} shift relatively to the solution levels. Consequently, under Fermi level pinning conditions the band bending and the photovoltage becomes independent of the potential of the electrolyte, remaining constantly small if the surface DOS is close to the CB (Figure 2.7b).

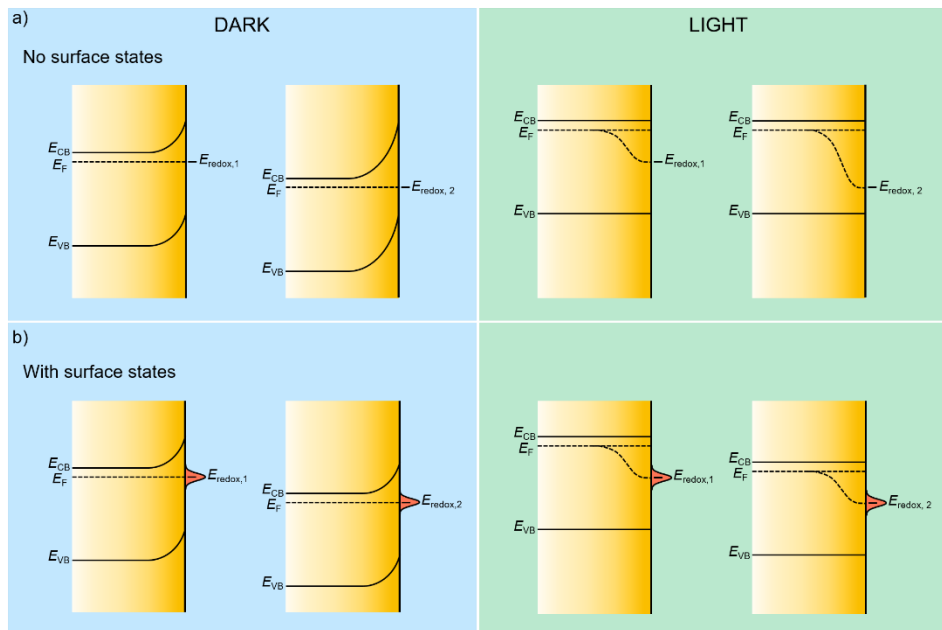


Figure 2.7 Sketches of the band energies of an n-type semiconductor after equilibration with two different electrolytes of different redox potentials $E_{redox,1}$ and $E_{redox,2}$, both in the dark (left) and under illumination (right), (a) in the absence and (b) in the presence of surface states at the SCLJ.¹⁹

As already mentioned, the charging of surface states corresponds to the charging of a surface state capacitance C_{ss} .^{6,18} This contribution to the interfacial capacitance is apparently zero in the potential range where the Fermi level is located away from the surface state level (i.e., in the region of the band edge level pinning). On the other hand, when the Fermi level is pinned at the surface state, the C_{ss} increases to its maximum value which is equivalent to the capacity C_H of the Helmholtz layer, because of the correspondence between the surface state charging and the Helmholtz layer charging in the Fermi level pinning condition. Since Mott-Schottky analyses (described in detail in Section 4.3.6) consist of measuring an electron-depleted space charge layer that is gradually polarized in the anodic direction, the presence of surface states that affect the SCLJ can have an important impact on the experimental response that is obtained from this kind of measurements. In fact, as long as the E_F is located away from the surface states, the interfacial capacitance is determined by the capacitance of the space charge region that obeys the Mott-Schottky relation (Eq. 2.15). As the E_F equilibrates with the surface states level, the interfacial capacitance corresponds to the capacitance of the compact Helmholtz layer (representing the maximum capacitance of the surface states) and remains constant throughout the potential range where the Fermi level is pinned. This corresponds to the observation of a flat region in the Mott-Schottky plot, in the same potential range as the Fermi level pinning condition is verified (Figure 2.8).

Once that the surface states are completely charged, a further increase in anodic polarization leads again to the capacitance of the space charge layer which varies according to the Mott-Schottky relation, represented by a second plot with non-zero slope, parallel to the previous one appearing prior the Fermi level pinning region.

As a result of anodic charging of the surface states, the flatband potential that is obtained from the Mott-Schottky plot is shifted towards the anodic direction meaning that, due to Fermi level pinning, it does no longer approximate the CB edge potential (E_{CB}) value like usual for n -type semiconductors, while rather resembling the surface states level potential.

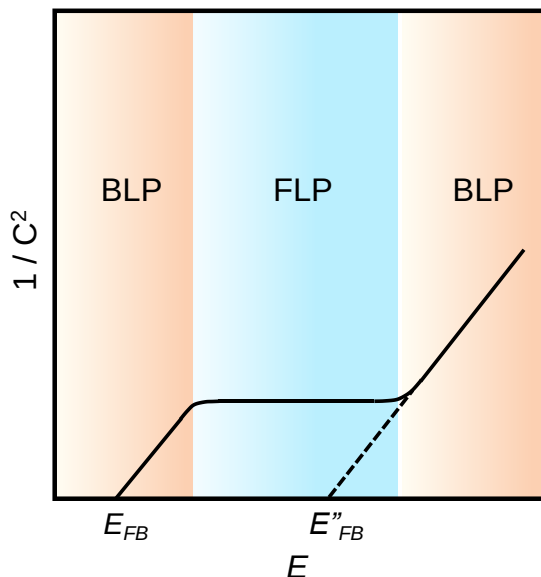


Figure 2.8 Mott-Schottky plot of an n -type semiconductor electrode in the presence of surface states, where BLP indicates the band level pinning region and FLP is the Fermi level pinning region. E_{FB} is the flatband potential determined before the Fermi level pinning region, while E''_{FB} is the flatband potential measured after anodic charging of the surface states.¹⁸

The above discussion highlights the strong impact of surface states on the intrinsic electrochemical properties of semiconductors which can be extracted by means of Mott-Schottky analyses (see Section 4.3.6). Although the impact played by surface states at the SCLJ has been recognized, their nature (*i.e.* if they are intrinsic surface states, already present in the dark and due to crystalline defects at the semiconductor surface, or light-induced states) and role are still under debate.^{1,19–25}

2.3 Solar PEC water splitting

In the next, further insights on the mechanism of solar assisted water splitting conducted with the simplest S2 single photoabsorber approach, introduced at the beginning of this chapter, will be provided on the basis of the previously discussed semiconductor/electrolyte junction properties, without and under the effect of an external applied potential. Then, we will extend the discussion to bias-unassisted solar water splitting carried out with the more complex D4 tandem PEC cell.

2.3.1 Bias-assisted PEC water splitting: the S2 approach

Given the larger overpotential for oxygen evolution compared to that required for hydrogen production from protons reduction, the OER reaction at the photoanode is the major bottleneck of the overall water splitting process. For this reason, massive efforts have been devoted to the improvement of semiconductor materials acting as photoanodes with the aim to overcome the limitations of water oxidation in PEC devices. Therefore, in the following we will refer to a S2 scheme based on an absorber material acting as photoanode, connected to a Pt wire as counter electrode and to a reference electrode through a potentiostat, in a three-electrode configuration cell (see Section 4.3.2 for a complete description).

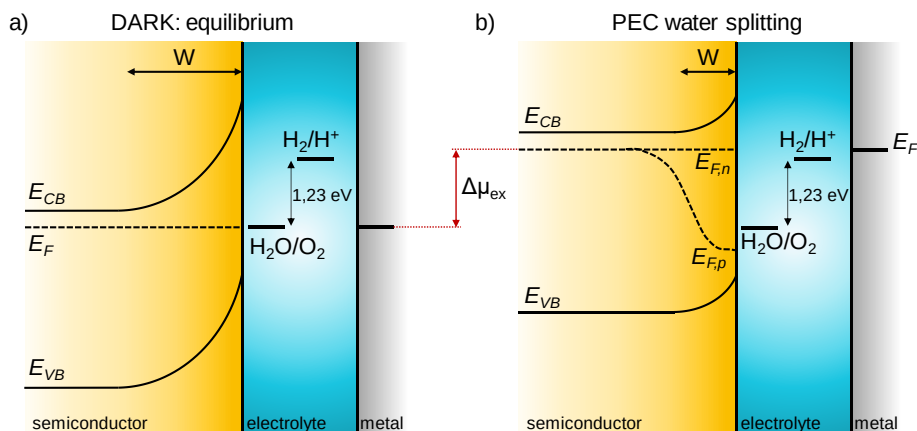


Figure 2.9 Band diagram for an S2 single photoabsorber PEC cell based on an n-type semiconducting photoanode that is electrically connected to a metal counter electrode, at equilibrium in the dark (left) and under illumination (right).⁶

In the ideal case of water splitting conducted with a single photoabsorber according to the S2 scheme, two absorbed photons are required to produce one molecule of H_2 . At open circuit potential (i.e., no current flow) in the dark, the Fermi levels of the semiconductor and metal, which are electrically connected, adjust to a value close to the electrochemical potential of the dominant redox species in solution (Figure 2.9a).

Under absorption by the photoelectrode of photons with energy $h\nu \geq E_g$, which induce the generation of electron–hole pairs, the Fermi level rises, with a consequent decrease in band bending, and splits near the semiconductor/electrolyte interface into quasi-Fermi levels for electrons and holes, separated by the internal photovoltage $\Delta\mu_{\text{ex}}$ (Figure 2.9b). This also corresponds, in a PEC cell, to the photoelectrochemical potential between the SCLJ and the counter electrode. The space charge field in the depletion region of width W promotes the separation of the photogenerated electrons in the CB from their corresponding holes in the VB.

For PEC water splitting to occur without any external bias according to the S2 scheme, the photoelectrode should generate, upon absorption of two photons, sufficient free energy $\Delta\mu_{\text{ex}}$ to overcome the 1.23 V required to split water plus the electrochemical overpotentials η_{ox} and η_{red} , for the oxidation and reduction reactions, respectively, and other energy losses. Moreover, thermodynamically speaking, a PEC cell can perform unassisted solar water splitting if electrons are generated with an energy higher than $-qE^0(H^+/H_2)$ and holes with an energy lower than $-qE^0(H_2O/O_2)$ i.e., in other terms, if the quasi-Fermi levels of electrons and holes straddle the water reduction and oxidation potentials, respectively.^{16,26} However, the only semiconductor materials that satisfy this requirement exhibit a band gap energy too large to absorb a significant part of the solar spectrum (for example, SrTiO_3 , SiC) or are unstable in aqueous solutions (e.g., Cu_2O , CdS). Conversely, it mostly happens that semiconductors having a proper band edge for water reduction are not suitable for water oxidation, and vice versa: non-oxide semiconductors tend for example to possess a sufficiently high E_{CB} to perform proton reduction, whereas oxide-based semiconductors exhibit an enough low E_{VB} for water oxidation.⁶ The application of an external bias between the photoelectrode and the metal counter electrode can help to both increase band bending in the space charge region, thus enhancing photogenerated charge separation, and compensate for eventual potential deficiencies given by an unfavourable thermodynamic location of the semiconductor quasi-Fermi levels with respect to the hydrogen and oxygen evolution potentials.

When a photoanode is polarized by a potentiostat anodically (more positive) or cathodically (more negative) than the flatband potential – where the conduction and valence bands are flat throughout the semiconductor and there is no current flow through the system – the Fermi level and the CB and VB in the bulk of the semiconductor move along with the vacuum (reference) level, while the energy levels at the surface stay fixed. Since polarization of the irradiated photoanode induces a significant variation in the quasi-Fermi level of holes while the position of the quasi-Fermi level of electrons stays almost unchanged,¹ the increase in external chemical potential $\Delta\mu_{\text{ex}}$ that can result from an anodic polarization leads to a progressive rise in band bending, which drives the separation of the photogenerated electrons from the corresponding holes.

However, even with the help of an external bias, the achievement of high solar-to-chemical conversion efficiencies with a single photoabsorber has not yet been

accomplished since the other important requirement of a substantial solar light harvesting should be also taken into account.

The solar-to-hydrogen (STH) conversion efficiency, which is a commonly adopted metric to quantify the overall efficiency of a PEC water-splitting device exposed to broadband solar Air Mass 1.5 Global (AM 1.5 G) illumination in a two-electrode configuration under zero bias conditions, can be calculated as:²⁷

$$\eta_{STH} = \frac{J_{op}[mA \cdot cm^{-2}] \times 1.23 [V] \times FE}{P [mW \cdot cm^{-2}]} \quad (2.18)$$

where J_{op} is the operating photocurrent density, FE the Faradaic efficiency (*i.e.* the conversion efficiency of free electrons to hydrogen product through the electrochemical reaction) and P the total integrated power input density.

For unassisted simultaneous water oxidation and reduction with a single absorber semiconductor, a relatively low maximum η_{STH} of 11.6% has been predicted with a minimum E_g value of 2.2 eV.^{4,5,16,28} Therefore, PEC water splitting efficiencies with a single semiconductor junction such that $\eta_{STH} \gg 10\%$ are far to be achieved.⁴

Therefore, to date, the identification of a single material capable of performing S2 water splitting at high solar-to-chemical conversion efficiencies, thus simultaneously offering significant solar light harvesting, appropriate conduction and valence band energy levels as well as adequate stability in the harsh operating conditions, has proven to be a very difficult task.

2.3.2 Dual-absorbing (D4) tandem cell for PEC water splitting

One possible solution to address the challenge of developing sufficient available free energy $\Delta\mu_{ex}$ for PEC solar hydrogen production, while also harvesting an appreciable amount of the solar spectrum, is represented by the two-photoelectrodes D4 approach or dual-absorbing tandem cell,^{5,29–31} which is capable of carrying out efficient unassisted water splitting by efficiently exploiting light irradiation. Moreover, with both electrodes capable of light harvesting and charge carriers couples generation, the holes produced at the photoanode and the electrons photoexcited at the photocathode can directly take part in water oxidation and reduction, respectively, which therefore are conducted separately. This allows overall water splitting to occur without the need of an external bias, which is required instead in the S2 approach to enhance charge separation.

The tandem system consists of an *n*-type semiconductor photoanode and a *p*-type semiconductor photocathode of different band gap energies E_{g1} and E_{g2} , respectively, with $E_{g1} > E_{g2}$ to harvest complementary portions of the solar spectrum, connected to each other in a “wired” configuration, as shown in Figure 2.10. In this way, a larger part of the solar spectrum compared to the S2 system can be exploited although resulting in sufficient $\Delta\mu_{ex}$ generation for carrying out unassisted water splitting, while appropriate quasi-Fermi levels positions with respect to the water reduction and oxidation potentials are preserved.

As indicated by the adopted D4 connotation, four photons must be absorbed (two by each absorber photoelectrode) to produce one H_2 molecule.

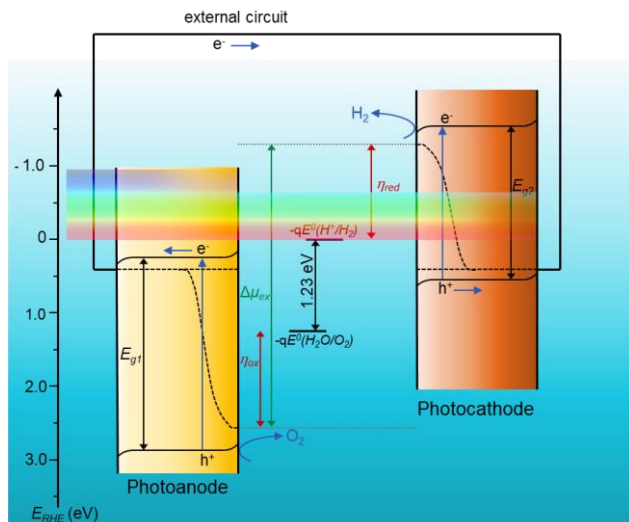


Figure 2.10 Schematic representation of a PEC tandem cell for overall water splitting in the “wired” configuration, with the photoanode and the photocathode semiconductor materials characterized by band gap energies E_{g1} and E_{g2} , so that $E_{g1} > E_{g2}$.³¹

This scheme can be realized by taking advantage of two possible configurations. The simplest one consists in placing the two photoelectrodes side-by-side, with a resulting maximum STH conversion efficiency of 16.6%, which represents only a moderate increase over the single absorber approach (exhibiting a maximum STH conversion efficiency of 11.6% for $E_g = 2.2$ eV), with the difficulty that a band gap as low as 1.4 eV should be employed for both semiconductors.

However, in the preferred configuration solar photon harvesting is optimized by placing the two photoelectrodes one on top of the other, so that the incident light can be harvested by each of them sequentially.^{16,32} In this way, the higher energy photons (corresponding to the wavelengths smaller than $\lambda_1 = hc/E_{g1}$) are absorbed by the first electrode stricken, *i.e.* the photoanode with larger band gap E_{g1} , while the remaining lower energy photons with $\lambda > \lambda_1$ are transmitted by the first electrode and absorbed by the photocathode, possessing a narrower band gap $E_{g2} < E_{g1}$.⁶ This design greatly increases the maximum theoretical STH conversion efficiency compared to both the single photoelectrode approach and the dual-absorbing side-by-side configuration. Indeed, the maximum predicted STH conversion efficiency for the D4 tandem cell with optimized E_g for both the top and the bottom photoelectrodes, according to the different calculation models employed (Weber and Dignam,¹⁶ Bolton,^{33,34} Lewis *et al.*³⁵), varies from at least 20% to even 30% depending on the selected conditions, *i.e.* the band gap energies of the two photoelectrodes and the assumed energy loss due to overpotentials.^{5,16,33,35–37}

In summary, this result accounts for the larger advantage of the stacked tandem configuration over both the single absorber S2 approach and the dual-absorbing side-by-side configuration, and underlines the requirement of optimized narrow band gap energies for these maximum efficiencies to be reached, *i.e.* representing a significant challenge for materials development. In this regard, an overview of the most attractive semiconductors currently preferred to play the most challenging role of photoanode in the above-described tandem PEC cell configuration will be provided in the next chapter.

An essential requisite for the realization of the most efficient D4 tandem cell with the two photoelectrodes in stacked configuration is the high transparency of the top photoanode in the wavelength range outside its band gap (E_{g1}), in order to optimize the transmission of photons with energy lower than E_{g1} and thus their harvesting by the bottom photocathode. To this aim, the preparation of optically transparent photoanodes with a planar structure should be preferred over the employment of nano- or micro-structuring techniques, which are usually resorted to overcome charge carriers transport limitations in semiconductors, while presenting the serious side-effect of light scattering which reduces the number of photons reaching the bottom photoelectrode.^{6,31,38–40}

The development and optimization of optically transparent photoanodes with a flat morphology, suitable to be employed as top photoelectrodes in the preferred tandem PEC cell architecture, by means of an easily scalable synthesis protocol, has been chosen as the object of study in the work presented in this thesis.

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Chapter 3

New generation of photoanodes for PEC oxygen evolution

3.1 Requirements for efficient photoelectrodes

In this section the requirements that a semiconductor must fulfil to be considered as a good material for PEC water splitting will be dealt in detail.¹ First of all, the band gap extent, which determines the photons energy range accessible to the material, should be narrow enough to maximize the absorption in the visible light range, representing most of the solar emission spectrum, as shown in Figure 3.1. It should be indeed bear in mind that the longest wavelength (λ_{max}) that a semiconductor of band gap E_g can absorb is limited by the relation $\lambda_{\text{max}} = hc/E_g$, where h is the Planck's constant and c the speed of light. Therefore, longer wavelengths with less energy are not useful for the semiconductor absorption.

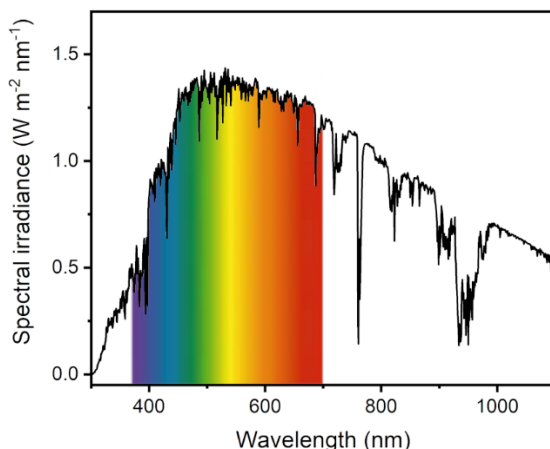


Figure 3.1 Reference Air Mass (AM) 1.5G solar radiation spectrum underlying the useful and predominant visible light region.²

On the other hand, as stated in the previous chapters, a minimum band gap is required for delivering the free energy necessary to drive the water splitting reaction, also known

as semiconductor photovoltage. In this regard, it is necessary to take into account the thermodynamic potential of 1.23 V for water splitting plus the thermodynamic losses (0.3–0.4 eV)³ and the overpotentials necessary to ensure sufficiently fast reaction kinetics (0.4–0.6 eV).^{4,5} As a result, the semiconductor should possess a band gap of at least 1.9 eV, which corresponds to an absorption onset at 650 nm, with an upper limit of 3.1 eV and a minimum absorption onset at 400 nm, since the intensity of sunlight at wavelengths below this value rapidly drops. As a consequence, the semiconductor band gap has to offer a trade-off between light absorption and photovoltage.

Moreover, to achieve a STH efficiency of 10% considered the threshold for practical applications, it's necessary to gain a minimum photocurrent density of 8.1 mA cm⁻², *i.e.* corresponding to a maximum band gap of *ca.* 2.3–2.4 eV. This energy interval is consistent with the prediction of Murphy *et al.* of a hypothetically ideal material with a band gap of ~2 eV for a maximum STH efficiency of 16.8%.⁴ Of course, as already discussed in the previous chapter, higher efficiencies can be obtained by exploiting multiple band gap energies as in tandem systems.

According to the second requirement, the semiconductor band edges, and in more stringent terms the quasi-Fermi levels for electrons and holes ($E_{F,n}$ and $E_{F,p}$, respectively) should straddle the water reduction and oxidation potentials, respectively. This means, specifically, that E_{CB} or $E_{F,n}$ in the quasi-Fermi levels description, should be above $E(H^+/H_2)$, while E_{VB} should lie below $E(O_2/H_2O)$. As shown in Figure 3.2 reporting the band-edge positions of various semiconductors, along with the reduction and oxidation potentials of water, few semiconductors satisfy this requirement, and the ones doing that have a too large band gap (*e.g.*, SrTiO₃, SiC) or are unstable in aqueous solutions (CdS).⁶ The reported band diagram also suggests that non-oxide semiconductors generally exhibit highly negative E_{CB} , which makes them particularly suited to reduce water, whereas oxide semiconductors, with typically highly positive E_{VB} , are mainly employed to carry out water oxidation.

Additionally, charge transport within the bulk semiconductor needs to be highly efficient for allowing the photogenerated electrons and holes to reach the electrode/FTO or electrode/electrolyte interface, respectively, before recombining. The charge carriers transport properties of semiconductor photoelectrodes can be determined by either the intrinsic electron and hole mobilities related to the electronic structure of the material⁷ or extrinsic factors such as shallow donors/acceptors and recombination centers.

In the case of metal oxides, where the conduction and valence bands are usually composed of metal 3d orbitals and oxygen 2p orbitals, respectively,⁸ electrons and holes mobilities are promoted by extensive overlap within each of these kinds of orbitals. Moreover, the presence of shallow donors or acceptors can contribute to further enhance the conductivity of a semiconductor, whereas defects with deeper lying energy levels usually act as recombination centers.

A further requirement concerns the interfacial charge transfer, corresponding for an *n*-type semiconductor to hole transfer across the semiconductor/electrolyte interface. This process should be fast enough to avoid the accumulation of carriers at the surface, possibly determining a decrease of the electric field and a concomitant detrimental increase in charge recombination. Furthermore, a sufficiently fast interfacial charge transfer should also avoid any anodic or cathodic decomposition reaction leading to the undesired photocorrosion of the photoelectrode.

The relative kinetics of charge transfer across the interface and of the decomposition reaction is indeed an important issue to evaluate the chemical stability of the electrode both in dark and under illumination, which severely limits the choice of photoactive materials. Photocorrosion of an *n*-type photoanode (*p*-type photocathode) occurs when photogenerated holes (electrons) may oxidize (reduce) the semiconductor first rather than water. The general rule is that a photoanode is stable with respect to hole oxidation if its oxidation potential (Φ_{ox}) is more positive than either the oxygen evolution potential $E(\text{O}_2/\text{H}_2\text{O})$ or the semiconductor E_{VB} . A photocathode is stable with respect to electron reduction, if its reduction potential Φ_{red} is more negative than either the hydrogen evolution potential or its E_{CB} .⁹

In this frame, oxide semiconductors are more stable photoanodes than non-oxide semiconductors (*e.g.*, Si, GaAs, GaP, CdSe), which are instead more prone either to corrode or oxidize when they are in direct contact with an aqueous solution, or to form an electrically-insulating passivation layer which prevents electron transfer across the semiconductor/electrolyte interface. In fact, as shown in Figure 3.2, oxides semiconductors usually possess a E_{VB} which is far more positive than the OER potential, so that photogenerated holes are thermodynamically more prone to oxidize water rather than the metal cations composing the semiconductor itself. However, the general trend for oxide materials is that the stability against photocorrosion increases with increasing band gap. This is obviously in contrast with the requirement of visible-light absorption, although not compromising the extensive employment of semiconductor oxides-based materials.

Finally, for the semiconductor to be economically viable, materials composed of cheap and abundant element should be preferred, together with synthesis methods which can be easily processable on a large scale. To date, it is very hard to find an ideal semiconductor material for PEC water splitting, thus satisfying all the previous described requirements. This task is indeed considered as the “Holy Grail” in photoelectrochemistry.

Among semiconductors, metal oxides have emerged as the most suitable class of materials for water splitting, mainly thanks to their distinct stability towards the harsh oxidative conditions in aqueous solution and relatively low cost. In the following, we will focus the attention on *n*-type metal oxide-based semiconductors to be employed as photoanodes in the OER, which is the most challenging (rate-limiting) step of the overall

water splitting process, due to the slow kinetics which involves the transfer of four holes to yield one O_2 molecule.

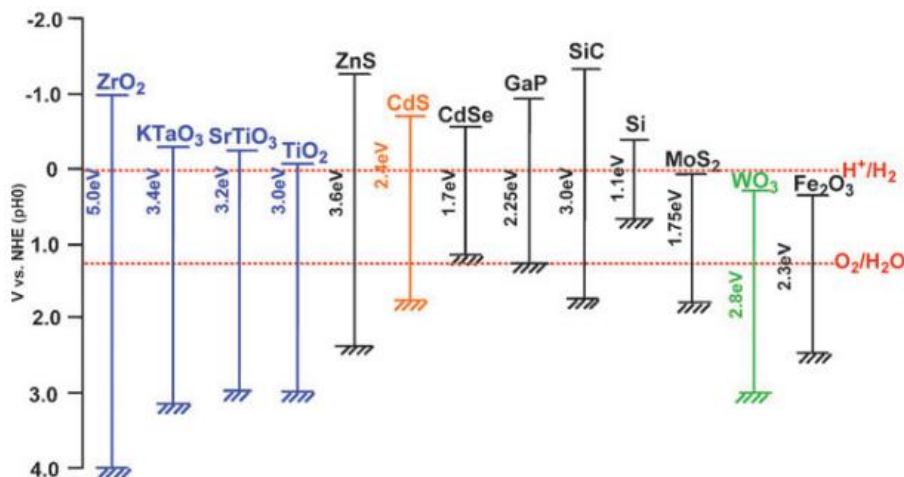


Figure 3.2 Band structure of different semiconductor materials with respect to the redox potentials of water splitting.¹⁰

3.2 Metal oxide-based semiconductors

Among the possible *n*-type semiconductors that have been investigated as photoanodes for the water oxidation half-reaction, transition metal oxides offer many unique advantages. First, they are generally stable in aqueous media during the harsh oxidative conditions of OER thanks to the relatively high electronegativity of oxygen which results in the formation of stable compounds based on O^{2-} anions,¹¹ combined with the fact that in most of metal oxides (such as WO_3 , Fe_2O_3 , $BiVO_4$ and $CuWO_4$) metals are in their higher oxidation states which make them not susceptible to further oxidation when used as photoanodes.¹²

Second, many of these materials possess relatively narrow band gaps in the 1.5–2.7 eV range which allow to optimize visible light absorption¹² of the top absorber photoanode in tandem PEC devices with the final aim to achieve at least 10% STH efficiency. Third, due to the primary O 2p character, the valence band of most of metal oxides locates at highly oxidizing potentials, *i.e.* at *ca.* 3V vs. NHE as depicted in Figure 3.2, thus energetically far below the thermodynamic potential of 1.23 V for oxygen to evolve. Therefore holes photoexcited in these materials can take advantage of a significant amount of overpotential (up to *ca.* 1.77 V) to drive water oxidation, when only 0.3–0.5 V is required,¹³ thus enabling metal oxides to easily overcome the kinetic barriers for OER.

The highly tunability of the band gap of transition metal oxides despite the almost unchanged highly oxidative E_{VB} position, is made possible by the fact that their electronic structure is such that while oxygen 2p states determine the valence band, *d* orbitals of one

or more metals define the composition of the conduction band. In this way, by tuning the transition metal cations, metal oxides with narrower band gap energies, although preserving a similar VB located at *ca.* 3 V vs. NHE, can be simply obtained through the lowering of the CB energy. Lastly, the composition of metal oxides is made of abundant and inexpensive elements which make the processing of these materials on a large scale easy and inexpensive.

Since the pioneering report of Fujishima and Honda on PEC water splitting by using TiO_2 ,¹⁴ early studies on oxide-based photoelectrodes have been focused on metal binary oxides, consisting of a single metal cation and an oxygen anion. In particular, the attention has been firstly devoted to the most stable WO_3 and Fe_2O_3 in addition to TiO_2 , prepared through solution-based processes, *e.g.* sol–gel, spray pyrolysis, or hydrothermal routes followed by thermal annealing, which allow to easily obtain oxide thin film electrodes without expensive processing techniques. However, these materials present some limitations which have compromised the achievement of photocurrents larger than 3 mA/cm^{-2} despite all the efforts made over decades of research.¹⁵

For example, the classic d^0 binary metal-oxide photoelectrodes which are TiO_2 ($E_g = 3.0\text{--}3.2$ eV), and WO_3 ($E_g = 2.7$ eV), have gathered great attention for decades thanks to their remarkable stability under PEC operation.^{16,17} It is indeed well-established that the O 2p character of the VB structure in transition metal oxides based on empty d bands (that is, with d^0 cations such as Ti^{4+} , W^{6+} , V^{5+} and Nb^{5+}), makes the valence band low in energy and stable towards oxidation under PEC operation. However, due to their high ionic character, these metal oxides suffer from band gaps too large to guarantee efficient exploitation of solar energy harvesting.

Consequently, the maximum STH efficiencies are limited to 2% and 5% when employing TiO_2 and WO_3 as photoanodes in a tandem cell, respectively. The relatively low efficiency exhibited by these metal binary oxides can be better compared in the graph of Figure 3.3, *i.e.* reporting the maximum tandem cell efficiencies in terms of both STH efficiencies and solar photocurrent in standard conditions, as a function of the band gap of the top photoabsorber.

Despite the many attempts devoted to narrow the band gap of these oxides by means of different doping strategies,^{17–19} none of these has proved successful to increase the energy conversion efficiency at a significant extent upon improved visible light harvesting,^{20,21} mostly due to the introduction of lattice defects as side-effect of atomic substitution, *i.e.* behaving as undesired recombination centers for the photogenerated charge carriers.

Fe_2O_3 with smaller band gap energy ($E_g = 2.1$ eV) has been examined as alternative stable oxide with a smaller band gap for increasing visible light absorption, and consequently obtaining STH efficiency up to 15% (see Figure 3.3).²¹ Apart from its good stability, despite the narrow band gap, as well as the ubiquity of iron in the earth's crust, short carrier lifetimes due to extensive recombination and/or poor transport properties

have emerged as major drawback that severely limits the experimental photocurrents of this material,²² which are still far away from the theoretical maximum limit despite the disparate efforts devoted to improve the Fe_2O_3 performance.

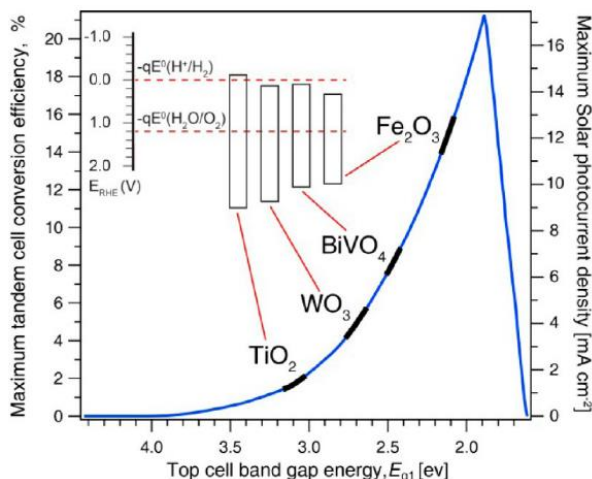


Figure 3.3 Maximum solar-to-hydrogen conversion efficiency and solar photocurrent as a function of the top cell band gap energy in a tandem cell. The band gap energies and efficiency range for commonly used semiconductor oxide photoanodes are also shown.²¹

It is worth noting that the use of other binary metal oxides such as ZnO , In_2O_3 , and Cu_2O as photoelectrodes for solar water splitting has been limited by their thermodynamically instability in aqueous solutions, which still represents a major issue despite the many attempts in developing surface protection layers to improve their stability.²³ Although efforts in the improvement of binary metal oxides are still ongoing, due to the above-mentioned issues which limit their use as photoanodes for water oxidation, the ideal material remains elusive. This has opened the way to investigate multinary (ternary, quaternary, *etc.*) metal oxides to be employed as photoelectrodes for PEC water splitting application.

Specifically, ternary and quaternary oxides are composed of two or three different metal ions, respectively combined in an oxide matrix. Therefore, thanks to the availability of more than 8000 and 700 000 combinations with ternary and quaternary compounds, respectively, their use instead of binary oxides (with which they are compared in Figure 3.4) provides more opportunities to tune the atomic composition and electronic structures of photoelectrodes, which can directly impact on the resultant photoelectrochemical properties.^{12,15,24}

Therefore, research on multinary metal oxides clearly opens up a huge number of possibilities in finding an ideal semiconducting material for solar water splitting. In the following sections, a brief excursus on some examples of the most attractive multinary metal oxides to date, which will be also the object of this thesis, first among all BiVO_4 , will be provided based on the most recent literature.

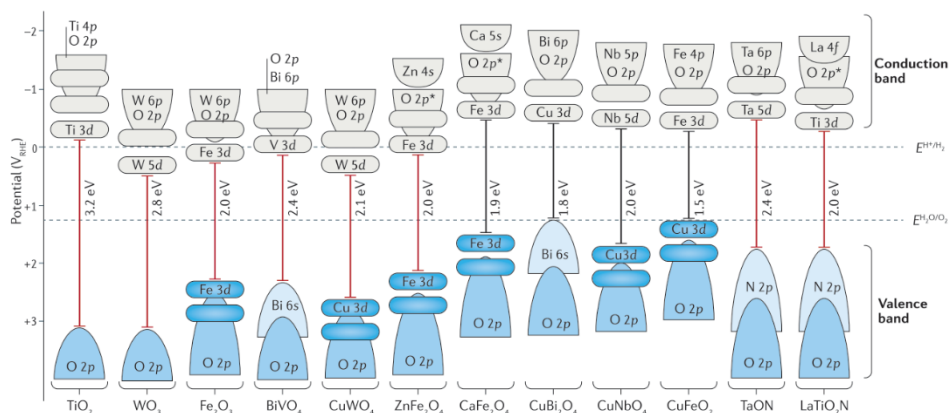


Figure 3.4 Band structure of common binary and ternary metal oxides and oxynitride semiconductors for PEC applications together with the water redox energy levels, expressed with respect to the reversible hydrogen electrode. The contributions of metal cation and oxygen anion states to the conduction and valence bands, as well as the band gap energy (indicated in red for n-type and in black for p-type) are also shown.¹¹

3.3 Multinary metal oxide semiconductors

To overcome the intrinsic limitations of binary metal oxides, an effective strategy is to combine multiple metal cations to form functionalized multinary oxides where the desired properties of different binary oxides are combined by appropriately selecting the metals. Specifically, one possibility is to engineer narrow band gap by mixing, for example, ns^2 cations (for example, Sn^{2+} and Bi^{3+}) with nd^0 cations (for example, V^{5+} , Ti^{4+} and Nb^{5+}), whose coupling between the s and the O 2p leads to an upward dispersion of the VB, whereas the coupling between the p band from the ns^2 cation and the d bands from the nd^0 cation keeps the CB edge lower in energy. In this way, ternary compounds such as $Bi_{20}TiO_{32}$, $SnNb_2O_6$ and $BiVO_4$ can be produced.

Bismuth vanadate ($BiVO_4$) is recognized as one of the most promising metal oxide photoanodes for OER known to date. In the next section, a brief overview on the crystal and electronic structures of this material in relation to its PEC properties is provided.

3.4 $BiVO_4$

$BiVO_4$, with a narrow band gap of about 2.4 eV in the most photoactive monoclinic scheelite phase, thanks to a valence band edge composed of a mixture of unhybridized O $2p_\pi$ and Bi 6s,¹¹ even though preserving a such energetically high conduction band edge located near 0 V vs. RHE that is favourable for H_2 evolution, could reach STH efficiencies of over 9%, corresponding to a theoretical maximum photocurrent density of 7.5 mA cm^{-2} (Figure 3.3), when used with a second absorber with $E_g < 1.9 \text{ eV}$ in a tandem cell.

3.4.1 Crystal and electronic structure

While naturally occurring as the pucherite mineral with an orthorhombic crystal structure, the two polymorphs of BiVO_4 prepared in the laboratory are the dreyerite with a tetragonal (zircon-type) crystal structure and the clinobisvanite, having a monoclinic (scheelite-type) crystal structure. A scheelite-type tetragonal crystal structure also exists, which is a slight modification of the monoclinic clinobisvanite BiVO_4 in terms of the atomic positions of Bi, V, and O. The lattice parameters of the different structure relative to the various BiVO_4 polymorphs are reported, together with the band gap energies, in Table 3.1.

Table 3.1 Crystal structure, lattice parameters and band gap of BiVO_4 polymorphs.^{15,25}

Phase	Crystal structure	Space group	a / Å	b / Å	c / Å	Band gap / eV
Pucherite	orthorhombic	<i>Pnca</i>	5.332	5.06	12.02	
Dreyerite	zircon-type	<i>I4₁/amd</i>	7.303	7.303	6.584	2.9
Clinobisvanite	monoclinic scheelite-type	<i>C₂/c</i>	7.247	11.697	5.09	2.4
Clinobisvanite	tetragonal scheelite-type	<i>I4₁/a</i>	5.147	5.147	11.72 16	2.34

In all BiVO_4 polymorphs each V ion is tetrahedrally coordinated by four O atoms (forming VO_4 tetrahedra), and each Bi ion is dodecahedrally coordinated by eight O atoms (in BiO_8 dodecahedra units). In the scheelite structure, each BiO_8 dodecahedral unit is surrounded by eight different VO_4 units. The only difference between the tetragonal and monoclinic scheelite structure is that the local environments of V and Bi ions are more significantly distorted in the monoclinic scheelite structure, so that the four-fold symmetry of a tetragonal system is absent (Figure 3.5a). For example, while in a tetragonal scheelite structure all four V–O bond lengths are equal and only two different Bi–O bond lengths exist, in a monoclinic scheelite structure there are two different V–O bond lengths and four different Bi–O bond lengths (Figure 3.5b). It is thanks to this distortion, able to enhance the local polarization and thus the electron–hole separation, that the BiVO_4 monoclinic scheelite structure has proved to be more photocatalytically active than the tetragonal scheelite phase.²⁶

On the other hand, the orthorhombic (Figure 3.5c) and zircon (Figure 3.5d) structure differs from the scheelite structure in the fact that each BiO_8 dodecahedral unit is surrounded by only seven or six VO_4 tetrahedral units, respectively. The zircon-type structure, which can be normally obtained at low synthesis temperatures, can be phase-transformed irreversibly to monoclinic scheelite at calcination temperatures in the 400–500 °C range, which are usually employed in all the synthetic strategies of BiVO_4 material. Interestingly, among the scheelite structures the tetragonal phase is considered

the less thermodynamically stable which undergoes reversible transition to the more stable monoclinic scheelite structure at 255 °C.

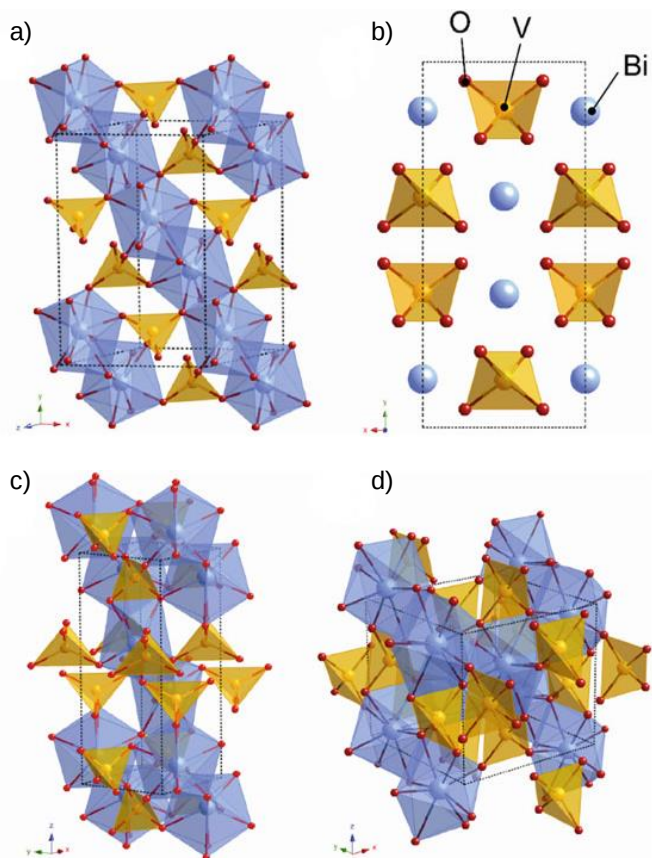


Figure 3.5 Crystal structures of different BiVO_4 polymorphs: (a) clinobisvanite (monoclinic scheelite) with (b) its side view (c-axis), (c) pucherite (orthorhombic) and (d) dreyerite (tetragonal zircon).¹⁵

According to what reported by the pioneer work of Kudo *et al.*, the superior photocatalytic activity of the monoclinic scheelite structure compared to the zircon-type structure of BiVO_4 is strongly correlated to the electronic structure of the material. Indeed, as shown in Figure 3.6, while in the zircon-type BiVO_4 the electronic transition occurring between the O 2p orbitals and the empty V 3d orbitals accounts for a band gap of 2.9 eV, the one verifying in the scheelite-type BiVO_4 and involving the Bi 6s or hybrid Bi 6s-O 2p orbitals and the empty V 3d orbitals gives rise to a narrower band gap energy of 2.4 eV, responsible for the enhanced photoactivity of the monoclinic scheelite structure.

While this attribution was initially supported by the density functional theory (DFT) study conducted by Walsh *et al.*,²⁷ in light of the more recent report of Zhao *et al.*,²⁸ the smaller band gap energy characterizing the monoclinic scheelite structure rather

originates from the crystal distortion which pushes the O 2p states upward and reduces the band gap. Therefore, the optical transition in the scheelite structure still accounts for a narrower band gap of 2.4 eV compared to the zircon type structure despite it now involves the filled O 2p_π and empty V 3d orbitals, thanks to the reduced energy difference between these levels. From now on, the discussion will be focused onto the monoclinic scheelite structure which is the one exhibiting the best PEC properties.

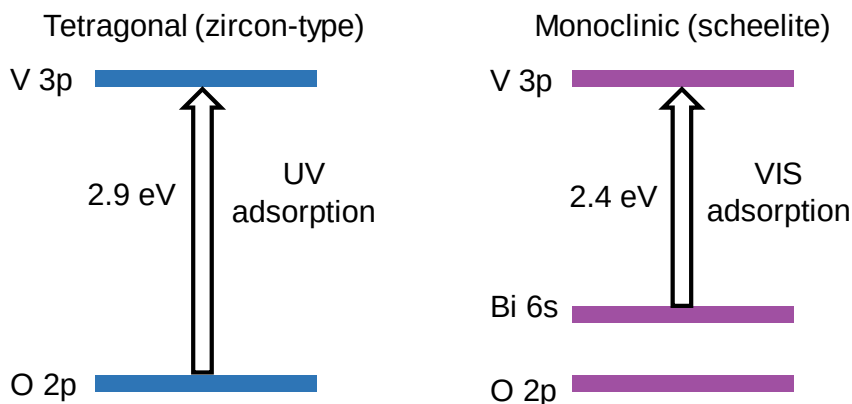


Figure 3.6 Schematic band structure of zircon- and scheelite-type BiVO_4 .

The nature of the optical transition of monoclinic scheelite BiVO_4 in relation to the direct character of its band gap, has been a topic of controversy in the literature. Recently, the indirect nature of BiVO_4 band gap has been assessed through a combination of experimental and theoretical studies²⁹ although a direct transition, responsible for the high absorption coefficient α (10^7 m^{-1}) of BiVO_4 , which is unusual for an indirect semiconductor, also persists at slightly higher energies of ca. 200 meV with respect to the main optical transition.

3.4.2 Photoelectrochemical properties

As already stated in the previous sections, BiVO_4 possesses many attractive features that make it a highly promising photoanode for solar water oxidation. It is composed of inexpensive elements and has a relatively narrow band gap of 2.4 eV with the VB edge, located at ca. 2.4 V vs. RHE, providing sufficient overpotential for holes to photooxidize water. Its CB edge is instead located at ca. 0 V vs. RHE, that is just short of the thermodynamic level for H_2 production and relatively very negative for an *n*-type semiconductor able to exploit visible light. Consequently, optimized BiVO_4 -based systems may be characterized by a flatband potential and a photocurrent onset potential as negative as 0.1 V and 0.25 vs. RHE, respectively.^{30–38} Such favourable photocurrent onset should correspond to the achievement of a photovoltage for water oxidation as high as 1 V, which is quite rare for photoanode capable of exploiting visible light.

Another extraordinary feature distinguishing BiVO₄ from other oxide-based photoanodes is its exceptionally η_{sep} which has been reported to reach values as high as $\geq 90\%$ at 1.23 V vs. RHE^{30,32,34} compared to the typically low $\eta_{\text{sep}} < 10\%$ at 1.23 V vs. RHE observed with other semiconductor materials. A further peculiar advantage of BiVO₄ is the lack of an extremely fast charge surface recombination in competition with the charge transfer kinetics at the electrode/electrolyte interface. Moreover, although being not thermodynamically stable against photocorrosion, the slow kinetics of this process in BiVO₄ is such that it can be suppressed as long as holes are quickly consumed by interfacial charge transfer reactions.²⁴

Despite the many advantages, BiVO₄ shows some major intrinsic limiting factors which are going to be discussed in the next, *i.e.* (i) slow hole transfer kinetics for water oxidation (ii) poor electrical conductivity and (iii) significant recombination of photogenerated electron–hole pairs. Several strategies that have been largely adopted to address these limitations will be also presented.

Although the use of a BiVO₄ photocatalyst for solar oxidation was first reported by Kudo *et al.* in 1998,³⁹ it is only since 2006 that the studies on BiVO₄ have focused on the preparation of electrodes that can be used as photoanodes for photoelectrochemical cells with appreciable photocurrents and quantum efficiencies.⁴⁰ The reported photocurrents, however, remained modest (several hundreds of $\mu\text{A cm}^{-2}$) until few years ago, when the main factors limiting the performance of BiVO₄ material were identified and photocurrents close to the theoretical maximum were thus attained.⁴¹

Among the above-mentioned issues, the large overpotential required to drive the OER, represented by the sluggish water oxidation kinetics leading to accumulation of the photogenerated holes at the surface, where they can recombine with the photopromoted electrons, is one of the main limitations of BiVO₄. The most effective and simple way used to diagnostic a poorly catalytic surface for water oxidation is to compare the photocurrent for water oxidation with that generated in the presence of holes acceptor molecules such as hydrogen peroxide, methanol and sulfite. These species have much faster interfacial hole transfer kinetics than water oxidation, so that 100% of the holes reaching the electrode/electrolyte interface can be assumed to be consumed by photooxidation, thus making the photocurrent achievable with hole acceptors the upper limit for water oxidation.

To overcome the large overpotential required to drive the OER, the modification of the BiVO₄ surface with various oxygen evolution co-catalysts (OECs) layers, such as the most common cobalt phosphate (Co-Pi)^{42–45} and dual-layer Fe and Ni oxy-hydroxides (Fe/NiOOH),^{32,41,46} but also Co-Bi, Ni-Bi, Co₃O₄, RhO₂, Pt, CoO, and FeOOH⁴⁷ has been applied.^{15,48} Interestingly, in addition to the well-established accelerated surface catalysis for the water oxidation reaction, as proved by the detected charge transfer efficiencies close to 100% upon OEC deposition, recent studies proved that the role of co-catalysts could be also to reduce surface recombination by either preventing back electron transfer

or chemically passivating surface traps.^{49,50} As a result, increased magnitude of photocurrent, shift of the photocurrent onset potentials towards the negative direction and improved stability of the BiVO₄ photoanodes are observed after OECs deposition.

Remarkably, a significant reduction of the overpotential for OER, represented by a cathodically shifted photocurrent onset, in addition to a reasonably enhanced photocurrent higher than 1 mA cm⁻² under standard conditions, was attained upon Co-Pi deposition onto BiVO₄ films.^{42,43} In particular, from the similarity of the recorded photocurrent with that found for bare BiVO₄ tested in the presence of H₂O₂, it was possible to demonstrate that the Co-Pi functionalized BiVO₄ electrodes almost completely eliminate performance losses due to electron-hole recombination at the SCLJ, while other factors, *e.g.* the transport of majority carriers, finally limit the overall efficiency of the material.⁵¹ This behaviour is in stark contrast with that of the visible absorber Fe₂O₃ binary oxide, *i.e.* still exhibiting an overpotential of about 300–500 mV even upon Co-Pi co-catalyst incorporation.

A recent work of van de Krol and co-workers, where the effects of Co-Pi co-catalyst were investigated more in depth by means of intensity modulated photocurrent spectroscopy (IMPS) technique, provides a compelling evidence that the main role of Co-Pi on BiVO₄ electrodes is to suppress surface recombination instead of enhancing the water oxidation kinetics by accelerating charge transfer to the electrolyte. This finding, which is surprising in light of the well-known traditional role of Co-Pi as electrocatalyst in enhancing the charge transfer rate constant for water oxidation, accounts also for the fact that, contrarily to earlier assumptions, the BiVO₄ photocurrent is mainly limited by surface recombination instead of surface reaction kinetics.⁴⁹

A further factor to be considered is that the effects produced by OECs strongly depend on the nature of the semiconductor/OEC interface. This is because the semiconductor/OEC interface or the OEC itself can affect the generation, separation, and recombination of photoinduced charge carriers in the semiconductor electrode.⁴⁸ A significative example has been reported by Choi *et al.*,³² who demonstrated the importance of minimizing recombination at the photoanode/OEC junction by comparing the effects of FeOOH and NiOOH OECs on water oxidation conducted by BiVO₄ photoanodes. Indeed, in the frame of this work, although FeOOH formed the best interface with the BiVO₄ film synthesized in that study, the electrodes with FeOOH and NiOOH consecutively deposited outperformed both BiVO₄/FeOOH and BiVO₄/NiOOH films. This result evidenced the possibility to exploit the advantages of both OECs, *i.e.* the minimum recombination exhibited by the BiVO₄/FeOOH interface and the fast water oxidation kinetics achieved by the NiOOH/electrolyte interface. On the other hand, the worst activity found with the opposite sequential OEC deposition in the BiVO₄/NiOOH/FeOOH electrode further supports the idea that the overall performance of a photoanode/OEC is significantly governed by their interface, which can be determinant for the extent of interface recombination (see Figure 3.7).^{24,32,48}

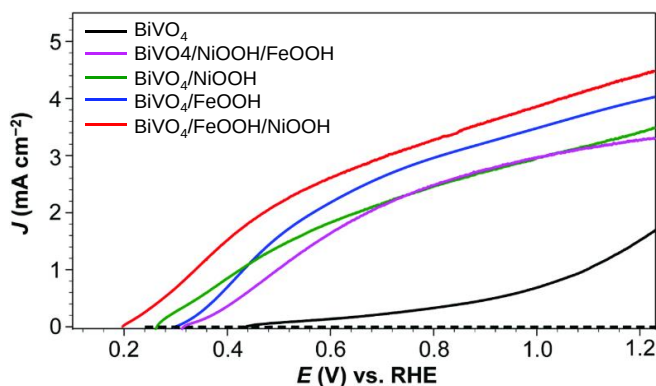


Figure 3.7 Effect of different OECs deposited onto a BiVO₄ electrode on the photocurrents for water oxidation.³²

The second important limitation of BiVO₄ is its poor charge transport properties. As usual in metal oxides, carrier transport occurs via a small polaron hopping conduction mechanism.⁵² As a consequence of the rather low charge carriers mobilities, a significant electron-hole couples recombination may occur in the material bulk before that charges reach the surface or interface, with a consequent decrease of charge separation efficiency. A mobility of 0.02 cm² V⁻¹ s⁻¹ was indeed reported for single crystal BiVO₄ which is one order magnitude smaller than for a polycrystalline BiVO₄,⁵³ that is in turn few orders of magnitude lower compared to other common metal oxides, such as ZnO (200 cm² V⁻¹ s⁻¹) and WO₃ (10 cm² V⁻¹ s⁻¹).

Doping has proved an effective way to increase the electronic conductivity and thus to compensate the relatively low charge carrier mobility in BiVO₄. Among the various metals screened (Mo, W, Fe, B, Cu, Zn, Ti, Nb, Sn, Co, Pb, Rb, Ru, Ag, Ga, Sr, Ir, Ta, Zr, Si and La),^{54,55} only Mo and W stand out as highly effective dopants for BiVO₄, producing significant performance improvements.^{44,56–58} Doping with the higher valence metals Mo and W, *i.e.* having 6 valence electrons and thus acting as donor-type dopants when substituting Bi³⁺ and/or V⁵⁺ in the BiVO₄ lattice (with typical dopant concentrations in the range of 1–10%), has proved an effective strategy to increase the carrier density and hence the conductivity σ in BiVO₄ electrodes,^{11,12,24,33,48} on the basis of the following relation:

$$\sigma = en\mu \quad (3.1)$$

where e is the elementary charge, n the concentration and μ the mobility of charge carriers. According to this relation, doping can further promote the material conductivity and therefore the charge transport, through the increase in charge carriers mobility.⁵⁶ Theoretical studies reported that the electron excess from W or Mo that localize on V atoms, thus forming V⁴⁺ centers and causing local structural distortions, should facilitate the small polaron hopping mechanism governing the charge transport in BiVO₄. In fact,

higher concentration of small polarons would lead to a larger overlap between them, thereby lowering the activation energy of the process.⁵⁶

A second effect of the doping-induced carrier density increase is the enhancement of the electric field in the space charge layer, which facilitates electron–hole separation in the space charge region. This results from the rise of the Fermi level of the *n*-type BiVO₄ upon donor dopants incorporation, which thus shifts in the negative direction along with the energy axis reported as V vs. RHE. As a consequence, the energy difference between the BiVO₄ Fermi level and the redox potential of the electrolyte (or any applied external bias) increases, so that band bending in the space charge region is significantly enhanced compared to the pristine material. However, according to Eq. 2.13, an increasing donor density is also responsible for the decrease of the space charge layer width, thus narrowing the region of the material in which the internal electric field ensures efficient charge separation.

Moreover, a dopant excess may produce impurities at the grain boundaries, *i.e.* acting as recombination or scattering centers, with a consequent reduction of the generated photocurrent. Therefore, the optimum dopant concentration that maximizes electron–hole separation should guarantee the balance between the favourable and unfavourable implications of doping, depending on various factors, such as the absorption coefficient of the host material, its minority carrier diffusion length and the morphology that affects the volume of the space charge layer.^{15,48}

One effective strategy to limit the space charge layer decrease, induced by dopant incorporation, has been the gradient doping, ensuring the formation of a distributed n^+-n homojunction as firstly reported by van de Krol and coworkers.⁵⁸ This concept consists of taking advantage of the mismatch in the Fermi energy level of several BiVO₄ layers with a varying dopant concentration, with the aim to distribute throughout the material bulk the internal electric field, arising at the interface of each couple of layers in contact. In this way, it was possible to significantly increase the charge carrier separation efficiency compared to an homogeneously W-doped BiVO₄, whose space charge layer is only present at the surface of the BiVO₄ electrode, and the photogenerated carriers are driven into the semiconductor bulk material by diffusion instead of the internal electric field.

This concept is better illustrated in Figure 3.8, where the formation of an homojunction between W-doped BiVO₄ (W:BiVO₄) and undoped BiVO₄ (Figure 3.8a), as well as the comparison of the energy band diagrams (Figure 3.8b) of an homogeneously doped W:BiVO₄ (left) and of a ten-step gradient-doped W:BiVO₄ (right) material, are shown. Afterwards, the concept of gradient dopant, as effective strategy to increase the charge separation efficiency in highly doped semiconductors, has been extended to several other semiconducting photoelectrodes.

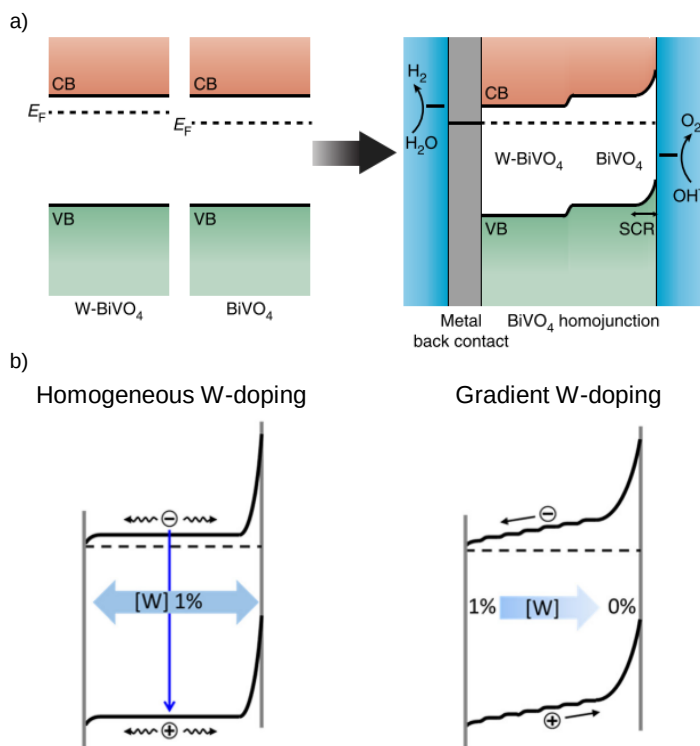


Figure 3.8 (a) Formation of a BiVO_4 homojunction based on the relative difference in Fermi level between W-doped BiVO_4 (W-BiVO_4) and undoped BiVO_4 . After contact, the equilibration of the Fermi level energy of the two electrodes leads to additional band bending on top of the existing one at the space charge region (SCR). (b) Energy band diagram of BiVO_4 with homogeneous W-doping (left) and gradient W-doping (right).^{12,58}

Despite the univocal identification of Mo and W metal ions as most effective donor dopants for BiVO_4 able to improve electron transport through the increase in carrier density, the debate on their additional roles is still open. In an early report Choi *et al.* ascribed the improved electron–hole separation, attained upon an optimum dopant level introduction, to the increased carrier density determined by means of Mott-Schottky analyses.³³

A recent study by Pattengale *et al.*, reporting Transient Absorption Spectroscopy analysis, demonstrated that the enhanced photocurrent observed upon increasing concentration has to be related not only to the enhanced carrier mobility (as a result of the increased electron density) but also to the improved charge separation efficiency, thanks to the diminishing of both electron and hole trap states upon Mo doping.⁵⁹

A similar ambivalent behaviour can be also found for the W doping, as demonstrated by the studies recently conducted by Zhao *et al.*⁶⁰ and Andreu and co-workers,⁶¹ where different roles played by W dopant on the PEC performance of BiVO_4 were identified in addition to the improved carrier density. Indeed, in the first case the incorporation of the

dopant was detected as beneficial also for the surface charge transfer efficiency in addition to the bulk properties, thanks to the induced lowering of the surface charge transfer resistance and formation of active surface states facilitating the charge transfer process.⁶⁰ In a similar way, the W doping strategy reported by Andreu *et al.* was found to affect both the bulk and the surface properties of BiVO₄ by suppressing the electron trapping processes occurring in both cases. In particular, the optimum doping level was found to correspond to that preserving enough high concentration of reactive sites in the material bulk in addition to a high film conductivity, while suppressing the recombination states located at the film surface.⁶¹

It is worth mentioning that the presence of surface states, usually denoted as SS, represents another crucial factor affecting the PEC performance for water oxidation of BiVO₄ and, more in general, of metal oxides. Intriguingly, the SS have been reported to influence charge transfer at the semiconductor/electrolyte interface because they can work as reaction sites (i-SS) and/or recombination centers (r-SS) on the electrode surface.⁶² The nature and the origin of these SS can be various: they can be intrinsic surface defects of the material acting as traps,⁶³ or surface-adsorbed intermediates species, likely surface hydroxyl groups and high-valent metal-oxo complexes, involved in the water oxidation reaction.^{64–66} The latter kind of SS, usually located just before the photocurrent onset potential, have proved to correspond to accumulated surface holes required to trigger the rather sluggish interfacial charge transfer reaction of water oxidation.^{64,67,68}

This was for example the case of hematite photoanodes, where Hamann and co-workers were able to detect, using *in situ* infrared spectroscopy, the formation of a high-valent iron-oxo intermediate as the product of the first hole-transfer reaction on the hematite surface in the water oxidation process, which appeared as a reversible oxidation of surface hydroxide species.⁶⁶ Specifically, they suggested that the hole trapping process into these SS is the necessary first step for water oxidation, which would proceed only after a build-up of the oxidized intermediates.⁶⁹

However, in comparison with hematite photoanodes, the presence of surface states affecting the BiVO₄ electrodes efficiency, and consequently strategies to control their effects on the resultant PEC performance, have been only scarcely investigated to date. Among the few examples, it should be mentioned the photocharging treatment reported by Smith *et al.*, *i.e.* a light-driven alteration of the surface of BiVO₄ favoured under alkaline conditions, able to limit the Fermi level pinning phenomenon normally affecting the surface of untreated BiVO₄ electrodes. The photocharging treatment, involving only the material surface while leaving the bulk properties unchanged, has been associated with the reduction (under illumination and alkaline conditions) of the surface vanadium ions from V⁵⁺ to V⁴⁺. This process has proved to induce higher photocatalytic properties thanks to the creation of oxygen vacancies, leading to the formation of oxy/hydroxyl-based water oxidation intermediates through adsorption of O²⁻ and OH⁻ species on the

electrode surface.⁷⁰ As a result of this surface treatment, a considerably increased photocurrent, a significant cathodic shift in the photocurrent onset potential, induced by the unpinning of the Fermi level of the material (*i.e.*, upon shift of the Fermi level towards the CB of BiVO_4), and an increased photovoltage have been observed,^{70,71} as illustrated in Figure 3.9.

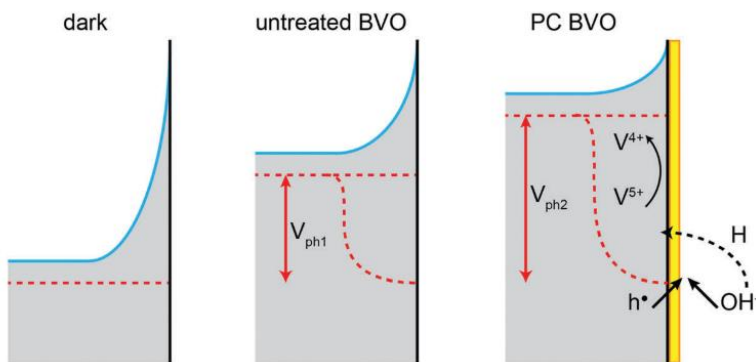


Figure 3.9 Band diagrams of BiVO_4 in the dark and under illumination, before and after the photocharging (PC) treatment.⁷⁰

As already mentioned, W doping of BiVO_4 was proposed by Andreu *et al.*⁶¹ as effective strategy to tune the electron trapping process occurring via reduction of V^{5+} species under illumination, both in the bulk and at the surface of the electrode. Indeed, while surface recombination at the r-SS centers has been reported to occur via the irreversible surface $\text{VO}_2^+/\text{VO}^{2+}$ redox process, the reactive sites i-SS arose from the adsorption of oxy/hydroxyl species at the surface through oxygen vacancies induced by the reversible $\text{V}^{5+}/\text{V}^{4+}$ reduction process in the material bulk. The W doping, which was found to suppress the electron trapping processes both in the bulk and on the material surface, was optimal at intermediate concentration ensuring the removal of r-SS centers while preserving the i-SS ones, as schematically represented in panel b) of Figure 3.10.

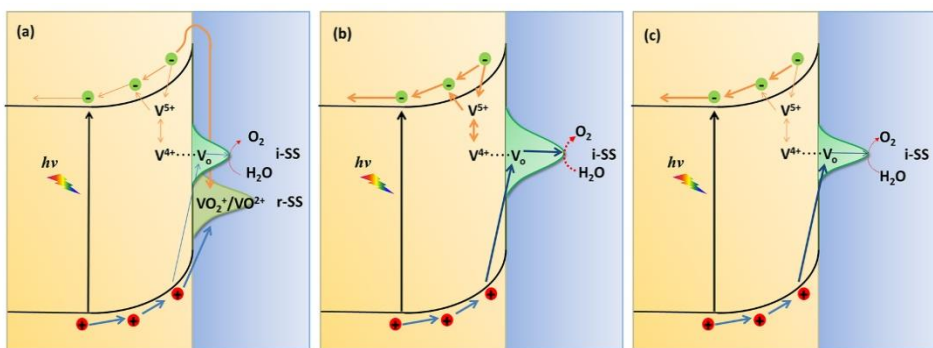


Figure 3.10 Schematic illustration of the W doping-induced electron trapping process proposed by Andreu *et al.*, as a function of (a) low, (b) intermediate and (c) high W doping level. Thicker arrows represent faster processes.⁶¹

Finally, a recent study of Durrant and co-workers reports about a thermally activated electron extraction from oxygen vacancies states, located just below the CB of BiVO₄, which is responsible for the performance enhancement attained in PEC water splitting with increasing the applied operative temperature. Specifically, this relies on the detection of localized electronic states V^{5+}_{OV}/V^{4+}_{OV} deriving from oxygen vacancies formation due to the *n*-type character of BiVO₄, leading to the localization of electrons on neighbouring vanadium sites, which are thus reduced from V^{5+} to V^{4+} . By means of combined optical and electrochemical analyses, these unoccupied/occupied oxygen vacancies states, lying energetically close (within ~ 0.2 eV) to the CB edge of BiVO₄, proved to have not any direct catalytic activity toward water oxidation. Rather, the authors associated the occupied oxygen vacancy states V^{4+}_{OV} in the bulk to deep hole traps, *i.e.* representing the primary loss pathway for the photogenerated VB holes. In fact, the so obtained oxidized V^{5+}_{OV} states, located at a potential more negative than the thermodynamic water oxidation potential of 1.23 V vs. RHE, result to be energetically unable to drive water oxidation. On the other hand, unoccupied oxygen vacancies V^{5+}_{OV} states, prevalently located in the space charge layer in the dark, behave as shallow electron traps, involved in a reversible detrapping process with low activation energy of ~ 0.2 eV, which can be overcome by thermal activation. Therefore, efficient electron extraction by the external circuit, which results in an enhanced PEC performance of BiVO₄ photoanodes, can be activated by higher operative temperatures.⁷²

In order to determine the optimal electrode thickness allowing an effective charge carriers separation, it is necessary to take into account the charge carriers diffusion length, being reported for BiVO₄ in the 70–200 nm range.^{11,42,52,53,73} Indeed, according to literature, the limit thickness value should correspond to the sum of the effective diffusion length (L_p) and the width of the depletion layer (W), the latter typically ranging from 3 to 36 nm for both pristine and doped BiVO₄.⁴² This means that, for a flat and compact BiVO₄-based film, a thickness of *ca.* 230 nm would be the upper limit for carrier transport to ensure efficient charge separation. However, from the optical point of view, in order to guarantee the complete absorption of all incident photons above the BiVO₄ band gap energy, a minimum threshold in the film thickness, based on the measurement of the light penetration depth (δ) of the film,⁷³ is required.

Nanostructuring has proved an efficient strategy to ensure that the film thickness does not exceed the carrier diffusion length, while still absorbing enough light. Therefore, in a nanostructured film, as long as the feature sizes are smaller than the diffusion length of the material plus its depletion width, most of the charge carriers can be collected at the surface or interface before they recombine, and high carrier separation efficiencies can thus be obtained.⁷⁴ Among several synthetic approaches employed for fabricating nanostructured BiVO₄, the first one reported by Choi and co-workers allowed to obtain nanoporous BiVO₄ (see Figure 3.11) with particle size in the ~ 70 –80 nm range through

an electrochemical deposition technique, guarantying the achievement of charge separation efficiencies as high as $> 90\%$ at 1.23 V .³²

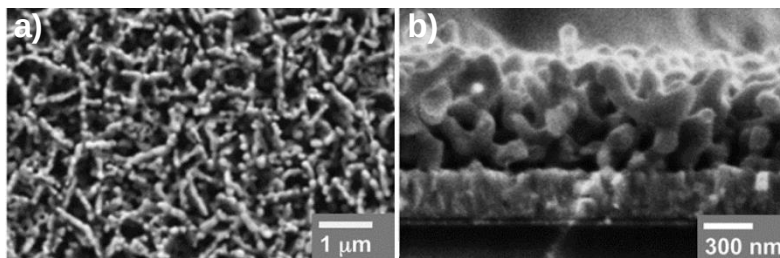


Figure 3.11 Morphologies of nanoporous BiVO_4 electrodes: (a) top view and (b) side-view SEM images.³²

Finally, electron–hole separation has been typically improved through the coupling of BiVO_4 with other metal oxide semiconductors to form heterojunction structures. Indeed, if coupled with a semiconductor whose CB is located at a more positive potential, a rapid electron injection from the CB of BiVO_4 into the CB of the other semiconductor can occur. In this way photogenerated electrons can be physically separated from the holes lying in the BiVO_4 VB, thus effectively reducing charge recombination.^{75,76} The most important example is the heterojunction with the larger band gap WO_3 semiconductor ($E_g = 2.7\text{ eV}$), usually denoted as $\text{WO}_3/\text{BiVO}_4$ heterojunction (Figure 3.12), which has proved to guarantee superior charge separation efficiency, and thus greatly higher overall PEC performance, compared to the two separate semiconductors.^{77–82}

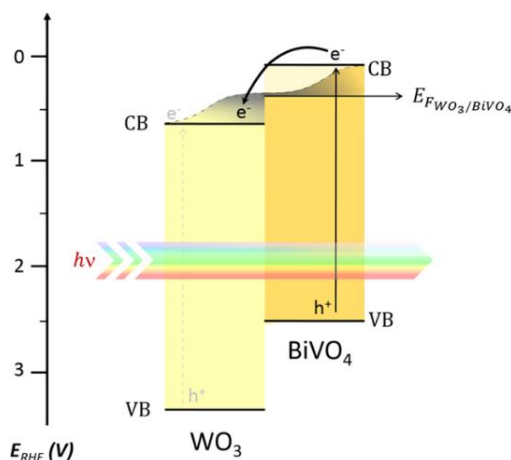


Figure 3.12 Type II band alignment in the $\text{WO}_3/\text{BiVO}_4$ heterojunction favouring the represented electron injection mechanism.⁷⁸

In particular, the $\text{WO}_3/\text{BiVO}_4$ heterojunction system takes advantage of the staggered (type II) band alignment between the two oxides, where both the CB and VB edges of WO_3 (located at *ca.* $+0.4$ and $+3.1\text{ V}$ vs. RHE, respectively) are lower in energy than those of BiVO_4 (lying at *ca.* $+0.02$ and $+2.4\text{ V}$ vs. RHE, respectively). This strategic band

alignment (see Figure 3.12) allows for facile electron injection of photoexcited electrons in BiVO₄ into the WO₃ CB, where their higher mobility leads to rapidly diffusion towards the external circuit, while holes can accumulate in the BiVO₄ counterpart. In this way, enhanced spatial charge separation in the coupled system, thanks to the lower carriers recombination, can be effectively achieved.

An intriguing case of study in literature has been represented by the heterojunction of BiVO₄ with TiO₂ (TiO₂/BiVO₄ heterojunction) in which case, despite the unfavourable Type I band alignment⁷⁵ predicted on the basis of the band edge positions of the pure oxides, which should prevent electron injection from BiVO₄ into TiO₂, enhanced PEC activity for the combined system relatively to the pure components has been often reported. Despite the origin of the experimentally observed enhancement has been variously attributed to different band alignments,^{75,83–85} the appealing “hot electron injection” mechanism proposed by Fu *et al.*,⁸⁶ i.e. based on the transfer of visible-light excited high-energy electrons in BiVO₄ towards the TiO₂ CB (Figure 3.13), has been recently confirmed in our labs.⁸⁷

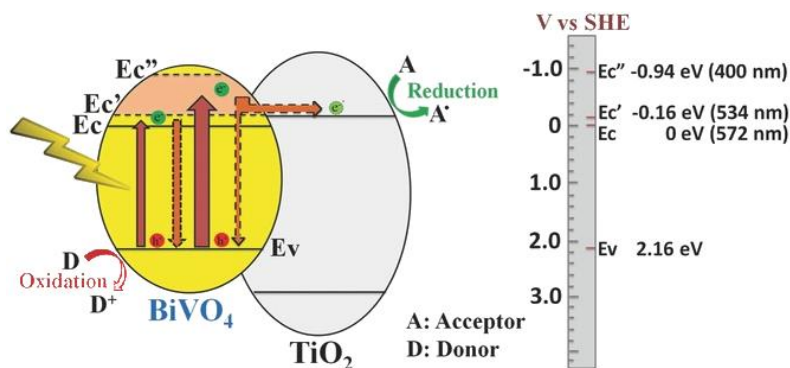


Figure 3.13 Schematic representation of transfer and separation of photogenerated high-energy electrons in TiO₂/BiVO₄ heterojunction nanocomposite under visible illumination.⁸⁶

As it will be detailed in Chapter 5, we were able to demonstrate the superior visible-light induced photocatalytic activity of BiVO₄, after coupling it with the more highly reductive TiO₂ semiconductor, by means of the reduction of methyl viologen, used as an electron acceptor probe having a reduction potential close to that of protons. The resulting electron transfer from photoexcited BiVO₄ to TiO₂, which is responsible for the prolonged lifetimes of electrons photoexcited into BiVO₄ CB, determines two beneficial effects: i) the TiO₂ visible light sensitization thanks to the excellent light harvesting properties of the BiVO₄ counterpart and ii) the production of highly reductive visible-light excited electrons, able to promote water reduction.

To date, one of the highest values of solar photocurrent ever reported for BiVO₄ photoanodes used as single photons absorber, obtained with nanoporous Mo-doped BiVO₄ films deposited onto a nanocone substrate and endowed with a FeOOH/NiOOH co-catalyst, corresponds to 6.0 mA cm⁻² at 1.23 V vs. RHE.⁸⁸ Moreover, a 6.7 mA cm⁻²

photocurrent, *i.e.* within 10% of the theoretical maximum, was achieved by employing a $\text{BiVO}_4/\text{WO}_3$ guest-host nanostructure modified with a Co-Pi OEC.⁸⁹ The onset potential reported for BiVO_4 is typically around 0.2–0.3 V vs. RHE,^{32,53,89} *i.e.* closer to its flatband potential (of *ca.* 0 V vs. RHE) with respect to what observed with other metal oxide photoanodes. Thanks to the relatively good matching of the onset potential with the material flatband, only a small applied external bias is required to achieve overall water splitting, thus making BiVO_4 a particularly well-suited candidate photoanode for tandem cell devices.

Finally, among the various demonstrations of unassisted solar water splitting tandem devices based on BiVO_4 , one of the most performing all-oxide tandem devices where a BiVO_4 -based photoanode is combined with a metal oxide Cu_2O photocathode, has been reported with a 3% STH efficiency.⁹⁰ Another example has been represented by a dual photoabsorber tandem device combining BiVO_4 and Fe_2O_3 photoelectrodes, with extended light harvesting, with a c-Si solar cell, exhibiting a STH efficiencies as high as 7.7%,³⁰ which thus approaches the theoretical maximum of 9%.¹¹ Further details on the realization of unassisted solar water splitting devices based on BiVO_4 -photoanodes will be provided in Section 3.7.

3.5 CuWO_4

Copper tungsten oxide is another much less studied example of semiconductor band gap engineering by combining metal cations to form a ternary oxide. With its relatively narrow band gap of 2.2–2.3 eV, it has been investigated as promising visible-light harvester derivative of the corresponding binary WO_3 . Indeed, compared to WO_3 ($E_g = 2.7$ eV), CuWO_4 not only allows utilization of a greater portion of visible light thanks to the smaller band gap energy, but is also highly chemically and photoelectrochemically stable in the more extended 7–9 pH range, while WO_3 is stable only in strongly acidic conditions. Despite the relatively narrow band gap allowing prediction of a maximum theoretical photocurrent density of 9 mA cm^{-2} ,⁹¹ the achievement of this predicted value has been to date prevented by multiple factors, *i.e.* the sluggish water oxidation kinetics, a low electronic conductivity causing poor charge separation in the bulk, the indirect band gap and the presence of midgap electronic surface states.^{11,12,24,91–95} Overall, these limiting factors account for a photocurrent density value at the thermodynamic water oxidation potential not larger than 0.5 mA cm^{-2} , and for a photocurrent onset potential several hundreds of millivolt more positive than the flatband potential.^{95,96}

3.5.1 Crystal and electronic structure

CuWO_4 has a triclinic crystal structure (space group $P\bar{1}$ with $a = 4.7026 \text{ \AA}$, $b = 5.8389 \text{ \AA}$, $c = 4.8784 \text{ \AA}$, $\alpha = 91.677^\circ$, $\beta = 92.469^\circ$ and $\gamma = 82.805^\circ$),⁹⁷ similar to monoclinic wolframite with an added Jahn–Teller distortion of Cu $3d^9$ reducing the cell symmetry,^{97–99} with deviation from 90° of both α and γ angles.

As shown in Figure 3.14, both Cu and W ions are coordinated octahedrally with six O atoms in an approximately hexagonal close-packing structure composed of a framework of oxygen atoms with the cations occupying half of the octahedral sites.⁹⁷ Cu and W form alternating sequence of layers between the oxygen sheets, giving rise to infinite zigzag chains formed by edge-sharing of alternating CuO_6 and WO_6 octahedra units. The existence of two kinds of connections between the CuO_6 octahedra in CuWO_4 has been reported to determine an antiferromagnetic behaviour.¹⁵

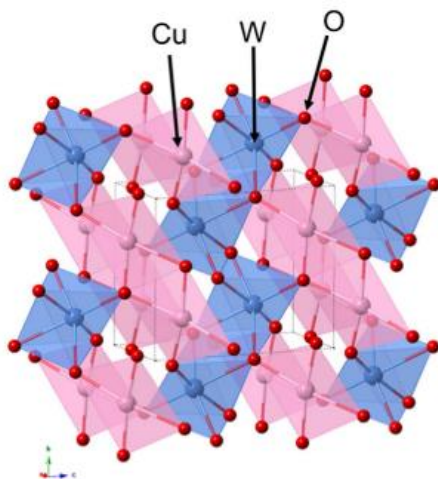


Figure 3.14 Crystal structure of triclinic CuWO_4 .¹²

Both experimental and theoretical studies agree in ascribing the reduced band gap of the ternary CuWO_4 to an upward shift of the VB of CuWO_4 with respect to that of WO_3 , mainly consisting of O 2p orbitals, due to the hybridization between the O 2p orbitals and Cu 3d orbitals of CuWO_4 (Figure 3.4), thus allowing an increased visible-light absorption range.¹⁰⁰

On the other hand, the composition of the CuWO_4 CB is still a topic under debate. While early studies, including the pioneering work of Bartlett *et al.*,¹⁰¹ accounted for a CB mainly composed of W 5d orbitals which makes the flatband potential of CuWO_4 perfectly matching that of WO_3 ^{93,99,101,102} (Figure 3.15), more recent works revealed the primary composition of the CB edge with Cu 3d orbitals, whose localized nature is responsible for the low charge carrier mobility and mid-gap state generation.^{93,95,103,104} The same Bartlett *et al.*, in a subsequent study conducted in 2013,¹⁰⁰ reported a new assessment of the electronic structure of CuWO_4 based on DFT calculations, where its CB was no longer nearly entirely W 5d in character.¹⁰¹ In fact, the incorporation of Cu 3d orbitals into the CB^{103,105} led to a shift of the dominantly in character W 5d CB towards more negative potential with respect to that of WO_3 . According to this model, a narrow CB predominantly composed of Cu $3d_{x^2-y^2}$ orbitals, that reside 0.4–1.0 eV lower in energy than the W 5d states,¹⁰⁰ was predicted (Figure 3.15).

In a more recent work of 2016,¹⁰⁵ Bartlett and co-workers confirmed the previous model accounting for a higher in energy empty W 5d band with respect to the unoccupied Cu 3d sub-band, which dominates the CB edge and acts as recombination centers of photogenerated carriers. At the same time, an upward shift of the VB due to the orbital mixing between O 2p and Cu 3d states was also predicted (Figure 3.15), with a resultant band gap decrease and a consequent better visible light exploitation.

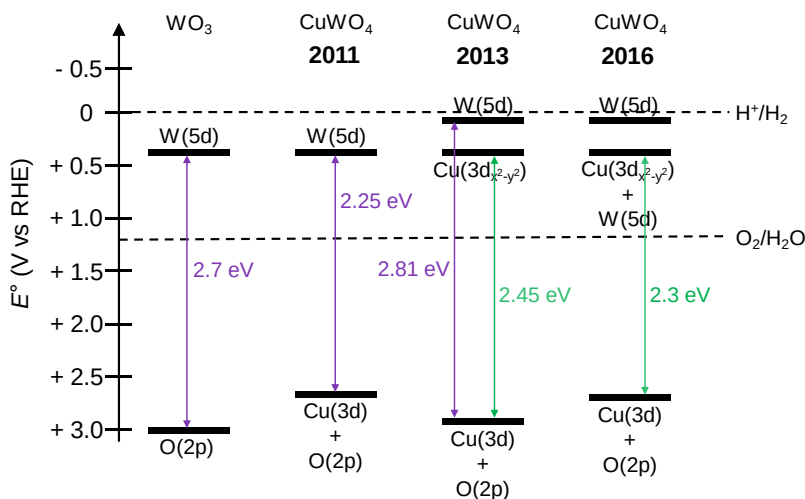


Figure 3.15 Electronic structures of CuWO₄ revisited in the years, compared to WO₃. Band edge potentials are referenced to the reversible hydrogen electrode (RHE).^{100,101,105}

Finally, the even more recent theoretical study conducted by Pacchioni *et al.*,¹⁰⁶ based on DFT calculations, revealed the presence of a narrow band originating from the Cu empty 3d levels having a low dispersion character due to the localized nature of the Cu 3d orbitals. This band is separated by a maximum of 3.6 eV from the top of the VB, which in turn consists of O 2p states mixed with Cu 3d states. In addition, a wider high-energy CB, *i.e.* dominated by W 5d states and Cu 3d states and separated by *ca.* 5 eV from the VB edge, was also predicted (see Figure 3.16). According to this model, the lowest excitation involves the electron transition from a mixed O 2p–Cu 3d state, within the not fully localized VB, to the very localized empty Cu 3d states, forming a narrow band due to their low overlap with the corresponding states of the neighbouring ions. In this way the conductivity in CuWO₄ should follow a different mechanism compared to classical conductivity, which is intermediate between that of a classical semiconductor and that of a Mott-Hubbard insulator, and well-described by a hopping process. The computation of the charge transition levels in CuWO₄ according to this model, within a fully *ab initio* approach, provided a theoretical band gap of 2.1 eV, in excellent agreement with the experimental observations of a band gap energy in the 2.1–2.3 eV range. It is worth noting that the relative position of the Cu 3d empty band from the top of the VB is a matter of controversy,¹⁰⁶ which has been the origin of the conflicting band gap values reported in

literature.¹² The electronic structure of CuWO_4 is complicated by the d^9 configuration of Cu^{2+} ions. The resultant open-shell configuration may thus lead to magnetic interactions influencing the orbital splitting. In light of this, CuWO_4 differs from the typical diamagnetic d^0 metal oxides such as WO_3 , TiO_2 and BiVO_4 , and is instead considered a Mott-Hubbard antiferromagnetic insulator similarly to Fe_2O_3 , being indeed both characterized by low charge carrier mobilities and short hole drift length, representing a fundamental shortcoming for their performance.^{93,100,101,106} This behaviour is typical of the first-row transition metals, whose unpaired spins are highly localized due to the compact radius of 3d orbitals and the strong overlap with bridging oxo ligands, thus leading to low carrier mobility in the bulk.^{93,95,101}

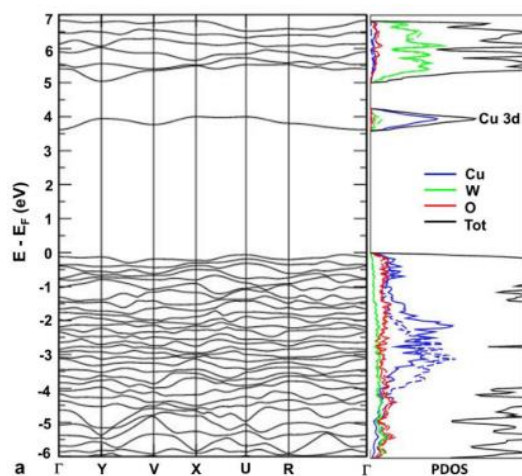


Figure 3.16 Band structure (left) and DOS (right) of the computed CuWO_4 unit cell with antiferromagnetic configuration.¹⁰⁶

Another limitation concerning the light harvesting capability of this material is represented by its indirect band gap energy and the consequent low absorption coefficient, so that $\alpha = 6600 \text{ cm}^{-1}$ at 400 nm with a further decrease to only 1715 cm^{-1} at 500 nm. This finding thus requires a thick CuWO_4 layer for optimizing its visible light absorption capability.^{11,12,93,95,100,101}

3.5.2 Photoelectrochemical properties

The research efforts focused on improving the PEC performance of CuWO_4 photoanodes for water oxidation have been intensified in the very few last years, with the pioneering work of Bartlett and co-workers in 2011, drawing attention to this material as a much more stable and better visible light absorber alternative to WO_3 for water oxidation in neutral pH conditions.¹⁰¹ Since that, several attempts have been addressed to mitigate the major limitation of this semiconductor, *i.e.* poor charge carrier transport within the material bulk due to low charge carrier mobility ($\sim 0.006 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and short charge diffusion length ($\sim 30 \text{ nm}$).¹⁰⁷ As a consequence, CuWO_4 -based materials generally

suffer of an extremely poor electron–hole couples separation and an inefficient charge carrier transfer at the electrode/electrolyte interface, possibly due to the presence of midgap surface states, acting as recombination centers.^{12,24,93,95}

Indeed, the studies on PEC water oxidation conducted with a CuWO_4 photoanode in the presence of Na_2SO_3 ,¹⁰⁸ which was found to be a more suitable hole scavenger compared to H_2O_2 generating the so-called current doubling effect,^{109,110} have shown a photocurrent enhancement compared to pure water oxidation only in the low bias region (<1.23 V vs. RHE). Comparable photocurrents for sulfite and water oxidation were instead detected in the high bias region (>1.23 V vs. RHE) as evidenced in Figure 3.17.¹⁰⁸ The behaviour observed over the entire potential region is a proof of the extremely poor charge separation as major challenge in the practical use of CuWO_4 -based photoanodes.

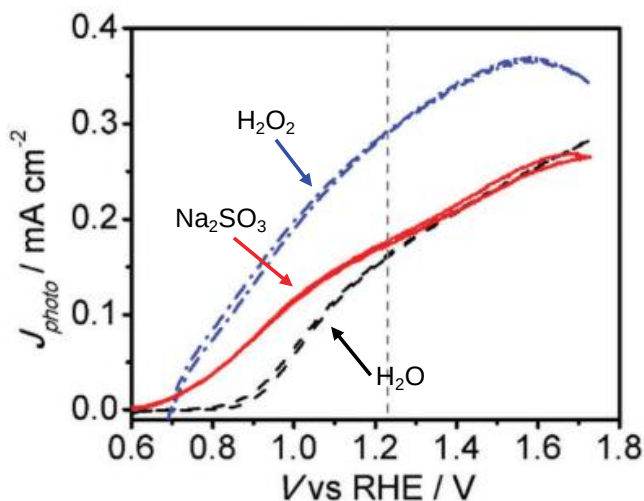


Figure 3.17 J - V curves of a CuWO_4 electrode immersed in a pH 9.0 KBi electrolyte in contact with H_2O (black dashed curve), Na_2SO_3 (red solid curve) and H_2O_2 (blue dash dot) under 1 sun illumination.¹⁰⁸

One approach to improve the low mobility of charge carriers due to the localized nature of the $\text{Cu}(3d)$ orbitals contributing to the CB, has been n -type doping. In this way, the resultant doping-induced carrier density increase may thus enhance the charge transport properties and, consequently, also electron–hole separation. Among the various attempts in doping the CuWO_4 lattice at the octahedrally coordinated Cu^{2+} with isovalent metal elements such as Zn, Co, Mn, and Ni, only Fe^{3+} loading has revealed successful in improving the PEC performance for both water and H_2O_2 oxidation. The doping with Fe^{3+} , chosen as a donor-type dopant at Cu^{2+} sites due to the relatively similar ionic radii between the two ions and the good compatibility with CuWO_4 crystal structure, has resulted in a 50% increase of charge separation efficiency and photocurrent at 1.23 V vs. RHE,¹⁰⁹ although the carrier separation efficiency remains below the 8% (Figure 3.18), thus suggesting that charge carriers still tend to recombine before reaching the electrode

surface. Concerning other metal doping attempts reported to date, it was found that Zn addition does not improve photocurrent densities, while Co behaves as a recombination center, through the possible introduction of additional, highly localized 3d midgap states acting as traps for the photogenerated couples, which thus quickly recombine before being collected to perform the oxidation reaction.¹⁰⁵ This behaviour has highlighted the need to properly select dopants for CuWO₄ matrix in order to avoid the introduction of additional and detrimental surface trap states.

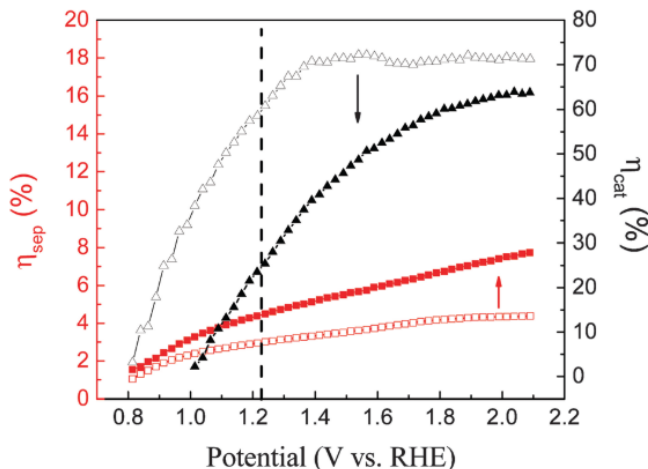


Figure 3.18 Separation efficiency (in red) and catalytic efficiency (in black) for pure CuWO₄ films (hollow data points) and 0.3% Fe-doped CuWO₄ films (solid data points) as a function of the applied potential. The black arrow downwards shows the decrease in catalytic efficiency upon doping, while the red arrow upwards shows the increase in separation efficiency upon doping.¹⁰⁸

Also the generation of oxygen vacancies induced by thermal treatment of CuWO₄ electrodes in a nitrogen¹¹¹ or hydrogen^{112,113} atmosphere has proved effective in improving the photoanodes PEC performance through the enhancement of the charge carrier density, accompanied by an increase in the concentration of W⁵⁺ in CuWO₄ material.¹¹² However, as reported by Diao *et al.*,¹¹² a modest increase in photocurrent density from 0.30 mA cm⁻² to 0.45 mA cm⁻² was provided by the optimized CuWO₄ after annealing in hydrogen atmosphere.

Fabrication of nanostructured films with a particle size smaller than the low charge carrier diffusion length of CuWO₄, corresponding to *ca.* 30 nm,¹⁰⁷ has been employed as an additional strategy to improve charge separation through the reduction of the migration distance of the photogenerated carriers. For example, Li *et al.* reported on a photoanode composed of vertically oriented CuWO₄ nanoflakes, with proper dimensions with respect to the carrier diffusion length, however still exhibiting a photocurrent density no higher than *ca.* 0.4 mA cm⁻² at 1.23 V vs. RHE.¹¹⁴

Coupling CuWO₄ in heterojunctions with other semiconductors is another way to overcome its fast charge recombination drawback and to simultaneously expand the

spectral range of light absorption gained by the photoanode material. Also in this case the most studied is the $\text{CuWO}_4/\text{WO}_3$ type-II heterojunction system (Figure 3.19a),^{115,116} providing a more effective electron-hole separation, and therefore enhanced PEC performance, compared to each of the two individual compounds. This is allowed by the staggered bands configuration allowing accumulation of holes on CuWO_4 and electrons on the WO_3 counterpart, where water oxidation and reduction can occur, respectively. An example is given by the $\text{CuWO}_4/\text{WO}_3$ heterojunction plates array films obtained via hydrothermal synthesis, able to produce a much higher photocurrent density of 1.21 mA cm^{-2} at $1.5 \text{ V vs. Ag/AgCl}$ with respect to that attained by pure CuWO_4 electrodes.¹¹⁷ The heterojunction between CuWO_4 with BiVO_4 ,¹¹⁸ represents another favourable Type II band-edge offsets system (Figure 3.19b), providing higher photocurrent production compared to the isolated constituents, either in Na_2SO_4 or NaHCO_3 electrolyte (buffered at pH 7).

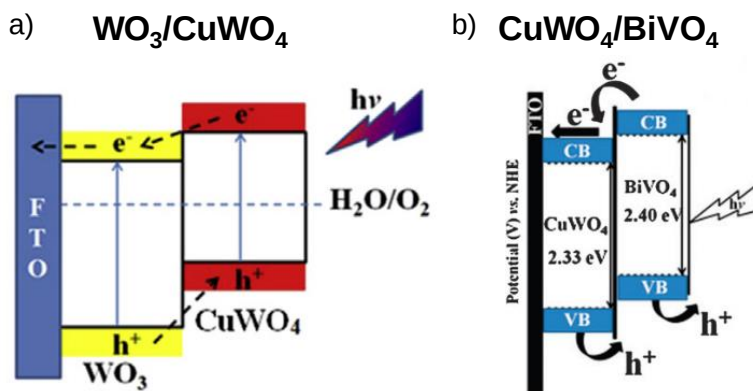


Figure 3.19 Schematic representation of the energy level diagram for the FTO/ $\text{WO}_3/\text{CuWO}_4$ and the FTO/ $\text{CuWO}_4/\text{BiVO}_4$ heterojunction systems.^{117,118}

The minor limitation of CuWO_4 material, *i.e.* the not so low charge transfer efficiency from the electrode surface to the electrolyte, seems not to be easily solved by depositing an OEC layer, as instead occurs with BiVO_4 photoanodes. This may be related to the presence of a large density of midgap states at the CuWO_4 surface.^{93,119} Indeed, there is only one case of study reporting a relevant photocurrent increase attained upon the incorporation of manganese phosphate (MnPO), as OEC, in both a single CuWO_4 or $\text{CuWO}_4/\text{WO}_3$ heterojunction system.^{105,116} Since it was reported that OER may proceed through a midgap state which dictates hole transfer rate for water oxidization,^{108,119} the selection of a proper co-catalyst, whose activation potential is compatible with the energy of the midgap state, is a critical point. While the existence and involvement of these surface states in water oxidation has been ascertained by different studies, the evaluation of the specific energetic location and the origin of such states is however elusive.^{91,93,95,105} In any case, the presence of surface states in CuWO_4 photoelectrodes have been identified as a possible origin of its typically low photocurrent generation.

The first demonstration of surface states in polycrystalline CuWO_4 film, reported by a comprehensive EIS study of Bartlett and co-workers,⁹³ accounts for the presence of permanent surface states detected in the 0.81–1.01 V vs. RHE potential region and responsible for Fermi level pinning. As a result, these surface states worked as detrimental charge carrier recombination centers, *i.e.* the photocurrent onset potential being ~ 400 mV shifted with respect to the materials CB edge energy. This behaviour has been attributed to slow water oxidation reaction proceeding through the midgap states. The occurrence of Fermi level pinning in the Mott-Schottky plot, recorded both in the dark and under illumination, suggested the permanent (and not light-induced) nature of the detected states. Intrinsic intra band gap states are a common feature of real materials and can arise from surface termination of the crystal lattice, defects at the surface, large differences between the bulk crystal and the surface composition, or even from donor species adsorbed at the electrode surface. Specifically, in the examined work they were identified with the strongly localized $\text{Cu}(3d)$ -based states arising from the $\text{Cu}(3d_{x^2-y^2})$ orbitals resulting from Jahn–Teller distortion of Cu^{2+} , which would lead to low carrier mobilities in the bulk as well as to surface recombination and poor carrier transport kinetics, responsible for the limited reaction rate.^{93,105} The resulting electronic structure of CuWO_4 under illumination is reproduced in Figure 3.20, where excitation in the bulk near the depletion region is followed by different possible charge transfer paths for both holes and electrons. Water oxidation can indeed proceed either directly, *i.e.* through the interaction with holes photogenerated in the valence band, or via midgap states where VB holes can be effectively trapped. Similarly, electrons photogenerated in the CB can migrate to the back-contact, recombine with holes lying in the VB or trapped at the midgap states, or even interact with surface intermediates formed during water oxidation reaction.⁹³

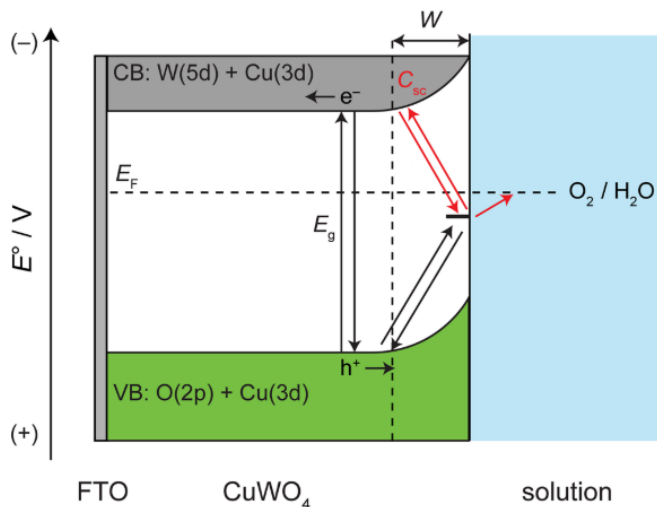


Figure 3.20 Proposed physical model for possible charge-carrier pathways in CuWO_4 : excitation, midgap state trapping and charge-transfer reactions to solution.⁹³

Conversely, by means of EIS measurements, Hamann and co-workers⁹¹ detected surface states of different nature, *i.e.* not Cu orbitals-based, in their CuWO₄ films. In this study, since surface states were observed only under electrochemical or photoelectrochemical water oxidation conditions, *i.e.* at a potential closely related to the water oxidation onset potential, it was deduced that they are not to be considered as intrinsic states but as water oxidation intermediate species, similarly to what observed with hematite electrodes.⁶⁶ However, also this kind of surface states may interact with photogenerated CB electrons, thus causing a delay in the photocurrent onset potential for water oxidation. An additional bias is in fact required to reduce the surface electron concentration and the undesired charge carrier recombination. Both the nature and the negative impact of these surface states on PEC water oxidation were further confirmed by two recent studies. These works shed light on the presence of intra band gap Cu²⁺/Cu⁺ states located 0.5 eV below the CB edge and responsible for the low charge carrier mobility and the marked photogenerated charge carriers recombination, both in the bulk and at the electrode/electrolyte interface.^{94,95} The surface states issue could be solved through the addition on the electrode surface of a suitable OEC. This species may in fact provide to photogenerated holes some alternative paths towards the electrode surface, with the main aim to circumvent surface recombination, even though this has revealed a very challenging goal.

Another optimization strategy of CuWO₄ material has concerned the further reduction of its already relatively small band gap by the partial replacement of W⁶⁺ with Mo⁶⁺ ions, with the main aim to further extend the visible light harvesting capability of the ternary oxide. The first related work dated back to 2013 and was reported by Choi *et al.*,¹²⁰ who obtained the optimum CuW_{0.35}Mo_{0.65}O₄ composite compound as solid solution starting from the CuWO₄ and CuMoO₄ precursors. The so obtained quaternary oxide photoanode showed a successful band gap decrease from 2.3 eV to 2.0 eV, as a consequence of the lowering of the CuWO₄ CB edge upon Mo⁶⁺ for W⁶⁺ substitution predicted by DFT calculations, as depicted in Figure 3.21. The consequent increase in photon absorption was also found to correspond to an effective enhancement in photocurrent generation from 0.06 to 0.15 mA cm⁻² at 1.23 V vs. RHE recorded with CuWO₄ and CuW_{0.35}Mo_{0.65}O₄ at pH 7, respectively.

In the following years, the investigation on this apparently promising quaternary oxide has been rarely persevered owing to the thermodynamically unfavourable energy position of the CB for solar H₂ reduction, which is even lower than that of CuWO₄, and to the difficulty in attaining pure-phase materials. However, very recently the interest on this material as photoanode for water oxidation has been renewed, and a larger improvement in photocurrent (passing from 0.07 to 0.46 mA cm⁻² at 1.23 V vs. RHE) compared to the pioneering work of Choi was obtained with an optimum 50% Mo for W substitution, and ascribed to both the improvement of photon utilization and to the increase in charge carrier concentration consequent to Mo atoms incorporation.¹²¹ Despite this, the incident

photon to current efficiency values obtained with the novel material were still low, suggesting that both light absorption and charge collection needed further improvements.

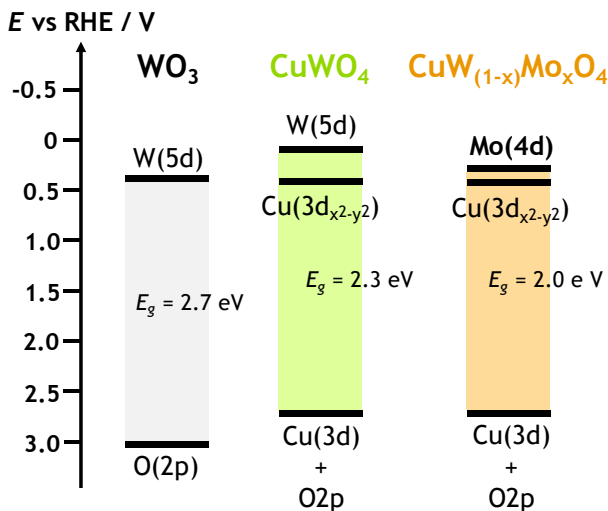


Figure 3.21 Schematic representation of the electronic structure of WO_3 , CuWO_4 and $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ pointing out the progressive reduction in band gap attained moving from the binary to the quaternary oxide.

The effectiveness of Mo doping of CuWO_4 material has also been coupled with the high specific area of nanostructured films with nanoflake morphology, providing a further enhancement in photocurrent up to 0.62 mA cm^{-2} at 1.23 V vs. RHE, upon incorporation of the optimum 32 at% Mo concentration. Also in this case, the observed improvement in activity has been ascribed to both the reduced band gap and significantly improved electron density.¹²² We further contributed to the development of this promising $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ quaternary oxide, through the demonstration of the effectively extended visible light photoactivity up to 650 nm for a 50% degree of Mo for W substitution, compared with pure CuWO_4 photoanode, which is photoactive only in the wavelength range below 550 nm. This was possible by means of a systematic investigation aimed at determining the optimum film thickness for maximized long-wavelength photons exploitation.¹²³ Further details about this study will be provided in Chapter 9.

Despite the above discussed strategies developed with the aim to improve the PEC properties of CuWO_4 photoanodes, a drastic overcoming of its severe bulk charge recombination limitation may be quite challenging.

A novel class of ternary metal oxides known as spinel ferrites will be presented in the next section as alternative family of metal oxides. These materials, although still exhibiting the same bulk separation issue than the above presented copper tungstate-based materials, possess a more favourable CB edge and band gap energy making them as more promising photoanodes for future applications.

3.6 ZnFe₂O₄

Zinc spinel ferrite (ZnFe₂O₄) belongs to the class of spinel ferrites of general formula MFe₂O₄ (M = Ba, Ca, Cu, Co, Mg, Mn, Ni, Zn), an emerging family of metal oxides that has recently drawn increasing attention in the solar energy conversion field thanks to their suitable light harvesting in the visible range ($E_g = 1.4\text{--}2.1$ eV), exceptional long-term photostability and abundant constituent elements.^{11,124,125} Among the spinel ferrites, ZnFe₂O₄ (ZFO) is an *n*-type semiconductor which has been explored as an alternative to α -Fe₂O₃ ($E_g = ca. 2$ eV) since, in addition to preserving the same desired properties as the binary oxide such as a similar band gap energy of *ca.* 2.1 eV, corresponding to a maximum photocurrent density of *ca.* 11 mA cm⁻²,¹²⁶ both the conduction and valence band edges are shifted towards the negative direction by approximately 200 mV, owing to strong hybridization with the Zn 3d states.^{11,127} This shift is also an indication of a more negative flatband potential, closer to the hydrogen evolution potential, according to which a lower external voltage is required for the water oxidation onset to be observed.¹²⁸ This feature makes ZnFe₂O₄ more thermodynamically suitable than Fe₂O₃ for being used in PEC water splitting. However, despite this advantage, the photocurrent density recorded with ZnFe₂O₄ is minor than that of the corresponding binary oxide,^{30,129,130} indicating that ZnFe₂O₄ photoanodes have not yet achieved to date their full potential in relation to both photocurrent onset potential and photocurrent density.

3.6.1 Crystal and electronic structure of spinel ferrites

Spinel ferrites are a class of metal oxides with general formula MFe₂O₄ where M = Zn²⁺, Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, which are known for their remarkable magnetic, catalytic, optical and electrical properties. Among the more general class of spinel metal oxides, having formula AB₂O₄ with A²⁺, B³⁺ and O²⁻ oxidation states, only iron-based spinels (AFe₂O₄ or MFe₂O₄) and cobalt-based spinels (CoB₂O₄) have been found to be photoactive for photocatalytic and PEC applications. As the majority of spinel compounds, spinel ferrites crystallize in the cubic crystal structure (space group *Fd3m*) with the oxygen anions arranged in a pseudo-cubic close-packed (ccp) lattice and the tetrahedral (A or M) and octahedral (B or Fe) cavities occupied by divalent or trivalent cations.^{12,131,132}

The cubic unit cell in AB₂O₄ compounds (Figure 3.22) is formed by 56 atoms: 32 oxygen anions distributed in a cubic close-packed structure and 24 cations occupying 8 of the 64 available tetrahedral sites (A) and 16 of the 32 available octahedral sites (B). Thus, the cell contains eight formula units ($Z = 8$) per cubic unit cell, each of which consists of 32 anions and 24 cations, for a total of 56 atoms, and corresponds to $[\text{Me}_8^{2+}]_A [\text{Me}_{16}^{3+}]_B [\text{O}_{32}^{2-}]_O$. The divalent metal cations commonly used in ferrites can be classified in those preferring A sites (Mn, Zn) and those preferring B sites (Co, Fe, Ni, Cr). Therefore, the crystal structure of spinel ferrites that takes into account all possible

configurations is given by the more general formula $[\text{Me}_{1-\delta}^{2+}\text{Fe}_{\delta}^{3+}]_{\text{A}}[\text{Me}_{\delta}^{2+}\text{Fe}_{2-\delta}^{3+}]_{\text{B}}\text{O}_4$ where δ refers to the *inversion parameter* or *degree of inversion*, which is a metric of cation disorder defined by the fraction of the tetrahedral sites (A) occupied by Fe^{3+} . This means that, in the prototypical normal structure of MFe_2O_4 ($\delta = 0$), Me^{2+} and Fe^{3+} cations occupy the tetrahedral (A) and octahedral (B) sites, respectively, whereas in the complete inverted structure ($\delta = 1$) A sites are occupied by Fe^{3+} and B sites are equally occupied by Zn^{2+} and Fe^{3+} . Spinel can also display a partially inverted structure, which is described by means of the δ parameter. The completely random distribution of Zn^{2+} and Fe^{3+} corresponds to $\delta = 0.67$.^{126,132,133} At standard conditions, the normal spinel structure is the more thermodynamically stable configuration for bulk ZFO. Nevertheless, it is known that ZFO does not usually exhibit a normal structure and the degree of inversion δ closely depends on various factors, such as site preferences of ions in terms of size, covalent bonding effects, crystal field stabilization energies and, especially, synthetic conditions.^{132,134}

The electronic band structure of ZnFe_2O_4 , the most widely studied spinel ferrite, as well as the spinel ferrites of interest in this thesis, is reported in Figure 3.4. For ZnFe_2O_4 materials a direct (E_g^d) and an indirect (E_g^i) optical band gap were experimentally determined, equal to 2.3 eV and 1.9 eV, respectively, regardless of the inversion degree.^{63,134} However, it must be noted that previous reports on different spinel ferrites have pointed out that light absorption via indirect transition does not effectively drive PEC processes.¹³⁵

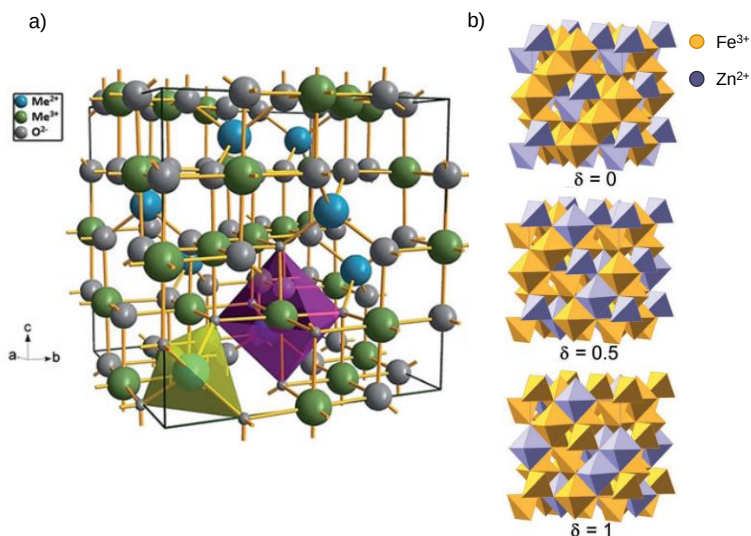


Figure 3.22 (a) The unit cell of MeFe_2O_4 spinel structure.¹³² (b) Crystallographic structures of the prototypical normal zinc ferrite spinel ($\delta = 0$), partially inverted ($\delta = 0.5$) and totally inverted ($\delta = 1$) zinc ferrite spinel (Fe^{3+} and Zn^{2+} polyhedrons occupation are indicated in yellow and purple, respectively).¹²⁶

3.6.2 Photoelectrochemical properties

Different strategies aiming at improving the intrinsic major challenges of ZnFe_2O_4 photoanodes for PEC water oxidation, *i.e.* the extremely poor bulk electron–hole separation in analogy with Fe_2O_3 and the lower charge carriers mobility compared to the binary oxide¹²⁸ ($3 \cdot 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $6 \cdot 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for ZnFe_2O_4 and Fe_2O_3 , respectively²⁴), have been developed, *e.g.* semiconductor heterojunctions formation, nanostructuring and post-synthesis reducing treatments.

The deposition of spinel ferrite thin films as overlayers onto conventional *n*-type metal oxides to form semiconductor heterojunctions, employed as photoanodes, has gained considerable interest. This strategy has been applied for ensuring multitude properties such as the enhancement of charge separation at the oxide heterojunction as in $\text{Fe}_2\text{O}_3/\text{ZnFe}_2\text{O}_4$,^{136–138} the sensitization of the primary oxide to visible light absorption as in $\text{TiO}_2/\text{ZnFe}_2\text{O}_4$,^{139–141} $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ ¹⁴² and $\text{ZnFe}_2\text{O}_4/\text{SrTiO}_3$ ¹⁴³ and, finally, the improvement of BiVO_4 stability in basic media, while simultaneously increasing light absorption, as in the $\text{BiVO}_4/\text{ZnFe}_2\text{O}_4$ heterojunction system.¹⁴⁴

Nanostructuring through various synthetic approaches has been largely adopted with the aim to improve the very modest performance of ZnFe_2O_4 as main active photoanode for PEC water oxidation. Among these, chemical vapor deposition¹⁴⁵ and atomic layer deposition on a nanostructured scaffold¹²⁸ have been employed to obtain nanostructured and macroporous thin films, respectively, with a resulting photocurrent density at the thermodynamic water oxidation potential of few hundreds of μA (*ca.* $300 \mu\text{A cm}^{-2}$). In the first case, the enhanced photocurrent for water oxidation observed with gradual decrease of the average feature size, has been ascribed to the improved photogenerated minority carrier collection at the electrode/electrolyte interface.¹⁴⁵ On the other hand, the 5-fold photocurrent increase attained in the latter work by employing a host-guest architecture, with extended light path compared to a flat film morphology, was attributed to the improved light-harvesting efficiency of the so-obtained absorber material.¹²⁸ Importantly, this study highlighted that, although a 200 mV more negative onset potential was found for ZnFe_2O_4 compared to Fe_2O_3 , thus allowing the water splitting reaction to proceed at a lower external bias, the net photocurrent density recorded with the ternary ZnFe_2O_4 still remained much lower than that produced by the binary oxide.

Nanostructured ZnFe_2O_4 electrodes in the form of nanorods (NR), fabricated directly on the electrode through an innovative chemical bath deposition route based on a β - FeOOH nanorod array precursor and followed by a rapid thermal annealing as schematically represented in Figure 3.23, were firstly reported by Kim and co-workers.^{146,147} Despite the application of post-synthesis treatments such as hybrid microwave annealing¹⁴⁶ with the aim to improve the film crystallinity, and annealing under hydrogen atmosphere¹⁴⁷ to create oxygen vacancies increasing charge carrier density and inducing surface defects passivation, the resulting solar water oxidation

photocurrent density of 0.35 mA cm^{-2} at 1.23 V vs. RHE was still far below the theoretical maximum value of $\text{ca. } 11 \text{ mA cm}^{-2}$.

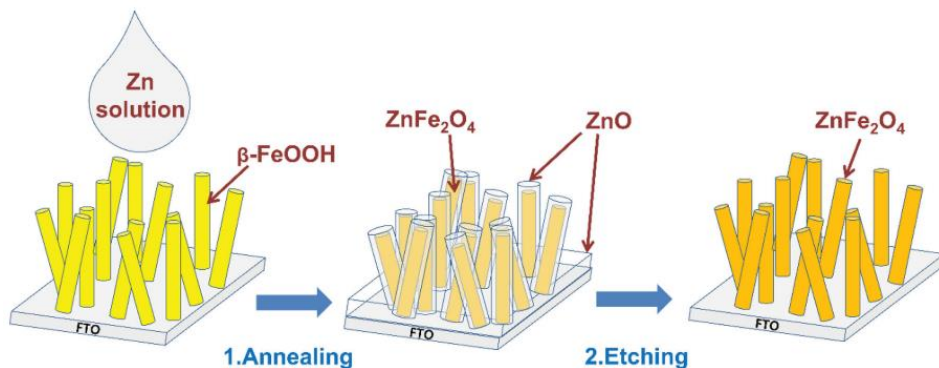


Figure 3.23 Fabrication of ZnFe_2O_4 photoanode with nanorod morphology through an all-solution process, based on a chemical bath deposition layer of $\beta\text{-FeOOH}$ coated with an excess of zinc nitrate, followed by rapid annealing and etching of the excess ZnO crust to afford the pure spinel ferrite film.¹⁴⁶

Although the deposition of a NiFeO_x OEC layer on ZnFe_2O_4 films prepared in the same way depicted in Figure 3.23, and subsequently reduced by a H_2 flux, led to an improved charge transfer efficiency at the electrode/electrolyte interface, the attained overall performance remained low. In this way, Sivula and co-workers⁶³ clearly demonstrated that a poor charge separation efficiency in the material bulk mainly limits the ZnFe_2O_4 performance.

In a more recent work, Sivula and co-workers¹²⁶ established a benchmark performance for solar water oxidation conducted with ZnFe_2O_4 NR films of 1 mA cm^{-2} at 1.23 V vs. RHE , with a photocurrent onset potential of 0.8 V vs. RHE (Figure 3.24). Interestingly, the authors discovered a strong correlation existing between the spinel inversion degree and the charge transport properties in ZnFe_2O_4 NR array electrodes, whose conductivity is based on a small polaron hopping mechanism.

The PEC performance observed with these ZnFe_2O_4 NR photoanodes (Figure 3.24a), synthesized through a similar procedure and followed by an optimizing post-synthesis annealing treatment under hydrogen atmosphere, was found to reflect an opposite trend correlating the spinel inversion degree or the film crystallinity with the applied annealing temperature (Figure 3.24b). Specifically, it was shown that films with a relatively poor film crystallinity but a higher spinel inversion degree (due to cation disorder) exhibited superior photogenerated charge separation efficiency and improved majority charge carrier transport with respect to ZnFe_2O_4 electrodes characterized by higher crystallinity and a lower inversion degree. These latter materials achieved instead better charge injection efficiency at the electrode/electrolyte interface (Figure 3.24c).

Therefore, since charge separation in the bulk (rather than holes transfer efficiency at the electrode surface) represents the major factor influencing the photoactivity of these

materials, the electronic structure arising from cation disorder and accompanying the normal-inverse spinel transition, which should aid charge transport via a hopping mechanism, may enhance the overall PEC performance of ZnFe_2O_4 NR films for solar water oxidation (Figure 3.24d). The so obtained record performance was even higher than that achieved with the synergistic modifications applied by Lee *et al.* in a recent work,¹⁴⁸ where a photocurrent density no higher than $\text{ca. } 0.9 \text{ mA cm}^{-2}$ at the thermodynamic water oxidation potential was achieved despite the multitude strategies adopted, such as the already mentioned hybrid microwave annealing and hydrogen treatment, together with the insertion of a TiO_2 underlayer and the deposition of a NiFeO_x OEC layer.

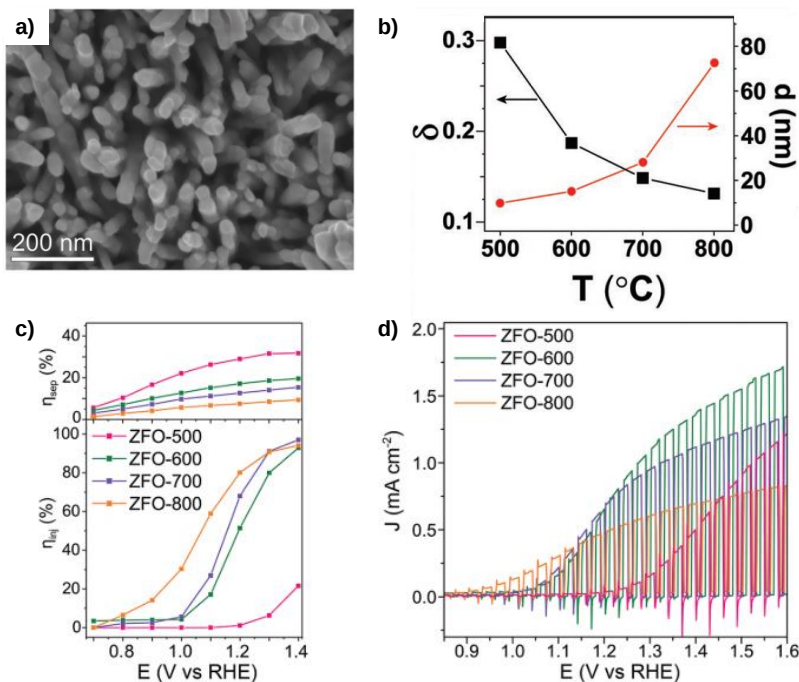


Figure 3.24 Main results of the ZFO NR photoanodes study. (a) Scanning electron microscopy image of the optimum ZFO film annealed at 600 °C. (b) Inverse trend of the spinel inversion degree, δ , (square markers) and of the estimated crystalline domain size, d , (circle markers) as a function of the ZFO synthesis temperature. (c) Estimated charge separation efficiency, η_{sep} , and minority charge carrier injection efficiency, η_{inj} . (d) Current-voltage plots in 1 M NaOH under chopped 1 sun illumination (100 mW cm^{-2}).¹²⁶

It is worth noting that the intriguing results of Sivula *et al.* demonstrate that the factors affecting small polaron-based charge transport can be significantly different from those controlling charge transport through the conduction band, which is generally hindered by structural disorder. They also open the question if the small polaron-based charge transport favoured by cation disorder in NR films plays also critical role in determining the overall PEC properties of flat films, which should be preferred for implementation in tandem devices thanks to their minimized light scattering.

In this context, Sivula and co-workers also developed a generalized solution-based approach for preparing non-light scattering ternary oxide thin films, with the main goal of being employed as photoanodes in tandem devices for solar water splitting.^{149,150} Thanks to the resulting flat morphology, the so obtained films proved also ideal model systems to study the individual effects produced on the electrode's performance by various synthetic parameters, such as annealing temperature, hydrogenation as post-synthesis treatment and film thickness, regardless of the advantageous minor travel distance for photogenerated charge carriers (aiming at reducing electrons-hole bulk recombination) induced by nanostructured architectures.

The so performed optimization study thus allowed to reveal the fundamental role played by the electrode morphology in determining which structural parameter (*i.e.* film crystallinity or structural disorder) mainly impacts on the overall PEC performance, as a function of the material annealing temperature. It was indeed found that, contrary to what observed with ZnFe_2O_4 NR electrodes, in the presence of a flat electrode morphology a satisfied photocurrent improvement can be attained as a result of the combined effects induced by a high film crystallinity (due to the rise in the annealing temperature), a reductive post-synthesis treatment under hydrogen atmosphere and a proper film thickness increase. Interestingly, these results shed light on the fact that the dominant role exerted by structural disorder over film crystallinity on the charge transport properties of ZnFe_2O_4 electrodes with nanorod morphology, cannot be extended to flat films, where PEC performance is instead controlled by the degree of film crystallinity. Specifically, a higher crystallinity is beneficial for the enhancement of the electrode performance over a wide range of flat film thickness. Details about this study will be provided in Chapters 10 and 11.

A further attempt applied to improve the poor bulk charge transport of these materials by increasing the majority carrier density, was represented by Ti^{4+} replacement for Fe^{3+} ions in ZnFe_2O_4 electrodes.¹⁵¹ The modest photocurrent density resulted after applying this doping strategy, together with the lack of beneficial shift in the photocurrent onset potential, account for the ineffectiveness of this strategy when solely applied.

The above discussed approaches suggest that the combination of multiple strategies is strictly required for further improving the performance of ZnFe_2O_4 photoanodes for PEC water oxidation. Specifically, remarkable advances in light absorption capability,¹²⁸ bulk charge separation¹⁴⁵ and photocurrent onset potential^{63,151} will be necessary in order to implement the use of ZnFe_2O_4 as the primary photon absorber in a photoanode system.

3.7 Tandem devices with multinary metal oxides

Within the material class of multinary metal oxides, BiVO_4 is the only one so far employed as photoanode in PEC tandem devices, thanks to its previously discussed unique advantages. In particular, the favourable photocurrent onset potential made BiVO_4 one of the most developed and highest performing metal oxide-based photoanodes. On

the other hand, despite the many efforts already spent in improving the performance of copper tungstate-based materials and spinel ferrites, their implementation in tandem devices is still far to be realized and further optimization strategies are required at this aim.

Among the most notorious examples of BiVO₄-based PEC tandem devices to date realized, the ternary oxide was combined: *i*) as a Co-Pi-catalyzed gradient doped W:BiVO₄ photoanode with a thin-film amorphous silicon solar cell (STH efficiency of 3.6-4.9%),⁵⁸ *ii*) as a guest-host mesoporous WO₃/BiVO₄ with a dye-sensitized solar cell (STH efficiency of 5.7%),¹⁵² *iii*) with a lead-halide perovskite (STH efficiency of 2.5%)¹⁵³ and *iv*) in the form of BiVO₄-Fe₂O₃ dual absorber photoanode with a Si-based multi-junction cathode (STH efficiency of 7.7%).³⁰

Specifically, tandem solar water splitting devices were realized by combining BiVO₄-based photoelectrodes with a double-junction GaAs/InGaAsP (STH efficiency of 8.1%),⁸⁹ with a chalcogenides-based photocathode (STH efficiency of 0.67%)¹⁵⁴ and with a Cu₂O photocathode. Importantly, the last example accounts for either the first demonstration of an all-oxide tandem device (STH efficiency of ~0.5%)¹⁵⁵ or the maximum solar-to-hydrogen conversion efficiency achieved with an all-oxide tandem device (STH efficiency of ~3%).⁹⁰ Therefore, BiVO₄-based tandem devices allowed to overcome the efficiency of tandem devices based on the well-studied binary metal oxides Fe₂O₃ and WO₃.¹⁵⁶

In a typical D4 dual-absorber tandem cell described in Section 2.3.2, where an *n*-type photoanode and a *p*-type photocathode are connected in a stacked configuration, the photovoltages of the two photoelectrodes add up while the same photocurrent must flow through both of them. The efficiency of the device is maximized when the overlap of the absorption regions of the two absorbers is minimized, while the overlap of the photocurrent-voltage (*J*-*V*) curves of the two photoelectrodes, monitored in a three-electrode configuration cell, is the largest possible, as described in the following.¹⁵

The operation of a D4 tandem cell can be indeed determined from the overlap of the *J*-*V* curves of the two electrodes (Figure 3.25), through their crossing point which provides the operating photocurrent of the tandem cell, *J*_{op}, while the sum of the photovoltages of the two photoelectrodes corresponds to the photovoltage of the overall device, *V*_{ph}, shown in Figure 3.25b for a device realized with photoanode A.

In order to evaluate which photoanode should be coupled, on the basis of its photovoltage, to a such photocathode with the aim to maximize the STH efficiency of the resulting PEC tandem device, it should be mentioned that the photovoltage gain for water oxidation (*V*_{ph,a}) corresponds to the difference between the photocurrent onset potential for water oxidation and the thermodynamic potential for water oxidation, 1.23 V vs. RHE (see Figure 3.25b). Therefore, the three hypothetical photoanodes compared in Figure 3.25a are such that, A and B have the same band gap (as shown by the achievement of the same photocurrent value in the high potential region, where photocurrent should be

mainly limited by photon absorption) but different photocurrent onset potential V_{on} (and, specifically, $V_{on,A} < V_{on,B}$). Photoanode C has the same photocurrent onset potential of B ($V_{on,B} = V_{on,C}$), but smaller band gap (as resulting by its higher photocurrent generation in the high bias region).

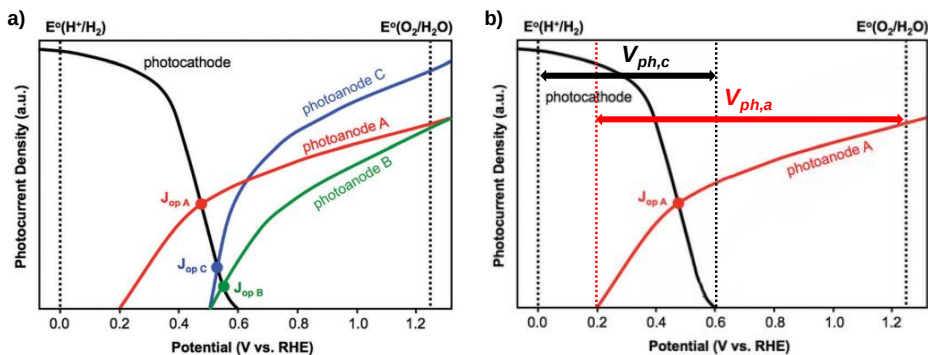


Figure 3.25 (a) Efficiency of a tandem PEC device realized by combining a photocathode with three hypothetical photoanodes, represented by the overlap of the corresponding J – V curves which provides the J_{op} of each resulting cell. (b) The same scheme for a tandem cell realized by coupling the photocathode with photoanode A. The overlap region between the photovoltages delivered by the photocathode and the photoanode, named $V_{ph,c}$ and $V_{ph,a}$, respectively, is related to the efficiency of the overall device.²⁴

According to the above definition of photovoltage for water oxidation, we can estimate the maximum photovoltage for each of the represented photoanodes at ~ 1 V in case of photoanode A and at ~ 0.7 V for photoanodes B and C. Correspondingly, when these photoanodes are combined with any given photocathode like that reported in Figure 3.25 (which can achieve a photovoltage for H_2 evolution, $V_{ph,c}$ of 0.6 V), the maximum operating photocurrent density (J_{op}) for the complete PEC tandem device can be determined by the crossing point between the photoanode and the photocathode J – V curves.¹⁵⁷ Therefore, when comparing the photoanodes A and B (with $V_{on,A} < V_{on,B}$), A can achieve a much higher J_{op} than B, accompanied by a relatively higher STH efficiency (since multiplying J_{op} by 1.23 V provides the STH efficiency of PEC unassisted solar water splitting, according to Eq. 2.18). Photoanode A still provides larger J_{op} and thus higher STH with respect to photoanode C, having a smaller band gap but minor photovoltage.

In order to maximize solar to hydrogen conversion efficiency, the above comparison clearly underlines the importance of achieving high photocurrent density in the low bias region of the J – V curve for each half reaction, in terms of both early photocurrent onset and high fill factor. The most negative photocurrent onset potential that can be achieved by a photoanode is given by its flatband potential E_{FB} , which can be attained only in the absence of surface recombination losses. Moreover, since E_{FB} is not an intrinsic property of a semiconductor, as it can change with varying the carrier density, it is common to refer to the CB edge of a semiconductor, which corresponds to the upper limit of the E_{FB}

position and, therefore, dictates the maximum photovoltage that can be achieved by a given photoanode.

In light of the above discussion, the CB edge position represents a further critical factor to be considered in the evaluation of a photoanode, in addition to the band gap energy dictating the maximum photocurrent density that can be generated by a given material, and the photogenerated charge separation and transfer efficiencies, providing the fraction of carriers that can be effectively utilized for photocurrent generation.

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Chapter 4

Experimental methods and set-ups

4.1 Photoanodes synthetic method

All metal oxide photoanodes investigated in this thesis have been synthesized as compact thin films with a flat morphology, coated on a transparent Fluorinated Tin Oxide (FTO) conductive substrate. The sought planar geometry has provided an excellent optical transparency in the wavelength range outside of their band gap. This characteristic, which makes the greatest discrepancy between flat and nanostructured electrodes, is a crucial requirement to fill for the realization of tandem cells where the semiconductor materials with larger band gap, which are usually those suitable for water oxidation, are employed as top photoelectrodes to optimize solar photon harvesting.¹

In addition to minimize undesired light scattering which may prevent photons to reach the bottom photoelectrode, in the work presented in this thesis compact films photoanodes have been preferred over porous electrodes also because they are more suitable for quantitative impedance analyses. In fact, in contrast with porous films which should be entirely immersed into the electrolyte to be tested, compact films can be easily sealed by gently pressing them against an o-ring. This provides firstly the exact determination of the film area that is exposed to the electrolyte, which is essential for donor density calculation from Mott-Schottky analyses. Moreover, this way makes also the illuminated area to coincide with the wetted film area, to minimize dark current contributions to the total current.²

To promote the formation of an Ohmic contact at the semiconductor/back-contact interface to allow charge extraction by the counter electrode, conductive substrates have been employed as back-contact. Among the optically transparent substrates required for allowing the back illumination of the sample, fluorine-doped tin oxide (FTO) and indium tin oxide (ITO) are the most commonly used thanks to their high band gap in the 3-4 eV range, which make them transparent in the visible range ($T > 75\%$ for 400–900 nm). In the work presented in this thesis, FTO has been chosen as coating of the glass substrates due to its higher thermal stability and chemical resistivity compared to ITO substrates.³ Moreover, classic FTO coatings are stable at high temperatures (up to 600-700 °C) by

preserving their conductivities if the applied annealing treatment is sufficiently short (less than about 30 min).

Thin films of the desired oxide semiconductor materials have been obtained by depositing the corresponding aqueous based precursor solutions onto transparent FTO substrates by means of spin coating technique, followed by a suitable annealing treatment allowing particles growth and crystallization.

4.1.1 Spin coating technique

Spin coating is a simple and inexpensive largely used technique for the fabrication of uniform thin film in the micrometer to nanometer thickness range. It proved particularly advantageous in ensuring highly controlled and reproducible depositions of thin films with high structural homogeneity.

Overall, in this technique an excess amount of the coating solution is deposited on the substrate, which is then rotated at a high speed in the 1000–8000 rpm range, in order to uniformly spread the solution across the substrate surface.

More specifically, a typical spin-coating process consists of four basic stages (Figure 4.1). In the deposition stage, the coating precursor solution is dispensed on the top of the substrate which is fixed to a plate through a vacuum. The amount of the deposited liquid depends on its viscosity and on the size of the substrate to be coated. In the acceleration stage (also known as spin-on), the solution is made to spread uniformly over the substrate, due to centrifugal force. Afterwards, the coated substrate is spun at a higher speed, thus allowing the solution to flow radially outward and the excess liquid to move towards the perimeter where it leaves as droplets (spin-off stage). Finally, a thin film is formed via solvent evaporation or drying, occurring throughout the overall process and promoted by the rapid rotation.⁴ The rate of solvent evaporation depends on the solvent volatility, vapour pressure and ambient conditions.

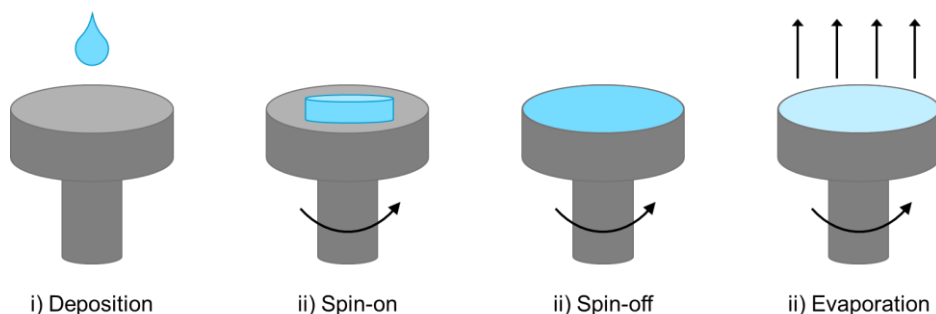


Figure 4.1 Schematic representation of the different stages of spin coating procedure onto a substrate.

The thickness of the resulting deposited layer is determined by multiple parameters, *e.g.* the viscosity and concentration of the coating solution, the rotation speed and the spin time. For example, high spin speed and longer spin time result in the layer thinning, while

an increase in the viscosity and concentration of the solution account for the layer thickening. Therefore, a fine control of the film thickness is possible by managing the various parameters involved in the procedure.

The dependence of the layer thickness on the cited different parameters is well described by the following equation:⁵

$$h = \left(1 - \frac{\rho_A}{\rho_A^0}\right) \cdot \left(\frac{3\eta m}{2\rho_A^0 \omega^2}\right)^{\frac{1}{3}} \quad (4.1)$$

where h is the thickness, ρ_A is the density of the volatile solvent, ρ_A^0 its initial value, η is the solution viscosity, m is the evaporation rate and ω the angular speed. By incorporating the different experimental parameters in a constant, the previous equation can be reduced to:

$$h \propto \frac{1}{\sqrt{\omega}} \quad (4.2)$$

where the coating thickness varies with the spin speed ω according to the $-1/2$ power. This means that the thickness that can be achieved from a given solution spans a relatively narrow range, thus allowing a precise control of the film thickness. The main control parameters of the spin coating process are discussed below.

Acceleration

An accurate control of the acceleration of the substrate towards the ending spin speed is important to define the final properties of the coated film, since the drying process already begins in the first part of the spin cycle. The acceleration step can help to uniformly coat the precursor paste on the substrate surface, which may prove challenging due to the topographical features that the substrate can retain from its prior processing. This may occur through the twisting force applied on the paste during the acceleration stage which aids the dispersal of the paste itself.

Spin speed

The high spin speed step is one of the most important factors since it affects the degree of centrifugal force applied to the liquid as well as the characteristic turbulence of the air immediately above it, thus defining the range of thicknesses that can be achieved from a given solution. In fact, the film thickness is given by the balance between the outward force which spreads the fluid towards the edge of the substrate and the drying rate that affects the viscosity of the paste, which in turn opposes the flow of the liquid over the surface. Generally, the range of working spin speeds span from a minimum of 500 rpm to a maximum of 8000 rpm. Uniform films can be easily attained from about 1000 rpm upwards, by adopting particular care in downing the speed up to 500 rpm.

Spin time

This parameter is generally set to keep the substrate spinning until the film is fully dry, which depends on the boiling point and vapour pressure of the solvent, as well as on the ambient conditions (temperature and humidity) around the substrate during the spin

process. Usually, a spin coating duration of 30 seconds is adequate for most of the processes, while in certain cases when drying takes particularly longer (for example with higher boiling point solvents and/or lower vapour pressure), additional drying steps are required.

Moreover, it's important to choose the proper spin coating method to dispense the solution, which can be either "static" or "dynamic". In a static dispense, the solution is placed upon the substrate and the entire substrate is covered before starting the rotation. The spin coater is then started and ought up to the required speed as fast as possible. In a dynamic dispense, the substrate is firstly started spinning and allowed to reach the desired spin speed before the solution is dispensed on the centre of the substrate. In this mode, the centripetal force can pull the solution from the middle of the substrate across the entire area before the beginning of the drying process. This is a particularly advantageous method when the fluid or substrate itself has poor wetting abilities and can eliminate voids that may otherwise form.

In both cases after the deposition the amorphous spin coated film is dried at temperatures higher than ambient conditions and finally annealed to crystallize. Repeated depositions followed by thermal treatment can be carried out to increase the films thickness as desired. It is worth noting that the control of the film thickness, as great advantage offered by this deposition technique, is crucial for the resultant final PEC activity.

The best thickness for a given semiconductor material should ensure optimal photon utilization without compromising efficient charge diffusion across the film. For this requirement to be satisfied, the charge collection length, given by the sum of the depletion layer, W , and the diffusion length of minority carrier, L_p , should be longer than the light penetration depth, $\delta = \alpha^{-1}$, where α is the optical absorption coefficient of the material.

Experimental methods and set-ups

All the photoanode films investigated in this thesis have been prepared by means of spin coating deposition of aqueous based precursor solutions of the desired metal oxide, onto a 2.5 cm x 2.5 cm transparent glass substrates coated by FTO (referred also as FTO substrates throughout the text). A classic Laurell spin coating model has been employed, in either a static or a dynamic mode, with an *ad-hoc* optimization of the process parameters, by varying the spin rate in the 500-8000 rpm range. Prior to deposition, the FTO substrates were firstly cleaned by 30 min-long subsequent sonication cycles in a soap/water mixture and in ethanol. Afterwards, the clean FTO substrates underwent a 15 min-long UV-cleaner ozone or plasma-cleaning treatment to remove any contaminant organic species deposited onto the FTO surface, which can compromise the uniformity of the deposition, or to increase the substrate wetting ability. The deposited films underwent first a calcination treatment to burn off all the organic material and a subsequent annealing treatment, at a higher temperature depending on the examined

material, to allow the amorphous film to crystallize (Figure 4.2). The solution concentration and the number of deposition steps were also varied up to the obtainment of the desired film thickness.

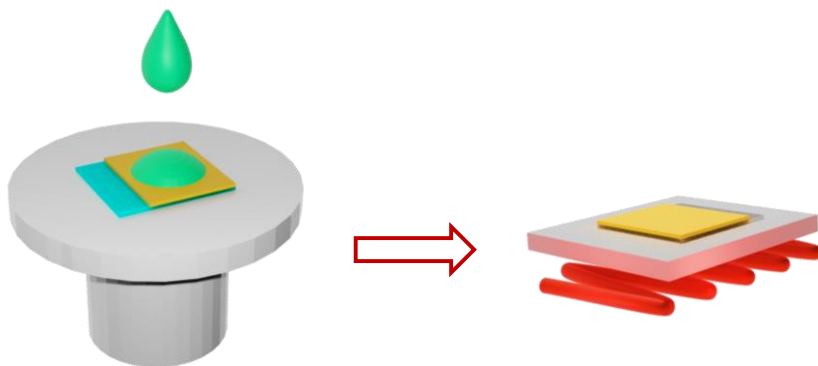


Figure 4.2 Schematic representation of the here employed experimental method of spin coating onto FTO glass substrates and subsequent annealing treatment.

4.2 Physical characterization methods

4.2.1 X-ray diffraction (XRD)

X-Ray diffraction (XRD) is a non-destructive structural characterization technique used for identifying the crystal phase of a material and for quantitative determination through the use of a refinement method (e.g. the Rietveld refinement), providing information on the crystallite size, atomic disorder and phase composition.

The diffraction arises from the interferences of a beam of monochromatic electromagnetic radiation (X-Rays), which is elastically scattered by the electron density of atoms in a periodic lattice. Constructive and destructive interferences between the diffracted X-rays occur when the wavelength of the incident radiation is of the same order of magnitude as the distance d between the parallel crystallographic planes where atoms are arranged (in the order of angstroms).

The condition to observe constructive interferences between the diffused waves, giving rise to the characteristic diffraction pattern of a material phase, is notoriously provided by the Bragg's law:⁶

$$n\lambda = 2d\sin\theta \quad (4.3)$$

where λ is the wavelength of the incident beam, d is the distance between two crystallographic planes, θ is the angle of the incident beam on the crystallographic plane, and n is a positive integer number providing the order of the reflection. According to this law, whose schematic illustration is reported in Figure 4.3, constructive interferences between diffracted X-rays can be observed when the difference in optical path between two X-Ray beams is an integer multiple of the incident radiation wavelength.

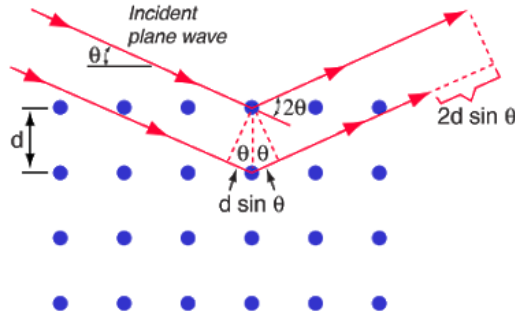


Figure 4.3 Representative sketch of the diffraction of X-Rays (red lines) by a crystalline lattice of ions (blue circles) according to the Bragg's law.

During a measurement, the wavelength of the X-Ray beam is kept constant, while the θ angle is varied. For each θ angle satisfying the Bragg's law, a peak or reflection in the diffractogram can be observed and the corresponding inter-plane distance d can be calculated. A typical diffraction pattern consists of the plot of the reflected intensities as a function of the detecting angle 2θ , comprehensive of both the incident and the diffraction angles. The entire set of reflections of a diffractogram associated with the different crystallographic planes, is therefore indicative of the crystalline phase of a material, which can be identified through the comparison with database diffractograms. When multiple crystalline phases are present, the experimental diffractogram is the sum of the diffractograms of the different phases.

A widely used refinement method for quantitative phase determination of a heterogeneous polyphasic sample is the Rietveld refinement.⁷ It is based on the construction of a fitting model for the entire diffractogram whose parameters are refined and optimized by minimizing the differences between the experimental pattern and the calculated model diffractogram, according to the following expression:

$$\Phi = \sum_{i=1}^n W_i (Y_i^{obs} - Y_i^{calc})^2 \quad (4.4)$$

where W_i is the weight assigned to the i^{th} data point, Y_i^{obs} is the integrated intensity of the observed i^{th} peak and Y_i^{calc} is the integrated intensity of the calculated i^{th} peak.

Experimental methods and set-ups

XRD technique has been employed throughout all this thesis as a fundamental characterization method of the phase purity and structure of the investigated materials. XRD patterns of thin film samples were generally recorded using a Philips PW1820 diffractometer operating at 40 mA and 40 kV, equipped with a Cu-sealed tube that provided $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) as X-ray emitting source.

XRD data of thin films electrodes reported in Chapter 7, 10 and 11 were collected during my internship in the group of Prof. Sivula at the EPFL of Lausanne, by using a Panalytical Empyrean diffractometer system (Theta-Theta, 240 mm) equipped with a

PIXcel-1D detector, in Bragg-Brentano geometry (including hybrid monochromator) and parallel beam optics. A detailed structural analysis by Rietveld refinement was also performed on Powder XRD (PXRD) data reported in Chapter 11, with the aim to extrapolate information on the crystalline domain size and the cation disorder of the investigated samples.

4.2.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM)^{8,9} is an imaging technique based on the interaction of a beam of accelerated electrons with matter to magnify nanoscopic samples, thus providing information on their topography (surface features), morphology (particles shape and size) and elemental composition. Compared to the counterpart optical microscopy, whose resolution is limited by the wavelength λ of visible light radiation (400-700 nm), SEM can reach image resolution down to a few nanometers, thanks to the use of accelerated electrons instead of visible-light photons as incident source. This is possible thanks to the wave-particle duality of electrons, according to which high-energy electrons with wavelengths much smaller than those of visible-light photons can be produced through acceleration under high voltages. This is shown by the following relationship resulting from the De Broglie equation for electron wavelength:

$$\lambda_e = \sqrt{\frac{150}{V}} \quad (4.5)$$

where V represents the accelerating potential and λ_e the electron wavelength. The electron-matter interaction can generate different kinds of signals as represented in Figure 4.4a, which can be collected by different detectors.

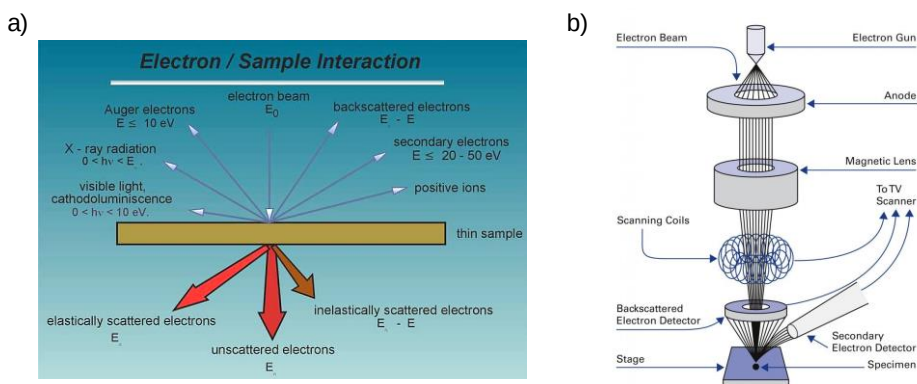


Figure 4.4 (a) Different signals generated from the interaction of a high-energy beam of electrons with a thin specimen, which can be detected by different types of electron microscopes and (b) schematic diagram of the core components of a SEM microscope.

While the transmission electron microscopy (TEM) counterpart exploits three kinds of transmitted electrons (unscattered, elastically scattered and inelastically scattered electrons), SEM operates with two types of electronic signals that are emitted from the

surface of the bombarded sample. These can be divided in: *i*) secondary low-energy electrons (SE) generated by inelastic interactions (*e.g.* electrons ejected from loosely bound outer shell or valence electrons with energy < 0.50 eV) and *ii*) backscattered electrons (BSE), *i.e.* generated by an elastic deflection of primary electrons scattered through of 90° - 180° and emerging back out of the specimen surface. Therefore, a SEM signal can be detected on the same side as the incident beam if the sample is conductive enough to evacuate the incident electrons.

The SE mode is the most common type of signal used for SEM image processing, which accurately produces the topological contrast of the sample such as surface texture and roughness. The BSE mode mostly involves the detection of the signal resulting from the interaction of incident electrons with energy higher than 50 eV with deeper atoms, which is proportional to the average atomic number on the interaction volume. Therefore, in BSE mode the image contrast varies as a function of the atomic number, thus allowing distinction between the boundary of different elements and providing significant information about the structures of the sample surface.

A typical SEM microscope, shown in Figure 4.4b, is composed of the electron gun, *i.e.* the electron source and accelerating anode which can be either of thermoionic or field emission type, electromagnetic lenses to focus the electron beam onto the specimen, a vacuum chamber housing the specimen stage and a selection of detectors to collect the signals emitted from the specimen. Ultra-high vacuum conditions (10^{-7} - 10^{-8} Pa) are required to avoid any kind of collision between the electrons beam and air molecules. While in typical SEM the electron beam is produced by resistive heating with a thermionic filament, in the more advanced field emission microscopes (FESEM) a potential difference between the anode and the cathode is used, instead of heating, to produce the electron beam. The images obtained with the field emitter are typically characterized by higher magnification and better resolution than SEM images resulting from thermionic sources.

Experimental methods and set-ups

SEM images reported in this thesis have been recorded with a model LEO 1430 scanning electron microscope operating at a 10 kV accelerating voltage and at 8 mm working distance. SEM images presented in Chapter 7, 10 and 11 were collected during my internship in the group of Prof. Sivula at the EPFL of Lausanne, by using a Zeiss Gemini 300 scanning electron microscope in HV mode. Field emission scanning electron microscope images were acquired using a SEM Field Emission ZEISS Supra40 scanning electron microscope. In any case, either top view or cross-sectional images have been recorded.

4.2.3 X-Ray photoelectron spectroscopy (XPS)

X-Ray photoelectron spectroscopy (XPS)^{10,11} is a quantitative surface spectroscopy technique providing information on the elementary composition, oxidation states and chemical environment of the surface top (10-200 Å) of a material. It is based on probing the kinetics energy (E_k) of the core electrons which are ejected from the surface atoms of a material under stimulation of an X-ray photon of energy $h\nu$ greater than the binding energy (E_b) of the electron in the atom (photoelectric effect). From the measured kinetics energy and from the known energy of the incident X-Ray beam, it is thus possible to determine the binding energy of each emitted electron according to the following equation:

$$E_b = h\nu - (E_k + \Phi) \quad (4.6)$$

where Φ is a correction factor of the spectrophotometer accounting for the work function of the solid. According to the elemental-sensitive character of the binding energy, it can be then utilized for the identification of unknown elementary surface composition. Useful information can be therefore extrapolated from the energetic and spatial distribution of the emitted core electrons.

In a typical XPS spectrum reporting the electron counts as a function of their binding energy, the peaks displayed at specific E_B values, which are characteristic of the atomic composition of the analyzed sample, allow elemental identification. Moreover, the relative shift in peaks position, known as chemical shift, is indicative of the local chemical environment, *i.e.* the formal oxidation state of the atom and its chemical bonding state in the specimen.

Quantitative analysis can be also performed by integrating the XPS signals to estimate the relative abundance of several elements, thus allowing the determination of the empirical chemical formula of the sample.

Moreover, a further kind of analysis providing a cross-sectional profile of the elemental and chemical composition of the material implies its surface etching with a beam of Ar^+ ions during XPS spectra acquisitions.

Experimentally, XPS spectra can be obtained by recording the number of photoelectrons emitted as a function of their kinetic energy using an appropriate electron energy analyser. Monochromatic soft X-rays with an energy of 200-2000 eV (typically produced by the K_α transition of Al or Mg) are usually employed, and measurements are conducted under high-vacuum conditions (normally 10^{-7} Pa) to allow electrons travelling through the energy analyzer to the detector without interference from gas phase collisions.

Experimental methods and set-ups

X-ray photoelectron spectroscopy (XPS) analyses reported in Chapter 7 were performed with PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany), in collaboration with Dr. Mounir Driss Mensi during my internship in the group of Prof. Sivula at the EPFL of Lausanne. Measurements were carried out by using

a monochromatic Al K α X-ray source of 24.8 W power with a beam size of 100 μm . The spherical capacitor analyzer was set at 45% take-off angle with respect to the sample surface. All peaks were calibrated using adventitious C 1s peak of 284.8 eV to correct charge shift of binding energies after deconvolution. Depth profile analysis was performed by etching the material with an Argon ion sputter gun, at a ~ 5.8 nm/min rate (calibrated on SiO₂), with a sampling depth of ~ 60 nm.

4.2.4 Ultraviolet-visible absorption spectroscopy (UV-Vis)

UV-Vis absorption spectroscopy allows to monitor the change in light absorption caused by electronic transitions inside the material, as a function of the wavelength. For transparent materials as it is the case of the optically transparent thin films investigated in this thesis, light absorption can be described in terms of transmittance (T) or absorbance (A), which are related each other as reported below.

The transmittance, defined as the fraction of light intensity (I) transmitted by the sample with respect to the incident light intensity (I_0) after its interaction with light, can be described by the Lambert-Beer law, reported in Eq. 4.7. This states that the ratio I/I_0 depends on the path length of light through the sample (h), the absorption cross section of the electronic transition (σ), and the difference in the population of the initial (N_1) and the final (N_2) electronic states:

$$T = \frac{I_t}{I_0} = e^{-\sigma(N_1-N_2)h} \quad (4.7)$$

The absorbance A , which is the parameter that is commonly referred to when evaluating the UV-Vis absorption spectra of samples, is related to T through the Beer's law, expressed as:

$$A = -\log T = -\log \frac{I_t}{I_0} \quad (4.8)$$

The absorption coefficient α of a semiconductor material is defined by:¹²

$$\alpha = \frac{4\pi k_e}{\lambda} \quad (4.9)$$

where k_e is the extinction coefficient of a semiconductor and λ the radiation wavelength.

The expression for α of a transparent film can be derived from Eq. 4.7 as follows:

$$\frac{I_t}{I_0} = e^{-\alpha h} \quad (4.10)$$

with $\alpha = \sigma(N_1-N_2)$. By combining Eqs. 4.10 and 4.8 it is possible to simply relate α to the measured absorbance and the film thickness, h , as follows:¹³

$$\alpha(\text{cm}^{-1}) = \frac{\ln(10) \times A}{h(\text{cm})} \quad (4.11)$$

A more accurate estimation of the absorption coefficient of transparent thin materials requires to take into account also the loss in reflectance, so that:

$$\frac{I_t}{(I_0 - I_r)} = e^{-\alpha h} \quad (4.12)$$

The parameter α can thus be expressed in terms of both transmittance T and reflectance $R = I_r/I_0$, with I_r being the reflected light intensity, as follows:

$$\alpha = -\frac{1}{h} \ln \left(\frac{T}{1-R} \right) \quad (4.13)$$

A useful parameter to evaluate the efficiency of the photon absorption process occurring within a sample, is the absorptance denoted as $A\%$ or η_{e^-/h^+} , defined as the fraction of photons absorbed per photons impinging on the sample or, analogously, the fraction of electron-hole (e^-/h^+) pairs generated per incident photon flux. It can be estimated from the measured absorbance of the sample according to:^{13,14}

$$A\% = \eta_{e^-/h^+} = 1 - \frac{I_t}{I_0} = 1 - 10^{-A} \quad (4.14)$$

When the material is characterized by strong light scattering, the Lambert-Beer law is no longer applicable and the loss in absorption due to the dispersion of the radiation needs to be taken into account. The different components that incident light can split into after interaction with the sample are summarized in the following relationship:

$$1 = A + T + R \quad (4.15)$$

where A is the absorptance, T the transmittance and R the reflectance. Eq. 4.15 indicates that, once the incident radiation reaches the sample, it is partly absorbed, partly transmitted and partly reflected (or dispersed). The last phenomenon can occur either as a specular reflection of the radiation with respect to the incidence angle (specular reflectance R_s), or through dispersion of the radiation in many directions (diffuse reflectance R_D).

Generally, UV-Vis absorption spectra of transparent samples are acquired by measuring the T using a basic spectrophotometer consisting of a light source, a monochromator, a sample holder and a detector, and are usually reported as plot of the absorbance as a function of the wavelength. On the other hand, in the case of highly scattering samples (Eq. 4.15), an integrating sphere is required to capture the photons reflected in all directions, thanks to the use of a highly dispersive coating material with poor light absorption.

However, undesired Fabry-Perot interference fringes, *i.e.* manifesting as an oscillatory signal that convolutes the data during transmission measurements, can arise also in the case of very thin samples. In this case it is recommended to perform UV-Vis measurements with a diffuse reflectance or absorption configuration.¹³

UV-Vis absorption spectroscopy proves also as a convenient method to estimate the band gap of a semiconductor, by probing the electronic transitions between the valence band and the conduction band. This analysis is usually carried out by referring to the Tauc plot relationship:

$$(h\nu\alpha)^{\frac{1}{n}} = (h\nu - E_g) \quad (4.16)$$

where $h\nu$ is the incident photon energy, α is the absorption coefficient of the semiconductor material, E_g is the semiconductor optical band gap energy and n is a constant parameter denoting the nature of the band gap transition. Generally, for allowed transitions dominating the basic absorption processes, direct and indirect transitions are described by $n=1/2$ or $n=2$, respectively. By knowing α it is thus possible to extrapolate E_g from the plot of $(h\nu\alpha)^{1/n}$ versus $h\nu$, by determining the energy value where the linear part of the plot intercepts the x-axis.

It is worth noting that, in some cases, *e.g.* when the semiconductor excitation does not occur between the valence band maximum and the conduction band minimum, since it rather involves defect bands or $d-d$ transitions, the so determined optical band gap does not necessarily correspond to the electronic band gap, though still being a good approximation.

Experimental methods and set-ups

The UV-Vis absorption spectra presented in this thesis have been mostly recorded in the transmission mode using a Jasco V-670 spectrophotometer. The measurements of T% and R% reported in Chapter 11 were performed in the Laboratory of Prof. Sivula using a UV-3600 (Shimadzu) spectrometer equipped with an integrating sphere, with the final aim to apply Eq. 4.13 for the α calculation of the investigated films.

4.2.5 Raman spectroscopy

Raman spectroscopy¹⁵ is a complementary technique to UV-Vis absorption spectroscopy allowing to observe lower energy transitions, such as vibrational and rotational modes, from the analysis of the scattered instead of the absorbed photons. It relies on the inelastic scattering occurring when the energy of the incident photon of a monochromatic laser source differs from the energy difference between the ground and the excited states of the sample, so that photon absorption cannot occur. During inelastic Raman scattering, a quantized exchange in energy of the incident radiation with the sample occurs, which results in an energy shift between the incident and the scattered photons, known as Raman shift $\Delta\nu$ and defined as:

$$\Delta\nu = \nu_0 - \nu_1 \quad (4.17)$$

where ν_0 is the excitation wavenumber of the incident radiation and ν_1 is the wavenumber of the scattered photon monitored by the detector.

The Raman shift reflects the energy of the stimulated vibrational or rotational transition of the sample (*i.e.*, the energy spacing between two rotational or vibrational levels) and corresponds to a peak in the Raman spectrum. Specifically, the scattering of the radiation can be described by three different contributions: *i*) the *Rayleigh scattering* (or elastic scattering) occurring when the incident and the scattered photons have the same energy, *ii*) the *Stokes Raman scattering*, a kind of inelastic scattering where the scattered

photons have lower energy than the incident photon and iii) the *anti-Stokes Raman scattering*, consisting of photons which are inelastically scattered with an energy higher than the incident photons. These phenomena correspond to the three different situations depicted in Figure 4.5. While inelastic Raman scattering is such that the excited sample decays to a different rotational or vibrational state than that occupied in the ground state, in Rayleigh scattering the excited species returns to its original energy state.

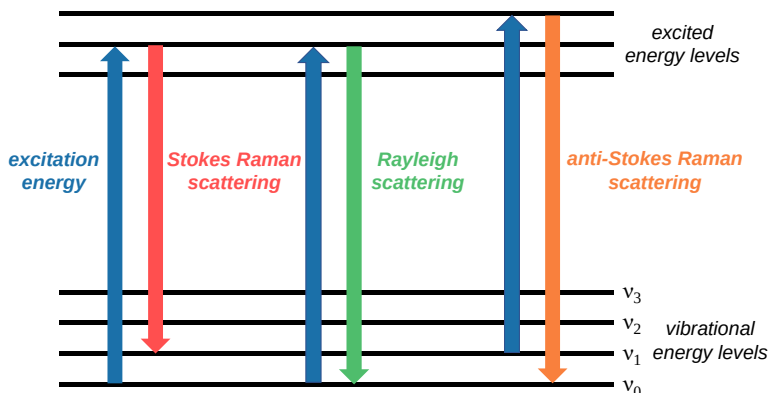


Figure 4.5 Schematic representation of the main transitions among vibrational energy levels involved in the Raman signal.

Commonly, in Raman spectra the number of photons reaching the detector is plotted as counts per second (c.p.s) against the Raman shift $\Delta\nu$. Compared to XRD, Raman does not require the same high degree of sample crystallinity, as it monitors short-range transitions on the scale of chemical bonds. The evaluation of the inelastic Raman-active modes that are excited during a Raman experiment provides a fingerprint of the analysed compound (either in the form of species in solution or amorphous/crystalline solid), thus allowing both the material identification and the test of its phase purity.

Experimental methods and set-ups

The Raman spectra presented in Chapter 7, 10 and 11 were acquired with a LabRam spectrometer (Jobin Yvon Horiba) in the Laboratory of Prof. Sivula. The excitation line was provided by an Ar laser (532.19 nm).

4.2.6 Transient absorption spectroscopy (TAS)

Ultrafast transient absorption spectroscopy has proved a powerful technique to reveal several photoinduced energy transfer processes such as those related to photosynthesis, taking place from hundreds of ps down to less than 50 fs.¹⁶ The detection of such ultrafast processes, *e.g.* the very early events taking place within light-harvesting antenna complexes, has been enabled by the advent of ultrashort tunable laser systems in 1990,¹⁷ with a high time resolution scale (sub 50 fs).

TAS has become a powerful tool to reveal also the ultrafast processes occurring in semiconductor materials after photon absorption, usually taking place in the sub-ps to few

ps timescales, such as separation and recombination of photogenerated electron/hole couples, excitons evolution, and electrons or holes injection or trapping. Therefore, the possibility to study these processes which drastically dictate the overall photoelectrochemical performance, determines the fundamental role of time-resolved spectroscopy in the optimization of PEC devices through the understanding of their limits.

The principle of TAS, also known as pump-probe spectroscopy, illustrated in Figure 4.6, consists of excitation of the sample by means of a monochromatic energetic pump pulse which trigger the investigated photoinduced process, followed by a weak probe pulse sent through the sample with a time delay τ with respect to the pump pulse. The probe pulse then reaches the detector, thus allowing to monitor the evolution of the system in its excited state.

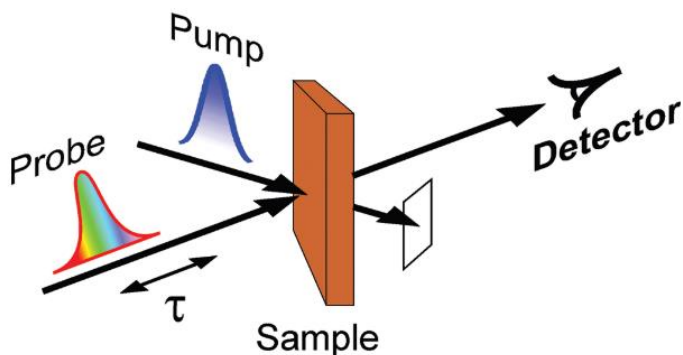


Figure 4.6 Simplified scheme of a pump-probe experiment.¹⁸

The temporal resolution of such experiments depends on the time duration of the pump and the spectral resolution of the probe. Ideally, very short pump pulses and broadband probes are required in order to investigate ultrafast dynamics. However, regarding bandwidth, the pump pulse should not be too broad in order to enable selective excitation of the desired optical transition, thus calling for a compromise between temporal and spectral resolution, while a broadband probe (as short as possible) is required to investigate ultrafast dynamics over a wide range of the UV-Vis-IR spectrum.^{18,19}

The measured parameter is a difference absorbance spectrum ΔA (or change in optical density ΔOD), corresponding to the difference between the absorption spectra of the sample in its excited state and ground state. By recording a ΔA spectrum at each time delay between the pump and the probe, which is varied over the scan, a $\Delta A(\tau, \lambda)$ profile as a function of both time and wavelength can be obtained. From the overall profile, the transient spectra and the transient kinetics traces can be extracted and separately analysed. The first ones, corresponding to the ΔA profiles recorded over a range of varying probe wavelengths at constant τ values, allow to evaluate the processes and species contributing to the change in optical density. The kinetics profiles extrapolated by keeping constant

instead the probe wavelength, allow to monitor the dynamics evolution of the transient species involved over time, *e.g.* charge recombination in a semiconductor material.

The different processes that contribute to the observed ΔA spectra can appear as either negative or positive features, as described in the following. The ground state bleaching process (GSB), corresponding to the ground state depopulation upon excitation of the pump pulse, induces a negative signal at wavelengths equal or shorter than the ground state optical transition. This is due to the minor ground state absorption of the sample in the excited state than before pump excitation. A different possible kind of negative signal is that corresponding to stimulated emission (SE), in which case a photon from the probe pulse can induce emission of another photon from the excited state of the sample to the ground state. Since the photon coming from SE is emitted in the same direction as the probe photon, this process results in an increase of light intensity on the detector, leading to a negative ΔA signal. Contrarily to GSB signal which can be expected to be ubiquitous, SE occurs only for optically allowed transitions and, when present, resembles the fluorescence spectrum profile of the excited sample, *i.e.* being Stokes shifted with respect to the ground-state bleaching. A positive signal can be instead induced by excited state absorption (ESA), consisting of an allowed optical transition occurring from the excited state of the sample towards higher excited states, and enabled by absorption of the photons of the probe pulse with proper energy. The photoinduced absorption process, which is not necessarily observed, can occur in any wavelength region corresponding to optically allowed transitions, and depending on the energy location of the density of states of the system. It should be noticed that in both SE and ESA processes the intensity of the probe pulse is so weak that the excited-state population is not appreciably affected by these processes. A simplified energy diagram with each of the above described processes and the corresponding signals induced in a ΔA spectrum are illustrated in Figure 4.7.

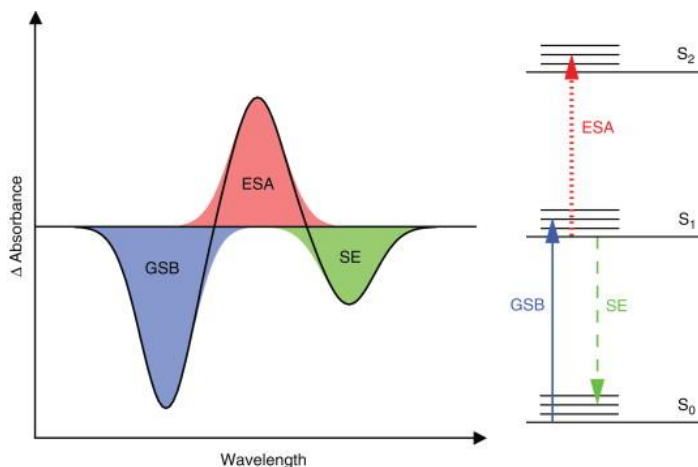


Figure 4.7 Possible types of ΔA signals observable in a transient absorption spectrum (left), and energy level scheme of the corresponding processes (right): ground-state bleaching (GSB), stimulated emission (SE) and excited state absorption (ESA).²⁰

Compared to the counterpart time-resolved fluorescence, time-resolved absorption spectroscopy also allows the detection of the evolution of non-emissive states and dark states.

Transient absorption data analysis

The TA data can be processed either by singular value decomposition of the $S(\lambda, \Delta t)$ matrix, *i.e.* by extracting and analysing single slices at a given λ or τ from the whole data matrix, or by means of the global analysis technique.^{21,22} The first method consists in analysing the TA spectra reporting the signal as a function of wavelength for a given τ , parallelly to the kinetic traces describing the evolution of the system over time at a specific probe wavelength value.

The global analysis approach consists in fitting the whole $S(\lambda, \Delta t)$ matrix considered as a set of $S_i(\lambda, \Delta t_i)$ spectra measured at the specified Δt_i delays. The fitting model $\hat{S}(\lambda, \Delta t)$ is made of a minimal basis set of spectral shapes $B_j(\lambda)$ with $j=1, \dots, N$ and, concerning the Δt -dependence, of a set of N exponentially decaying coefficients. It can be thus represented as the sum of exponentially decaying functions convolved with the impulse response function (IRF), $i(t)$:

$$\hat{S}(\lambda, \Delta t) = \sum_{j=1}^N B_j(\lambda) \cdot \left(\exp\left(-\frac{\Delta t}{\tau_j}\right) \circ i(t) \right) \quad (4.18)$$

where $1/\tau_j$ is the rate of the exponential decay relative to the j component and the symbol ' $\circ$ ' indicates the convolution with the IRF ($i(t)$). In a global analysis run, N can be selected on the basis of statistical or physical considerations. Therefore, a kinetics model consisting of N exponential decays and corresponding amplitudes, should be employed to fit the data, thus providing a set of N spectral shapes $B_j(\lambda)$ and time constants τ_j . Moreover, from the global fitting procedure, also the parameters of a Gaussian impulse response function (IRF), and of a polynomial dispersion function accounting for chirping of the probe pulse, are identified.

The basis set $B_j(\lambda)$ can be represented in two formally different, but physically equivalent, ways, according to whether the spectral shapes are meant to be characteristic of electronic structures that either interconvert sequentially or decay in parallel. The basis elements of the former case are known as Evolution-Associated Spectra (EAS) while the latter representation, to which the model presented in Eq. 4.18 refers, results in a collection of Decay-Associated Spectra (DAS). It is worth noting that the two approaches differ in the spectral shape only, while the same time constants can be identified with both types of representation.

The DAS scheme provides a physical interpretation in terms of specific contributions to spectral changes in different delay intervals or, stated otherwise, of the loss or gain of absorption with a certain lifetime, assembling into the evolving pattern of ΔA spectra. EAS, instead, reflects mixtures of difference spectra of individual electronic states, thus being more intuitively representative of the actual evolution of the spectral shape.

Therefore, the application of such approaches in a least square fitting process by means of variable projection is the principle of global analysis, which results in the estimated rate constants, *i.e.* the reciprocal of the lifetimes for the different electronic structures, as well as in their DAS and EAS spectra.

Experimental methods and set-ups

The set up employed for transient absorption (TA) experiments described in Chapter 8 is illustrated in Figure 4.8. A CPA (chirped pulse amplification) Ti:sapphire laser system (Libra, Coherent) delivering 4 mJ, 100 fs pulses at a fixed wavelength of $\lambda = 800$ nm, with 1 kHz repetition rate, was used as power source.

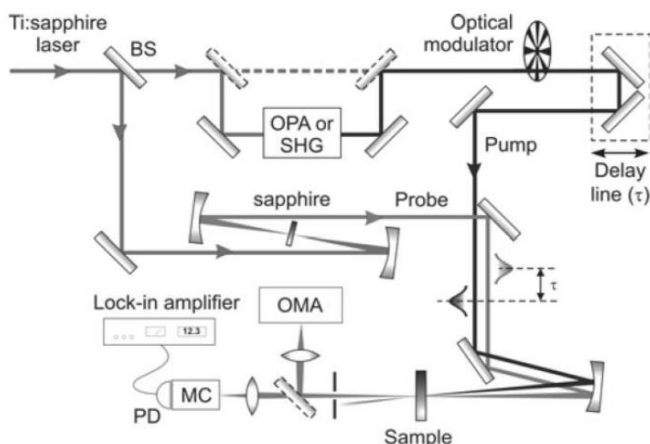


Figure 4.8 Femtosecond pump-probe experimental setup with broadband detection using white light generation. Here, BS is the beam splitter, OMA the optical multichannel analyser, MC the monochromator and PD the photodiode.¹⁹

A 400 μ J fraction of the laser energy was used for the experiment, which was in turn split into a 95% and a 5% fraction by a beam splitter (BS). The more intense 95% fraction was used as pump after being frequency doubled to $\lambda = 400$ nm by either a second harmonic generator (SHG) consisting of a nonlinear β -Barium Borate crystal only capable of frequency doubling, or by an optical parametric amplifier (OPA) allowing to tune the pump energy over the entire visible spectrum. The less intense 5% fraction was instead focused on a CaF_2 crystal to generate the white light continuum probe, covering the 380–680 nm wavelength range. To avoid the pulse chirping effects during the white light generation, according to which the blue light is generated later with respect to the longer wavelength photons, the white light was collected and focused on the sample using only reflective optics.

The passage of the pump was regulated by an optical modulator (chopper) which was set at the same frequency as the laser pulse repetition rate (1 KHz). The delay of the pump with respect to the probe pulses was realized by sending the pump through an optical delay line consisting of a retroreflector mounted on a high-precision motorized computer-

controlled translation stage, before being focused on the sample. Since half of the pump shots was blocked by the chopper, while the broadband probe pulse entirely reached the sample, its attenuated spectrum measured by an optical multichannel analyzer (OMA) corresponded to an alternatively excited and not excited sample. In this way, ΔA spectra at a fixed pump-probe delay can be obtained by subtracting pump-on and pump-off spectra. The temporal resolution of this experiment, limited by the chirp of the white light probe, is usually around 100 fs.

Other experimental details are reported in Chapter 8. All these measurements were carried out in collaboration with the group of Prof. Giulio Cerullo at the Polytechnic University of Milan. Global analysis of the TAS data sets was performed using the Glotaran program.^{21,22}

4.3 Photoelectrochemical characterization methods

In this section, the techniques and the equipment employed to perform photoelectrochemical experiments in the presented work thesis will be described. PEC experiments carried out on the investigated photoelectrodes consisted of probing the performance of each sample in a three-electrode cell configuration under operating conditions, *i.e.* in an aqueous electrolyte solution, under the application of a potential scan (as in voltammetry), a constant bias (as during potentiostat chronoamperometry) or a bias perturbation (as in electrochemical impedance spectroscopy), both in the dark or under light irradiation. Specifically, the standard solar simulated AM 1.5 G (1 Sun) light irradiation conditions, also referred as full lamp irradiation, have been employed in almost all cases except for Incident Photon to Current Efficiency (IPCE) measurements, which were conducted under monochromatic light irradiation.

Moreover, the experimental set-ups adopted for measurements carried out at the University of Milan and in the group of Prof. Sivula at the EPFL of Lausanne, differing in the employed PEC cell, illumination source and potentiostat, will be described.

4.3.1 Back vs. front illumination

The extent of the generated photocurrent often depends on the illumination direction of the electrode, being thus an indication of electron or hole transport limitations in the material bulk. When an *n*-type semiconductor photoanode is irradiated from the back-side, *i.e.* light hits the substrate prior the photoelectrode (Figure 4.9a), most of the incident light is absorbed near the FTO substrate instead of the film surface, and there is a higher density of photogenerated charge carriers closer to the back-contact than to the SCLJ. Consequently, electrons only need to travel a very short distance to reach the back-contact, where they are extracted by the external circuit to be injected into the counter electrode for hydrogen evolution. On the other hand, holes, which under back illumination are generated far from the surface, must be able to diffuse through the bulk of the material without recombining, in order to reach the SCLJ where they can participate to water

oxidation. Therefore, in a photoanode irradiated in back configuration, the hole diffusion length should be greater than or equal to the film thickness, for holes to reach the SCLJ before recombining in the material bulk. Conversely, for a photoanode illuminated from the front-side, *i.e.* when light hits directly the photoelectrode (Figure 4.9b), most of the incident light is absorbed near the surface of the film, with a consequent larger density of photogenerated charge carriers near the SCLJ than at the back of the electrode. In this case, a relatively small hole diffusion length is enough for holes to reach the SCLJ, while electrons need to cross the bulk of the material to reach the substrate back-contact where they are extracted. Therefore, in a photoanode irradiated in front configuration, the electron diffusion length should be greater than or equal to the film thickness, for electron transport in the material bulk to occur efficiently.

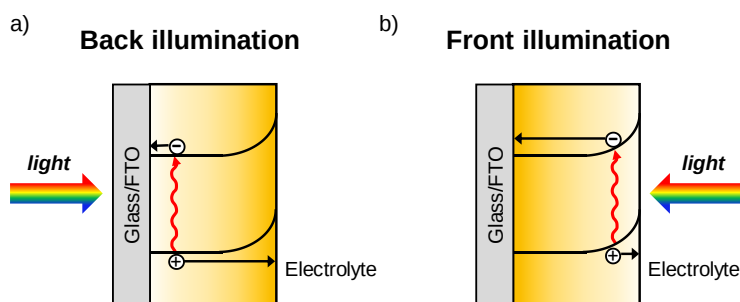


Figure 4.9 (a) Back-side (with illumination through the substrate) and (b) front-side (with illumination through the film) irradiation configurations.²

The evaluation of the carrier diffusion length, which is given by $L = (D\tau)^{1/2}$ where $D = kT\mu/e$ is the diffusion coefficient and μ the carrier mobility, is an important criterium to determine the optimum thickness of a semiconductor material film, in order to guarantee maximum absorption of light without compromising efficient transport of the photogenerated charge carriers. Moreover, the choice of the illumination configuration can be related to which one between the minority and majority charge diffusion lengths predominantly affects charge transport in the bulk.

4.3.2 Three-electrode cell configuration

The performance of the investigated photoanodes was tested in the three-electrode configuration cell, described in the following. Here, the current flowing between the working electrode (WE), represented by the semiconductor electrode itself, and the counter electrode (CE) composed of a platinum wire, is probed under polarization of the WE with respect to the reference electrode (Ref), composed of an Ag/AgCl filled with 3 M or a saturated KCl solution and characterized by a fixed potential. The three electrodes are plunged into an aqueous electrolyte solution and placed into either a custom-made glass cell, equipped with two quartz windows, or a “cappuccino cell”, each of them being connected to a potentiostat. In both the employed cells, the photoanode can be irradiated

either through the film, with incident light crossing firstly a quartz window and the electrolyte (front illumination), or through the transparent FTO substrate (back illumination). The irradiated area of the film in contact with the electrolyte is 0.28 cm^2 or 0.7 cm^2 in the glass cell depending on the use of a shielding mask (under back-side irradiation) or not (under front-side irradiation), respectively. That area corresponds to 0.25 cm^2 in the cappuccino cell, regardless of the employed irradiation configuration.

In the actual operative conditions, *i.e.* photoelectrochemical water splitting reaction, an aqueous electrolyte solution was employed, selected in each case depending on the tested material. In pure water oxidation conditions, where the solvent and the active species to be reduced or oxidized coincide, supporting ions are anyway required due to the poor conductivity of water, to guarantee the attainment of the desired current flow.

In addition, PEC tests were also conducted in the presence of a suitable sacrificial redox agent acting as hole scavenger toward the photoanode, as main oxidizable substrate in solution. It is well known that the photooxidation of a hole acceptor is characterized by a much faster interfacial hole transfer kinetics than water. Therefore, the comparison of photocurrents for water oxidation with those generated in the presence of hole scavengers is a useful simple method to diagnostic any interfacial charge transfer limitation, *i.e.* to assess whether the poor catalytic nature of the photoelectrode is the main limiting factor for photocurrent generation, rather than bulk transport and separation processes.¹⁴

The different electrolyte solutions employed in this thesis were selected in relation to the pH range of stability of the tested semiconductor material. For BiVO_4 , exhibiting stability in a wide (3–11) pH range, neutral pH conditions, which are those usually employed in overall water splitting on tandem devices, were preferred. A 0.5 M Na_2SO_4 solution or a 0.5 M Na_2SO_3 solution, buffered at pH 7 with a 0.5 M potassium phosphate (KPi) buffer, have been employed for testing BiVO_4 -based electrodes in either pure water oxidation or sacrificial redox conditions, respectively (Chapter 5, 6 and 7). The addition of a pH buffer solution is commonly used also to avoid local pH fluctuations in the main species solution. Copper tungstate-based materials (Chapter 8 and 9) were tested both in a pure 0.1 M K_3BO_3 (KBi) solution and in the presence of different hole scavengers, buffered by the KBi solution at pH 9. Finally, water oxidation on zinc spinel ferrite electrodes (Chapter 10 and 11) was performed in a 1 M NaOH solution, both in the absence and in the presence of a 0.5 M Na_2SO_3 solution as hole scavenger.

The potentials measured vs. the Ag/AgCl reference electrode are conveniently referred to the Reversible Hydrogen Electrode (RHE) for a pH-independent metric, according to the Nerst equation:²³

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^0 + 0.059 \times \text{pH} \quad (4.19)$$

where $E(\text{Ag/AgCl})$ is the recorded potential versus the experimentally employed reference electrode, $E^0(\text{Ag/AgCl})$ is the standard potential of the Ag/AgCl redox couple (0.210 V vs. NHE), RT/nF is equal to 0.0591 at room temperature and the pH is that of

the employed electrolyte solution. In the RHE scale, $E(\text{H}^+/\text{H}_2) = 0 \text{ V}$ vs. RHE and $E(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V}$ vs. RHE, irrespective of the pH. This makes this scale more convenient to be used than the NHE one, where $E(\text{H}^+/\text{H}_2) = 0 \text{ V}$ only at unit activity of the H^+ ions and the dissolved H_2 gas.²

4.3.2.1 Custom-made glass cell

The single-compartment glass cell employed in this thesis, provided with an Ag/AgCl reference electrode (3.0 M NaCl) and a platinum wire, is shown in Figure 4.10. The cell is equipped with two windows that host the photoanode and a quartz dish (20 mm diameter), located in figure on the right side and on the left side, respectively. An adequate sealing of the cell is pursued using an o-ring tightened through a Rotulex clip on both the film and the quartz window sides, to avoid leaking of the electrolyte. The three electrodes are thus connected to the potentiostat through electrical clips. In order to know the actual irradiated film area, a shielding mask was placed onto the non-conductive glass side of the photoelectrode when exposing it to light illumination in back-side configuration. This way allows to avoid any poor irradiation uniformity of the electrode and provides a constant irradiated area of $\sim 0.28 \text{ cm}^2$. In this configuration, the power density of the incident light was calibrated to reach 100 mW cm^{-2} (1 Sun) at the photoanode surface location in both back- and front-side configurations, using a silicon photodiode detector.

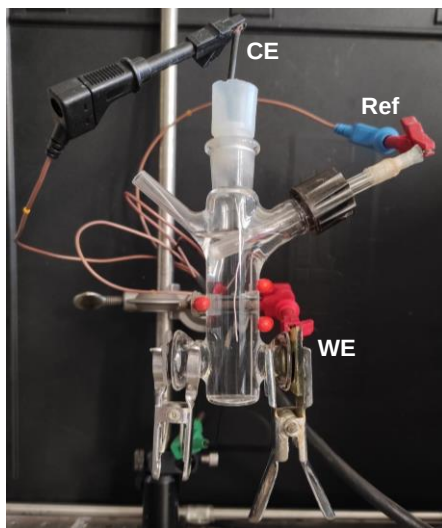


Figure 4.10 Custom-made glass cell equipped with the tested photoanode as working electrode, an Ag/AgCl reference electrode and a platinum wire as counter electrode.

4.3.2.2 Cappuccino cell

The “cappuccino” cell (Figure 4.11) is a more practical PEC cell made of polyether ether ketone (PEEK), a chemically resistant inert polymer, and designed by the Laboratory of Photonics and Interfaces (LPI) group at EPFL. In addition to the superior

handling, its main advantages compared to the glass cell are its smaller electrolyte volume (*ca.* 10 mL), which minimizes the incident light losses when passing through the electrolyte solution before reaching the sample, as well as the correspondence between the illuminated sample area and the wetted area by the electrolyte. Moreover, it ensures small characteristic distances between the electrodes which minimize ohmic losses. On one side (front of the cell), the cell is endowed with a 20 mm diameter quartz window pressed against an o-ring by a metallic window part (see Figure 4.11a), which allow for photoelectrochemical characterization. On the other side (back of the cell), a threaded ring presses an O-ring seal on the cell body (see Figure 4.11b).

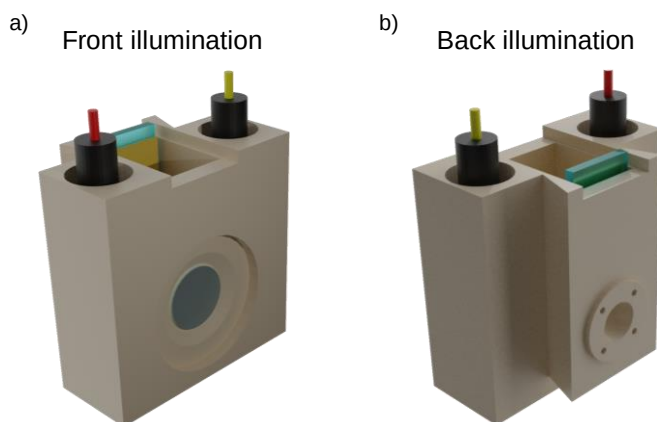


Figure 4.11 “Cappuccino cell” from the (a) front-side and (b) back-side.

This cell is conveniently provided of two samples insertion configurations. One of them, particularly suitable for nanostructured films which cannot be easily sealed with an o-ring, consists in clamping the sample from the top in a miniature steel vise, which is then plunged into the electrolyte solution on both sides. To switch from one irradiation configuration to the other, the clamped sample can be simply lifted out of the cell and rotated by 180°. However, the wetted area in this configuration is $\sim 2\text{--}3$ times larger than the illuminated area. In the other configuration which was adopted in this thesis, the electrode is pressed against an o-ring on the cell body by the threaded ring mounted on the back-side of the cell, by turning the film surface towards the inner of the cell to ensure the contact with the electrolyte. In this way, a constant 0.25 cm^2 irradiated area is provided under both back- and front-side configurations, which is further the same as the wetted area of the film. In this mode, front-side illumination can be realized with incident light passing through the glass window (Figure 4.11a), while back-side irradiation occurs through the threaded ring mounted on the back-side of the cell (Figure 4.11b). Moreover, switching from back- to front-side configuration can be realized by simply rotating the cell by 180°, without losing in optical alignment or light intensity. The working electrode should be grabbed from the uncoated top part serving as electrical contact for external connection. The reference and counter electrodes are placed into the two compartments

located on the WE sides, as shown in Figure 4.11. Light calibration was made by providing a photon flux equal to the AM 1.5 G spectrum according to the method reported in Section 4.3.3 (Experimental set-ups), by placing a Si photodiode instead of the cell onto the cell holder, in correspondence of the film position under both back- and front-side irradiation configurations.

4.3.3 Voltammetry and chronoamperometry

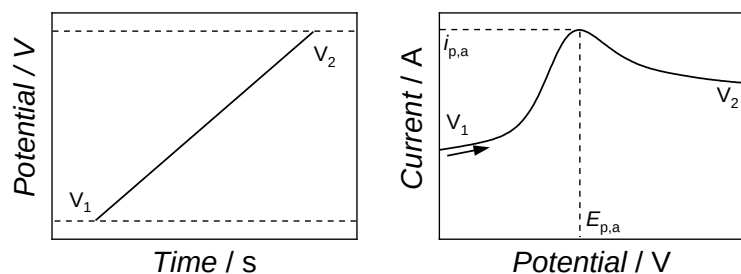
The most employed electrochemical techniques, in this thesis, to probe the performance of the investigated photoanode materials under solar simulated irradiation is linear sweep voltammetry (LSV) belonging, together with cyclic voltammetry (CV) which was employed to a minor extent, to the voltammetry class methods. Here, the change in current flowing through the electrode is monitored upon variation of its potential over time (Figure 4.12). In both LSV and CV a linear potential sweep is applied between the working electrode and the reference electrode. On the other hand, Chronoamperometry works in potentiostatic conditions, *i.e.* by monitoring the current flowing through the sample over time at a constant applied bias. In the following, a brief description for each of these techniques is reported.²⁴

In LSV analyses (Figure 4.12a), the current produced while sweeping the potential of the working electrode at a constant scan rate, usually between 10 and 50 mV s⁻¹, is monitored as a current-voltage (*J-V*) curve, which is positive in case of a photoanode material. From these measurements, a wide range of information can be attained on the photoelectrode performance, such as: *i*) the photocurrent onset potential, *i.e.* the potential where a non-negligible photocurrent rises, *ii*) the “fill factor”, *i.e.* the slope of the *J-V* curve indicating the efficiency of holes/electrons exchange with the electrolyte at the SCLJ, *iii*) the saturation photocurrent density, *i.e.* the plateau photocurrent reached at high bias when hole transfer efficiency is maximum and *iv*) transient spikes, indicating recombination. Considering the extensive use of *J-V* curves in this thesis as a fundamental step in the characterization of the studied photoanode materials, Section 4.3.3.1 adapted from the work of Sivula *et al.*²⁵ will be devoted to discuss in detail the different kinds of information that can be extrapolated from this analysis.

Cyclic voltammetry is a sweep technique where, analogously to LSV, the applied potential is linearly changed at a constant scan rate while recording the current between the photoanode and the counter electrode. Differently from LSV, the potential in CV is varied between two values according to a triangular profile where, once the second potential value is reached, the scan is reversed and the voltage is swept back to its initial value (Figure 4.12b). For the simple case of a reversible single electron transfer reaction, the CV is made of an anodic and a cathodic peak. This technique is commonly used to probe the reversibility of redox processes, to get information about the potential at which they occur and to evaluate the stability of an electrode towards electrochemical cycles. Moreover, it is also employed to distinguish capacitive processes (also known as “non-

faradaic”), which do not involve any charge transfer reaction while rather inducing charge accumulation/depletion on the electrode or electrolyte side, from faradaic processes resulting from electrochemical reactions at the electrode surface. In the case of reversible processes, where the current (I) depends linearly on the scan rate (v), symmetrical CV profiles with respect to the potential axis can be observed. The non-reversible faradaic processes give rise to non-symmetrical CV profiles with a peak.

a) Linear Sweep Voltammetry



b) Cyclic Voltammetry

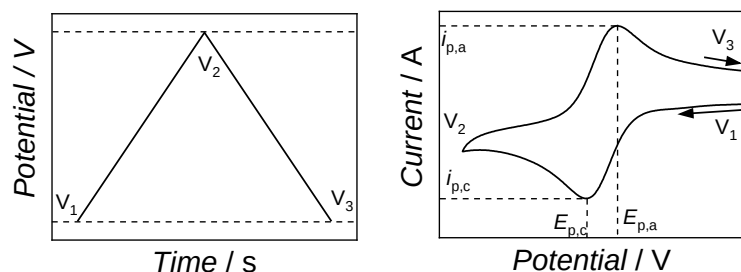


Figure 4.12 Potential-Time signals and Current-Potential plots of a reversible electrochemical process for (a) Linear Sweep Voltammetry and (b) Cyclic voltammetry.

In chronoamperometry (CA) measurements the current flow is monitored over time while keeping the electrode potential at a constant value (Figure 4.13). When applied on photoelectrodes, this technique is generally employed to probe the photocurrent produced under illumination. For electrodes suffering from a sluggish water oxidation kinetics such as BiVO_4 photoanodes, it is common to observe a characteristic transient spike and overshoot after switching the light on and off, respectively, which are indicative of extensive electron-hole recombination.²⁶ The transient photocurrent upon switching light on corresponds to a rapid displacement of photogenerated holes towards the electrode surface, where they accumulate due to the sluggish hole transfer kinetics. On the other hand, the photocurrent observed in steady-state conditions corresponds to holes that are successfully transferred to the electrolyte, when charge recombination is no longer a competitive process. In this thesis, CA technique has been employed to test the stability of the investigated photoanodes under operating conditions, *i.e.* in the water oxidation reaction conducted at 1.23 V vs. RHE, under 1 Sun illumination, and to determine the

incident photon to current efficiency (IPCE) of the electrode under monochromatic light, which refers to the charge collected for incident photon, as described in Section 0.

Chronoamperometry

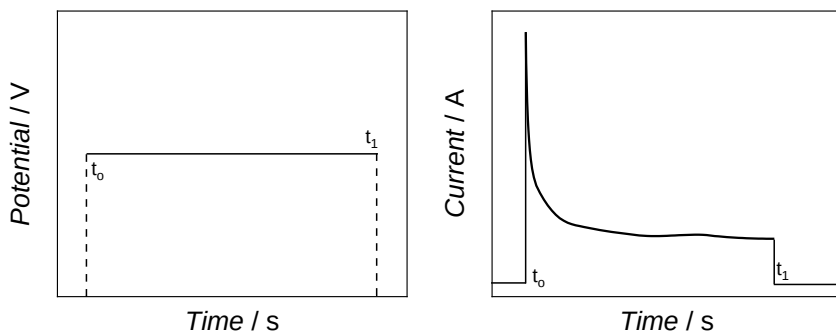


Figure 4.13 Potential-Time signal (left panel) of the corresponding chronoamperometry plot (right panel).

4.3.3.1 Current-voltage curves characteristics

The measurement of the photocurrent density produced by the photoelectrode in contact with the electrolyte, as a function of the applied potential, is the most employed method for characterizing the PEC performance of a photoanode (or photocathode). A positive photocurrent should be expected upon application of an increasing bias to an *n*-type photoanode, while a negative photocurrent should be observed upon scanning the potential from a higher to a lower value on a *p*-type photocathode. In the following, the fundamental concepts on the behaviour of a photoelectrode under applied bias are applied to *n*-type photoanodes (as objects of interest of this thesis) undergoing anodic polarization with respect to the flatband potential, to interpret the features of the resulting *J-V* plots.

As shown in Figure 4.14a, when the photoelectrode is polarized at its E_{FB} , the conduction and valence bands are flat throughout the semiconductor, indicating that no band bending occurs at the SCLJ, as well as the lack of electric field in assisting the separation of the photogenerated electrons and holes. As the electrode is polarized with an increasing anodic potential with respect to the E_{FB} , the Fermi level of the photoanode, together with the conduction and valence bands, are brought down below the flatband level, leaving unchanged the energy levels at the surface. This polarization induces a progressive increase in band bending and in charge separation of the photoproduced electron-hole couples, thanks to the generation of a space charge field extending over a region of width W at the SCLJ. In the limit of a thin film where the light absorption rate is independent of depth into the material and the diffusion length of photogenerated carriers is small, the increase in photocurrent should be proportional to W , which in turn rises with the square root of the applied voltage.

Often, metal oxides photoanodes exhibit an overpotential towards the water oxidation reaction (η_{ox}) which directly corresponds to an anodic shift of the photocurrent onset with

respect to their flatband potential, giving rise to a J - V curve shape well represented by the red curve in Figure 4.14b.^{25,27} The real J - V plot deviates from the ideal case of zero overpotential represented by the green J - V curve in Figure 4.14b, where the photocurrent onset coincides with the flatband potential, and progressively higher photocurrent values can be measured at all potentials more anodic than E_{FB} .

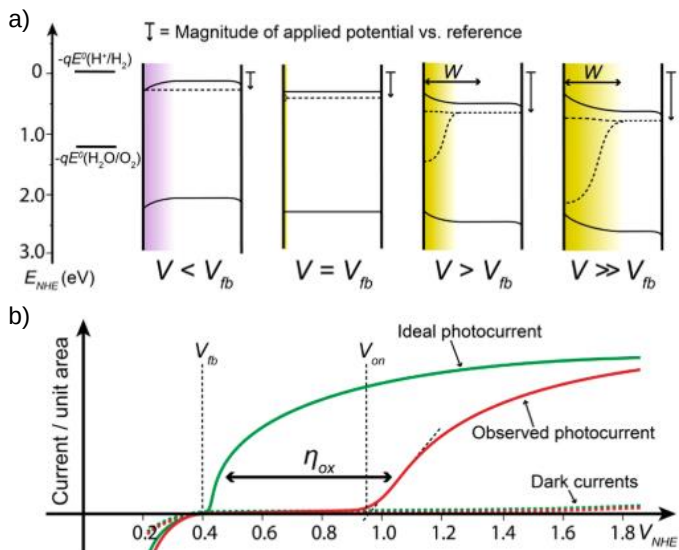


Figure 4.14 (a) Electron energy diagram of an n-type semiconductor photoanode under polarization at different potentials V , with respect to the flat band potential, V_{fb} . (b) Ideal vs. actual J - V curves where the photocurrent onset shifts from V_{fb} in the ideal case to V_{on} in the real case, due to the electrode overpotential for water oxidation.²⁵

The two different photocurrent onset potentials exhibited by the real and the ideal curves also result in a different “fill-factor”, which reflects the competition between the SCLJ processes occurring at early potentials, *i.e.* the reverse recombination of surface holes with conduction band electrons, and water oxidation. Therefore, a different potential is required, in the real and ideal cases, for the photocurrent to saturate to a maximum value known as saturated photocurrent density (J_{eq}) or steady-state photocurrent. The J_{eq} in case of the real J - V curve is indeed reached only at very positive biases, where increased band bending reduces electrons concentration at the electrode surface, so that water oxidation can outcompete recombination. Under steady-state conditions, the produced photocurrent becomes therefore limited by bulk recombination.^{25,28}

The overpotential required for the high demanding water oxidation reaction is usually ascribed to the kinetic limitations due to the involvement of four photogenerated holes to evolve one molecule of O_2 . However, electronic surface traps can be an additional loss mechanism which justifies the large difference in overpotential observed with different metal-oxides based photoanodes (for example between TiO_2 and WO_3 where $\eta_{ox} = 0.2$ V

and Fe_2O_3 where $\eta_{\text{ox}} = 0.5\text{--}0.6$ V).²⁵ It has indeed shown that the delay in water oxidation onset is often associated with the accumulation of photogenerated holes at the electrode surface, manifesting as a capacitance. As already reported in Chapter 2, surface states (SS), due to either oxygen vacancies or crystal defects located at the SCLJ, can be responsible for Fermi level pinning (FLP). The presence of SS in metal oxide photoanodes at intra band gap energies, can be therefore detected through electrochemical impedance spectroscopy (EIS) measurements from the change in slope of the Mott-Schottky plot or as a capacitance peak around the water oxidation onset, according to what explained in Section 4.3.6. It is well known that any applied bias to the electrode under FLP conditions does not induce the generation of a space charge field and consequent band bending able to separate the photogenerated couples, until surface states are totally charged. This is schematically shown for an *n*-type photoanode in Figure 4.15, reporting three different situations: *i*) the electrode polarized at its E_{FB} (Figure 4.15a), *ii*) the electrode polarized at $E > E_{\text{FB}}$, with partly emptied surface states and still without any induced band bending (Figure 4.15b) and *iii*) band bending generation after that surface states are completely emptied (Figure 4.15c). It results that the presence at the SCLJ of a large amount of SS strongly affects the photocurrent onset potential.

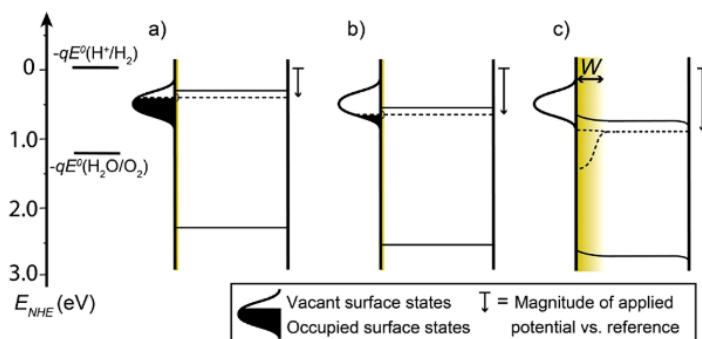


Figure 4.15 Electron energy diagram of an *n*-type semiconductor photoanode under polarization at different potentials in the presence of surface states that cause Fermi level pinning. The electrode is polarized (a) at its V_{fb} , (b) at $V > V_{\text{fb}}$ where surface states commence to empty, but no band bending can be still observed and (c) at $V \gg V_{\text{fb}}$ where surface states are emptied and band bending is induced.²⁵

The overpotential of a photoanode towards water oxidation can be evaluated by comparing the photocurrent onset potential of the corresponding *J*-*V* curves to that observed in performing the electrochemically less demanding oxidation reaction of a hole scavenger. A good hole scavenger, such as H_2O_2 and Na_2SO_3 , is indeed both kinetically and thermodynamically easier oxidizable than water, as shown by the following reactions:^{29–31}



Therefore, thanks to the faster oxidation kinetics, all photogenerated holes that reach the surface can be consumed in the hole scavenger oxidation without being lost due to surface recombination. Indeed, it is well-established that in the presence of a good hole scavenger exhibiting an interfacial charge injection yield ~ 1 , the photocurrent onset potential may provide a rapid estimation of the flatband potential of the electrode.³² In fact, under these conditions the potential where the photocurrent disappears can be considered close to that where bands become flat and no minority carriers can reach the electrode surface, which is properly the E_{FB} . This is the case of hematite photoanodes, where the photocurrent onset potential for H_2O_2 oxidation well approximates the material flatband, indicating that photogenerated holes are already available for oxidation at this potential.

The delay in photocurrent onset observed with pure water oxidation with respect to that of a good sacrificial agent, is an indication of the sluggish water oxidation kinetics, which represents a severe limit to photocurrent generation at early bias values. This phenomenon can be appreciated from the comparison of the photocurrent onsets recorded with hematite photoanodes for H_2O (blue curve in Figure 4.16) and H_2O_2 (red curve in Figure 4.16) oxidation.

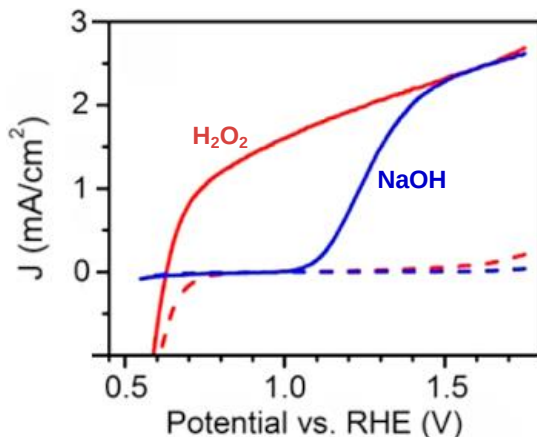


Figure 4.16 J-V curves in the dark (dashed lines) and under simulated solar illumination (solid lines) for hematite photoanodes in contact with H_2O_2 hole scavenger (red lines) and with a non-sacrificial electrolyte aqueous solution (blue lines).^{25,29}

Moreover, Figure 4.16 shows that it is only at very high bias that the water oxidation photocurrent density approaches the saturated photocurrent density exhibited by H_2O_2 oxidation. This is due to the increased band bending at high bias, able to reduce the extent at which surface electron–hole recombination occurs, thus inducing an abrupt increase in the portion of surface reaching holes that can successfully perform water oxidation. It follows that, in the high potential region, photocurrent generation is no longer dictated by surface charge recombination, while becomes limited by charge transport and recombination in the bulk.²⁹

Therefore, the use of a suitable hole scavenger enables the investigation of the PEC properties of the examined electrodes without any complication from surface recombination and poor catalysis. It is worth noting that J - V measurements recorded in the presence of a good hole scavenger provide the upper limit of the performance for pure water oxidation when the electrode surface is functionalized with an efficient co-catalyst for OER.²³ However, it is worth noting that, unless the charge injection yield is very close to 1, the photocurrent onset potential can deviate from the actual E_{FB} even if the oxidation of the sacrificial species is faster than water oxidation. Finally, as discussed in Section 4.3.4, the use of a suitable hole scavenger also allows to decouple the contributions of the bulk and surface processes on the overall observed PEC performance.

Experimental set-ups

Photoelectrochemical measurements under AM 1.5 G solar simulated light for the research work presented in this thesis were performed in the three-electrode configuration cell described in Section 4.3.2, using either the custom-made glass cell or the cappuccino cell, endowed with an Ag/AgCl reference electrode and a Pt wire counter electrode. Both the back (through the transparent electrode substrate) and the front-side (through a quartz window and the electrolyte) irradiation configurations have been adopted for measurements carried out with both kinds of cell. An example of the experimental set-up used in this thesis in performing PEC measurements under full lamp irradiation is shown in Figure 4.17.

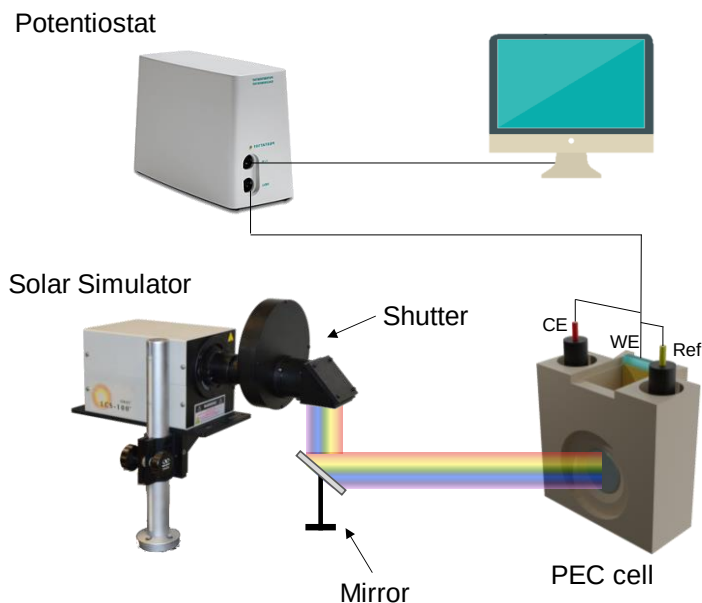


Figure 4.17 Example of the experimental set-up used in this thesis for PEC measurements carried out under full lamp irradiation. A solar simulated light source irradiates the three-electrode PEC cell, connected to a potentiostat.

a) Set-up in Milan

In the set-up used in Milan, an Oriel, Model 81172 solar simulator equipped with an AM 1.5 G filter has been employed as full lamp irradiation source (Figure 4.18) combined with the glass cell. The most recent experiments and control measurements have been carried out with a LCS-100 Solar Simulator Model 94011A-ES (Newport) equipped with an electronic shutter, in combination with a cappuccino cell. The power density of the incident light was calibrated to 100 mW cm^{-2} as described in Section 4.3.2.1 using a Thorlabs PM200 power meter equipped with a S130VC power head with Si photodiode detector. The electrical bias was set by connecting the cell to an Autolab PGSTAT 12 (EcoChemie, Utrecht, The Netherlands) potentiostat controlled by the NOVA software.

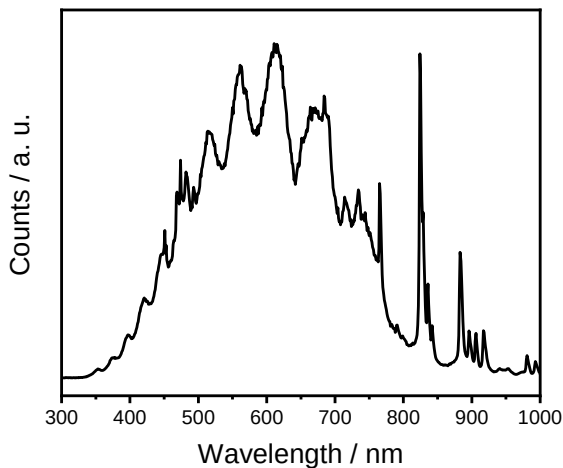


Figure 4.18 Emission spectrum of an AM 1.5 G solar simulator.

b) Set-up in Lausanne

The set-up employed for experiments presented in Chapter 7, 10 and 11 carried out in the group of Prof. Sivula at EPFL, consisted of a cappuccino cell illuminated by a 1000 W Xe arc lamp (Newport Oriel) and connected to a BioLogic SP-500 potentiostat. Chopped light illumination has been provided by a custom-made electronic shutter. The position of the sample with respect to the lamp source was calibrated by using a Si photodiode to provide a photon flux equal to the AM 1.5 G spectrum for $h\nu$ larger than the band gap of the tested material, as reported by Prévot *et al.*³³ Briefly, according to this method, the Xenon arc lamp spectrum was calibrated in order to gain the same number of photons as the AM 1.5 G spectrum between 300 nm and 850 nm (Figure 4.19).

The expected photocurrent produced by the diode under illumination by the calibrated Xe arc lamp, is given by the product of its incident photon to current efficiency (IPCE) spectrum with the calibrated lamp spectrum after integration over the 300-850 nm range, according to the following equation:

$$J_{ph}^{tot} = \int_{300}^{850} [IPCE(\lambda) \times N_{photons}^{AM\ 1.5}(\lambda) \times e] d\lambda \quad (4.23)$$

In this way, the sample can be placed at the position where the photodiode provides the so calculated photocurrent under illumination.

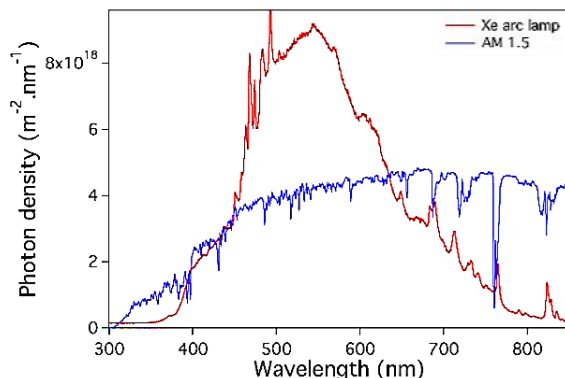


Figure 4.19 Calibration of the Xe arc lamp emission spectrum (red line) with the solar AM 1.5 G spectrum (blue line) for the number of incident photons emitted in the 300-850 nm range.³³

PEC techniques performed under full lamp irradiation

The *J-V* curves reported in this thesis were acquired as multiple consecutive scans both in the dark and under 1 Sun irradiation. In the latter case, either a constant illumination or a chopped light irradiation, attained by switching the light on and off at a constant frequency by means of an electronic shutter, have been employed. The estimation of the photocurrent which is effectively produced by an electrode from the conversion of the absorbed photons, was attained by comparing the *J-V* curves acquired under continuous light illumination with those performed in the dark. The same information can be directly obtained from the chopped LSV plots where light and dark intervals are alternated. In this case, a sharp increase in the current density is observed when light is on, and a subsequent sharp decrease in the measured current density, directly related to the dark current, occurs when light is turned off. Since any dark current shown by a photoelectrode at a given potential is usually a sign of corrosion, a minimized dark current density in the potential range swept should be observed for a material to be considered stable.

LSV measurements were recorded in both non-sacrificial electrolytes as well as in the presence of a hole scavenger, with an average of 5 consecutive scans for each kind of LSV measurement to ensure the attainment of a stabilized photocurrent. In each scan, the starting potential has been set to the open circuit potential (OCP) of the tested electrode, measured either in the dark or under illumination, or to a fixed value close to the material flatband. It is worth reminding that the OCP of an electrode in the dark is determined by the equilibrium potential of the main redox species in the electrolyte solution. The OCP of the electrode under illumination assumes a more negative value than that determined in the dark, being provided by the condition where the net current is zero. The upper potential value of each LSV scan has been chosen depending on the employed electrolyte

solution and the tested material, so to avoid the arise of a non-negligible dark current contribution. For example, non-sacrificial electrolyte solutions offer the possibility to screen a wider potential window than sacrificial agents-containing electrolytes, undergoing self-oxidation earlier. The potential scan rate was varied between 10 and 20 mV s^{-1} .

The acquired J - V curves were exploited to estimate the photocurrent onset potential, *i.e.* the potential where the photocurrent arises, extrapolated from the tangent line to the current-voltage curve, according to what reported in literature.³⁴ The goodness of the SCLJ properties was also evaluated from the fill factor of the curves of the tested photoanode. Finally, the photocurrent value extrapolated at the thermodynamic water oxidation potential and the saturated photocurrent density value attained with each tested electrode were evaluated and compared within a series of materials and with literature values.

Cyclic voltammetry measurements in the dark were employed *i)* to estimate the double layer capacitance for electrochemical active surface area (ECSA) estimation (Chapter 6 and 7), *ii)* to shed light onto the faradaic charge transfer processes occurring at the electrode surface towards specific electron donor species (Chapter 6) and *iii)* to localize bands edge positions and intra band gap states within the investigated semiconductor (Chapter 8). In the first case, the capacitive current was recorded at different scan rates ranging from 5 to 100 mV s^{-1} , in a narrow potential window (a few tens of millivolt) centered around the OCP of the investigated system, where no faradaic processes occur. In the other two cases, the CV traces were spanned over a wider potential window, useful to identify the anodic and cathodic processes occurring upon the electrode polarization, far from its flatband potential.

Chronoamperometry measurements (Chapter 6) were carried out in operating conditions, *i.e.* water oxidation under AM 1.5 G irradiation, at the thermodynamic water oxidation potential of 1.23 V vs. RHE. These measurements were exploited to evaluate the steady-state photocurrent, corresponding to the flux of holes that are successfully transferred to the electrolyte once that electron-hole recombination at the electrode surface is suppressed, and the stability of the electrode over time under operating conditions.

4.3.4 Charge separation and charge injection efficiencies

The comparison of the J - V curves acquired under non-sacrificial conditions and in the presence of a suitable hole scavenger, is a first simple method to decouple the contributions of bulk recombination and surface injection to the overall performance of a photoanode, as a function of the applied potential.

The measured photocurrent for water splitting, $J_{photo}^{H_2O}$, can be expressed in terms of efficiencies of three different processes, according to the following equation:²⁹

$$J_{photo}^{H_2O} = J_{abs} \times \eta_{sep} \times \eta_{inj} \quad (4.24)$$

Here, J_{abs} is the rate of photon absorption expressed as a current density. η_{sep} is the charge separation efficiency in the material bulk, corresponding to the fraction of photogenerated holes that successfully reach the electrode/electrolyte interface without recombining with electrons in the bulk. η_{inj} is the charge injection efficiency to the electrolyte, *i.e.* the fraction of surface reaching holes that are effectively transferred to the electrolyte to oxidize water, without recombining with electrons at surface trap states.

The predicted photocurrent density J_{abs} , based on the number of absorbed photons, can be calculated by integrating the experimental absorbance spectrum of the sample with respect to the AM 1.5 G solar spectrum, as follows:^{33,35}

$$J_{abs} = q \int_{\lambda_1}^{\lambda_2} \Phi_{AM\ 1.5}(\lambda) LHE(\lambda) d\lambda \quad (4.25)$$

where $\Phi_{AM\ 1.5}(\lambda)$ is the photon flux density under standard conditions (AM 1.5 G, 100 mW cm⁻²) at each wavelength, in units of photons number per second per m² per nm, while q is the electron charge (1.602·10⁻¹⁹ C). LHE is the light harvesting efficiency or absorptance of the electrode, defined as the fraction of electron-hole pairs generated per incident photon flux,¹⁴ calculated from the absorbance A of the film according to the following relationship:³³

$$LHE = absorptance(\lambda) = \frac{I_{absorbed}(\lambda)}{I_{incident}(\lambda)} = 1 - 10^{-A(\lambda)} \quad (4.26)$$

When performing the oxidation of a hole acceptor with fast interfacial charge transfer kinetics (*e.g.* H₂O₂ or Na₂SO₃) so that surface recombination is suppressed and $\eta_{inj} = 1$, J_{photo} can be expressed as:

$$J_{photo}^{H_2O_2} = J_{abs} \times \eta_{sep} \quad (4.27)$$

From Eq. 4.27 the charge separation efficiency can be simply calculated from the ratio between $J_{photo}^{H_2O_2}$ and J_{abs} . The charge injection efficiency into water can be instead pursued by dividing Eq. 4.24 by Eq. 4.27, *i.e.* from the ratio between $J_{photo}^{H_2O}$ and $J_{photo}^{H_2O_2}$. The expressions for η_{sep} and η_{inj} are therefore:

$$\eta_{sep} = \frac{J_{photo}^{H_2O_2}}{J_{abs}} \quad (4.28)$$

$$\eta_{inj} = \frac{J_{photo}^{H_2O}}{J_{photo}^{H_2O_2}} \quad (4.29)$$

4.3.5 Incident photon to current efficiency (IPCE)

The incident photon to current efficiency (IPCE), also known as external quantum efficiency (EQE), measures the efficiency of the photoactive system in terms of photocurrent collected per incident photon flux, as a function of the illumination wavelength. It is given by the following formula:^{14,36}

$$IPCE(\lambda) = \frac{\text{electrons cm}^{-2} \text{ s}^{-1}}{\text{photons cm}^{-2} \text{ s}^{-1}} = \frac{|J_{\lambda}(\text{mA cm}^{-2})| \times 1239.8 \text{ (V nm)}}{P_{\lambda}(\text{mW cm}^{-2}) \times \lambda(\text{nm})} \quad (4.30)$$

where J_{λ} is the measured photocurrent density at each wavelength, 1239.8 V nm represents the product between the Planck's constant, h , and the speed of light, c , λ is the irradiation wavelength and P_{λ} is the power of incident light measured at the corresponding wavelength.

Interestingly, the measured IPCE accounts for the efficiencies of three main processes involved in the observed photoelectrochemical activity, *i.e.* *i*) photon absorptance, *ii*) charge transport to the solid-liquid interface, and *iii*) efficiency of interfacial charge transfer.¹⁴ Therefore, the difference between the measured IPCE and the maximum value of 100% reflects the sum of the incident photons that are lost due to both reflection and transmission, and the number of photogenerated electron-hole pairs that recombine before being injected into the external circuit.²

However, to understand the intrinsic performance of a material, it is necessary to correlate the conversion efficiency only to the absorbed photons, by thus considering the losses in reflected or transmitted photons. To this aim, it is useful to estimate the internal quantum efficiency (IQE), also known as absorbed photon to current conversion efficiency (APCE), which describes the photocurrent collected per incident photon absorbed.^{2,14,23,36} It can be obtained by dividing the IPCE at each wavelength by the absorptance at the corresponding wavelength, as follows:

$$IQE(\lambda) = \frac{IPCE(\lambda)}{1 - 10^{-A(\lambda)}} \quad (4.31)$$

where $A(\lambda)$ is the absorbance of the electrode at each wavelength.

It is worth noting that, thanks to the correction for both reflection and transmission losses, the IQE is a more useful parameter than IPCE. In fact, while the latter provides the maximum possible current that can be extracted by a photon source, the determined IQE value allows to directly evaluate charge carrier recombination within the semiconductor.² The evaluation of IQE is a particularly useful tool to determine the optimal thickness of a thin film which maximizes the path length for photon absorption, while still ensuring a minimal effective charge transport distance within the material.

A valuable information from the IPCE spectrum is the prediction of the maximum obtainable photocurrent under AM 1.5 irradiation, which can be calculated by multiplying the IPCE value measured under monochromatic light by the AM 1.5 photon flux at each wavelength, followed by integration over all wavelengths:^{2,36}

$$J_{AM\ 1.5} = \int (IPCE(\lambda) \times \Phi_{AM\ 1.5}(\lambda) \times e) d(\lambda) \quad (4.32)$$

where $J_{AM\ 1.5}$ is the total photocurrent density under solar irradiation (mA cm^{-2}), $\Phi_{AM\ 1.5}(\lambda)$ is the photon flux of the solar irradiation ($\text{photons m}^{-2} \text{s}^{-1}$) which can be calculated from tabulated solar irradiance data,³⁷ and e is the elementary charge (C). The resulting integrated photocurrent density should match that measured at the same bias under actual AM 1.5 conditions, if the sample exhibits a linear response. Indeed, the presence of surface states or a sluggish surface oxidation kinetics may cause large deviations between the predicted solar photocurrent and the actual value recorded under full lamp irradiation.² For example, due to the poor water oxidation kinetics of BiVO_4 electrodes without any added co-catalyst overlayer, a *ca.* 8-fold higher predicted photocurrent has been found at low light intensities compared to the experimental AM 1.5 photocurrent.²⁶

Experimental methods and set-ups

The incident photon to current efficiency have been measured through a chopped chronoamperometry scan performed under monochromatic light irradiation selected through a monochromator, using the three-electrode configuration either in the glass or in the cappuccino cell. It is worth noting that the monochromatic light intensities used in IPCE have been 2 orders of magnitude lower than the 100 mW cm^{-2} provided by the solar simulator. In this way, the current density generated under a constant bias at various wavelengths has been probed. The photocurrent associated with the redox reaction occurring at the electrode surface was evaluated from the difference between the steady-state current, recorded at each wavelength, and the steady-state background dark current.

The IPCE has been thus obtained according to Eq. 4.30, from the ratio between the photocurrent, converted into an electrons flux, and the flux of incident photons, obtained from the calibrated power of the light source. The IQE has been then calculated by applying Eq. 4.31. The analyses have been carried out both in non-sacrificial electrolytes and in the presence of a suitable hole scavenger, under back- and front-side irradiations. A typical setup for such measurements is shown in Figure 4.20.

a) Set-up in Milan

In the IPCE set-up used in Milan, where measurements were performed in the three-electrode configuration glass cell, monochromatic light source was provided by a 300 W Xe lamp (Lot-Oriel) equipped with a LOT-Oriel Omni- λ 150 monochromator to filter out a narrow part of the spectrum centered around the wavelength of interest. A Thorlabs SC10 automatic shutter was used to control the exposure of the sample to the light at a constant frequency. The applied potential was controlled by an Autolab PGSTAT 12 (EcoChemie, Utrecht, The Netherlands) potentiostat. Long-pass filters have been used to filter the higher orders of the diffracted light by the monochromator grating. The intensity of the incident light was measured with the Thorlabs PM200 silicon photodiode, which provides the incident light intensity (in Watts) for each single wavelength, using an

internal calibration curve. Chopped chronoamperometry measurements have been performed with 20 s of light alternate to 20 s of dark, by scanning the wavelength of the incident light with a 10 nm step-size within the 300-700 nm range, depending on the tested material.

b) Set-up in Lausanne

In the set-up employed in Lausanne for the IPCE measurements presented in Chapter 7, the three-electrode configuration cappuccino cell controlled by the BioLogic SP-500 potentiostat was used. Monochromatic illumination was provided by a 75 W Xenon tunable PowerArc illuminator (Optical Building Blocks) and the photon flux at each wavelength was measured with a photodiode power sensor (S120VC, Thorlabs). The wavelength of the incident light was varied between 570 and 300 nm with a 5 nm-step variation.

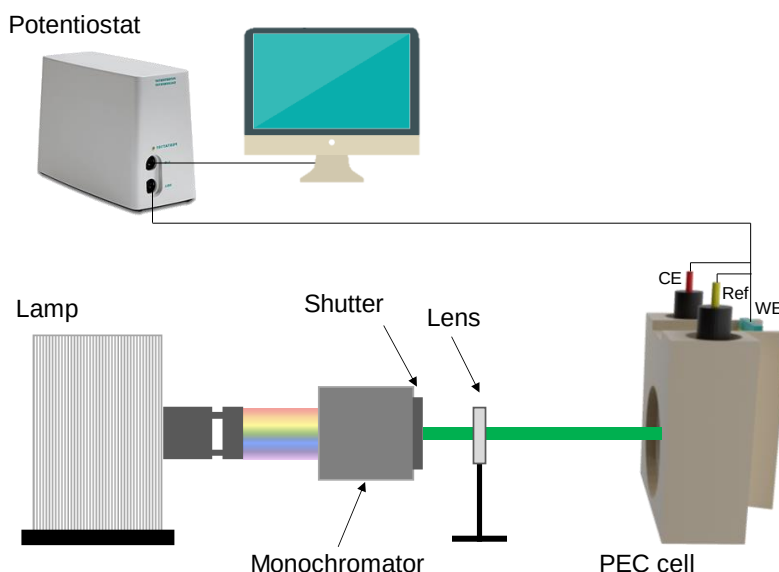


Figure 4.20 Example of the experimental set-up used in this thesis for IPCE measurements carried out under monochromatic light irradiation.

4.3.6 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy is a powerful technique working in the frequency domain, for the characterization of electrode processes and complex interfaces. It relies on probing the complex response of an electrode to a sinusoidal modulation of the applied potential, at different frequencies (typically in the 10 mHz – 3 MHz range). The variation of the excitation frequency allows the resolution of processes with different time constants. A small potential perturbation, typically in the 5-10 mV range, is required for single process evaluation in the potential domain. Under these conditions, the potential-current dependency of the electrochemical system can be approximated as linear

and treated according to the Ohm's law, accounting for the linear interdependency between potential perturbation and current response.

The sinusoidal perturbation of the potential $E(t)$ induces a sinusoidal current $I(t)$ of the same frequency (ω) superimposed onto the steady-state current with a phase shift (ϕ) with respect to the potential, as shown by the following equations:

$$E(t) = |E_0| \sin(\omega t) \quad (4.33)$$

$$I(t) = |I_0| \sin(\omega t - \phi) \quad (4.34)$$

where E_0 and I_0 are the amplitudes of potential and current, respectively, and $\omega = 2\pi f$ stands for the radial frequency expressed in rad/s (while f is the frequency expressed in Hz).

The electrochemical impedance of the system is defined analogously to the Ohm's law ($R = E(t)/I(t)$) as:

$$Z(\omega) = \frac{E(t)}{I(t)} = \frac{|E_0| \sin(\omega t)}{|I_0| \sin(\omega t - \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t - \phi)} \quad (4.35)$$

In polar coordinates the potential and the current response can be represented by vectors of length $|E_0|$ and $|I_0|$ rotating counter clockwise at the radial frequency ω . Using Euler's relationship $\exp(jx) = \cos(x) + j \sin(x)$, these functions are most easily described by using complex numbers:

$$E(t) = |E_0| \exp(j\omega t) \quad (4.36)$$

$$I(t) = |I_0| \exp(j\omega t - j\phi) \quad (4.37)$$

And the impedance can be expressed as a complex function:

$$Z(\omega) = \frac{|E_0| \exp(j\omega t)}{|I_0| \exp[j(\omega t - \phi)]} = \frac{|E_0|}{|I_0|} \exp(j\phi) = |Z_0| \exp(j\phi) \quad (4.38)$$

which can be expressed as the sum of a real (Z') and an imaginary part (Z'') at a certain ω .^{38,39}

$$Z(\omega) = |Z_0| \exp(j\phi) = |Z_0| (\cos\phi + j \sin\phi) = Z' + j Z'' \quad (4.39)$$

with $Z' = |Z_0| \cos\phi$ and $Z'' = |Z_0| \sin\phi$.

One common way to visualize the electrochemical impedance data is given by the Nyquist plot, consisting of plotting the negative imaginary impedance component ($-Z''$) against the real component (Z') at each excitation frequency. It should be noted that each point on the Nyquist plot represents the impedance at one frequency. Typically, the impedance response of the system to the high frequencies perturbation can be found on the left side of the plot, while the low frequency modulation response is located on the right side of the spectrum.

The analysis of the frequency-dependent response of the system can help to separate different processes such as charge transport, charge trapping and charge transfer at the interface with the electrolyte, accounted by the presence of more than one semicircle in the Nyquist plot and occurring on different temporal scales. For example, since bulk recombination (< 100 ns) and surface processes (100 ms – 1s) typically occur in distinct

time scales, they can be associated with the high and the low frequency response ranges of the plot, respectively.

EIS data are commonly analysed by fitting it to a suitable equivalent electrical circuit model to extract the elements, arranged in parallel and in series, which are related to the basic electronic processes of charge accumulation (capacitances), and charge recombination and transfer (resistances), occurring inside the electrode under operating conditions. Notably, elements or circuits connected in series are known to model processes occurring consequently, whereas elements or circuits connected in parallel simulate processes occurring simultaneously.

An important contribution for a PEC system, which must be deconvoluted from the total resistance, is represented by the interfacial charge transfer resistance R_{ct} , providing information about the charge transfer rate for electrochemical reactions. The capacitance of a semiconductor, corresponding to a charge storage mechanism, is determined by different contributions: *i*) the dielectric capacitance, associated with an internal electrical field produced by spatial charge separation, and represented by charge storage across the semiconductor space charge region (C_{sc}) or across the Helmholtz double layer (C_H), and *ii*) the chemical capacitance, resulting from the variation of the chemical potential or carrier concentration due to charge storage in surface states.³⁶ In the following, two of the most common equivalent circuits, also employed in this thesis, are presented in relation to the corresponding Nyquist plot.

The simplest equivalent circuit shown in the inset of Figure 4.21, known as Randles circuit, accounts for the modelling of the electrode/electrolyte interface. In this case, R_s simulates the ohmic resistance (composed of the solution, wires and other uncompensated resistances), C_{dl} simulates the double layer capacitance at the SCLJ (associated with the depletion and Helmholtz layers of opposite charge), which is charged simultaneously with the occurring electrochemical reaction. The double layer capacitance is in parallel with R_{ct} , the resistance associated with the charge transfer across the SCLJ. The Nyquist plot for a simplified Randles cell is always a semicircle, whose diameter is equal to the charge transfer resistance, as represented in Figure 4.21.

The Randles model has been adopted in the impedance measurements reported in Chapter 6 and 8, where the non-ideal behaviour of a semiconductor, resulting in a flattening of the Nyquist semicircle, was taken into account by introducing a Constant Phase Element (CPE) in replacement of a pure capacitive element to describe the double layer capacitance (Figure 4.21). The impedance of a real capacitor CPE is given by:³⁹

$$Z(\omega) = \frac{1}{Q} (j\omega)^{-n} \quad (4.40)$$

where Q is a constant and $0 < n < 1$. The case $n = 1$ recovers a perfect capacitor.

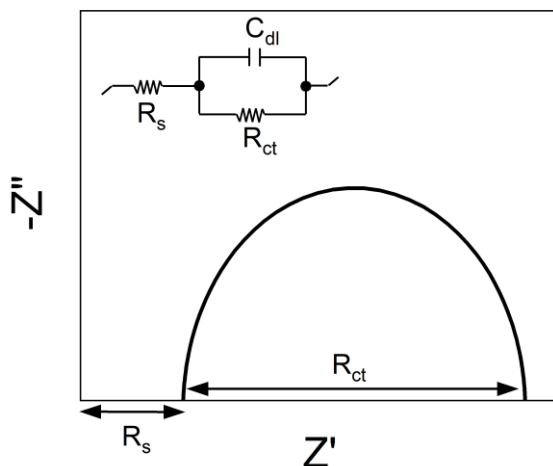


Figure 4.21 Nyquist plot composed of one single semicircle fitted by a classic Randles circuit (inset).

When more than one semicircle occurs in the impedance spectrum, an equivalent circuit containing more elements should be used. The presence of a second semicircle is usually due to a two-step reaction process, in which case an intermediate state is involved. This can be represented by states located within the energy gap at the semiconductor surface, adsorbed molecules as reacting intermediates of the reaction or by reactions proceeding through more than one electron.

In Chapter 7 and 11, a modified Randles equivalent circuit represented in the inset of Figure 4.22 has been employed to fit Nyquist plots characterized by two semicircles as that shown in Figure 4.22, likely due to the involvement of intra band gap surface states. Here, the high frequency arc should refer to the space charge capacitance in the semiconductor material, while the low frequency arc conveys information on the capacitance of surface states.

The modified Randles circuit depicted in Figure 4.22 has been firstly reported to describe charge transfer from the surface to electrolyte species dominated by surface states, which competes with the rate of electrons and holes trapping.⁴⁰ Moreover, it has been largely employed in literature with many metal oxide electrodes where surface states act as intrinsic electron traps promoting charge recombination at the electrode surface,⁴¹ rather than as intermediate states, formed under light irradiation, that trigger water oxidation.^{40,42,43} Moreover, the same model circuit can be also used to describe the situation where an increase in hole density, due to charging of the surface states, causes the stabilization of C_{sc} and a displacement of the Mott-Schottky plot due to Fermi level pinning,⁴⁰ as described in the following paragraphs.

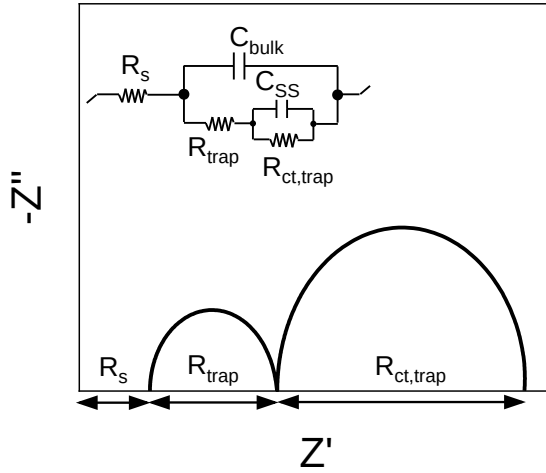


Figure 4.22 Nyquist plot composed of two semicircles fitted by a Modified Randles circuit (inset).

In the model represented in Figure 4.22, R_s is a series resistance associated with charge transfer through the external circuit and the bulk of the semiconductor, C_{bulk} is the bulk capacitance, so that $C_{\text{bulk}}^{-1} = C_{\text{SC}}^{-1} + C_H^{-1}$, where C_{SC} corresponds to the capacitance of the depletion layer inside the semiconductor and C_H to the Helmholtz layer capacitance inside the electrolyte, R_{trap} is the parallel resistance of hole trapping to surface states, C_{ss} is the built-up capacitance induced by the interfacial accumulation of charges in surface states and $R_{\text{ct,trap}}$ is the charge transfer resistance to water oxidation occurring through surface states.

The most common use of impedance measurements aims to determine the space charge capacitance. The differential space charge capacitance, C_{SC} , is expressed by the dependence of the space charge density, Q_{SC} , on the potential difference across the space charge region, $\Delta\Phi_{\text{SC}}$, formed under depletion of the majority carriers from the interfacial SCLJ:

$$C_{\text{SC}} = \frac{\partial Q_{\text{SC}}}{\partial \Delta\Phi_{\text{SC}}} \quad (4.41)$$

In the situation of no charge storage in surface states, the changes in applied potential occur almost entirely across the space charge region inside the semiconductor material, leaving unchanged the interfacial potential drop in the Helmholtz layer (since the Helmholtz capacitance C_H is generally much larger than C_{SC}). Under these conditions, $\Delta\Phi_{\text{SC}} = E - E_{\text{FB}}$ where E is the electrode potential and E_{FB} is the flatband potential.

The potential dependence of C_{SC} is described by the Mott-Schottky (M-S) equation, here reported for an n -type semiconductor:^{23,44}

$$\frac{1}{C_{\text{SC}}^2} = \frac{2}{qN_D A^2 \varepsilon_r \varepsilon_0} \left(E - E_{\text{FB}} - \frac{kT}{q} \right) \quad (4.42)$$

where N_D is the donor density corresponding to the majority charge carrier density, *i.e.* electrons in an n -type semiconductor, ε_r is the relative permittivity of the semiconductor,

ϵ_0 is the vacuum permittivity, A is the surface area, q is the electron charge, k is the Boltzmann constant and T the temperature. It should be noted that the electrode area A in Eq. 4.42 corresponds to the actual surface area of the electrode and not to the geometric surface area, unless the investigated film has a flat surface or electrodes with identical surface morphologies are compared.

Therefore, the plot of $1/C_{sc}^2$ as a function of the applied potential (M-S plot), allows to extrapolate N_D from the slope of the resulting straight line, and E_{FB} from its intercept with the potential axis. Moreover, the sign of the slope indicates the type of intrinsic doping of the semiconductor since a positive slope should be observed for n -type materials whereas p -type electrodes exhibit a negative slope.

It is well-known that both the N_D and the Fermi level can be affected by the semiconductor extrinsic doping, which changes the distribution of electrons within the solid. Consequently, the flatband potential, which is defined as the potential where the Fermi energy lies at the same energy as the solution redox potential, so that no net charge transfer occurs, can be influenced by the doping of the material.⁴⁵ The determination of the E_{FB} of an electrode is of extreme importance in PEC water splitting since, in addition to providing a relative measure of the semiconductor reducing power, it corresponds to the earliest potential value where the photocurrent onset for water oxidation can be observed.

The flatband potential and donor density values extrapolated by means of the Mott-Schottky analysis can be also employed to determine the width of the depletion region W , as a function of the applied potential, as follows:

$$W = \left(\frac{2(E - E_{FB})\epsilon_r\epsilon_0}{qN_D} \right)^{\frac{1}{2}} \quad (4.43)$$

In an ideal semiconductor, whose space charge is balanced by the counter-charge in the electrical double layer formed in the electrolyte, the surface ionic charge is determined by the acid/base or ion-exchange properties of the surface. In this regard, oxide electrodes usually exhibit a Nernstian pH dependence of the flatband potential due to the change in surface dipole. However, in the presence of a high density of surface states causing Fermi level pinning, the variation in surface charge of the semiconductor upon varying the applied potential is such that the potential drop occurs across the Helmholtz double layer rather than the space charge region of the electrode. This effect appears as a flat region in the M-S plot arising from the almost constant value of the total capacitance.⁴⁴

The surface states responsible for this effect can be either intrinsic to the semiconductor, if they correspond to crystal imperfections and surface damage originating from the break of the periodic crystal symmetry at the material surface, or extrinsic if they arise from the contact of the electrode surface with adsorbates or electrolyte species, both in the dark and under illumination. Anyhow, surface states may play a key role in the kinetics of the interfacial reactions occurring in the semiconductor,

by acting either as intermediate species of the reaction or by inducing charge trapping responsible for the overpotential required to observe the photocurrent onset.^{36,44}

Impedance spectroscopy is a powerful tool to probe the density of surface states by monitoring the surface state capacitance C_{SS} as a function of the applied bias. This chemical capacitance is the third contribution to the overall capacitance of a semiconductor material, and can be expressed under equilibrium conditions in the dark as follows:^{36,40}

$$C_{SS} = A_S q N_{SS} \frac{\partial f_{SS}}{\partial E_{F,n}} = A_S \frac{N_{SS} q^2}{k_B T} f_{SS} (1 - f_{SS}) \quad (4.44)$$

where N_{SS} is the density of the surface states, f_{SS} is the fractional occupancy of the state and $E_{F,n}$ is the electron Fermi level of the surface state. According to Eq. 4.44 the C_{SS} traces a peak with respect to Fermi level variation at the point $E_{F,n} = E_{SS}$, where E_{SS} is the energy level of the surface state.

The expression for the surface state capacitance arising from water photooxidation conditions is more complex than that measured in the dark (described by Eq. 4.44), since under light irradiation the occupation probability of surface states, f_{SS} , is not only affected by the trapping of majority carriers, but also by the photogenerated minority carriers.⁴⁶

The surface state capacitance can be probed through a voltage scan of the capacitance at intermediate frequencies to remove the effect of C_{bulk} . The measurement of the C_{SS} can be then used to calculate the density of surface states (DOS), expressed as a Gaussian distribution, $g_{SS}(E_{F,n})$, through the following relationship:⁴⁰

$$C_{SS} = q g_{SS}(E_{F,n}) \quad (4.45)$$

This approach has proved effective in revealing either intrinsic surface states already present in the dark, acting as electron traps which promote charge recombination at the surface of CuFeO_2 *p*-type photocathodes,⁴¹ or intermediate species for the water oxidation reaction, such as surface hydroxyl groups and high-valent metal-oxo complexes, as reported for Fe_2O_3 ⁴⁰ and CuFe_2O_4 photoanodes.⁴² A good indication of the presence of surface states is the matching between the energetic location of the build-up of the surface state capacitance under water photooxidation, which corresponds to accumulated holes at the electrode/electrolyte interface, and the potential range of Fermi level pinning in M-S plots. Moreover, any eventual correspondence between the potential range of the C_{SS} peak and that of the photocurrent onset in *J-V* plots, may suggest that water oxidation should mainly proceed through surface trapped holes, whose accumulation is a prerequisite to trigger the water oxidation reaction.^{40,42}

Experimental methods and set-ups

EIS measurements have been carried out either in the dark or under illumination conditions, in which case the technique has been referred to as photoelectrochemical impedance spectroscopy (PEIS). EIS and PEIS experiments in this thesis have been performed with the aims to i) investigate the charge transfer processes characteristics

occurring at the electrode/electrolyte interface, *ii*) measure the depletion capacitance according to the Mott-Schottky relationship and *iii*) detect any surface states accumulation at the SCLJ by probing the surface state capacitance as a function of the applied potential.

In Chapter 6, EIS measurements were carried out both in the dark and under AM 1.5 G irradiation in the three-electrode glass cell connected to a Metrohm Autolab PGSTAT302N potentiostat, either in a 0.5 M Na_2SO_3 solution buffered at pH 7 with a 0.5 M potassium phosphate (KPi) buffer, or in a 0.5 M Na_2SO_4 N_2 -purged solution. Each EIS spectrum was recorded at different applied potentials by sampling sixty frequency values in log10 frequency domain (single sine, logarithmically distributed) from 100 kHz to 0.1 Hz with a 10 mV amplitude, and was fitted by means of the Z-View software (Scribner Associates, Inc.) using the classic Randles equivalent circuit $R_s(R_{ct}, CPE)$ reported in Figure 4.21.

PEIS experiments presented in Chapter 7 and 11 were carried out in the Laboratory of Prof. Sivula. Those concerning Chapter 7 were performed in either a 0.5 M Na_2SO_4 solution or in a 0.5 M Na_2SO_3 solution buffered at pH 7 with 0.5 M KPi, using the cappuccino cell connected to a Bio-Logic SP-500 potentiostat coupled with the EC-Lab (V11.12) electrochemical platform. During each PEIS scan, a voltage perturbation within a frequency range from 1 MHz to 0.05 Hz was applied with a 25 mV sinusoidal amplitude. PEIS experiments reported in Chapter 11 were carried out with the same set-up in 1M NaOH electrolyte solution at pH 14, by scanning the potential modulation frequency between 160 Hz and 50 mHz. The so acquired PEIS data were fitted by employing the modified Randles circuit in Figure 4.22 by means of a custom program written with the Python programming language by Boudoire *et al.*⁴⁷

Mott-Schottky measurements presented in Chapter 8 were performed by acquiring a series of potentiostatic EIS spectra with a Parstat potentiostat in a 0.3 M Na_2SO_4 solution (pH 7), using a potential perturbation amplitude of 10 mV in the 100 kHz – 0.1 Hz frequency range. A Randles equivalent circuit model, where the double layer capacitance is replaced by a CPE to consider the morphological heterogeneities of the film, was employed to fit the data. The fitting was carried out by means of a Matlab-based program.

4.3.7 Intensity modulated photocurrent spectroscopy (IMPS)

Intensity modulated photocurrent spectroscopy (IMPS) is a powerful frequency-domain technique allowing to clearly distinguish the processes occurring in the bulk of the semiconductor and at the interface with the electrolyte, by measuring the frequency-dependent magnitude and phase shift of the photocurrent generated by intensity-modulated light.⁴⁸

IMPS technique takes advantage of the modulation of the light intensity to modulate in turn the surface concentration of the photogenerated carriers, instead of the reaction rate constant as in EIS experiments. The small amplitude modulation of the light intensity

results in a modulation of the photocurrent with the same frequency but characterized by different magnitude and phase. The in-phase and out-of-phase components result in a complex photocurrent whose real and imaginary parts can be plotted in a Nyquist plot, at different applied potentials.⁴⁹

According to the generalized IMPS theory proposed by Peter *et al.*,^{48,50} the IMPS response $J(\omega)$ of a photoelectrode in a small modulation depth regime can be expressed as:

$$J(\omega) = J_h \times \frac{k_{tran} + i\omega \left(\frac{C_H}{1 + \frac{C_H}{C_{SC}}} \right)}{k_{tran} + k_{rec} + i\omega} \times \left(\frac{1}{1 + (i\omega\tau)^\alpha} \right) \quad (4.46)$$

where J_h denotes the hole (minority carriers) current towards the electrode/electrolyte interface and τ is the mean transit time for photogenerated electrons. k_{tran} and k_{rec} are the pseudo-first order charge transfer and recombination rate constant, respectively. C_{SC} and C_H represent the capacitances of the space charge layer and of the Helmholtz layer, respectively. α ($0 < \alpha \leq 1$) is a non-ideality factor accounting for the deformation of the semicircles in the Nyquist plots. Therefore, through extrapolation of the pseudo-first order k_{tran} and k_{rec} rate constants, the above model is particularly useful for analysing the competition between hole transfer to the electrolyte and surface recombination at the electrode/electrolyte interface.

IMPS data presented in Chapter 11 are fitted with a phenomenological model similar to that proposed by Klotz *et al.*,^{51,52} based on two resistor–capacitor (RC) responses, which has been developed by Boudoire *et al.*:⁴⁷

$$J(\omega) = \frac{J_h}{1 + (i\omega\tau_h)^{\alpha_1}} + \frac{J_r}{1 + (i\omega\tau_r)^{\alpha_2}} \quad (4.47)$$

where J_h is the bulk photocurrent available for water oxidation and J_r is the photocurrent losses due to surface recombination. τ_h and τ_r are the corresponding time constants referring to processes occurring in the bulk of the photoanode before surface recombination (bulk hole current) and charge recombination at the surface, respectively. Compared to the pioneering Peter's model characterized by a large variability of the fitting results due to the presence of 6 parameters to determine, in the model employed in this thesis only 4 fitting parameters are required to describe the IMPS data.

An example of the application of this model to IMPS data presented as a Nyquist plot of the complex photocurrent response at a certain applied potential, is provided in Figure 4.23. Here, the negative semicircle located at the higher frequency values of the complex plane corresponds to the processes occurring with shorter time constants, which are charge generation and transport in the bulk of the electrode. Consequently, the diameter of the negative semicircle indicates the magnitude of the bulk photocurrent J_h , which is available for water oxidation in the absence of surface recombination. The positive

semicircle appearing at the lower frequency values is representative of surface recombination occurring with a longer time constant compared to the bulk processes. The surface semicircle amplitude provides therefore a direct estimation of J_r .

The difference between J_h and J_r , extrapolated from the amplitude of the high frequency and low frequency semicircles, respectively, provides the magnitude of the steady-state photocurrent (J_{eq}) generated by the flux of holes that are successfully transferred to the electrolyte, without undergoing surface recombination.⁵³

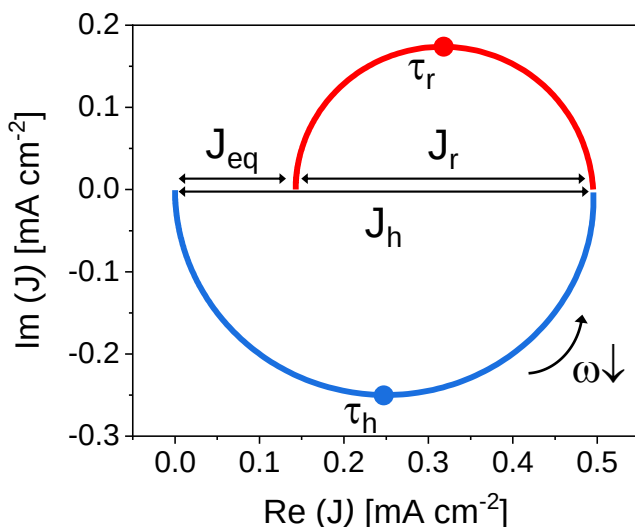


Figure 4.23 IMPS data represented as a Nyquist plot of the complex photocurrent at a given applied potential, fitted by means of the phenomenological model described in Eq. 4.47.

By combining Eq. 4.46 and Eq. 4.47 it is possible to derive the pseudo-first order rate constants, k_{tran} and k_{rec} , appearing in Peter's model (Eq. 4.46), after the extrapolation of the (four) fitting parameters of the here employed model Eq. 4.47. This can be made according to the following relationships:

$$k_{tran} = \frac{1}{\tau_r} \frac{J_h - J_r}{J_h} \quad (4.48)$$

$$k_{rec} = \frac{1}{\tau_r} \left(1 - \frac{J_h - J_r}{J_h} \right) \quad (4.49)$$

Furthermore, IMPS analyses allow also to calculate the charge separation (η_{sep}) and charge injection (η_{inj}) efficiencies under true operation conditions, which are instead typically estimated from measurements conducted in the presence of a sacrificial redox agent²⁹ (see Section 4.3.4).

It is worth noting that measurements under redox sacrificial conditions, where surface recombination should be suppressed and the bulk photocurrent is entirely accessible to the interfacial oxidation reaction, may not properly reflect the effective photocurrents produced in true water oxidation conditions.⁵² Indeed, hole scavengers may alter the

electrochemical reaction occurring at the electrode/electrolyte interface through the change of the surface properties such as band-bending and charge accumulation, which may in turn influence the hole current. In this regard, IMPS analyses performed *in operando* should provide a more accurate estimation of the sought quantities.

According to Peter's approach (Eq. 4.46), the surface charge transfer efficiency, η_{inj} , can be expressed in terms of the phenomenological rate constants k_{tran} and k_{rec} , as follows:⁵⁴

$$\eta_{inj} = \frac{k_{tran}}{k_{tran} + k_{rec}} \quad (4.50)$$

By substituting Eqs. 4.48 and 4.49 in Eq. 4.50, the expression for η_{inj} becomes:

$$\eta_{inj} = \frac{J_h - J_r}{J_h} \quad (4.51)$$

while the charge separation efficiency, η_{sep} , simply corresponds to:

$$\eta_{sep} = \frac{J_h}{J_{abs}} \quad (4.52)$$

where J_{abs} is the maximum photocurrent expected to be produced by the investigated electrode based on its absorption properties, calculated according to Eq. 4.25.

Experimental methods and set-ups

IMPS measurements presented in Chapter 11 have been performed in collaboration with the group of Prof. Sivula, with the aim to validate the bulk charge separation and surface charge injection efficiencies calculated from sacrificial redox measurements. In IMPS the modulation of light intensity requires a sinusoidally potential perturbation by an arbitrary function generator of a light emitting diode (LED) source, superimposed on a DC background.

The IMPS experiment presented in this thesis was performed using a customized light modulation system with 4 Cree XLamp MC-E LEDs. The blue LED as light source was powered at a DC background of 3.4 V. The sinusoidal modulation (200 mV) of the light intensity was controlled by an arbitrary/function generator (Tektronix AFG3021C), with a modulation depth of 10% and a frequency range from 100 kHz to 50 mHz.

A three-electrode cappuccino cell was used, connected to a Thompson Electrochem potentiostat (model 251) to control the applied potential on the working electrode. The photocurrent response was recorded by a digital oscilloscope (Tektronix DPO7254C) via a 50 Ω resistor (Velleman E6/E12) in series with a platinum counter electrode.

IMPS data were processed and fitted with the model shown in Eq. 4.47 using a custom program written with the Python programming language by Boudoire *et al.*⁴⁷

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Chapter 5

Sensitizing effects of BiVO₄ in the TiO₂/BiVO₄ heterojunction

5.1 Abstract

BiVO₄ is an efficient and stable visible light active photoanode material. However, due to its unfavorable conduction band position which falls below the H₂ reduction potential, it fails to carry out the complete water splitting reaction. On the other hand, larger band gap TiO₂ is able to photocatalytically split water, thanks to its negative conduction band energy. Aiming at verifying the possibility of sensitizing TiO₂ with BiVO₄ and employing the so obtained composite material in photocatalytic water splitting under visible light, we prepared and photoelectrochemically characterized TiO₂/BiVO₄ heterojunction electrodes. The photocatalytic reduction of methyl viologen, an electron acceptor probe with a reduction potential close to that of protons, was used to evaluate the reducing ability of the photoactive materials under visible light. An apparently counterintuitive electron transfer from photoexcited BiVO₄ to the TiO₂ conduction band occurs in the TiO₂/BiVO₄ heterojunction, resulting in TiO₂ sensitization and production of highly reductive electrons, which appears to be favored by the band alignment occurring at the heterojunction.

5.2 Introduction

In the search for semiconducting oxides acting as efficient photoanodes for water oxidation,¹⁻³ BiVO₄ is still the most promising choice.^{1,4-7} Apart from its benchmark stability and excellent visible light conversion efficiency, it affords favourable bands edge location: the VB edge provides sufficient overpotential for holes to photooxidize water whereas the CB edge, located just below the thermodynamic level for H₂ evolution,⁴ enables water splitting at modest external bias compared to most of the visible-light responsive photoanodes.^{1,8,9} Furthermore, thanks to the relatively narrow band gap of *ca.* 2.4 eV in the monoclinic scheelite phase, BiVO₄ can absorb up to 11% of the solar spectrum, *i.e.* a larger fraction compared to the widely employed UV-absorber TiO₂.⁸⁻¹⁰

On the other hand, TiO₂, the most largely employed, stable and cost-effective photocatalyst, possesses a CB potential of -0.16 V vs. NHE (in the more photoactive anatase phase),¹¹ which is negative enough to reduce water. However, its relatively high energy band gap of 3.2 eV (anatase phase) makes it active only under UV light, which is only 3% of the solar spectrum incoming on the earth.¹² In this context, many strategies have been employed to make TiO₂ visible light-active,^{13–15} in particular through the insertion of dopant species,^{11,16,17} which may extend light absorption through the introduction of defective sites, and dye sensitization.¹⁸ However, an excess of dopant impurities, acting as charge recombination centres, can have detrimental effects on TiO₂ photoefficiency,¹⁶ while organic dye sensitizers are known to undergo photodegradation over time.¹⁵

Hence, the use of visible light responsive transition metal oxide semiconductors, which are stable under oxidative conditions, together with coupling different semiconductor materials in heterojunction systems,^{19,20} is an attractive strategy to extend the sensitivity of photocatalytic materials and improve their functionality. In fact, in these composite systems a more effective electron-hole separation may be achieved, which guarantees longer lifetime of the photogenerated charges and a generally enhanced photocatalytic performance with respect to the individual components.^{20,21}

For instance, coupling TiO₂ with WO₃ was demonstrated to limit the undesired recombination of photogenerated charge carriers, with the photoexcited electrons being efficiently transferred from the TiO₂ to the WO₃ CB. However, this also results in an undesired decrease of their reducing power.^{22,23} Moreover, Fe₂O₃²⁴ and chalcogenide semiconductors, such as CdSe,²⁵ characterized by smaller band gaps compared to TiO₂, were employed as sensitizers of transparent oxides to extend their photoactivity in the visible region. However, similarly to WO₃, Fe₂O₃ is not a good candidate to preserve the potential of TiO₂ for overall water splitting due to its too low CB edge energy,²⁶ while chalcogenide materials, though having an ideal CB position for H₂ generation,¹ are unsuitable because of their instability under water oxidation conditions.

In this frame BiVO₄, with its narrower band gap and good stability, emerges as a promising candidate to broaden the photoactivity of TiO₂ possibly without significant loss of reducing ability,²⁷ since the BiVO₄ CB edge is located only *ca.* 0.2 eV below that of TiO₂.²⁸ By coupling titanium dioxide with bismuth vanadate in the TiO₂/BiVO₄ heterojunction, visible light sensitized TiO₂ can be obtained which, thanks to its high reduction potential, can be employed for up-hill processes such as water splitting into H₂ and O₂, under visible light irradiation.²⁹ In such a system, the excellent visible light harvesting properties of BiVO₄ may be combined with the TiO₂ CB potential suitable for proton reduction. However, on the basis of the relative band edge positions of pure TiO₂ and BiVO₄, a Type I band scheme¹⁹ should be predicted for this heterojunction system which, under visible light irradiation, would result in the accumulation of photopromoted electrons and photogenerated holes on the BiVO₄ side. Even though electron injection

from the low-lying CB of BiVO₄ to the more negative CB of TiO₂ is in principle thermodynamically unfavoured, evidence that this may occur has been recently reported^{30–40} and ascribed either to the presence of a Type II instead of the predicted Type I band alignment,^{31,32,34,36,38–43} or to an unidentified defect-mediated charge transport pathway.³⁰ Moreover, evidence was provided for transfer into TiO₂ of high-energy electrons visible light excited in BiVO₄, with an unexpected activity in PEC water oxidation and photocatalytic production of H₂.³³

Inspired by this intriguing phenomenon, we investigated the TiO₂/BiVO₄ heterojunction trying to shed light on the mechanism through which high-energy electrons photoexcited in BiVO₄ under visible irradiation transfer into more reductive TiO₂. Optically transparent films of the composite system and of the pure components, for comparison, were prepared by spin coating deposition of precursor solutions through a low-cost and time saving process. Optically transparent photoelectrodes can be exploited in dual absorber tandem cells, in which two or more absorbing materials are sequentially stacked to maximize light absorption in the overall device.⁹ The combination of PEC characterization and methyl viologen photocatalytic reduction tests provides evidence that highly reducing electrons, photopromoted in BiVO₄ under visible light irradiation, may transfer to TiO₂. The so realized heterojunction might in principle act as a stand-alone composite photoanode able to carry out complete solar water splitting.

5.3 Experimental section

5.3.1 Chemicals and materials

The following chemicals, purchased from Sigma Aldrich, were employed as supplied: titanium diisopropoxide bis(acetylacetonate) (TIPA), 75 wt% in isopropanol, ammonium metavanadate, bismuth(III) nitrate pentahydrate (98%), poly(vinyl alcohol) >99%, citric acid (99%), glacial acetic acid, sodium sulfate, methyl viologen (MV²⁺), nitric acid 68%, isopropanol and ethanol (99%). Anhydrous sodium sulfite was purchased from Alfa Aesar; fluorine-doped tin oxide (FTO) glass, 2 mm thick, was purchased from Pilkington Glass (TEC-7).

5.3.2 Photoelectrodes preparation

Titanium dioxide films were prepared under nitrogen atmosphere inside a glove box, starting with 1:3 dilution of TIPA with isopropanol, followed by spin coating the so obtained solution onto FTO at 2000 rpm for 30 s. Prior to deposition, the FTO glass was cleaned by 30 min-long sonication in a soap solution, then washed carefully, sonicated in ethanol for 30 min and dried in air. After coating, the film was dried for 1 h at 70 °C and then annealed for 1 h at 500 °C.

Bismuth vanadate films were prepared as reported elsewhere.²⁸ In a typical synthesis, 0.002 mol of Bi(NO₃)₃ and NH₄VO₃ were dissolved into 6 mL of 23.3% HNO₃ containing 0.004 mol of citric acid acting as a stabilizer. After complete dissolution of the precursors,

0.04 g of poly(vinyl alcohol) and 0.25 mL of acetic acid were added to 1.0 mL of the above solution to obtain a denser paste. A BiVO₄ layer was obtained by spin coating the paste at 4000 rpm for 30 s onto clean FTO, previously treated with acetone. The so obtained films were then dried in air for 1 h at 70 °C and annealed in air for 1 h at 500 °C.

The TiO₂/BiVO₄ films were obtained by coating a TiO₂ electrode prepared as described above with the BiVO₄ dense paste. Then, the composite films underwent the same thermal treatment used for single BiVO₄ films. An inverse BiVO₄/TiO₂ heterojunction photoanode was also prepared by covering a FTO/BiVO₄ electrode with a TiO₂ film, followed by thermal treatment.

The FTO/WO₃/BiVO₄ and CdS electrodes employed in MV²⁺ photocatalytic reduction tests were prepared through spin coating and chemical bath deposition,^{44,45} respectively.

5.3.3 Physical and photoelectrochemical methods

UV–visible absorption spectra were recorded using a Jasco V-670 spectrophotometer. The crystalline phase of the materials was determined through X-ray powder diffraction (XRPD) analysis using a Philips PW1820 with Cu K α radiation at 40 mA and 40 kV. Images showing the morphology and the cross section of the electrodes were obtained using a scanning electron microscope (SEM, model LEO 1430, Zeiss) operating at a 10 kV accelerating voltage, at an 8 mm working distance.

PEC measurements were carried out using the three-electrode glass cell described in Section 4.3.2.1 with an Ag/AgCl (3.0 M NaCl) reference electrode and a platinum gauze as a counter electrode, connected to an Autolab PGSTAT 12 (EcoChemie, Utrecht, The Netherlands) potentiostat. The photoanodes were tested under back-side illumination (*i.e.*, through the FTO/TiO₂, FTO/BiVO₄ or FTO/TiO₂/BiVO₄ interface), in contact with a 0.5 M Na₂SO₃ aqueous solution buffered at pH 7 with a 0.5 M potassium phosphate buffer (KPi), acting as hole scavenger. The light source was an Oriel solar simulator (Model 81172) providing AM 1.5 G simulated solar illumination with 100 mW cm⁻² intensity (1 sun). All semiconductor oxides are stable at neutral pH and no noticeable degradation was observed under irradiation. The potential vs. Ag/AgCl was converted into the RHE scale using Eq. 4.19. All RHE values refer to pH = 0, *i.e.* they coincide with SHE values.⁴⁶ The linear sweep voltammetry (LSV) scans for each material were recorded at 10 mV s⁻¹ starting from the open circuit potential after 5 min irradiation, up to 0.7 V vs. Ag/AgCl, in order to avoid the electrochemical oxidation of sulfite.

The incident photon to current efficiency (IPCE) was measured both in 0.5 M aqueous Na₂SO₃ buffered at pH 7 with 0.5 M KPi and in 0.5 M aqueous Na₂SO₄, using the same single-compartment three-electrode glass cell. The IPCE was calculated using Eq. 4.30.

5.3.4 Photocatalytic tests

A 25×8 mm² film was placed in a 100 mm thick vacuum cuvette containing 3 mL of 1.0 mM MV²⁺ solution in ethanol. The light source was a 200 W Xe lamp equipped with a water filter (Lot Oriel) and a 420 nm cutoff filter (Thorlabs), in order to cut the IR and the UV portion of the emission spectrum, respectively, and to obtain visible irradiation with 30 mW cm⁻² power intensity. By this way MV²⁺ self-reduction, occurring under irradiation with wavelength up to 390 nm, and the direct excitation of TiO₂ were both excluded. The light power intensity was checked using a Thorlabs PM200 power meter equipped with a S130V C power head with a Si detector. Before each experiment, the vacuum cuvette was filled with the MV²⁺ ethanol solution in a N₂ purged glove box, in order to remove any trace of O₂, possibly acting as undesired electron acceptor during the photoreduction experiment. The same film area was irradiated in all experiments, by selecting it through a mask. The increase in concentration of the reduced methyl viologen (MV⁺) species was monitored during the experiment by recording, at selected time intervals, the absorption spectrum of the solution, which assumes an increasing blue colour under irradiation.

5.4 Results and discussion

5.4.1 Photoelectrodes characterization

The X-ray powder diffraction patterns of the TiO₂, BiVO₄ and BiVO₄/TiO₂ electrodes are reported in Figure 5.1a. The pattern observed for BiVO₄ fits well with that relative to the monoclinic structure, while the characteristic (101) reflection of TiO₂ anatase at 2θ = 25.5° is evident in both the individual TiO₂ film and the composite material, as shown in the inset of Figure 5.1a. Other reflections typical of anatase cannot be appreciated due to their lower intensity and to the overlap of some of them with more intense signals originated from FTO. The XRPD spectrum obtained with the combined BiVO₄/TiO₂ material, *i.e.* with TiO₂ as top layer, exhibits the reflection patterns of both components, indicating that no other phase was formed upon coupling the two oxides.

The absorption spectra of pure TiO₂ and BiVO₄ films and of both TiO₂/BiVO₄ and BiVO₄/TiO₂ heterojunctions are reported in Figure 5.1b. The TiO₂ thin film is transparent in the visible range; its absorption onset, at *ca.* 400 nm as expected from the 3.2 eV band gap of TiO₂ anatase, overlaps with interference fringes. The BiVO₄ photoanode (band gap of 2.4 eV) absorbs in the visible range up to *ca.* 500 nm. Lower absorption is obtained in this region when BiVO₄ is coupled with TiO₂ in both TiO₂/BiVO₄ and BiVO₄/TiO₂ heterojunctions, as shown in Figure 5.1b. This unexpected phenomenon, in which a coloured film loses absorption when covered with a transparent layer, may find an explanation in electronic structure effects consequent with the equilibration of the Fermi levels of the two oxides. Furthermore, the absorption onset of both coupled systems is

seemingly shifted to higher energy values with respect to that of individual BiVO_4 , which might also be related to Fermi levels equilibration effects at the heterojunction.

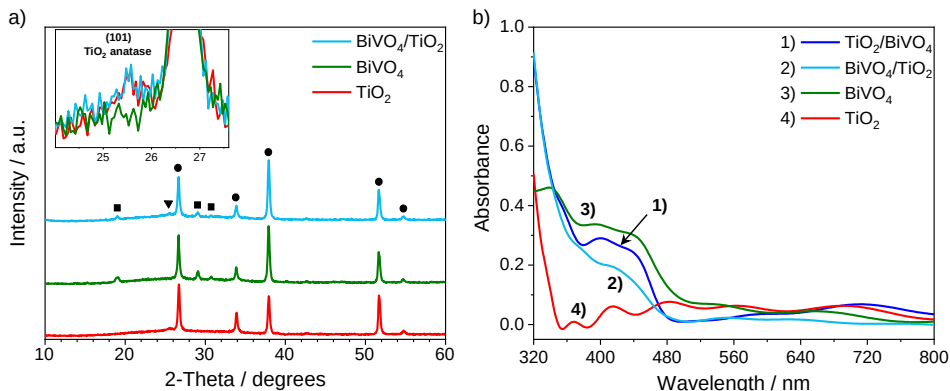


Figure 5.1 (a) X-ray powder diffraction patterns of the TiO_2 , BiVO_4 and $\text{BiVO}_4/\text{TiO}_2$ heterojunction films, where ● refers to FTO, ■ to BiVO_4 and ▼ to anatase TiO_2 reflections. Inset: enlargement of the 24.0 – 27.5° 2θ range, with the characteristic (101) reflection of anatase TiO_2 . (b) Absorption spectra of 1) $\text{TiO}_2/\text{BiVO}_4$ and 2) $\text{BiVO}_4/\text{TiO}_2$ heterojunctions, 3) BiVO_4 and 4) TiO_2 .

The top view SEM images of the BiVO_4 and $\text{TiO}_2/\text{BiVO}_4$ heterojunction films are reported in Figure 5.2. They show an aggregated network of particles, with the BiVO_4 film (Figure 5.2a) characterized by a worm-like shape morphology similar to that obtained in previous studies,^{28,44} and by a discontinuous coating of the FTO underlayer. Differently, in the $\text{TiO}_2/\text{BiVO}_4$ heterojunction film (Figure 5.2b) the FTO asperities are completely covered by the TiO_2 and BiVO_4 layers. Moreover, the BiVO_4 top layer in the composite system appears as a compact film, which completely covers the TiO_2 layer due to the different affinity of BiVO_4 for TiO_2 rather than for FTO.

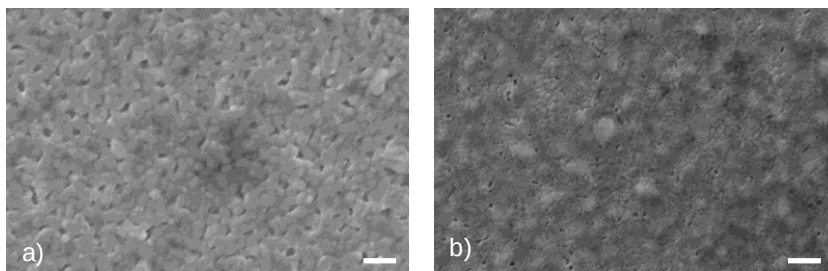


Figure 5.2 Top view SEM images of (a) BiVO_4 and (b) $\text{TiO}_2/\text{BiVO}_4$ heterojunction photoanodes. The scale bar is 500 nm.

From the cross section SEM images shown in Figure 5.3 a thickness of ca. 55, 60 and 100 nm was calculated for the BiVO_4 , TiO_2 , and overall $\text{TiO}_2/\text{BiVO}_4$ layers, respectively, by subtracting the average thickness of FTO (546 nm, obtained from Figure 5.3a) from the average thickness of the FTO/ BiVO_4 , FTO/ TiO_2 and FTO/ $\text{TiO}_2/\text{BiVO}_4$ systems (Figure 5.3b, c and d, respectively). The so calculated thickness for the bare BiVO_4 film is in accordance with that obtained for BiVO_4 films prepared by the same procedure.²⁸

Furthermore, the thickness of the TiO₂/BiVO₄ heterojunction system is in line with the thickness of the single component layers.

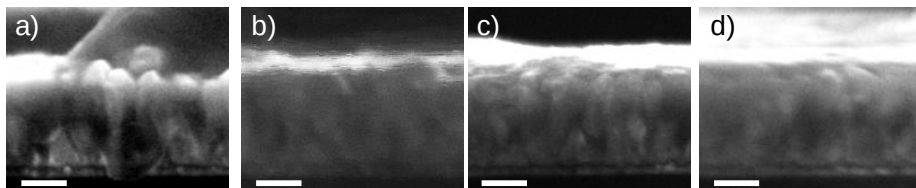


Figure 5.3 Cross section SEM images of (a) clean FTO, (b) BiVO₄, (c) TiO₂ and (d) TiO₂/BiVO₄ heterojunction photoanodes. The scale bar is 250 nm.

5.4.2 Photoelectrochemical performance

The PEC performance of the investigated TiO₂/BiVO₄ heterojunction as photoanode material was compared with that of single TiO₂ in contact with a Na₂SO₃ solution at pH 7 (0.5 M KPi). In the presence of this hole scavenger the performance of the heterojunction electrode is not affected by the typically slow water oxidation kinetics at the BiVO₄ surface.³¹ As PEC experiments were performed by irradiating the photoanodes through the FTO/oxide film interface, in the composite material visible light first passed through the TiO₂ film and promoted electrons in BiVO₄, close to the interface between the two semiconductors. Thus, the mobility of the electrons photopromoted in the CB of BiVO₄ was not affected by its poor electron transport properties.^{47,48}

The LSV plots recorded with the TiO₂ and the TiO₂/BiVO₄ photoanodes, under both full lamp solar simulated irradiation and visible light irradiation at $\lambda > 420$ nm, are shown in Figure 5.4a. Under full lamp irradiation the TiO₂ photoanode produced a relatively small photocurrent, as expected from its limited ability to absorb solar radiation (see Figure 5.1b), and no appreciable photocurrent was produced under visible light irradiation, as expected. Under full lamp irradiation, *i.e.* under conditions of simultaneous excitation of both semiconductor oxides, the photocurrent produced at 1.0 V vs. RHE by the TiO₂/BiVO₄ heterojunction photoanode was 10-fold higher than that produced by the TiO₂ photoanode, thanks to the ability of BiVO₄ in absorbing a larger part of the solar spectrum. The combined photoanode thus exhibits considerable photoactivity even under visible light excitation ($\lambda > 420$ nm), which can be absorbed by BiVO₄ only.

Since the procedure here adopted for the preparation of TiO₂ films even in the composite system ensures the formation of compact and pin hole-free TiO₂ layers, electrons visible light excited in BiVO₄ can flow to the FTO glass only through the TiO₂ film. Therefore, assuming a Type I band alignment between the two semiconductor counterparts in the composite system, due to the *ca.* 0.2 eV energy mismatch between the CB of TiO₂ and BiVO₄, only the electrons with an energy excess with respect to the CB edge of BiVO₄ (0.02 V vs. RHE at pH 0²⁸) are able to transfer to the more negative CB of anatase TiO₂ (−0.16 V vs. RHE at pH 0¹¹). For this reason, a relatively lower photocurrent density value is expected with the TiO₂/BiVO₄ heterojunction compared to

pure BiVO₄ photoanodes.³⁶ Alternatively, if a Type II band alignment exists between BiVO₄ and TiO₂, such that electron transfer from the BiVO₄ to the TiO₂ is favourable, the above described behaviour can be attributed to photogenerated carrier recombination at the TiO₂/BiVO₄ interface.

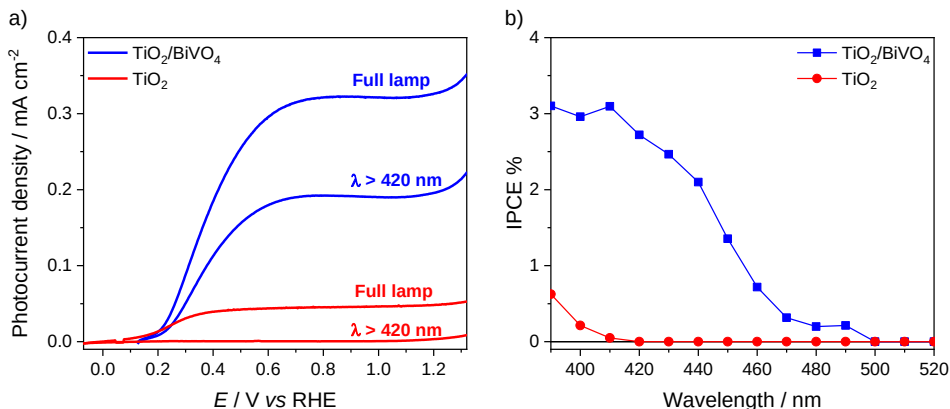


Figure 5.4 (a) Linear sweep voltammetry (LSV) and (b) incident photon to current efficiency (IPCE) analyses at 1.0 V vs. RHE of TiO₂ and of the TiO₂/BiVO₄ heterojunction, in 0.5 M Na₂SO₃ buffered at pH = 7 with 0.5 M potassium phosphate.

The LSV analyses reported in Figure 5.4a also show that the TiO₂ photoanode exhibits a much more negative photocurrent onset with respect to that found for the TiO₂/BiVO₄ heterojunction. The photocurrent onsets measured by this way provide a good indication of the flat band potential (E_{FB}) of the material.^{28,49} In order to ascertain the E_{FB} position of the investigated heterojunction with respect to those of the two individual components, we recorded their open circuit potentials (OCP) under 5 min long solar simulated irradiation (1 sun),⁵⁰ in contact with the Na₂SO₃ electrolyte solution. We obtained OCP values of 0.003 V, 0.203 V and 0.253 V vs. RHE (pH 0) for the TiO₂, TiO₂/BiVO₄ heterojunction and BiVO₄ electrode, respectively, with the heterojunction OCP value in line with a CB edge alignment which follows the equilibration of the Fermi levels of the two oxides in the heterojunction.

The IPCE plots reported in Figure 5.4b evidence that TiO₂ is active only up to 410 nm, consistently with its 3.2 eV band gap, while it becomes photoactive under visible light irradiation when coupled with BiVO₄, acting as visible light sensitizer up to 490 nm.

The visible light sensitizer role of BiVO₄ in the composite system is evident also from the IPCE in water splitting measured at 1.23 V vs. RHE with the electrodes in contact with a Na₂SO₄ aqueous solution, shown in Figure 5.5. The null conversion efficiency of TiO₂ in the visible region is confirmed. Since BiVO₄ alone is photoactive up to 520 nm,²⁸ the energy difference between the photocurrent onsets of pure BiVO₄ and of the TiO₂/BiVO₄ heterojunction composite system may correspond to the extra energy required for visible light excited electrons in BiVO₄ to be injected into the TiO₂ CB. The lower photoactivity of the two BiVO₄-containing coloured materials compared to those

obtained in contact with the Na₂SO₃ solution should be ascribed to the slow water oxidation kinetics typical of BiVO₄, in the absence of any hole scavenger or co-catalyst for oxygen evolution.^{51,52} Furthermore, under such unfavorable oxidation kinetics conditions, the IPCE values obtained with the TiO₂/BiVO₄ heterojunction up to ca. 480 nm are higher not only than those obtained with TiO₂, but also compared to those obtained with single BiVO₄, suggesting that partial charge separation occurs in the composite system.

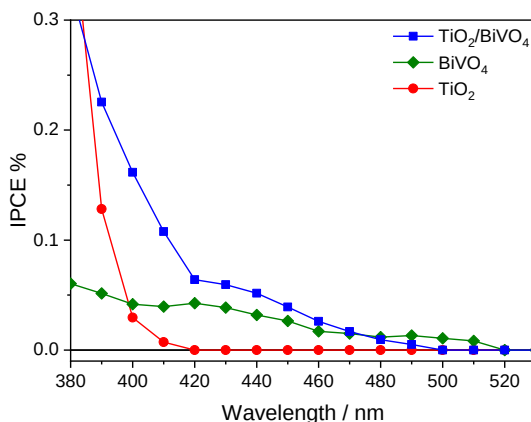


Figure 5.5 Incident photon to current efficiency (IPCE) analysis of TiO₂, BiVO₄ and of the TiO₂/BiVO₄ heterojunction at 1.23 V vs. RHE, in 0.5 M Na₂SO₄.

5.4.3 Photocatalytic methyl viologen reduction tests

Photocatalytic methyl viologen reduction tests were performed to investigate the photocatalytic reduction ability of the TiO₂/BiVO₄ heterojunction in comparison with that of other commonly employed semiconductors.^{53–56} The mono-electron reduction of the almost colourless MV²⁺ to the blue MV^{•+} reduced form (Figure 5.6), occurring at –0.03 V vs. NHE,^{57,58} was monitored by measuring the absorption of a 1.0 mM solution of MV²⁺ in ethanol under visible light irradiation ($\lambda > 420$ nm). Such irradiation conditions prevent MV²⁺ self-reduction, occurring under UV irradiation and, in the case of the TiO₂/BiVO₄ electrode, exclude the direct excitation of TiO₂ which, due to its negative CB potential, would induce MV²⁺ reduction very efficiently.

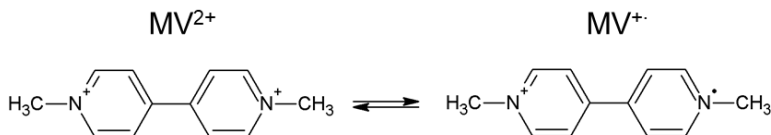


Figure 5.6 Reduction reaction of methyl viologen (MV²⁺) to its mono-electron reduced MV^{•+} form.

The experiment was carried out with the tested film initially in contact with the MV²⁺ solution under nitrogen atmosphere, in order to avoid the reversible oxidation of the MV^{•+} species in the presence of oxygen.⁵³ In addition to the investigated TiO₂/BiVO₄

heterojunction, other common semiconductors with known CB potential location were tested for comparison, *i.e.* the pure TiO₂ and BiVO₄ components having a CB potential edge at *ca.* -0.16 V (in the anatase phase)¹¹ and 0.02 V²⁸ vs. NHE, respectively, the WO₃/BiVO₄ heterojunction, known for its excellent charge separation properties,⁵⁹ with a CB edge at *ca.* 0.19 V vs. NHE,²⁸ and CdS, characterized by extended absorption in the visible up to *ca.* 550 nm⁶⁰ and by a highly negative CB potential of *ca.* -0.4 V vs. NHE,⁶¹ *i.e.* significantly more negative than the reduction potential of the MV²⁺/MV⁺ couple. The photocatalytic reduction efficiency of all investigated materials was tested under 2 h-long irradiation, up to the attainment of a plateau.

The absorption spectra of the probe solution recorded at different time during the photoreduction experiment in the presence of the TiO₂/BiVO₄ heterojunction and of the pure BiVO₄ are shown in Figure 5.7a and b, respectively. The formation of the blue reduced MV⁺ species was testified by the absorbance increase over time, which clearly occurred at a higher rate when the experiment was carried out with the TiO₂/BiVO₄ coupled system. Thus, the composite material is clearly more efficient than pure BiVO₄ in MV²⁺ reduction.

Figure 5.7c reports the MV⁺ maximum absorbance at 606 nm vs. the irradiation time plots for all tested semiconductor materials, providing information on their relative photocatalytic reduction efficiency under visible light irradiation. As expected, TiO₂ shows negligible photoactivity. Indeed, despite its highly negative CB potential, its poor visible light absorption ability limits its activity under the here employed irradiation conditions, in line with the IPCE results shown in Figs. 5.4b and 5.5. Also the WO₃/BiVO₄ heterojunction shows little photoactivity despite it absorbs light up to *ca.* 500 nm and possesses excellent charge separation properties.^{28,44} The limiting factor should be thus identified in this case with the much more positive CB edge position (0.19 V vs. NHE) of the WO₃/BiVO₄ heterojunction with respect to the reduction potential of MV²⁺. Furthermore, the WO₃/BiVO₄ heterojunction shows lower ability in MV²⁺ reduction than individual BiVO₄ (Figure 5.7c), supporting a downward BiVO₄ flat band equilibration when the WO₃/BiVO₄ heterojunction is formed.²⁸ This rules out the hypothesis that the improved charge separation typical of heterojunction systems is sufficient to explain the higher photocatalytic activity in MV²⁺ reduction obtained with the TiO₂/BiVO₄ heterojunction compared to the single components. Indeed, Figure 5.7c shows that after 1 h-long visible light irradiation, the MV⁺ concentration attained in contact with the TiO₂/BiVO₄ heterojunction is 10- and 3-fold higher than in contact with the TiO₂ and BiVO₄ films, respectively. The TiO₂/BiVO₄ heterojunction exhibits high MV²⁺ reduction ability, which is lower only to that of CdS, having a CB potential significantly more negative than the reduction potential of the MV²⁺/MV⁺ couple. This demonstrates that under visible light irradiation highly reducing electrons are produced in the TiO₂/BiVO₄ heterojunction, at a more negative potential than those visible light promoted in single BiVO₄.

As expected, the highest photoreduction efficiency was attained with the semiconductor systems having the most negative CB edge value. Therefore, by comparing the photocatalytic tests results with the CB edge position values reported in the literature, the apparent relative scale shown in Figure 5.7d can be drawn for the CB edge energy of the tested materials, with respect to the reduction potential of the MV²⁺/MV^{•+} couple. Thus, only CdS and TiO₂ have a CB edge potential negative enough to efficiently photoreduce MV²⁺. BiVO₄, although having a slightly more positive CB potential, is still able to photoreduce MV²⁺, thanks to electrons photoexcited above the CB edge having higher energy compared to the MV²⁺/MV^{•+} couple reduction potential. On the other hand, the CB potential of the WO₃/BiVO₄ heterojunction is more positive than that of BiVO₄ and this results in a low MV²⁺ reduction efficiency.

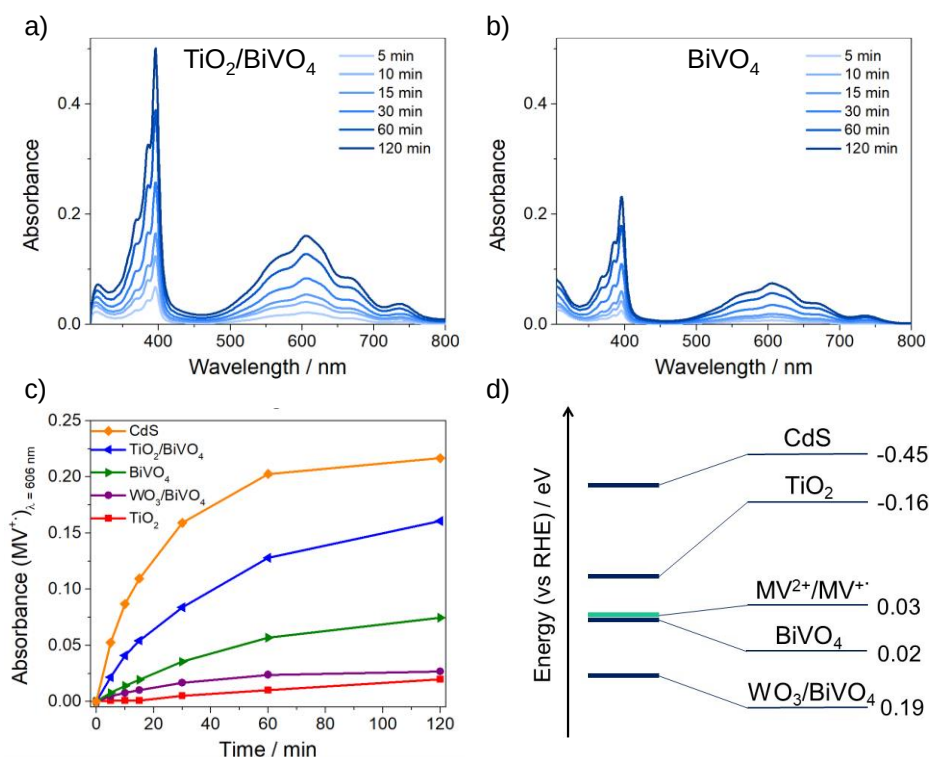


Figure 5.7 Absorption spectra recorded during methyl viologen (MV²⁺) photoreduction experiments in the presence of (a) the TiO₂/BiVO₄ heterojunction and (b) pure BiVO₄. (c) Kinetic profiles (maximum MV^{•+} absorbance at 606 nm vs. time plots) obtained with different semiconductor systems in photocatalytic MV²⁺ reduction tests. (d) CB energy scale of the tested semiconductor systems compared to the MV²⁺/MV^{•+} reduction potential. All potential values for CdS,⁶¹ TiO₂,¹¹ MV²⁺/MV^{•+},^{57,58} BiVO₄ and the WO₃/BiVO₄ heterojunction,²⁸ are taken from the literature.

5.4.4 Proposed mechanism

Visible light excited electron injection from the CB of BiVO₄ to the CB of TiO₂ is required to explain the unexpected PEC performance, as well as the visible light photocatalytic activity in MV²⁺ reduction, of the TiO₂/BiVO₄ heterojunction. PEC analysis of the TiO₂/BiVO₄ heterojunction under visible light irradiation ($\lambda > 420$ nm) indeed demonstrates that photopromoted electrons resulting from the selective excitation of the BiVO₄ layer can effectively transfer to TiO₂.

In the Type I band alignment based on the band edge positions of the two isolated semiconductors,^{11,28} which is schematically represented in Figure 5.8a, only electrons photopromoted with enough energy above the BiVO₄ CB bottom to reach the same energy level as the TiO₂ CB bottom, can be successfully transferred. The required energy excess can be quantified on the basis of the results of the IPCE analyses shown in Figs. 5.4b and 5.5, and it should be around 0.2 eV, *i.e.* the energy difference associated with the photocurrent onset of the TiO₂/BiVO₄ and BiVO₄ electrodes (490 and 520 nm, respectively). Therefore, if the transfer of these electrons from BiVO₄ to TiO₂ occurs efficiently, and an intimate contact between the two semiconductors is crucial to this aim, the charge couples photogenerated in BiVO₄ under visible light irradiation can be efficiently separated at the opposite sides of the heterojunction, with beneficial effects on photoactivity.

On the other hand, methyl viologen photocatalytic reduction tests in the absence of any external bias imply that the electron transfer towards the probe solution is mainly driven by the energy difference between the CB edge position of each photocatalyst system and the reduction potential of MV²⁺. Therefore, the higher efficiency of the TiO₂/BiVO₄ heterojunction with respect to pure BiVO₄ may only be ascribed to the actual involvement of visible light photopromoted, highly reducing electrons.

The increase of the reductive power of photopromoted electrons in the TiO₂/BiVO₄ coupled system can be also explained on the basis of the Fermi level equilibration between the TiO₂ and BiVO₄ components, which leads to the consequent shift towards a more negative value of the flat band potential at the heterojunction with respect to pure BiVO₄ (as confirmed by OCP values, see Section 5.4.2). In fact, the highly reducing electrons lying in the so obtained TiO₂/BiVO₄ CB should be more prone than those in BiVO₄ CB to reduce MV²⁺, with a consequent beneficial effect on the overall efficiency of the investigated process.

Therefore, based on the results of the photocatalytic reduction tests, a Type II band alignment depicted in Figure 5.8b and reported elsewhere,^{31,38,39,41–43} consequent to the Fermi level equilibration between the two semiconductors and responsible for the visible light induced higher reducing ability of the composite system with respect to individual BiVO₄, cannot be discarded.

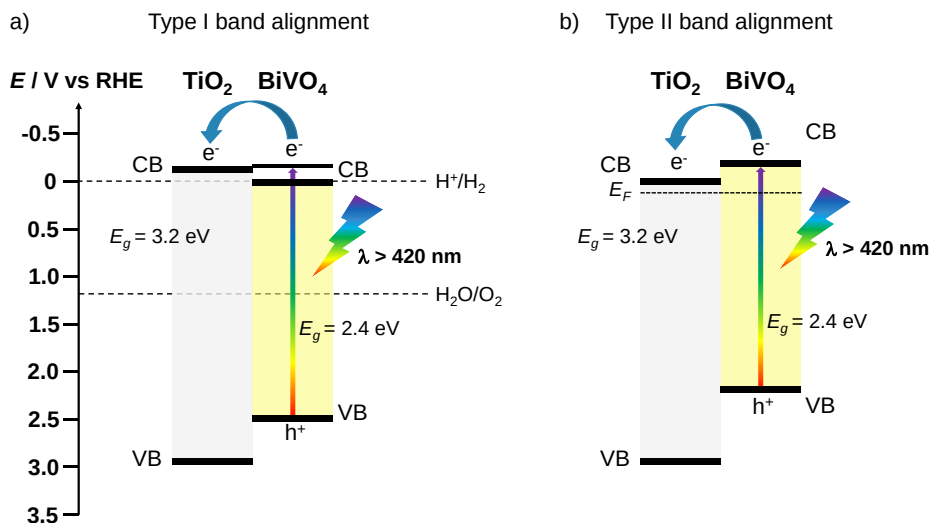


Figure 5.8 Proposed electron injection mechanism for the TiO₂/BiVO₄ heterojunction under visible light irradiation in the a) Type I alignment based on the band edge positions of the two isolated semiconductors and b) Type II alignment after the thermodynamic equilibrium (E_F represents the Fermi level of the TiO₂/BiVO₄ system).

5.5 Conclusions

The TiO₂/BiVO₄ heterojunction is a fascinating material which allows to exploit the excellent absorption properties of BiVO₄ to produce highly reductive electrons through TiO₂ sensitization under visible light. A counterintuitive electron transfer mechanism from BiVO₄ to TiO₂ is active in this system, which significantly deviates from predictions purely based on the CB edges location of the two isolated semiconductors. Methyl viologen reduction tests demonstrate the higher photocatalytic activity under visible light of the TiO₂/BiVO₄ heterojunction with respect to either individual components and also compared to the WO₃/BiVO₄ heterojunction, which is characterized by excellent charge separation but is affected by a lower reducing ability than individual BiVO₄. The TiO₂/BiVO₄ heterojunction system allows TiO₂ sensitization for solar energy storage applications and has the potential to carry out overall water splitting under visible light, even without the application of an external bias.

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Chapter 6

Unravelling the bulk and interfacial charge transfer effects of Mo⁶⁺ doping in BiVO₄ photoanodes

6.1 Abstract

The role of Mo⁶⁺ doping on the photoelectrochemical (PEC) performance of BiVO₄ photoanodes was investigated both in the presence and in the absence of sulfite as hole scavenger. Optically transparent, flat BiVO₄ photoanodes containing different amounts of Mo⁶⁺ dopant were synthesized by spin coating onto conductive substrates. Two opposite trends of the PEC *performance vs. doping degree* were found in the presence or absence of sulfite, in parallel with the opposite behaviour in interfacial charge transfer resistance determined by electrochemical impedance spectroscopy. In fact, increasing amounts of the Mo⁶⁺ dopant not only improve the electron transport in the BiVO₄ bulk by increasing its conductivity, as unequivocally ascertained through the employment of a Ni/Fe oxyhydroxide co-catalyst, but also facilitate the charge transfer at the electrode/electrolyte interface in the absence of hole scavenger. On the other hand, increasing the Mo⁶⁺ dopant amount in BiVO₄ induced an unexpected decrease in PEC performance per unit surface area in sulfite oxidation, as a result of enhanced interfacial charge transfer resistance. First evidence is thus provided of a different behaviour observed upon Mo⁶⁺ doping of BiVO₄ depending on the nature of the involved electron donor species, together with an intriguing multifaceted role played by Mo⁶⁺ doping in enhancing the PEC performance of modified BiVO₄ electrodes.

6.2 Introduction

In spite of the several attractive features exhibited by BiVO₄ as photoactive material described in Section 3.4 and resumed in the previous chapter, intrinsic limitations, such as poor electron transport leading to a low electron–hole separation yield and a sluggish water oxidation kinetics responsible for excessive surface charge recombination, hamper the achievement of the theoretical STH conversion efficiency limit of 9%.^{1–6}

While BiVO₄ combination with other semiconductors in heterojunctions^{7–9} and the incorporation of oxygen evolution co-catalysts (OECs)^{4,10–13} have been employed aiming at overcoming bulk charge recombination and speeding up the water oxidation kinetics at the electrode surface, respectively, nanostructuring and doping are promising strategies to alleviate the intrinsic electron transport limitations of pure BiVO₄.^{2,14–16} Nanostructuring was found effective in tackling the charge carrier transport limitations of BiVO₄ photoanodes,¹⁷ but it compromises the transparency of the electrode in the wavelength range outside its band gap, which is an important requirement for the dual absorbers cell configuration.^{18,19}

Doping with higher valent metal ions such as Mo⁶⁺ and W⁶⁺, with respect to both Bi³⁺ and V⁵⁺, has been extensively employed as the most successful doping strategy to increase the water oxidation activity of pure BiVO₄.^{3,5,15,16,20–25} Most commonly, the observed PEC performance enhancement has been associated with the alleviation of the intrinsic poor electron transport properties of the material, since the hexavalent ions can act as shallow donors which increase the majority carrier concentration and, consequently, the *n*-type conductivity in the bulk.^{6,25,26} For instance, by screening different Mo⁶⁺ doping degrees in electrodeposited BiVO₄ films, Choi *et al.* identified 3 at% doping as optimum in the presence of sulfite, with a significantly enhanced water photooxidation after coupling with an OEC. A more efficient electron–hole separation, resulting from improved electron transport upon Mo⁶⁺ doping, was identified at the basis of the increased activity.³ A similar explanation was invoked by Bard *et al.* for the 10 times higher photocurrent attained upon consecutive W and Mo co-doping of BiVO₄ with respect to pure BiVO₄, in both water and sulfite oxidation.²⁰

Despite the similarity in the function and ionic radii,²⁰ the Mo dopant was generally found to provide superior conductivity than the W dopant and, therefore, enhanced photoactivity.^{16,22,27,28} For instance, Parmar *et al.* reported that 2 at% Mo doped BiVO₄ films exhibit better performance than W doped electrodes, thanks to the higher donor capacity of Mo compared to W, to which corresponds a higher improvement in electron mobility.¹⁶ Moreover, the screening study of different dopants conducted by Yan *et al.* via density functional theory (DFT) calculations,²⁶ confirmed that Mo is a better *n*-type dopant than W for BiVO₄.

Moreover, in most cases the effects of BiVO₄ doping were screened either in pure water oxidation or in the presence of a sacrificial agent such as the sulfite anion, which of course implies the interaction of the photoanode with a species more easily oxidizable than water, possibly occurring through a different mechanism and with a different electron transfer kinetics. This means that the impact of doping on the BiVO₄ performance in water and sulfite oxidation can be different.²⁹

In the study presented in this chapter, we aim at elucidating the effects that Mo⁶⁺ doping has on the performance of BiVO₄ photoanodes in both sulfite and water oxidation, by directly comparing the relative trends in performance attained in the two reactions as

a function of the doping degree. The Mo⁶⁺ doping degree of BiVO₄ was systematically changed in photoanodes synthesized as optically transparent flat films deposited by spin coating of precursor solutions onto FTO conductive substrates. The PEC performance resulting from irradiation through both the *back*- and the *front*-side of the electrodes was tested in both a 0.5 M Na₂SO₄ aqueous solution (*i.e.*, in the water oxidation reaction) and 0.5 M Na₂SO₃ aqueous solution (*i.e.*, in sulfite oxidation), in relation to electrochemical impedance spectroscopy (EIS) measurements. Furthermore, insights into the bulk transport properties of the material under *in situ* conditions were obtained by modifying selected electrodes with Ni/Fe oxyhydroxide (NiFeO_x) OEC. The different *performance vs. doping degree* trends found for the two here investigated oxidation reactions indicate that specific interactions between the electrode and the oxidizable substrate occur, depending on both the dopant content and the nature of the electron donor species.

6.3 Experimental section

6.3.1 Chemicals and materials

The following chemicals, purchased from Sigma Aldrich, were employed as supplied: molybdenum oxide bis(2,4-pentanedione), ammonium metavanadate ($\geq 99\%$), bismuth(III) nitrate pentahydrate (98%), poly(vinyl alcohol) $> 99\%$ (PVA), citric acid (99%), glacial acetic acid, nitric acid 23.3%, sodium sulfate ($\geq 99\%$), anhydrous sodium sulfite ($\geq 99\%$), acetone, iron(II) sulfate heptahydrate ($\geq 98\%$), nickel(II) sulfate pentahydrate ($\geq 99\%$). Fluorine-doped tin oxide (FTO) glass, 7 Ω ·sq, 2 mm thick, was purchased from Pilkington Glass (TEC-7).

6.3.2 Photoelectrodes preparation

Pure BiVO₄ (BV) films were prepared as reported elsewhere.³⁰ In a typical synthesis, 0.002 mol of Bi(NO₃)₃ and NH₄VO₃ were added to 6 mL of 23.3% HNO₃ containing 0.004 mol of citric acid acting as stabilizer. After complete dissolution of the precursors, a denser paste was obtained by adding 0.04 g of poly(vinyl alcohol) (PVA) and 0.25 mL of acetic acid to 1.0 mL of the above solution. The mixture was stirred overnight to allow dissolution of the thickening polymeric agent. A BiVO₄ layer was obtained by spin coating the so obtained paste at 4000 rpm for 30 s onto clean FTO, previously treated in acetone. The so obtained films underwent a calcination treatment at 70 °C for 1 h to burn off all the organic material, followed by annealing at 500 °C for 1 h in air. Prior to deposition, the FTO glass was cleaned by 30 min-long sonication in a soap solution, followed by careful washing, sonication in ethanol for 30 min and drying in air. The clean glass slices then underwent a 15 min-long UV-cleaner ozone treatment to remove any organic species deposited onto the FTO surface.

Mo⁶⁺ doped BiVO₄ precursor solutions containing nominal Mo to V (or equivalently Mo to Bi) molar ratios equal to 0.3, 0.5, 0.7, 2, 3 and 6 at% were prepared by substituting the proper amount of the molybdenum precursor to both Bi and V precursors, to obtain a

Mo_{2x}Bi_(1-x)V_(1-x)O_(4+2x) nominal composition. Afterwards, a denser paste was obtained from each precursor solution through PVA addition and single layer films with different Mo⁶⁺ doping percentages were synthesized by spin coating the corresponding paste onto clean FTO, followed by thermal treatment, as for pure BiVO₄ electrodes. Doped monolayer BiVO₄ materials were labelled X Mo:BV, with X referring to the nominal atomic Mo⁶⁺ dopant amount.

A mixed nickel and iron oxyhydroxides co-catalyst layer was deposited on pure and representative Mo⁶⁺ doped BiVO₄ electrodes by a previously described PEC method.³¹ The so obtained photoanodes were named as X Mo:BV_NiFeO_x, with X referring to the nominal atomic Mo⁶⁺ dopant amount.

6.3.3 Physical and photoelectrochemical methods

The crystalline phase of the materials was determined through X-ray diffraction (XRD) analysis using a Philips PW1820 instrument with Cu K α radiation, at 40 mA and 40 kV. Field emission scanning electron microscope (FESEM) images were acquired using a SEM Field Emission ZEISS Supra40 scanning electron microscope operating at a 10 kV accelerating voltage, at a 8 mm working distance. Atomic force microscopy images were collected by means of a AFM/STM Thermomicroscope CP-Research. UV–visible absorption spectra were recorded in the transmittance mode using a Jasco V-670 spectrophotometer.

PEC measurements were carried out using the three-electrode glass cell described in Section 4.3.2.1, with each of the tested films acting as working electrode, an AgCl/Ag (3.0 M NaCl) electrode as reference electrode and a platinum gauze as a counter electrode, all connected to a Metrohm Autolab PGSTAT302N potentiostat/galvanostat. PEC tests were performed in both back- and front-side irradiation configuration, *i.e.* under illumination either through the FTO substrate or the electrode/electrolyte interface, respectively. The photoanodes were in contact with either a 0.5 M Na₂SO₃ aqueous solution, acting as supporting electrolyte and hole scavenger, and buffered at pH 7 with a 0.5 M potassium phosphate buffer, or with a 0.5 M Na₂SO₄ electrolyte solution, where only water oxidation can take place. The irradiation source was an Oriel, Model 81172 solar simulator providing AM 1.5 G solar simulated illumination with 100 mW cm⁻² intensity (1 sun). All tested electrodes are stable at neutral pH and no noticeable degradation was observed under irradiation. The applied potential vs. AgCl/Ag was converted into the reversible hydrogen electrode (RHE) scale using Eq. 4.19.

Linear Sweep Voltammetry (LSV) was performed with a 20 mV s⁻¹ scan rate starting from the open circuit potential (OCP), determined for each film after 5 min irradiation, up to 1.3 V vs. RHE and 1.8 V vs. RHE in 0.5 M Na₂SO₃ and 0.5 M Na₂SO₄ solution, respectively. A narrower potential window was investigated in the presence of the Na₂SO₃ hole scavenger to avoid the generation of a significant dark current resulting from the oxidation of the SO₃²⁻ anion. Five consecutive LSV scans were recorded for each sample

in each employed electrolyte solution and irradiation configuration to allow the stabilization of the system; only the last stabilized J - V curve was taken into account. Cyclic voltammetry (CV) curves in the dark were acquired in previously N_2 -purged 0.5 M Na_2SO_3 and 0.5 M Na_2SO_4 electrolyte solutions, at a 50 mV s^{-1} scan rate. Chronoamperometry (CA) measurements were performed in a 0.5 M Na_2SO_4 solution at 1.23 V vs. RHE, under back-side AM 1.5 G irradiation.

Incident photon to current efficiency (IPCE) measurements were carried out in either 0.5 M Na_2SO_3 or 0.5 M Na_2SO_4 solutions at 1.0 V vs. RHE and 1.23 V vs. RHE, respectively, under front-side monochromatic irradiation, using the same three-electrode glass cell employed in AM 1.5 G solar simulated experiments. The IPCE was calculated using Eq. 4.30. Internal quantum efficiency (IQE) curves were calculated by normalizing the IPCE curves for the photons effectively absorbed by the material, calculated from the absorbance spectra (Eq. 4.31).

6.3.4 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were conducted both in the dark and under back-side AM 1.5 G irradiation using a single-compartment three-electrode glass cell, either in 0.5 M Na_2SO_3 or in 0.5 M Na_2SO_4 N_2 -purged solutions. Each tested BiVO_4 -based film acted as the working electrode (0.7 cm^2 geometric area), a platinum gauze acted as the counter electrode and an AgCl/Ag (3.0 M NaCl) equipped with a salt bridge was the reference electrode. All measurements were acquired with a Metrohm Autolab PGSTAT302N potentiostat/galvanostat equipped with a frequency response analyzer module (FRA32M) connected to the cell.

A first set of data was recorded, for each BiVO_4 -based electrode, under back-side irradiation (100 mW cm^{-2}) at 1.0 V vs. RHE, corresponding to the highest “operative potential” of the working electrode selected for triggering the sulfite oxidation reaction in a 0.5 M Na_2SO_3 solution, which undergoes self-oxidation earlier than water in Na_2SO_4 solution. Each EIS spectrum was recorded by sampling sixty frequencies (single sine, logarithmically distributed from 10^5 Hz to 0.1 Hz ; 10 mV amplitude).

Mott-Schottky (M-S) analyses were carried out in the dark and in a 0.5 M Na_2SO_4 N_2 -purged solution, to estimate the flat band potential (E_{FB}) and the electron donor density (N_{D}) of all investigated electrodes. Impedance spectra were recorded at a bias potential ranging from 0 to 1.2 V vs. RHE, by scanning 30 single sine frequencies between 10^4 Hz to 0.03 Hz (logarithmically distributed; 10 mV amplitude). Each tested material was first conditioned at 1.23 V vs. RHE for 30 s and then at the selected potential for 30 s. During the entire EIS measurement, a flux of N_2 was maintained on the solution surface.

EIS spectra were fitted by means of the Z-View software (Scribner Associates, Inc.) through the simple equivalent circuit $R_s(R_{\text{ct}}, \text{CPE})$ that does not model any mass transport limitation. In particular, R_s is the serial resistance (accounting for all ohmic resistances in the electrochemical system), R_{ct} represents the charge transfer resistance associated with

the faradaic reaction and CPE is the constant-phase element accounting for the double layer capacitance (C_{dl}). To properly draw the Mott-Schottky plots ($C^{-1/2}$ vs. applied potential), the effective capacitance, C , was calculated from CPE parameters as described in literature.³²

6.4 Results and discussion

6.4.1 Photoelectrodes characterization

The XRD patterns of the electrodes (Figure 6.1) identify the most active monoclinic scheelite BiVO₄ structure in all cases,^{2,33} without evidencing any impurity phase or compound. Thus, neither structural changes nor crystalline MoO₃ can be detected upon dopant incorporation into BiVO₄, up to the here employed highest level.^{3,27} This rules out that phase conversion to the less active tetragonal structure of BiVO₄, which is reported to take place for Mo contents in BiVO₄ above 6 at%,³ occurred for any of the here investigated doping percentages.

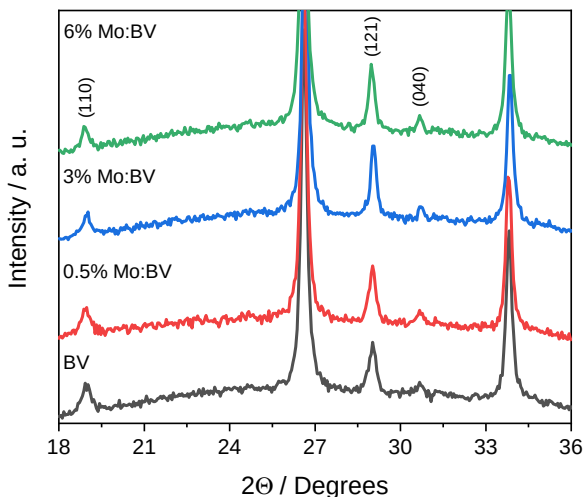


Figure 6.1 XRD patterns of i) BV, ii) 0.5% Mo:BV, iii) 3% Mo:BV and iv) 6% Mo:BV.

The dopant incorporation was proved by the energy-dispersive X-ray spectroscopy (EDX) mapping analyses reported in Figure 6.2, where a homogeneous distribution of the Bi, V and Mo elements was detected for the doped samples. The total average Mo concentration in the synthesized films, accounting for both bulk and surface doping, was checked by means of ICP-AES analyses carried out by dissolving the FTO covering films in a 23% HNO₃ solution. The so determined Mo atomic percentages (with respect to the total Bi and V amount) in the investigated films are collected in Table 6.1. For each photoanode the actual Mo content was found to be systematically lower than the nominal value, which can be ascribed to an intrinsic loss and evaporation of the Mo dopant during the synthesis and annealing processes,³⁴ though progressively increasing with increasing nominal Mo⁶⁺ content.

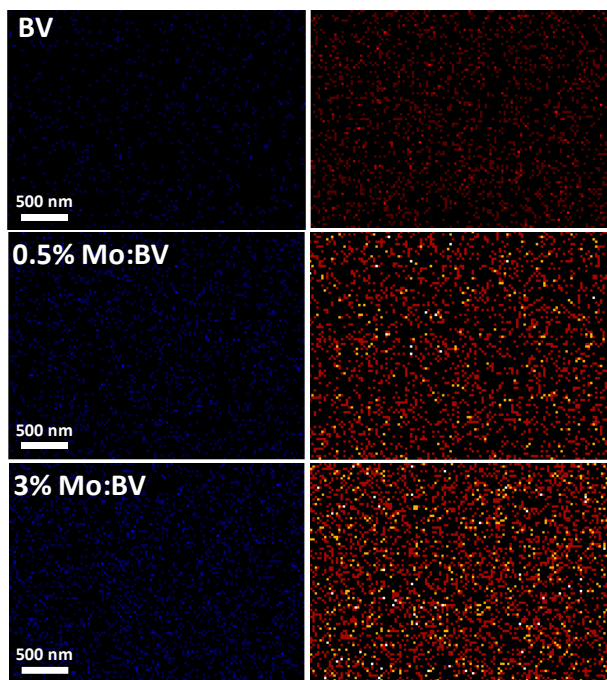


Figure 6.2 Energy-dispersive X-ray spectroscopy (EDX) images of pure, 0.5 at% and 3 at% Mo^{6+} doped BiVO_4 films. Red, Blue and yellow colours refer to Bi, V and Mo elements, respectively.

Table 6.1 Comparison between the nominal and the experimental atomic percentages of Mo^{6+} obtained from ICP-AES analyses.

Nominal Mo in solution / at%	Mo in films by ICP-AES / at%
0	n.d.
0.5	0.35 ± 0.06
0.7	0.77 ± 0.10
2	1.60 ± 0.01
3	2.92 ± 0.20
6	4.34 ± 0.22

FESEM analyses were conducted in order to examine the morphology of the investigated films. As evidenced by the so-obtained top view micrographs for BV, 0.5% Mo:BV, 3% Mo:BV and 6% Mo:BV shown in Figure 6.3a, the morphology of the synthesized films considerably changed upon dopant incorporation, as already reported in previous studies.^{23,35} The small grains almost spherical in shape, characterizing the pure BiVO_4 film, turn into a continuous network of interconnected worm-like shaped features upon introduction of 0.5 at% Mo^{6+} (Figure 6.3a, parts i) and ii), respectively), similar to

those previously reported for BiVO₄-based films.^{8,15,30} Then, the Mo⁶⁺ content increase to 3 at% and 6 at% values (Figure 6.3a, parts iii) and iv), respectively) induces a further change in morphology, with the worm-like features aggregating in almost spherically shaped, *ca.* 100 nm sized isolated nanoparticles.

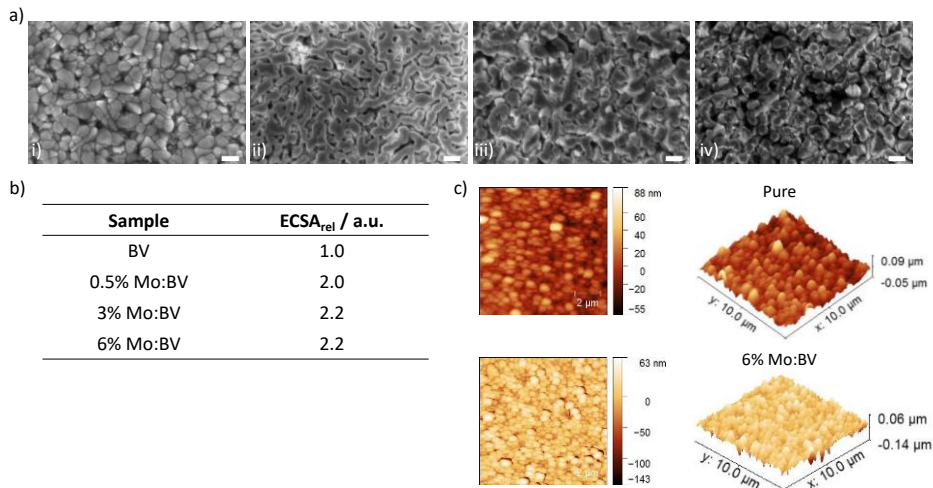


Figure 6.3 (a) Top view FESEM images of i) BV, ii) 0.5% Mo:BV, iii) 3% Mo:BV and iv) 6% Mo:BV, with a scale bar of 300 nm; (b) relative electrochemical active surface area (ECSA) of the same films, calculated with respect to the pure BV one. (c) Atomic force microscopy (AFM) surface topography of pure BV and 6% Mo:BV.

This phenomenon is paralleled by a significant change in the real surface area of the examined films upon dopant incorporation, as demonstrated by the electrochemical active surface area (ECSA) measurements detailed in Appendix A. In fact, a double relative ECSA, almost invariant with the Mo⁶⁺ amount, was found for the most representative doped electrodes (0.5% Mo:BV, 3% Mo:BV and 6% Mo:BV), taking pure BV as the reference (Figure 6.3b). In line with this, AFM analyses (Figure 6.3c) estimated a lower root-mean-square (RMS) factor for pure BV compared to the 6% Mo:BV film, *i.e.* 13.5 nm and 15.5 nm, respectively.

UV-vis absorption spectra of all synthesized photoanodes, reported in Figure 6.4, exhibit the typical BiVO₄ absorption profile with a maximum at 420 nm and the absorption onset at *ca.* 500 nm, in agreement with the 2.4 eV band gap energy of BiVO₄.³⁶ A good transparency at wavelengths longer than the absorption onset can be appreciated for all samples, with a slightly pronounced absorption tail probably due to light scattering.

All BiVO₄ films were *ca.* 70 nm thick, as previously measured for BiVO₄ films previously synthesized in the same way³⁷ and showing an identical absorbance at the 420 nm absorption maximum as the here investigated materials.

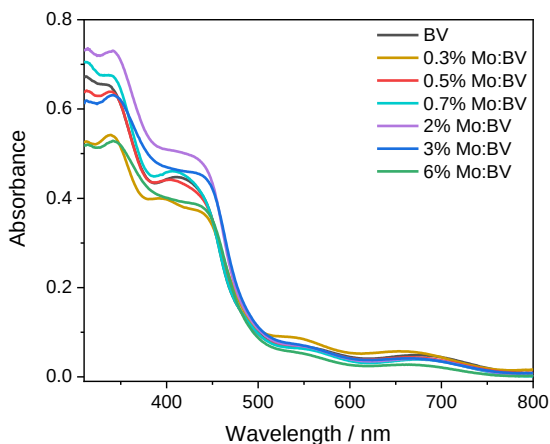


Figure 6.4 UV-vis absorption spectra of all synthesized films recorded in the transmittance mode.

6.4.2 Charge transfer features towards water molecules and sulfite ions

The electrochemical portrait of the BiVO_4 -based electrodes was first pursued by investigating their electrochemical fingerprints and their charge transfer properties towards the specific electron donor species involved in PEC investigations, *i.e.* water and the sulfite anion, which was used as a hole scavenger. Figure 6.5 collects the cyclic voltammograms recorded with pure BiVO_4 and with the most highly doped electrode, in 0.5 M Na_2SO_4 and in a pH 7 buffered 0.5 M Na_2SO_3 solution, in the absence of irradiation.

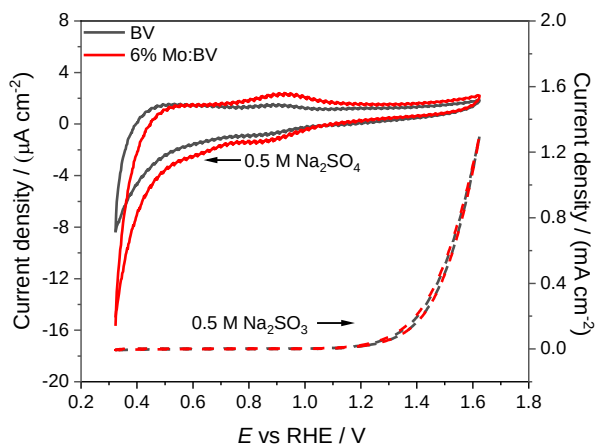


Figure 6.5 Cyclic voltammograms (sweep rate: 50 mV s^{-1}) of two representative electrodes: pure (gray lines) and 6 at% Mo^{6+} doped BiVO_4 (red lines), recorded in 0.5 M Na_2SO_4 (continuous lines, ordinate to the left) and in 0.5 M Na_2SO_3 (dashed lines, ordinate to the right) aqueous solutions, in the dark.

In both aqueous media (not evident in Figure 6.5 in the curve recorded in the Na_2SO_3 solution, due to the more expanded photocurrent density scale), a characteristic peak

couple at *ca.* 0.85 V vs. RHE was systematically detected, independently of the presence of Mo⁶⁺ ions in the BiVO₄ matrix, which has been ascribed to the redox V⁴⁺/V⁵⁺ couple.³⁸ Besides this fingerprint, no massive water oxidation was detected in Na₂SO₄ solution, even at the most positive 1.6 V vs. RHE potential, corresponding to an overpotential of *ca.* 400 mV with respect to its thermodynamic value. This points to a significantly high activation barrier for the oxygen evolution reaction on BiVO₄-based electrodes.^{4,13}

On the contrary, an evident anodic current starts to flow at around 1.4 V vs. RHE when working in the presence of sodium sulfite. The potential onset is compatible with the oxidation of SO₃²⁻ ions (*E* = 1.16 V vs. RHE at pH 7³⁹), confirming the electron donor ability of sulfite ions towards bismuth vanadate electrodes, with a just *ca.* 200 mV overpotential.

Therefore, sulfite ions can effectively be used as hole scavenger in PEC tests for both pure and Mo-doped BiVO₄ electrodes to facilitate the charge transfer process at the electrode/solution interface in aqueous medium and overcome the sluggish water oxidation kinetics.

6.4.3 Photoelectrochemical performance

The PEC performance of all synthesized photoanodes was investigated in both water and sulfite oxidation reactions to distinguish the effects induced by Mo doping on the bulk and on the surface properties of BiVO₄ photoanodes. In fact, the water oxidation photocurrent density can be described as $J_{\text{H}_2\text{O}} = J_{\text{abs}} \eta_{\text{inj}} \eta_{\text{sep}}$, where J_{abs} is the theoretical maximum photocurrent density, η_{inj} the charge transfer efficiency at the electrode/electrolyte interface and η_{sep} the charge separation efficiency in the bulk of the semiconductor material.

The sulfite anion is both thermodynamically and kinetically more oxidizable than water. Thus, its use as sacrificial electron donor enables efficient filling up of surface reaching photoproduct holes, hampering back electron-hole recombination, which is instead favored in the case of a sluggish electron transfer reaction at the electrode/solution interface.^{3,13,40,41} Therefore, in the presence of the Na₂SO₃ hole scavenger, a 100% charge injection yield (η_{inj}) can be assumed⁴¹ and the above relationship is reduced to $J_{\text{Na}_2\text{SO}_3} = J_{\text{abs}} \eta_{\text{sep}}$, with the observed photocurrent becoming an index of the bulk charge separation efficiency. Therefore, PEC performances attained toward sulfite oxidation can in principle provide direct information on the effects that Mo⁶⁺ doping exerts on the intrinsic material bulk properties of the prepared BiVO₄ electrodes,^{3,42} without the potentially interfering influence of the poor water oxidation kinetics at the electrode/electrolyte interface.

On the other hand, when PEC water oxidation is carried out in non-sacrificial conditions, the sluggish holes injection kinetics at the BiVO₄ electrode surface represents the rate determining step of the overall anodic photocurrent production.²

6.4.3.1 Sulfite oxidation

J-V curves recorded with all prepared photoanodes in the sulfite-containing solution under front-side irradiation are collected in Figure 6.6a. The similar absorption properties of all tested electrodes (Figure 6.4) allow to directly correlate the obtained photocurrent density values to the intrinsic structural and surface properties of the investigated materials.

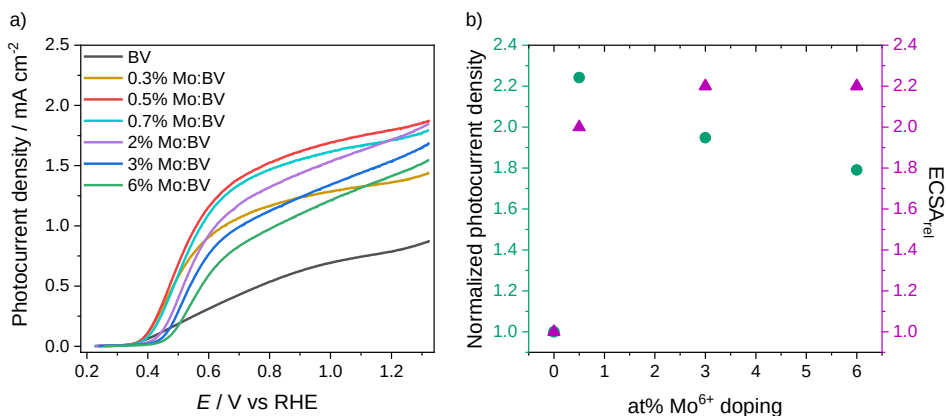


Figure 6.6 (a) Linear sweep voltammetry (LSV) scans under front-side irradiation for all investigated electrodes in 0.5 M Na_2SO_3 solution buffered at pH 7 with a 0.5 M potassium phosphate solution and (b) comparison between the relative ECSA and the normalized photocurrent density, calculated as the ratio between the values recorded at 1.23 V vs. RHE under front-side irradiation with representative Mo^{6+} doped BiVO_4 electrodes and that achieved with the pure BV electrode.

First of all, an anodic photocurrent typical of *n*-type response at potentials more positive than the flatband potential (located at *ca.* 0.1 V vs. RHE according to the Mott-Schottky analysis performed in this study, see Section 6.4.4.1 and Figure 6.11a) can be observed in all recorded LSV scans in Figure 6.6a, indicating that the electrodes work as photoanodes transferring the photogenerated holes to a hole acceptor at the semiconductor/electrolyte interface.⁴³ Furthermore, the typical *J-V* curve shape observed in sulfite oxidation carried out with BiVO_4 photoanodes¹³ was attained in all cases. This curve is characterized by a good fill factor consisting of a steep photocurrent onset (fast charge transfer) and subsequent achievement of an almost saturation photocurrent (diffusion limit).

The LSV curves shown in Figure 6.6a reveal a photocurrent density increase upon molybdenum incorporation in the BiVO_4 photoanode. The plots also evidence a bell-shape trend of the *performance vs. doping degree*, similar to that reported elsewhere,⁴³ with a maximum of *ca.* 1.8 mA cm^{-2} recorded at the formal water oxidation potential of 1.23 V vs. RHE⁴⁴ with the 0.5% Mo:BV electrode. This photocurrent density is double compared to that obtained with the pure BV electrode. The performance decrease for higher doping indicates that the introduction of an excess of Mo^{6+} ions can be

accompanied by other factors limiting the overall photocurrent, such as the presence of Mo⁶⁺ impurities, acting as detrimental recombination centers.^{2,3,45,46}

The observed PEC performance improvement towards sulfite oxidation upon dopant incorporation can be related to the doubled electrochemical active surface area (ECSA) of the doped photoanodes compared to the pure BV material (see Figure 6.3b). By comparing the ratios between the photocurrent density at 1.23 V vs. RHE attained with the 0.5 at%, 3 at% and 6 at% Mo:BV electrodes and that recorded with the pure BV film with the corresponding relative ECSA (see Figure 6.6b), evidence is provided that the relative photocurrent density increase attained with the optimized 0.5% Mo:BV electrode can be mainly ascribed to its double ECSA value. This is indeed well reflected by the closeness of the values attained for the current ratio and the relative ECSA in Figure 6.6b.

A drop of photocurrent density ratio occurs by further increasing the dopant content, accounting for the lack of any favourable impact of Mo⁶⁺ doping on Na₂SO₃ oxidation for dopant amounts larger than 0.5 at%. This finding appears in contrast with the results provided by the EIS analyses reported in Section 6.4.4.1, which demonstrate an increase in majority carrier density upon molybdenum doping corresponding to an enhanced film conductivity, accompanied by an improved electron transport in the material bulk. The lack of evidence of this behavior in the presence of the sulfite hole scavenger, which is supposed to point out the effects of doping onto the bulk material properties by favouring hole transfer at the electrode surface, may account for specific detrimental interactions of highly doped electrodes with sulfite ions and evidence the crucial role played by the exposed real surface area in the evaluation of the effective PEC performance of each electrode.

Another undesired effect of molybdenum incorporation in the presence of the sulfite hole scavenger is the positive shift in the photocurrent onset, obtained as the crossing point between the tangent line to the *J-V* curve and the baseline in the low applied potential region,⁴⁷ occurring with increasing dopant content with respect to pure BV (Figure 6.6a). This phenomenon, associated with a limited photocurrent generation, can be related to the undesired factors accompanying an excessive dopant addition (*i.e.* the presence of Mo-based traps at the grain boundaries),³ or to a decreased width of the depletion region,⁴⁸ induced by the progressively enhanced majority charge carrier density upon increasing dopant amount (Section 6.4.4.1).^{2,3,11} In this picture, the best performing 0.5% Mo:BV electrode exhibits the less positive potential onset among the doped electrodes, located at *ca.* 0.4 V vs. RHE.

The above discussion refers to PEC performances recorded under front illumination, in which electrons are photoexcited close to the electrode/electrolyte interface and have to cross the material bulk to reach the FTO contact, in contrast with back-side illumination (irradiation through the FTO substrate), where electrons are photopromoted close to the FTO back-contact and can be directly injected into the external circuit.^{1,3,49}

Therefore, a comparison between back and front irradiation performances as a function of the doping degree should provide information on the benefits that n -type Mo^{6+} doping has on the bulk charge transport properties of BiVO_4 . As shown in Figure 6.7, a similar *performance vs. doping degree* trend to that observed under front-side irradiation, characterizes also the J - V curves for sulfite oxidation acquired under back illumination.

Furthermore, as typical of BiVO_4 -based materials suffering from inefficient electron transport in the bulk, the performances attained under back irradiation were systematically higher than those attained under front irradiation (Figure 6.7). This phenomenon, ascribable to the longer average distance that photogenerated electrons must travel to reach the FTO back-contact in front irradiation configuration,^{1,29,42,49} suggests that electron transport in the bulk still represents a major limiting factor for photocurrent generation also in the presence of the Mo^{6+} dopant.^{1,3,22} However, a minimized discrepancy between the back and the front photocurrent can be observed for 3 at% Mo^{6+} incorporation, appearing as the optimum doping degree to improve electron conductivity and transport in the here investigated BiVO_4 -based photoanodes.^{5,16,23,35}

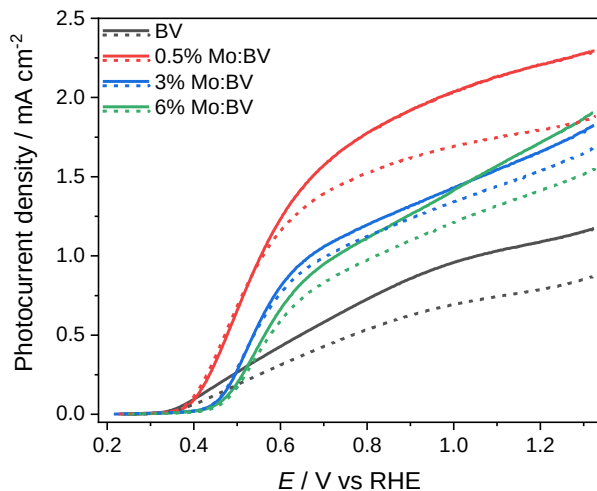


Figure 6.7 Comparison between the LSV curves recorded under back- (continuous lines) and front-side (dashed lines) irradiation with selected electrodes, in 0.5 M Na_2SO_3 solution buffered at pH 7 with a 0.5 M potassium phosphate solution.

Figure 6.8a shows the incident photon to current efficiency (IPCE) measurements conducted at 1.0 V vs. RHE in the Na_2SO_3 electrolyte solution, while the internal quantum efficiency (IQE) plots, derived from IPCE data through normalization for the absorbance spectra of the corresponding electrodes, are shown in Figure 6.8b. These data, accounting for the fraction of absorbed photons which actually generate photocurrent, allow to directly get insight on how charge recombination processes intrinsically affect the overall performance of the materials.

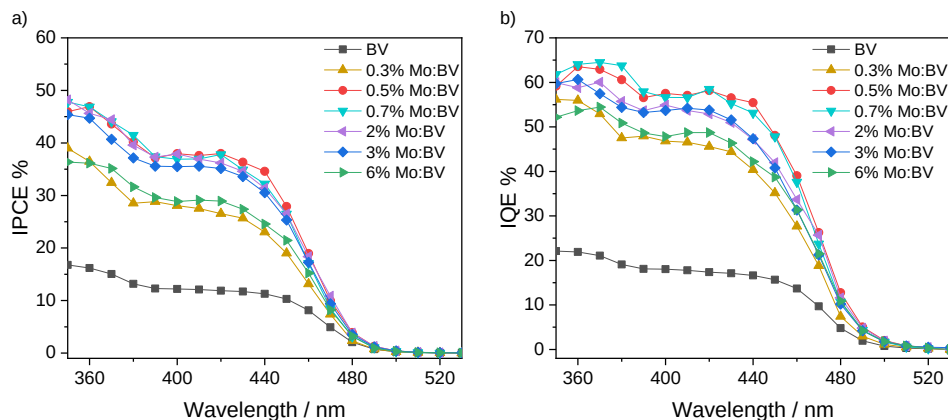


Figure 6.8 (a) Incident photon to current efficiency (IPCE) analyses recorded at 1.0 V vs. RHE under front-side irradiation with all investigated electrodes in 0.5 M Na_2SO_3 solution buffered at pH 7 with a 0.5 M potassium phosphate solution and (b) corresponding internal quantum efficiency (IQE) plots.

The same bell-shaped *performance vs. doping degree* trend with maximum for an intermediate 0.5–0.7 at% dopant content is confirmed by the monochromatic IQE plots. Also in this case, the 3.5-fold IQE enhancement with respect to the pure BV attained at 420 nm with the optimized 0.5% Mo:BV electrode (accounting for a *ca.* 60% internal conversion efficiency) does not represent a so significant improvement intrinsic of the doped material, if the doubled ECSA exhibited by Mo^{6+} doped electrodes is taken into account.

However, a minor discrepancy in activity between the intermediate and the higher doping degrees can be detected from the monochromatic IQE curves compared to full lamp LSV analyses, which should be ascribed to the lower light intensity used in the former (few mW cm^{-2}) with respect to that employed in LSV measurements under AM 1.5 G (100 mW cm^{-2}) irradiation. Indeed, the majority of the electron-hole couples generated under relatively higher light intensity¹ can undergo easier recombination in the presence of a high dopant content, potentially acting as detrimental trap at the grain boundaries and at the interface.^{2,3}

Finally, no change in the photocurrent onset response, located at *ca.* 500 nm for all the tested electrodes (Figure 6.8), was induced by dopant incorporation, indicating that Mo^{6+} doping does not affect the band gap energy of BiVO_4 photoanodes, in line with their absorption spectra.

6.4.3.2 Water oxidation

Since surface processes are typically much slower (timescale from 100 μs to 1 s) than bulk recombination processes (timescale typically below 100 ns),⁴ in the absence of a hole scavenger or co-catalyst for water oxidation holes extraction at the material/electrolyte interface should be the main limiting factor to the observed

performance.^{4,11} Therefore, PEC data acquired in Na_2SO_4 electrolyte allow to examine how the interfacial hole transfer kinetics, dominating the photoresponse of the investigated photoanodes, is affected by the presence of the dopant, in a wider applied potential window compared to that of sulfite oxidation, which undergoes self-oxidation earlier than water.

The LSV and IQE plots recorded with all synthesized films under front-side irradiation are collected in Figure 6.9.

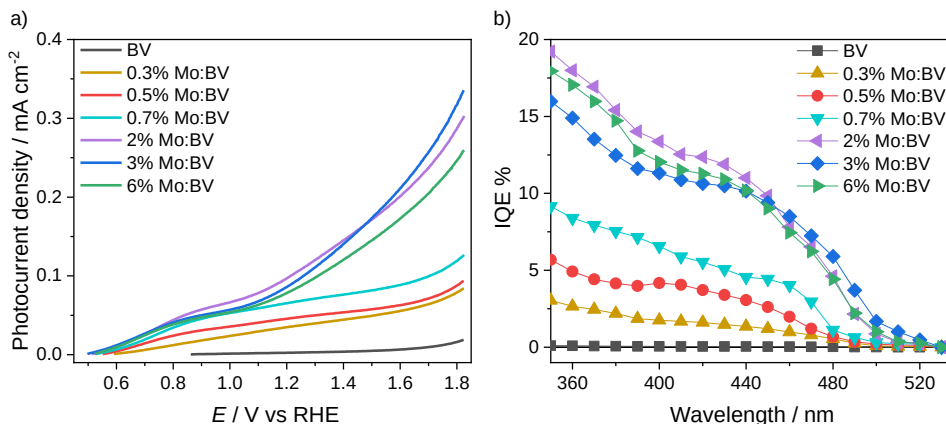


Figure 6.9 (a) LSV and (b) IQE plots recorded at 1.23 V vs. RHE under front-side irradiation with all investigated electrodes in 0.5 M Na_2SO_4 solution (pH 7).

Firstly, photocurrent showed lower absolute values with respect to those attained in Na_2SO_3 solution for both doped and pure BiVO_4 electrodes. Indeed, while the maximum photocurrent density recorded with Mo^{6+} doped BV materials in water oxidation (Figure 6.9a) is *ca.* one order of magnitude lower than the photocurrent density attained in the presence of Na_2SO_3 (Figure 6.6a), the pure BV electrode practically exhibits no photoactivity in the absence of a hole scavenger, similarly to previous reports.⁴⁰ This can be ascribed to the pile up of holes at the BiVO_4 surface due to the sluggish water oxidation kinetics which may cause severe recombination issues, further limiting also the charge transport efficiency.^{1,2,11,40,42} Furthermore, the photocurrent onset potential observed with all materials in water is considerably larger than for sulfite oxidation, implying that larger overpotentials are necessary to separate the photogenerated charges to effectively enable holes consumption in the water oxidation reaction (compare Figure 6.9a with Figure 6.6a).^{40,50}

However, the overall improvement induced by Mo^{6+} doping in water oxidation is far more pronounced than in the presence of the hole scavenger. Indeed, the negligible photocurrent obtained with pure BV was enhanced up to *ca.* 120 $\mu\text{A cm}^{-2}$ at 1.23 V vs. RHE (Figure 6.9a) and a IQE of 12% was attained at 420 nm (Figure 6.9b) upon Mo^{6+} incorporation, in addition to a progressive negative shift (*i.e.*, to lower supplied energy) of the photocurrent onset potential with increasing dopant content (Figure 6.9a).

In this way, in the water oxidation reaction an inverse trend of the *performance vs. doping degree* was attained compared to that observed in contact with the Na₂SO₃-containing solution, with an almost monotonic photoactivity increase with increasing the doping extent.

Furthermore, while comparable photocurrent values were recorded at the thermodynamic threshold potential of 1.23 V vs. RHE regardless of the nominal Mo⁶⁺ content of the electrodes, an abrupt photocurrent increase was obtained for highly doped systems (2–6 at% of Mo⁶⁺) in the high applied potentials region of the *J-V* curves in Figure 6.9a. This means that at sufficiently high applied bias, where water oxidation may outcompete surface recombination due to an increased band bending in the material, a relatively large Mo⁶⁺ dopant amount is essential in order to gain relevant and beneficial effects, promoting the interfacial water oxidation kinetics at the electrode/electrolyte interface.

The same behavior is shown by the IQE plots in Figure 6.9b at the relatively low 1.23 V vs. RHE bias since, in this case, surface recombination is limited by the low intensity of monochromatic incident light.¹ Thus, the dopant has a beneficial role on interfacial charge transfer even at low applied potentials.

Therefore, Mo⁶⁺ doping of BiVO₄ produces a *ca.* two orders of magnitude photocurrent density increase with respect to that obtained with pure BiVO₄, which cannot be explained with the relatively modest ECSA increase attained upon doping, as in the case of the results attained in sacrificial conditions. Moreover, the lack of such a high improvement when in sulfite oxidation, *i.e.* under conditions in which surface recombination is negligible and bulk properties of the material should be determinant, excludes that the main effects of doping are limited to the material bulk, especially in the water oxidation reaction.

Conversely, the different behaviors observed in the two employed test reactions strongly suggest that, in conditions of sluggish water oxidation kinetics at the film surface, the dopant should play its main role in improving hole transfer at the film/electrolyte interface instead of improving bulk transport properties. This conclusion is indirectly supported by the still higher performance attained under back- rather than front-side irradiation, even for the most highly doped materials (Figure 6.10a), indicating that the poor electron transport in the material bulk has not been efficiently overcome upon doping.

The stability over time towards water oxidation of the pure BV electrode and of some representative doped films was tested through 4 h-long chronoamperometry (CA) measurements at 1.23 V vs. RHE under full lamp irradiation, as reported in Figure 6.10b. In all cases, the photocurrent response reached a steady-state value after an initial activation time of *ca.* 1 hour. The stable photocurrent value was quickly recovered even after a 180 s-long polarization in the absence of irradiation, indicating that light activation of each electrode has a long-lasting effect. The extent of photocurrent improvement

achieved after the photoactivation period clearly depends on the doping degree, leading to a photocurrent density of *ca.* 0.8 mA cm^{-2} with the 3% Mo:BV doped electrode, which thus appears as the best performing photoanode in pure water oxidation.

The record steady-state photocurrent reached upon light activation and polarization is 7-fold higher than the transient photocurrent generated with the same (3 at% doped) electrode during LSV measurements, at the same applied potential. This indicates that additional factors related to the irradiation conditions, such as light intensity and exposition time, other than the doping degree and the nature of the electrolyte solution, play a fundamental role in determining the overall observed photoactivity, as a result of complex interconnected mechanisms.

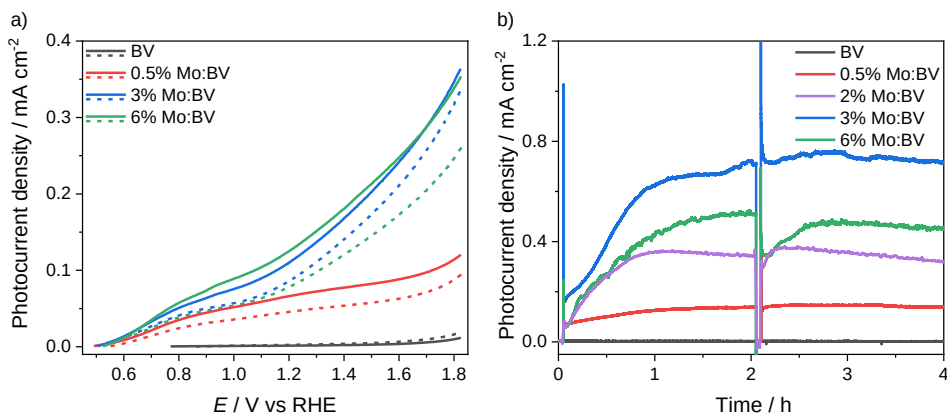


Figure 6.10 (a) LSV plots recorded with selected electrodes under back-side (continuous lines) and front-side (dashed lines) irradiation in $0.5 \text{ M Na}_2\text{SO}_4$ solution (pH 7). (b) Chronoamperometry (CA) measurements for the pure, 0.5 at%, 2 at%, 3 at% and 6 at% Mo^{6+} doped BV films under back-side irradiation in the same electrolyte solution.

6.4.4 Electrochemical impedance spectroscopy analysis

6.4.4.1 Mott-Schottky analysis

Mott-Schottky (M-S) analysis is one of the most effective and commonly employed strategy to obtain information on the electronic characteristics of intrinsic and extrinsic semiconductor electrodes. Accordingly, it has already been used to investigate the role of Mo^{6+} doping on the electronic features of BiVO_4 electrodes, for example to estimate the majority carrier density (N_D) in the material bulk and the flatband potential (E_{FB}).^{2,3,23,35,45,51} The method implies the treatment of capacitance data obtained through EIS. In particular, it relies on measuring the capacitance of the space charge region (C_{SC}), naturally built in the outermost layer of a semiconductor in contact with an electrolyte, as a function of an externally applied potential.⁵⁰ Under specific conditions, the space charge capacitance of the semiconductor, dielectric in origin and corresponding to the transfer of charges from the bulk of the absorbing layer to the electrolyte through the semiconductor–liquid junction (SCLJ),⁵² gives rise to a line in the Mott-Schottky plot,

describing how C_{SC} varies with the applied voltage E_{appl} throughout the depletion layer, according to Eq. 6.1 (valid for n -type semiconductors):

$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon_r \varepsilon_0 q N_D} \left(E_{appl} - E_{FB} - \frac{kT}{q} \right) \quad (6.1)$$

where C_{SC} (F cm⁻²) is the space charge capacitance normalized for the electrode geometric area, ε_r the relative permittivity of the semiconductor (*ca.* 70 for BiVO₄⁵³), ε_0 the permittivity of vacuum (8.85 10⁻¹⁴ F cm⁻¹), q the elementary charge, N_D the donor density, k the Boltzmann constant and T the absolute temperature. Hence, at a given T and pH of the electrolyte solution, E_{FB} can be obtained by extrapolating to zero the linear part of the C_{SC}^{-2} vs. E_{appl} plot (and correcting the intercept for $kT/q \approx 25$ mV at room temperature), whereas N_D can be directly estimated from the slope of the linear region of the plot, to which it is inversely proportional. Moreover, the evaluation of E_{FB} , corresponding to the voltage at which the potential drop in the space charge layer is zero and the semiconductor bands are flat, provides a good estimation of the conduction band (CB) edge for a highly doped semiconductor.

Figure 6.11a shows the M-S plots relative to pure BV, 0.5% Mo:BV, 3% Mo:BV and 6% Mo:BV electrodes in contact with the Na₂SO₄ solution in the absence of irradiation, obtained by fitting the related EIS spectra at each single potential with the $R_s(R_{ct},CPE)$ equivalent circuit shown in the inset of Figure 6.11a. In this model, R_s is the solution resistance, CPE the constant phase element describing the space charge capacitance (see Experimental Section for more details) and R_{ct} the charge transfer resistance.

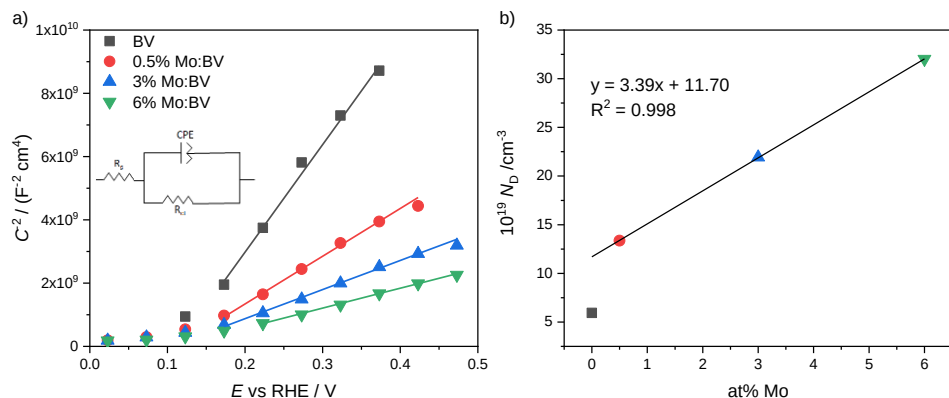


Figure 6.11 (a) Mott-Schottky plots measured in the dark in 0.5 M Na₂SO₄ solution for the pure, 0.5 at%, 3 at% and 6 at% Mo⁶⁺ doped BV photoanodes. The plotted space charge capacitance (C_{SC}) values were obtained from the corresponding CPE values of the $R_s(R_p, CPE)$ equivalent circuit, after normalization for the geometric area of the electrodes. (b) Plot of donor density (N_D) values vs. the Mo⁶⁺ content of the investigated photoanodes.

The linear region of the plot exhibits a positive slope for all samples, confirming the n -type character of the synthesized semiconductor materials. The estimated values of both E_{FB} and N_D parameters of the investigated photoanodes is provided in Table 6.2.

Table 6.2 E_{FB} and N_D parameters estimated from M-S analysis.

	E_{FB} vs. RHE / V	$10^{19} N_D / \text{cm}^{-3}$
BV	0.09	5.9
0.5% Mo:BV	0.09	13
3% Mo:BV	0.08	22
6% Mo:BV	0.08	32

A flat band potential of *ca.* 0.09 V vs. RHE in a neutral 0.5 M Na₂SO₄ solution was obtained for pure BV, similarly to previously reported values.^{13,15,42} No significant change in the flat band potential was evidenced upon Mo⁶⁺ incorporation,^{2,3} in perfect line with the absorption (Figure 6.4) and IQE analyses (Figure 6.9b) accounting for a band gap of *ca.* 2.4 eV, independent of the Mo⁶⁺ doping level.

On the other hand, a progressively less steep slope of the M-S regression lines can be observed when passing from pure BV to increasingly doped films (Figure 6.11a), pointing to a gradual increase of the donor density upon dopant addition (from $5.9 \cdot 10^{19} \text{ cm}^{-3}$ for pure BV to $32 \cdot 10^{19} \text{ cm}^{-3}$ for 6% Mo:BV; Table 6.2), according to the *n*-type character of the Mo⁶⁺ dopant^{25,54} and in agreement with literature reports.^{2,3,23,27,29,51} The linear increase of the donor density with the percent amount of Mo⁶⁺ dopant reported in Figure 6.11b is in agreement with the absence of any exogenous peak in the XRD spectra (Figure 6.1) of the doped samples, and points to an incorporation of Mo⁶⁺ ions into the crystal structure of BiVO₄ without any segregation effect even for the higher dopant amounts. An increase in donor density should correspond to an enhancement of the film electrical conductivity (σ), according to Eq. 6.2:^{11,55}

$$\sigma \sim N_D q \mu \quad (6.2)$$

where q is the elementary charge and μ the electrons mobility. Thus, the obtained result is also an indirect evidence of the electron transport improvement in the material bulk upon incorporation of increasing Mo⁶⁺ concentrations.^{2,3,11,55}

6.4.4.2 Photoelectrochemical impedance spectroscopy analysis

The influence of the Mo⁶⁺ dopant amount on the interfacial charge transfer properties of BiVO₄ photoanodes in relation to the two investigated oxidation reactions was further elucidated by directly comparing the corresponding electrochemical impedance spectra recorded in Na₂SO₃ and Na₂SO₄ electrolyte solutions *in operando* conditions, *i.e.* under AM 1.5 G full lamp irradiation (the actual conditions of PEC experiments conducted with full lamp illumination). In this case, the reference parameter R_{ct} stands for the charge transfer resistance associated with the photo-assisted oxidation reaction occurring at the electrode/electrolyte interface.

Figure 6.12 compares the Nyquist plots recorded in the presence of the two electrolytes at 1.0 V vs. RHE under AM 1.5 G illumination, after normalization for the

ECSA of each electrode, in order to rule out any possible contribution related to the increased real surface area occurring upon Mo^{6+} incorporation in BiVO_4 .

From a qualitative point of view, the semicircle diameter is equal to the charge transfer resistance (R_{ct}) associated with the oxidation reaction occurring at the electrode surface and its reduction is indicative of a faster interfacial charge transfer process.^{51,56} Overall, the far lower charge transfer resistances detected for sulfite compared to water oxidation can be related to the easier oxidation of sulfite itself and to the higher photocurrent response attained in its presence compared to water oxidation conditions (see Figure 6.12a vs. Figure 6.12b).

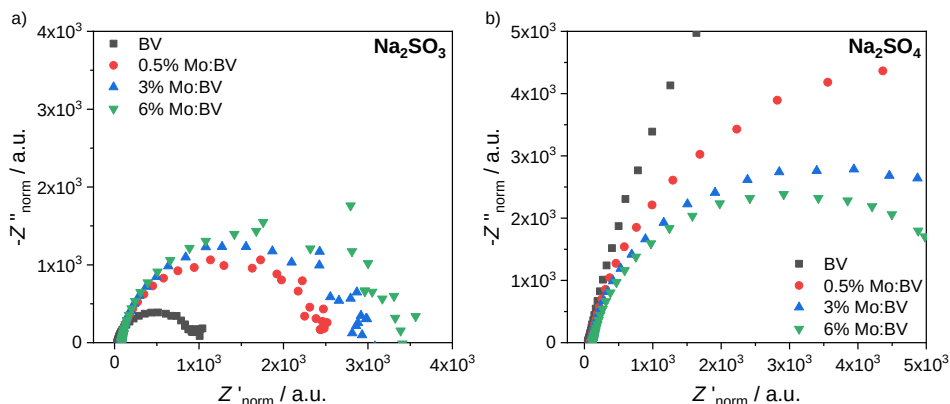


Figure 6.12 Nyquist plots normalized for the corresponding relative ECSA of the BV, 0.5 at%, 3 at% and 6 at% Mo^{6+} doped BV electrodes, recorded under AM 1.5 G irradiation in both N_2 -purged (a) 0.5 M Na_2SO_3 (buffered at pH 7) and (b) 0.5 M Na_2SO_4 aqueous solutions at 1.0 V vs. RHE.

In line with the results of PEC analyses, the presence of the Mo^{6+} dopant in BiVO_4 was found to have an opposite impact also on the charge transfer resistance towards the two oxidation substrates. In fact, a progressive R_{ct} decrease for water oxidation occurs by moving from pure BV to the most highly doped film, suggesting an improved charge transfer kinetics upon Mo^{6+} incorporation (Figure 6.12b). Differently, pure BV exhibits the highest intrinsic reactivity towards the sulfite electron donor, which dramatically diminishes with increasing Mo^{6+} content (Figure 6.12a).

Notably, the obtained trend in charge transfer resistance towards water oxidation resembles those commonly reported for pure and similarly modified BV photoanodes,^{51,57–59} while the opposite behavior found with the electrodes in contact with the sulfite electron donor has never been observed before, to the best of our knowledge.

The above described EIS results well reflect those of PEC tests in the two different electrolytes. Indeed, the performance trend obtained for sulfite oxidation, with an effective ECSA-normalized performance decrease occurring for dopant contents larger than 0.5 at% (Figure 6.6b), should be thus ascribed to the progressively higher interfacial charge transfer resistance towards sulfite oxidation with increasing doping degree. On the other hand, the remarkable photoactivity improvement in water oxidation upon Mo^{6+}

incorporation can be explained by the progressive decrease in charge transfer resistance at the electrode/electrolyte interface with increasing doping degree, instead of to the parallel slight ECSA increase. In addition, the effective majority carrier density (N_D) growth induced by the *n*-type character of the dopant (see Table 6.2 and Figure 6.11b), may be beneficial to the overall electron transport properties in the bulk material.

6.4.5 PEC performance of Ni/Fe oxyhydroxide modified electrodes

To shed light onto the effects that Mo^{6+} doping of BiVO_4 has on the bulk properties of the films in water oxidation, *i.e.* in the absence of any sacrificial agent, the investigated photoanodes were coupled with the Ni/Fe oxyhydroxide (NiFeO_x) OEC.^{13,60} In the absence of any OEC, charge transport in the BiVO_4 bulk is masked by the sluggish interfacial electron transfer kinetics dominating the overall activity in water oxidation, while in the presence of an OEC charge transport in the BiVO_4 bulk becomes the main factor limiting the performance of the material.

NiFeO_x is one of the most active co-catalysts for oxygen evolution,^{13,61–63} exploiting a synergistic effect of the Fe and Ni ions in reducing the activation energy of the water oxidation rate determining step,^{4,63} by mediating the hole extraction across the photoexcited semiconductor/electrolyte interface. The consequently much faster hole transfer to the electrolyte should result in *i*) an anticipated photocurrent onset potential, *ii*) a considerable increase of photocurrent, and *iii*) a better stability of the composite photoanode under simulated solar light conditions compared to bare photoanodes in contact with a non-sacrificial electrolyte.^{4,31,40,62} The upper photocurrent limit achievable in water oxidation with the support of an efficient OEC such as NiFeO_x may correspond to the photocurrent generated in the presence of a good hole acceptor such as Na_2SO_3 , so that the surface charge transfer efficiency can be assumed to be 100%.²

After PEC deposition of the NiFeO_x overlayer on the main representative electrodes,^{31,61,64} the co-catalyst was activated by performing consecutive LSV scans under full lamp irradiation during which the photocurrent was found to increase up to a steady-state value. The so recorded stabilized *J-V* curves are plotted in Figure 6.13a, together with the CA profiles acquired during stability tests performed at 1.23 V vs. RHE under continuous AM 1.5 G irradiation (Figure 6.13b).

The catalytic activity of the NiFeO_x overlayer towards O_2 evolution is confirmed by the shape of the *J-V* curves (Figure 6.13a), which is more similar to that attained in the presence of the sulfite hole scavenger (Figure 6.6a) than to that measured in the sodium sulfate electrolyte (Figure 6.9a). The good fill factor (*i.e.*, the sharp increase of photocurrent just beyond the onset potential) and the attainment of a sort of plateau photocurrent are two clear electrochemical signatures pointing to a fast, activation-free electron transfer reaction limited by mass transport phenomena.

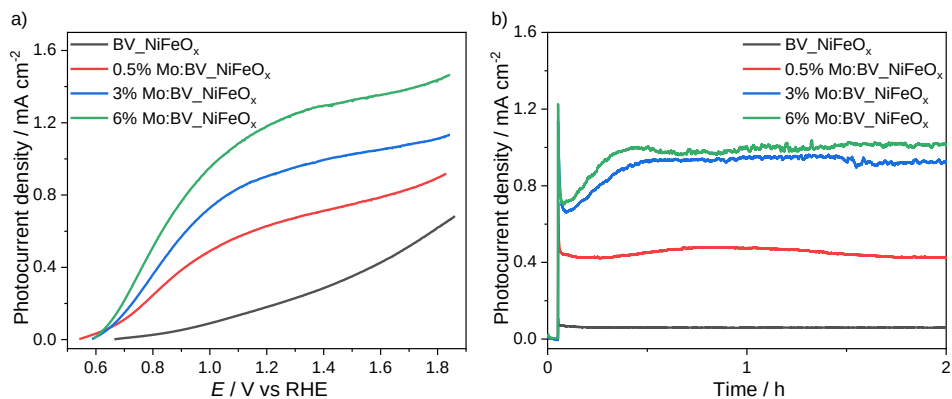


Figure 6.13 (a) LSV and (b) CA measurements at 1.23 V vs. RHE on the NiFeO_x -modified pure BV, 0.5 at%, 3 at% and 6 at% Mo^{6+} doped BV electrodes in 0.5 M Na_2SO_4 solution under back-side irradiation.

First of all, a considerable improvement in photocurrent was observed with the OEC modified photoanodes with respect to the corresponding bare electrodes tested in the same medium. Indeed, a photocurrent maximum value above 1 mA cm^{-2} was recorded at 1.23 V vs. RHE, both under transient and steady-state conditions (Figure 6.13a and b, respectively), without any prior activation period (under polarization and continuous illumination), which is instead required with the unmodified photoanodes in order to approach similar photocurrent values (Figure 6.10b).

The steady-state analysis under continuous irradiation (Figure 6.13b) reveals that the maximum photocurrent was achieved with the 3% Mo:BV_NiFeO_x electrode, 3 at% thus being confirmed as the optimal doping degree of BiVO_4 in water oxidation for both bare and co-catalyst modified BV electrodes. Moreover, by comparing the photocurrent density obtained at 1.23 V vs. RHE with the NiFeO_x -modified pure and 3 at% Mo^{6+} doped BV electrodes, *i.e.* corresponding to *ca.* $190 \mu\text{A cm}^{-2}$ and 1 mA cm^{-2} , respectively (Figure 6.13b), the intrinsic beneficial effect of Mo^{6+} doping on the performance of BV-based electrodes appears to be preserved also upon OER co-catalysts deposition.

By considering the PEC performances attained with NiFeO_x -modified photoanodes, the photoactivity improvement extent achieved with doped materials compared to pure BiVO_4 is parallel to the electron donor density (N_D) increase determined by EIS analysis for the corresponding bare materials (see Table 6.2). This matching indicates that the photoactivity enhancement observed with NiFeO_x -modified electrodes upon molybdenum doping should be mainly ascribed to an improved film conductivity and electron transport in the material bulk. By contrast, the *ca.* two orders of magnitude increased photocurrent in water oxidation attained with the doped electrodes compared to the pure BV in the absence of OEC overlayer, can be explained only by taking into account an important contribution of the Mo^{6+} dopant in improving the interfacial charge transfer kinetics at the electrode surface.

The impact of Mo^{6+} dopant on the bulk transport properties of the investigated photoanodes was further outlined by IQE analyses conducted with the NiFeO_x -coated electrodes in the Na_2SO_4 electrolyte after the 2-h long CA measurements (Figure 6.13b), in the two irradiation configurations (Figure 6.14). As expected, NiFeO_x -modified films showed overall higher efficiencies than those of the corresponding bare electrodes tested under the same conditions. Notably, the IQE plots recorded with the co-catalyst-modified photoanodes exhibit a clear inversion of the relative activity recorded in the two illumination modes, with the front irradiation efficiency reaching and also overcoming the back irradiation efficiency with increasing dopant content from 3 to 6 at%, while the performance under back irradiation of all photoanodes discussed so far was higher than under front irradiation.

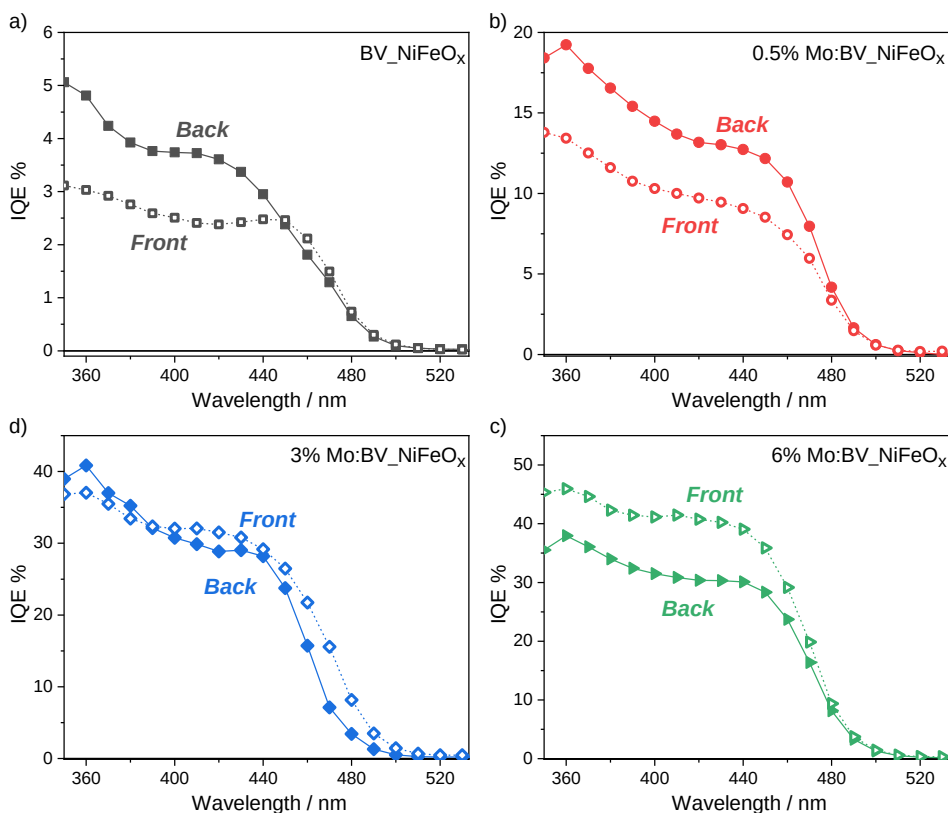


Figure 6.14 Comparison of the IQE plots resulting from IPCE analyses conducted under back- and front-side irradiation on the NiFeO_x -coated (a) pure BV, (b) 0.5 at%, (c) 3 at% and (d) 6 at% Mo^{6+} doped BiVO_4 electrodes at 1.23 V vs. RHE in 0.5 M Na_2SO_4 electrolyte.

This suggests that, upon the addition of a proper Mo^{6+} dopant amount and the deposition of an efficient OEC, the electron transport towards the FTO back-contact is no longer the main limiting factor for efficient charge separation in the bulk, which is instead actually controlled by hole transport towards the electrode/electrolyte interface. Thus,

relatively high degrees of Mo^{6+} doping play a key role in improving the transport of the majority charge carriers within the investigated films.

6.5 Role of Mo^{6+} doping in sulfite vs. water oxidation reactions

Despite the higher photoactivity shown by all investigated photoanodes in contact with the Na_2SO_3 rather than with the Na_2SO_4 solution, due to the easier oxidation of sulfite as hole scavenger with respect to water, an opposite trend in performance, *i.e.* a performance decrease with increasing doping degree, was found in sulfite oxidation, while a performance increase was attained in water oxidation. The larger effective surface area of doped electrodes compared to the pure BiVO_4 electrode assesses this behaviour. Indeed, as demonstrated by the data reported in Figure 6.6b, no significant improvement in the BV performance in sulfite oxidation was attained upon incorporation of a 0.5 at% dopant amount, while any further Mo^{6+} addition (3 at% or 6 at%) led to an activity lower than that of pure BV. On the other hand, the remarkable enhancement, with respect to pure BV, in the PEC performance in water oxidation recorded with highly Mo^{6+} doped photoanodes, is far above the ECSA increase consequent to dopant addition and should be thus explained in terms of a specific improvement induced by Mo^{6+} doping on the electronic properties of BiVO_4 .

Photoelectrochemical impedance measurements revealed that the two inverse trends in the *performance vs. doping degree* found in the two oxidation reactions should be ascribed to the opposite impact of the Mo^{6+} dopant on the interfacial charge transfer resistance towards the two target substrates. Indeed, in the absence of the sulfite sacrificial agent, *i.e.* when the performance is limited by the poor water oxidation kinetics instead of the charge transport in the bulk, the resistance towards hole transfer at the electrode/electrolyte interface progressively decreased with increasing the Mo^{6+} amount in BiVO_4 . On the other hand, the much higher charge transfer resistance towards the sulfite substrate exhibited by doped electrodes compared to the pure BV one, accounts for the performance decrease in sulfite oxidation upon increasing dopant addition, despite the increase in donor density detected from Mott-Schottky analyses.

The use of the NiFeO_x OEC to overcome the limits imposed by the sluggish water oxidation kinetics of BV materials provided insights into the role of the dopant in water oxidation under bulk charge transport control.^{4,29} In NiFeO_x -modified electrodes, beneficial effects in terms of enhanced electron conductivity in the bulk, were induced by increasing Mo^{6+} incorporation, in agreement with the progressively higher electron donor density estimated by means of Mott-Schottky analyses.

In the light of these results, bulk recombination issues should be definitively ruled out as possible cause of the unexpected behaviour of the here investigated BiVO_4 -based materials observed in Na_2SO_3 oxidation, which is instead related to the increase in charge transfer resistance at the film/electrolyte interface occurring upon Mo^{6+} addition. This specific and undesired phenomenon thus seems to prevail over the systematic and

significant beneficial effect that Mo^{6+} incorporation has on the BiVO_4 bulk charge transport properties.

6.6 Conclusions

The role of Mo^{6+} doping on the PEC performance of BiVO_4 photoanodes for water oxidation was investigated by means of a unique combination of morphological and PEC analyses. In order to discern the effects that doping BiVO_4 with Mo^{6+} has on the bulk transport properties of the material from those related to surface electron transfer, the electrodes were tested either in sulfite oxidation (in a Na_2SO_3 solution) or in water oxidation (in a Na_2SO_4 solution). This reaction was investigated either with the bare electrodes, *i.e.* under the limits of sluggish interfacial charge transfer kinetics, or under charge transport control in the bulk, employing NiFeO_x OEC-modified materials.

PEC tests of the two oxidation reactions evidenced two opposite trends in the *performance vs. doping degree*, reflecting the opposite trends in interfacial charge transfer resistance, detected through EIS measurements. Overall, while the interfacial charge transfer efficiency in sulfite oxidation diminishes upon doping BiVO_4 , both the reduced charge transfer resistance at the film/electrolyte interface and the improved film conductivity attained upon increasing Mo^{6+} incorporation are responsible for the considerably enhanced PEC performance in water oxidation attained with the doped materials compared to pure BV.

This investigation sheds light on the importance that surface area modifications occurring upon doping have in determining the electrode performance, especially in the oxidation of hole scavenger species such as sulfite ions. Moreover, unfavourable interactions occurring between the sulfite electron donor and Mo^{6+} doped BiVO_4 electrodes, possibly related to the dopant-induced change of surface states involved in the oxidation reaction, are clearly evidenced here for the first time. Understanding the nature of these phenomena is of crucial importance for engineering efficient photoanodes able to overpass the limits encountered in oxygen production through water splitting.

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Appendix A (Chapter 6)

A1 Electrochemical active surface area determination

Many parameters describing the performance of electrodes (including the PEC performance) are referred to the geometric area of the irradiated spot of the electrode put in contact with the electrolyte. Nevertheless, the geometric area (A_g) is simply the projection on a plane (parallel to the macroscopic phase boundary of the electrode) of the real surface area (A) actually involved in any PEC process. These two entities are related each other by the linear relationship $A = A_g \cdot f_r$, where f_r is the roughness factor.¹

Especially when comparing the activities of electrodes exhibiting substantial differences in morphology or structure, as it is the case for the examined Mo^{6+} doped BiVO_4 (BV) photoanodes, the calculation of the real surface area is necessary for a correct interpretation of the observed results. An effective *in situ* approach to estimate the real surface area of the electrodes is provided by the electrochemical active surface area (ECSA) obtainable from the capacitive current (*i.e.*, the non faradaic one) associated with the charging and discharging of the double layer built at the film/electrolyte interface.¹⁻³

A valuable way to measure the capacitive current is through cyclic voltammetry (CV),¹ by properly selecting a narrow potential window (a few tens of millivolt) centred around the open circuit potential (OCP) of the investigated system, in which no faradaic process can take place. Under this hypothesis, the recorded current is only capacitive (I_c) and it depends linearly on the potential sweep rate (v) according to $I_c = C_{DL} \cdot v$, where C_{DL} represents the double layer capacitance of the interface and corresponds to the $\text{ECSA} \cdot C_s$ product, with C_s being the intrinsic specific capacitance of the semiconductor material (typically in the $15\text{-}130 \mu\text{F cm}^{-2}$ range²).

Specifically, such measurements were performed with the investigated electrodes in the dark, using the glass cell configuration with a geometric area of 0.7 cm^2 . For each of the tested electrodes, four consecutive CV traces, centred around the OCP and spanned over a narrow potential window (between -0.05 V and $+0.05 \text{ V}$ vs. OCP) were recorded at six different potential scan rates, ranging from 0.005 to 0.075 V s^{-1} , as shown in Figure A1 for the pure BiVO_4 sample.

Unfortunately, the specific capacitance for BiVO_4 is not known in the open literature. Moreover, by considering that pretty low f_r can be obtained from these measurements by using a C_s value of $60 \mu\text{F cm}^{-2}$ (as generally reported for metal oxides-based materials),⁴ and that the actual determination of the absolute ECSA value for each electrode is out of our scope, *relative* ECSA values were determined for an internal comparison purpose,

assuming that the small amount of added Mo^{6+} does not significantly affect the charging mechanism of the oxide material.

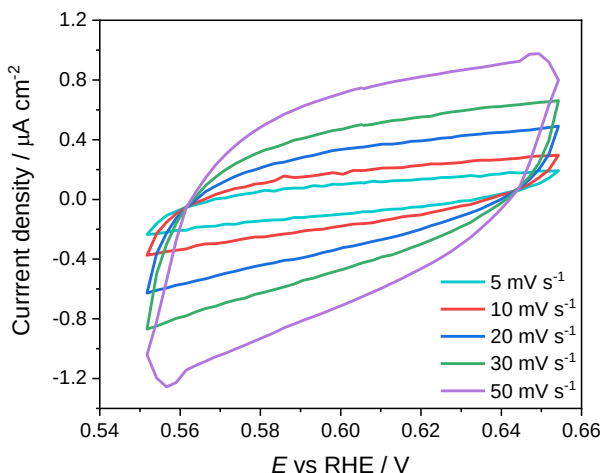


Figure A1 Cyclic voltammetry relative to the pure BiVO_4 electrode recorded in the range between -0.05 and $+0.05$ V vs. OCP, at different potential scan rates (ranging from 0.005 to 0.050 V s^{-1}).

In particular, relative ECSA values were thus obtained by evaluating the ratio between the C_{DL} slope attained for each investigated sample respect to pure BiVO_4 . In particular, such C_{DL} parameter is obtained as an average of the slopes (expressed in absolute value) obtained for the anodic and cathodic branches of the straight lines interpolating the recorded I_c values as a function of v , with I_c read in the middle of the CV potential window on the anodic and cathodic scan, respectively (see Figure A2).

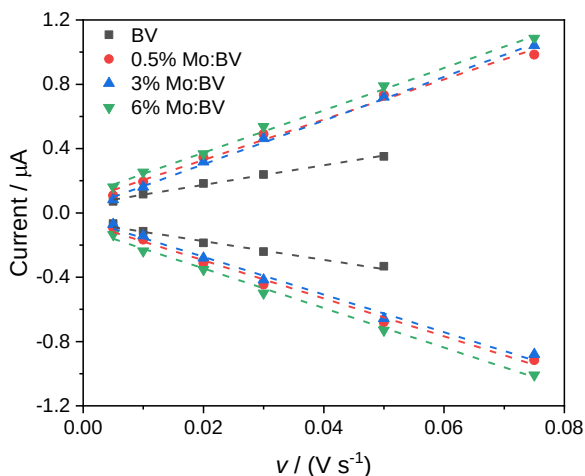


Figure A2 Capacitive anodic and cathodic current values recorded with the pure, 0.5 at%, 3 at% and 6 at% Mo^{6+} doped BV electrodes in a N_2 -purged 0.5 M Na_2SO_4 solution, as a function of the potential scan rates (ranging from 0.005 to 0.075 V s^{-1}). The reported current values were extrapolated at the open circuit potential (OCP) value from the corresponding cyclic voltammetry scans recorded in the range between -0.05 and $+0.05$ V vs. OCP.

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Chapter 7

Mo⁶⁺ doping-induced effects in BiVO₄ multilayer film photoanodes

7.1 Abstract

The major impact of Mo⁶⁺ incorporation onto the photoactivity of BiVO₄ thin film photoanodes has been unequivocally identified by means of a thorough structural, morphological and photoelectrochemical (PEC) investigation. While confirming the effects that the hexavalent metal ion has on the material bulk properties in terms of improved electron transport, PEC impedance spectroscopy (PEIS) also revealed the role that the Mo⁶⁺ dopant has on the surface properties of BiVO₄ photoanodes. The presence of intra band gap V⁵⁺/V⁴⁺ oxygen vacancies states, acting as traps of photogenerated electrons/holes in pure BiVO₄, was detected through the build-up of the interfacial surface state capacitance. The limited water oxidation activity of pure BiVO₄ was dramatically improved upon Mo⁶⁺ dopant incorporation at 3 at% degree, which was found to passivate the trap surface states, mitigating the V⁵⁺/V⁴⁺ redox process by supplying additional free electrons. The larger effect of the dopant on the film surface rather than in the material bulk was corroborated by XPS analyses revealing that most of the introduced Mo⁶⁺ ions are localized on the top surface of the photoactive film. Through a multilayer films study the optimum dopant content was identified, able to provide a more efficient charge carrier transport with respect to pure BiVO₄, while maximizing the absorption capability of the photoanodes. Overall, the results of structural, PEC and PEIS analyses conducted in both water and sulfite oxidation reactions revealed that the main positive impact of the Mo⁶⁺ dopant is exerted on the surface-related limitations affecting the overall PEC performance of BiVO₄ photoanodes.

7.2 Introduction

In addition to the commonly accepted role of Mo⁶⁺ and W⁶⁺ dopants as shallow donors able to increase the material conductivity by supplying additional free electrons, a wide number of further effects has been invoked to explain the significant improvement in PEC performance observed upon BiVO₄ doping with Mo⁶⁺. For example, according to the DFT

studies carried out by Park *et al.*¹ and Zhang *et al.*,² the gain in photoactivity attained upon W or Mo doping should be ascribed to lowering the activation energy for the polaron hopping mechanism, which drives charge transport in BiVO_4 . The improved performance observed by Yang *et al.*³ upon 3 at% Mo^{6+} doping was attributed to crystal deformation caused by the slightly larger tetrahedral ionic radius of Mo^{6+} compared to V^{5+} , which might improve the intrinsically poor electron mobility in BiVO_4 . Finally, Ager *et al.* ascribed the increase in photocurrent density achieved with the optimal 3 at% Mo doping level to a grain size growth, responsible for the reduction of the majority carrier transport limitations.⁴

In all cases, a conspicuous improvement in performance compared to pure BiVO_4 was attained by doping, but a comprehensive explanation for this is still lacking. The observed photoactivity increase depends on the dopant content and should result from the balance of different effects induced by this latter.

The Mo^{6+} dopant was also proposed to passivate trap sites and recombination centres at both grain boundaries and interfaces.^{5–7} The improved performance observed by Matt *et al.* in both sulfite and water PEC oxidation upon a 2 at% Mo^{6+} doping was indeed attributed to the passivation of recombination centres, rather than to an increased majority carrier concentration.⁵ The transient absorption studies of Pattengale *et al.* revealed that both electron and hole trapping sites, which inhibit electron–hole separation in the BiVO_4 bulk, are reduced upon Mo doping.⁸

Beyond the processes affecting the material bulk, the chemistry at the semiconductor–liquid junction (SCLJ) has huge impact on the efficiency of PEC devices, especially in the case of metal oxides such as BiVO_4 whose performance is limited by their sluggish water oxidation kinetics. Surface states proved to play a pivotal role in acting either as intrinsic traps or as photogenerated intermediates of the water oxidation reaction, likely surface hydroxyl groups and high-valent metal-oxo complexes.⁹ Thus, the identification of their specific function is quite difficult. In this regard, Smith *et al.* proposed the photocharging of BiVO_4 as an effective strategy to reduce surface recombination by promoting V^{5+} to V^{4+} reduction under prolonged light irradiation in alkaline conditions.¹⁰ Andreu *et al.* recently identified the V^{5+} to V^{4+} reduction as a bulk process leading to the formation of oxygen vacancies which can trigger hole transfer at the SCLJ through the adsorption of oxy/hydroxyl species. The W-doping strategy adopted in that case was found to suppress either the formation of the V^{4+} reaction sites in the semiconductor bulk or the undesired $\text{VO}_2^+/\text{VO}^{2+}$ trapping process at the film surface, with the optimum dopant amount allowing for an optimized balance between these two opposite effects.¹¹ Moreover, Durrant *et al.*¹² recently detected the presence of intra band gap $\text{V}_{\text{OV}}^{5+}/\text{V}_{\text{OV}}^{4+}$ oxygen vacancy states which have no catalytic activity toward water oxidation, but rather act as electron/hole traps. In fact, occupied $\text{V}_{\text{OV}}^{4+}$ states were the primary loss pathway for photogenerated valence band holes, while unoccupied $\text{V}_{\text{OV}}^{5+}$ states acted as shallow traps of conduction band electrons which control their extraction by the external circuit.

Despite various evidence of surface states in metal oxide-based materials, the unambiguous identification of their nature (for example, if they are intrinsic to the material or light-induced defects), location (bulk or surface defects) and function (*i.e.* if they act as traps or reactive sites) is still very challenging due to the multiple variables which affect all these factors, such as the kind of metal oxide itself, the synthesis/annealing conditions of the material and, eventually, the nature of the dopant.

Aim of the studies presented in this chapter is the identification of the different mechanisms responsible for the performance enhancement in water oxidation induced by Mo⁶⁺ doping of BiVO₄ photoanodes, both in the bulk and at the surface of the photoactive films. Compared with other reports¹³ and with the results presented in Chapter 6, the current investigation went more in depth into the role of Mo⁶⁺ doping in relation to the chemistry of surface states, during both water and sulfite oxidation, one of the most commonly employed hole scavengers for this photoanode material. At this aim, we adopted the EIS data analysis approach proposed by Bisquert to investigate the surface states involved in the water oxidation reaction with hematite-based photoanodes.⁹ In this way, we revealed the presence of surface states in our BiVO₄ photoanodes causing Fermi level pinning during water oxidation, due to accumulation of charges at the SCLJ, which can be passivated upon Mo⁶⁺ doping.

Furthermore, for each dopant amount introduced in BiVO₄ a multilayer films study was performed aiming at identifying the optimum film thickness able to maximize visible light absorption, without compromising the charge carrier transport in the bulk. Photoelectrodes of both pure and Mo⁶⁺ doped BiVO₄ were prepared by means of a well-established aqueous solution-based approach for pure BiVO₄ electrodes,¹⁴ differing with respect to that presented in Chapter 6 in the elimination of PVA as thickening agent in the precursor solutions, replaced by a multilayer spin coating deposition. The new approach guarantees the production of highly performing multilayer flat films with higher optical transparency than the previous PVA-containing ones presented in Chapter 6, which are thus more suitable to be employed in the dual absorber tandem cell configuration.

Notably, by the adopted synthesis strategy Mo⁶⁺ doped BiVO₄ photoanodes were obtained exhibiting a higher performance under front- rather than back-side irradiation, which confirms the successful improvement of the electron transport properties of the material. This study thus demonstrates the beneficial dual role of Mo⁶⁺ doping of BiVO₄, in improving the electron conductivity in the material bulk as well as in passivating the surface states accumulated at the electrode/electrolyte interface, which would hamper efficient PEC water oxidation.

The characterization analyses presented in this chapter were performed during my visiting period in the group of Prof. Sivula at the EPFL in Lausanne.

7.3 Experimental section

7.3.1 Chemicals and materials

The following chemicals, purchased from Sigma Aldrich, were employed as supplied: bismuth(III) nitrate pentahydrate ($\geq 98\%$), ammonium metavanadate ($\geq 99\%$), molybdenum oxide bis(2,4-pentanedione) ($\geq 99\%$), citric acid (99%), nitric acid 23.3%, sodium sulfate ($\geq 99\%$), anhydrous sodium sulfite ($\geq 99\%$), acetone. Fluorine-doped tin oxide (FTO) glass, 2 mm thick, was purchased from Pilkington Glass (TEC-7).

7.3.2 Photoelectrodes preparation

Pure BiVO₄ (BV) electrodes were prepared according to a previously described procedure.¹⁴ Typically, 0.002 mol of Bi(NO₃)₃ and NH₄VO₃ were added to 6 mL of 23.3% HNO₃ containing 0.004 mol of citric acid acting as a stabilizer. After complete dissolution of the precursors, a BV film layer was obtained by spinning 70 μ L of the so obtained solution onto clean FTO at 8000 rpm for 30 s with an acceleration rate of 6000 rpm s⁻¹. Prior to deposition, the FTO slices were soaked in acetone for a few seconds to increase the quality of the resulting film. The films were then dried at 250 °C for 10 min and annealed at 500 °C for 1 h in air. The thickness of the BiVO₄ layer was modulated by repeating the spin coating deposition and the thermal treatment up to 8 times. Prior to deposition, the FTO glass was cleaned by 30 min-long sonication in a soap solution, followed by careful washing, sonication in ethanol for 30 min and drying in air. The clean glass slices then underwent a 15 min-long UV-cleaner ozone treatment to remove any organic species deposited onto the FTO surface.

The Mo⁶⁺ doped BV electrodes were synthesized by substituting the proper amount of Bi and V precursors with that of the molybdenum precursor in the starting solution, in order to obtain nominal molar dopant contents of 0.5 at% or 3 at% (*i.e.*, mol (Mo) / [mol (Bi) + mol (V)] = 0.005 and 0.03), respectively. The so obtained precursor solutions were employed to prepare multilayer films of differently doped BV photoanodes, by repeating the same spin coating procedure and annealing treatment adopted for pure BV up to 8 layer depositions.

The synthesized multilayer films were labelled as nL_BV_X, with n referring to the number of coating layers and X standing for the nominal dopant (Mo) molar ratio.

7.3.3 Physical characterization methods

The crystalline phase of the materials was determined by collecting their XRD patterns using a Panalytical Empyrean system (Theta-Theta, 240mm) equipped with a PIXcel-1D detector, Bragg-Brentano beam optics (including hybrid monochromator) and parallel beam optics. Raman spectra were measured with a LabRam spectrometer (Jobin Yvon Horiba) using a 532.19 nm excitation line provided by an Ar laser. SEM images were acquired using a Zeiss Gemini 300 scanning electron microscope in HV mode.

UV–visible absorption spectra of the multilayer films were recorded in transmittance mode with a Jasco V-670 spectrophotometer. The AFM images of the films were measured using a Cypher S AFM from Asylum Research. X-ray photoelectron spectroscopy (XPS) analyses were performed with PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany) with a monochromatic Al $K\alpha$ source with 24.8 W power with a beam size of 100 μm . Depth profile analysis was performed by etching the material with an Argon ion sputter gun, at a rate (calibrated on SiO_2) of ~ 5.8 nm/min with a sampling depth of ~ 60 nm.

7.3.4 Photoelectrochemical methods

PEC experiments were carried out using the three-electrode cappuccino cell described in Section 4.3.2.2, by employing each of the BV-based photoanodes as working electrode, a Pt wire as counter electrode and a (Metrohm) Ag/AgCl (KCl sat'd) as reference electrode. The cell was connected to a BioLogic SP-500 potentiostat. A 1000 W Xe arc lamp (Newport Oriol), calibrated to the AM 1.5 G spectrum using a Si photodiode sensor (S120VC, Thorlabs), was exploited as light source for both photocurrent and impedance measurements.

During the tests, the BV-based photoanodes were illuminated from both the FTO substrate side (back irradiation) and the electrode/electrolyte side (front irradiation), with the electrode in contact with a 0.5 M Na_2SO_4 aqueous solution (pH 7). For the experiments conducted under sacrificial conditions, a 0.5 M Na_2SO_3 solution was employed, buffered at pH 7 through the addition of 0.5 M potassium phosphate (KPi). In all measurements the applied potentials, measured with respect to the Ag/AgCl reference electrode, were referred to the RHE scale using Eq. 4.19.

Linear sweep voltammetry (LSV) measurements under both back- and front-side irradiation were performed at a scan rate of 20 mV s^{-1} . Five consecutive LSV scans were recorded for each of the tested electrodes in each of the employed conditions, and no decay in photocurrent was ever observed.

Incident photon to current efficiency (IPCE) measurements were collected during either water or sulfite oxidation under both back and front irradiation, using the same three-electrode configuration cappuccino cell. Monochromatic irradiation for IPCE tests was provided by a 75 W Xenon tunable PowerArc source (Optical Building Blocks) and the photon flux at each wavelength was measured with the S120VC (Thorlabs) photodiode power sensor. The IPCE curves were calculated using Eq. 4.30. The internal quantum efficiency (IQE) plots were obtained by normalizing the corresponding IPCE curves for the photons absorbed by the material, obtained from the absorbance (A) spectrum, according to Eq. 4.31.

Photoelectrochemical impedance (PEIS) measurements were carried out using a Bio-Logic SP-500 potentiostat coupled with the EC-Lab (V11.12) electrochemical platform. During each PEIS scan, a voltage perturbation within a frequency range from 1 MHz to

50 mHz was applied with a 25 mV sinusoidal amplitude. A custom program written in the Python programming language was used to process and fit PEIS data.

7.4 Results

7.4.1 Photoelectrodes characterization

The crystal structure and phase composition of the three thickest 8L electrodes were determined by means of the X-ray diffraction (XRD) and Raman spectroscopy analyses reported in Figure 7.1.

The XRD pattern of each film in Figure 7.1a exhibits the standard pattern of monoclinic BiVO_4 (JCPDS 14-0688),^{1,15,16} with the main characteristic (110), (121) and (040) diffraction peaks located at *ca.* 18.9°, 28.9° and 30.5°, respectively. No impurity belonging to secondary phases, such as the less active tetrahedron and rhombohedron phases,^{17,18} can be detected except for the reflexes relative to the FTO substrate (marked with asterisks in Figure 7.1a). This means that no transformation of monoclinic BV occurs upon Mo^{6+} incorporation even at the highest dopant content, in agreement with earlier reports.^{1,7,18–21} Moreover, there are no peaks relative to crystalline MoO_3 , confirming the successful formation of a solid solution of Mo^{6+} -doped BV.^{7,20,22} All films exhibit sharp peaks with relatively high intensity, indicating high crystallinity (Figure 7.1a).

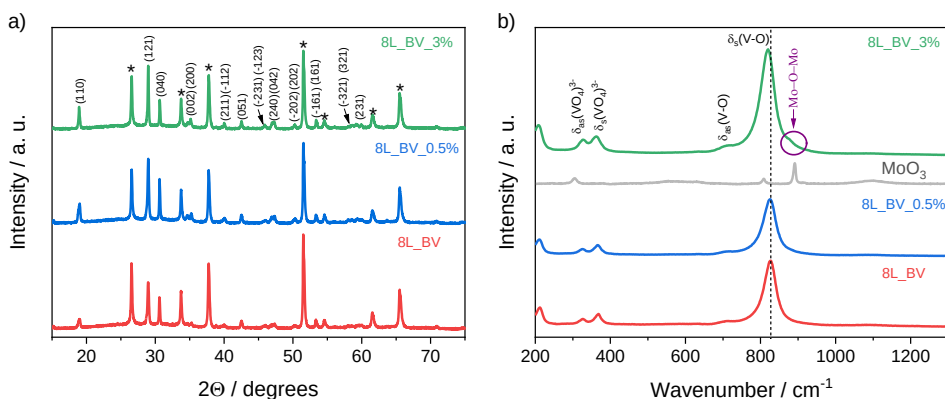


Figure 7.1 (a) XRD patterns and (b) Raman spectra of 8L_BV, 8L_BV_0.5% and 8L_BV_3%. The Raman spectrum of MoO_3 (grey trace) is also reported for comparison. The reflections relative to the FTO substrate are marked with an asterisk.

The slight (*ca.* 0.1°) shift of the (040) peak for highly doped 8L_BV_3% can be ascribed to the compressive lattice strain^{16,20} induced by the substitution of Mo^{6+} ions for relatively smaller V^{5+} ions (having a ionic radius of 0.41 Å and 0.35 Å, respectively¹). This causes the partial distortion of the VO_4^{3-} tetrahedron space lattice, which was found to enhance the electron mobility of BiVO_4 ,³ and suggests the succesful incorporation of Mo into the BiVO_4 lattice.¹¹ Furthermore, the progressive intensity increase of the XRD reflection at $2\theta = 18.9^\circ$ with increasing the dopant content (see Figure 7.1a) sheds light on a preferred BiVO_4 growth orientation along the (110) and (010) directions, attained

during the film annealing process under Mo⁶⁺ control, in agreement with a previous study.⁴

The Raman spectra of either the pure BV or the doped 8L films in Figure 7.1b show the typical modes of the BiVO₄ monoclinic phase,^{19,20} consistent with the XRD analysis results. The dominant Raman band at *ca.* 827 cm⁻¹ is assigned to the symmetric $\delta_s(\text{V-O})$ stretching mode of the VO₄³⁻ units and the weak shoulder at *ca.* 710 cm⁻¹ to the corresponding $\delta_{as}(\text{V-O})$ asymmetric mode. The weak bands at around 325 cm⁻¹ and 360 cm⁻¹ are identified as the asymmetric $\delta_{as}(\text{VO}_4^{3-})$ and symmetric $\delta_s(\text{VO}_4^{3-})$ deformation modes of VO₄³⁻, respectively, while the band at around 210 cm⁻¹ is ascribed to external (rotational or translational) modes. Interestingly, a progressive red shift of the $\delta_s(\text{V-O})$ stretching mode occurs upon incorporation of increasing amounts of the Mo⁶⁺ dopant, passing from 827 cm⁻¹ recorded for pure 8L_BV to 820 cm⁻¹ for highly doped 8L_BV_3%. This shift to lower wavenumbers was again attributed, as for the results of XRD analyses, to the Mo⁶⁺ for V⁵⁺ replacement in the BiVO₄ lattice,^{4,18–20,22–25} causing elongation of the V–O bond of the VO₄ unit due to the larger ionic radius of Mo⁶⁺ compared to V⁵⁺.¹ The Mo⁶⁺ for V⁵⁺ substitution and consequent formation of Mo–O–Mo bonds was further confirmed by the appearance of the Mo–O–Mo stretching mode^{17,19,22} at 890 cm⁻¹ in the Raman spectrum of 8L_BV_3%, easily identifiable from its comparison with that relative to the MoO₃ compound reported in Figure 7.1b, as reference.

The top-down scanning electron microscopy (SEM) images reported in Figure 7.2 for the 8L_BV, 8L_BV_0.5% and 8L_BV_3% electrodes account for a flat surface with uniform texture, *i.e.* composed of densely packed grains in the ~100–200 nm range (see Table 7.1), ensuring homogeneous coverage of the rough FTO surface and a high film compactness.

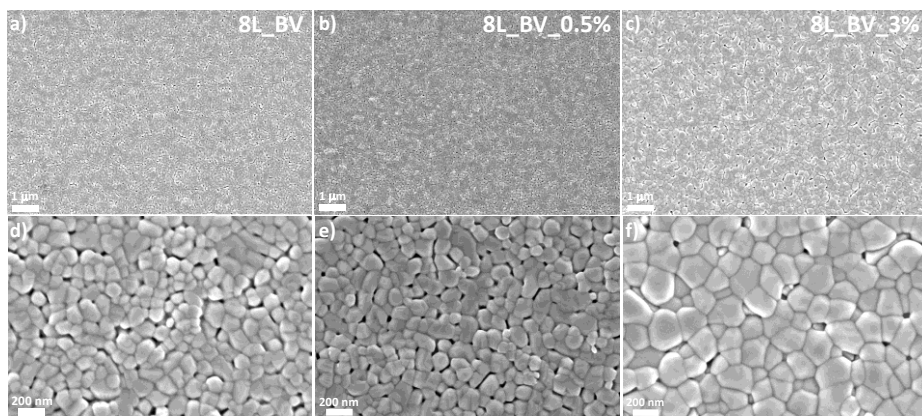


Figure 7.2 Top-down SEM images of 8L_BV (a,d), 8L_BV_0.5% (b,e) and 8L_BV_3% (c,f).

The high magnification images in Figure 7.2d–f reveal that a spherical-like nanoparticles shape characterizes all examined films regardless of the doping degree, in contrast with the BiVO₄-based films discussed in Chapter 6. In that case, an initial worm-

like porous structure was observed for the pure BV film up to a 0.5 at% Mo^{6+} doping degree, turning into a quasi spherical-like shape morphology for higher dopant amounts. The different morphology of the films produced in the two studies is probably a consequence of their different synthetic route. In fact, the previous study (Chapter 6) implied the use of polyvinyl alcohol (PVA) as thickening agent, whereas a multilayer deposition PVA-free method was employed in the present case. Despite the lack of substantial changes in film morphology and nanostructure, the SEM images at high magnification (Figure 7.2d-f) clearly show that the grain size increases with increasing dopant amount, possibly as a consequence of the peculiar Mo^{6+} -induced particles agglomeration process, as already reported for similar materials.^{4,7,19} This phenomenon was also evidenced for the 4L and 6L electrode series (Figure 7.3), as confirmed by the estimated nanoparticles size of the films reported in Table 7.1.

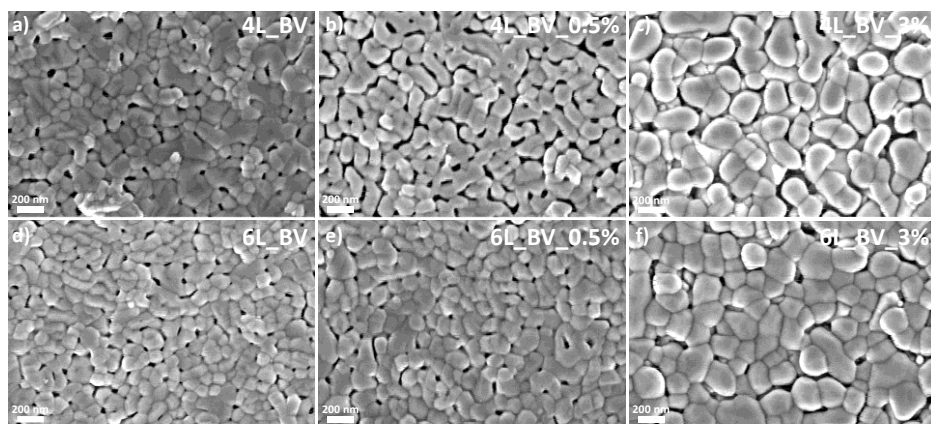


Figure 7.3 Top-down SEM images of (a) 4L_BV, (b) 4L_BV_0.5%, (c) 4L_BV_3%, (d) 6L_BV, (e) 6L_BV_0.5% and (f) 6L_BV_3%.

As shown in Table 7.1, among each electrodes series with the same number of film layers, the main significant increment in nanoparticles average size, compared to pure BV, can be attained with a 3 at% doping degree. Moreover, for a fixed relative nominal dopant content, no mean particles size increase with increasing number of film coatings was observed, except for the 8L_BV_3% photoanode, exhibiting a *ca.* 20% increase in the average grain size (*ca.* 190 nm) compared to that measured for the 4L_BV_3% and 6L_BV_3% electrodes (*ca.* 160 nm in both cases).

Table 7.1 Film grains size, in terms of particles diameter, measured by means of the ImageJ software. The grain size values and the relative errors are expressed in nm.

Electrode	4L	6L	8L
BV	107 ± 14	105 ± 16	104 ± 15
BV_0.5%	114 ± 16	122 ± 22	114 ± 13
BV_3%	160 ± 28	160 ± 23	194 ± 30

These observations suggest that the Mo⁶⁺ dopant can act, especially when in relatively high amount (*e.g.* 3 at%), as a nucleic site for interparticle aggregation,²⁶ leading to a denser film structure with reduced number of pin-holes between the sintered particles compared to pure BV. Moreover, the excess of dopant in the thickest 8L_BV_3% photoanode can promote further nanoparticles sintering between adjacent layers, thus explaining the observed increase in grain size passing from 6 to 8 layers.

The trend in grain size is reflected by the change in the real surface area of the electrodes, estimated through electrochemical active surface area (ECSA) measurements described in Appendix A. The relative ECSA values of 4L, 6L and 8L films, normalized with respect to that of pure 4L_BV, are collected in Table 7.2. From these values, an ECSA decrease is observed with increasing Mo⁶⁺ dopant amount for samples with the same number of layers, the highest variation being attained with the 8L films. Moreover, the slight decrease in ECSA of pure BV with increasing number of layers is progressively more evident with increasing the Mo⁶⁺ dopant content.

Table 7.2 Normalized relative electrochemical active surface area (ECSA) of the 4L, 6L and 8L electrodes.

Electrode	4L	6L	8L
BV	1	0.9	0.9
BV_0.5%	1	0.8	0.6
BV_3%	0.7	0.5	0.3

Thus, the combination of a relatively high Mo⁶⁺ dopant amount and a multilayer film approach increases the overall compactness and density of the photoactive film in the electrodes. In this way, the undesired direct exposure of FTO to the electrolyte solutions, possibly accompanied by detrimental internal short circuits, can be minimized,²⁷ with positive effects on the resulting overall PEC performance attained with the BiVO₄-based photoanodes.

However, though the particles sintering process is expected to promote the reduction of the grain boundaries, otherwise acting as recombination centres,^{4,28} the enhanced film compactness and concomitant decrease in pin-holes may hamper the electrolyte diffusion through the film network, with a consequent reduction of the electrode/electrolyte contact. Therefore, the observed PEC performance will be a result of such competitive phenomena.

Notably, the features sizes reported in Table 7.1 are comparable with the typical 70-100 nm charge diffusion length reported for BiVO₄-based electrodes,^{25,29,30} except for the 3 at% Mo⁶⁺ doped series (4L_BV_3%, 6L_BV_3% and 8L_BV_3%), having grain sizes far above this threshold value.

The average film thickness values of the thickest 8-layered photoanodes (8L_BV, 8L_BV_0.5% and 8L_BV_3%), evaluated by means of SEM cross-section images (Figure 7.4a-c), were all *ca.* 150 ± 15 nm, independently of the dopant amount.

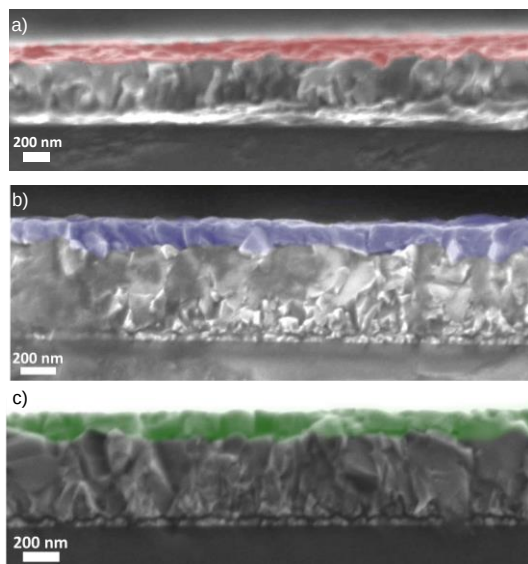


Figure 7.4 Cross section images of (a) 8L_BV, (b) 8L_BV_0.5% and (c) 8L_BV_3%.

The absorption coefficient (α) for each investigated samples series was estimated on the basis of the Lambert-Beer law^{31,32} according to Eq. 4.11, by considering the absorbance data at 420 nm acquired for the 8L thickest electrodes, and the experimental thickness estimated from cross section images in Figure 7.4.

The α values determined at 420 nm corresponded to 0.015 nm^{-1} , 0.020 nm^{-1} and 0.023 nm^{-1} for the pure BV, the 0.5 at% Mo^{6+} doped and the 3 at% Mo^{6+} doped films, respectively. The estimated thickness of all the investigated photoanodes, determined from the corresponding absorbance values at 420 nm, are collected in Table 7.3.

Table 7.3 Absorbance at 420 nm and estimated thickness for all BV, BV_0.5% and BV_3% film series.

Layers	Absorbance at 420 nm			Thickness / nm		
	BV	BV_0.5%	BV_3%	BV	BV_0.5%	BV_3%
1	0.12	0.27	0.18	19	32	18
2	0.37	0.44	0.51	57	52	51
3	0.40	0.67	0.73	62	79	73
4	0.60	0.80	0.88	92	95	88
6	0.83	1.10	1.34	128	129	134
8 [†]	0.97	1.30	1.49	150	150	150

[†]The thickness of the 8L_BV, 8L_BV_0.5% and 8L_BV_3% films were estimated from the cross section images reported in Figure 7.4.

In line with previous findings,¹⁹ the grain size enlargement with increasing Mo⁶⁺ dopant amount can be correlated to the progressive light absorption increase at wavelengths shorter than the BiVO₄ band gap absorption edge (ca. 520 nm for a 2.4 eV band gap), observed for the doped thick systems, as evidenced by the comparison of the absorbance spectra of the 8L_BV, 8L_BV_0.5% and 8L_BV_3% electrodes reported in Figure 7.5.

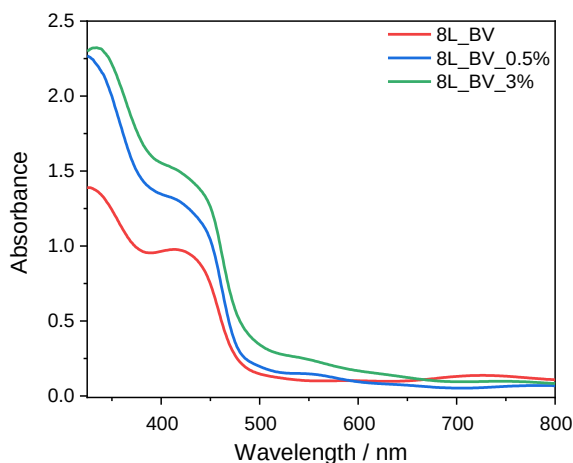


Figure 7.5 Comparison of the absorbance spectra (recorded in the transmittance mode) of the 8L_BV, 8L_BV_0.5% and 8L_BV_3% electrodes.

From the above reported absorption coefficients at 420 nm, the absorption depths, *i.e.* film thicknesses ensuring the absorption of 96%, 83% and 63% of incident 420 nm light, were calculated as $\delta = 3 \alpha^{-1}$, $\delta = 2 \alpha^{-1}$ and $\delta = \alpha^{-1}$, respectively.³² The obtained values for pristine BV, 0.5 at% Mo⁶⁺ doped and 3 at% Mo⁶⁺ doped films are reported in Table 7.4. In particular, the penetration depth δ (corresponding to 96% of absorbed light) of the incident 420 nm photons passed from *ca.* 200 nm for the pure 8L_BV electrode, in perfect agreement with literature values,^{30,32,33} to *ca.* 150 nm and 130 nm in the case of the 8L_BV_0.5% and 8L_BV_3% doped systems, respectively (see Table 7.4).

Table 7.4 Penetration depths, ensuring 96%, 83% or 63% absorption of incident 420 nm light, estimated for the BV, BV_0.5% and BV_3% films series.

Material	3 α^{-1} / nm (96% light absorption)	2 α^{-1} / nm (83% light absorption)	1 α^{-1} / nm (63% light absorption)
BV	200	134	67
BV_0.5%	154	102	51
BV_3%	130	87	43

A further effect of the particle size increase was a higher opacity of the films with a 3 at% Mo⁶⁺ content, resulting in a quite pronounced scattering tail appearing at wavelengths longer than the BiVO₄ absorption edge, as shown in Figure 7.5. Apart light scattering

effects, the absorption spectra of the investigated electrodes do not evidence any appreciable shift of the BiVO_4 absorption edge, suggesting that Mo^{6+} doping does not influence the band gap energy of the material, as reported elsewhere.^{18,34}

The AFM images reported in Figure 7.6 confirm the spherical shape of the nanoparticles composing all 8L_BV, 8L_BV_0.5% and 8L_BV_3% films, as well as the grain coalescence with increasing dopant amount. At the same time, the 3D surface topography images (Figure 7.6) reveal the presence of distinctive nanoislands on the film surface, progressively more extended and sharper as the particles dimension increases with increasing dopant amount. In parallel, the surface roughness, estimated through the RMS factor (see Figure 7.6) also increases with increasing dopant amount.

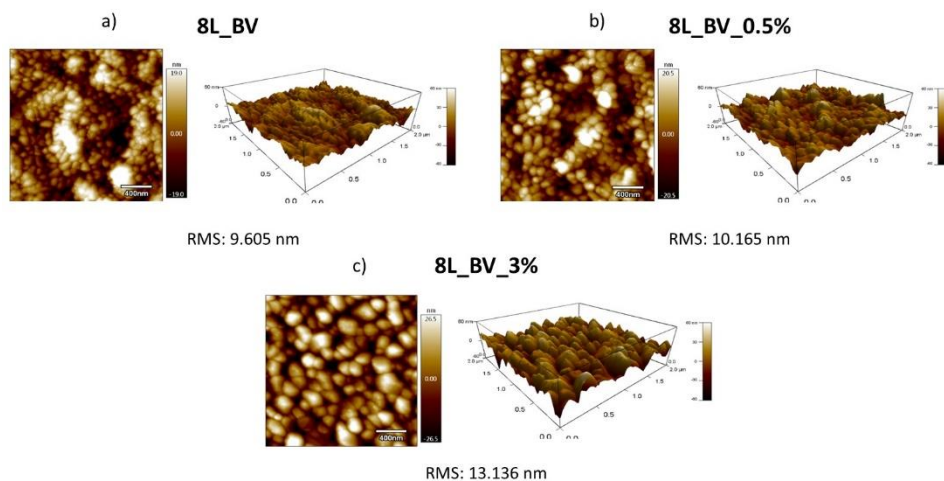


Figure 7.6 AFM images of (a) 8L_BV, (b) 8L_BV_0.5% and (c) 8L_BV_3% electrodes.

The elemental surface composition and chemical states of the 8L_BV, 8L_BV_0.5% and 8L_BV_3% films were investigated by means of X-ray photoelectron spectroscopy (XPS) analyses. The survey spectra of all examined samples revealed no contamination from other species, except for adventitious carbon. Figure 7.7 shows the XPS spectra relative to Bi 4f, V 2p, O 1s, and Mo 3d.

The characteristic spin-orbit doublet separation of the Bi 4f ($\text{Bi}4f_{5/2}$ and $\text{Bi}4f_{7/2}$) and V 2p ($\text{V}2p_{1/2}$ and $\text{V}2p_{3/2}$) signals typical of monoclinic scheelite BiVO_4 can be observed in all cases in good agreement with literature results.^{3,5,35,36} Looking at the pristine 8L_BV electrode, the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ core level peaks (Figure 7.7a), located at binding energies of 158.9 and 164.3 eV, respectively, confirm the presence of Bi^{3+} cations. The V $2p_{3/2}$ and V $2p_{1/2}$ core level peaks (Figure 7.7b) with binding energies of 516.7 and 524.3 eV, respectively, allow unambiguous assignment to V^{5+} . The O 1s signal (Figure 7.7c) at ca. 529.7 eV can be assigned to lattice oxygen (V–O), and the shoulder at around 532.3 eV to hydroxyl groups (–OH) on the BiVO_4 film surface,^{11,37,38} which can act as surface hole trapping sites, resulting in a Fermi level pinning effect at the

electrode/electrolyte interface.^{37,38} The intensity drop of the characteristic –OH signal component observed for the 8L_BV_3% sample indicates that the formation of these surface hole trapping sites is inhibited upon 3 at% Mo⁶⁺ incorporation (Figure 7.7c).

The main evidence of the successful Mo⁶⁺ doping of the investigated systems is provided by the presence of the two characteristics Mo 3d_{5/2} and 3d_{3/2} peaks, located at 232.1 eV and 235.1 eV, respectively, only in the XPS spectra of the two doped photoanodes (Figure 7.7d), with intensity progressively increasing with increasing nominal doping degree.^{3,18,26,35,36,39} At the same time, the fact that both 8L_BV_0.5% and 8L_BV_3% films show Bi 4f, V 2p and O 1s signals slightly shifted to higher binding energy with respect to the pure BV electrode (Figure 7.7a-c), due to the higher electronegativity of Mo⁶⁺ with respect to V⁵⁺, indicates the close interaction between Mo and the VO₄ tetrahedron, thus confirming the incorporation of Mo⁶⁺ ions into the BV lattice, in substitution of V⁵⁺ ions.^{20,37}

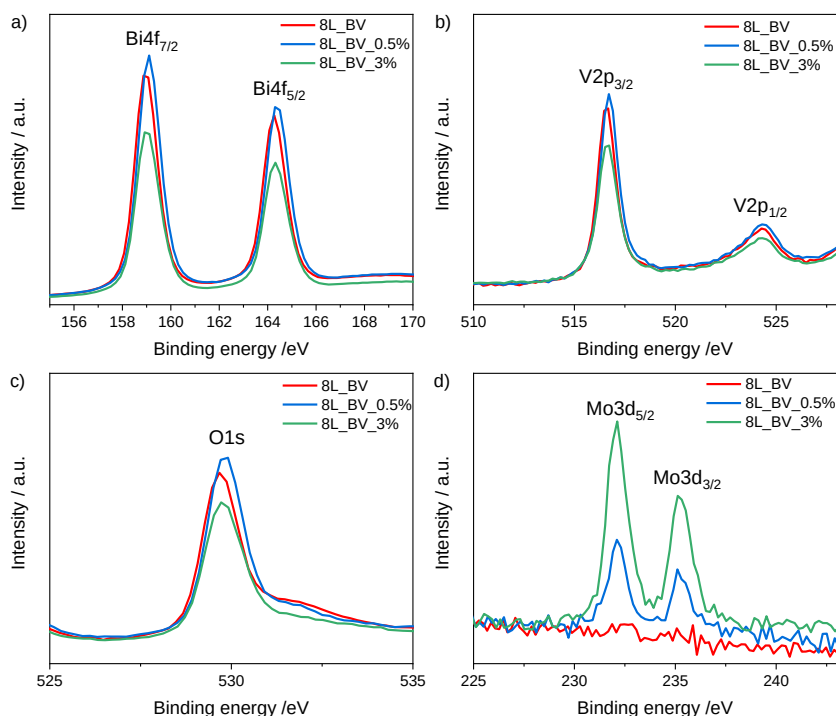


Figure 7.7 XPS spectra of the 8L films in the binding energy regions of the (a) Bi 4f, (b) Mo 3d, (c) V 2p and (d) O 1s signals.

The composition of the 8L films was also investigated at different etching depths by acquiring the XPS depth profiles after etching with Ar⁺ ions sputtering. The so recorded spectra in the Mo 3d binding energy region are collected in Figure 7.8. Notably, for both 8L_BV_0.5% and 8L_BV_3% electrodes the Mo 3d signal intensity tends to progressively decrease with increasing etching depth, the Mo content in the electrode bulk

being possibly below the detection limit of XPS analysis. Gradient doping is thus evidenced, so that within the 60 nm etching depth Mo⁶⁺ ions are almost all confined at the top of the film surface, especially for a relatively low doping degree (0.5 at%).

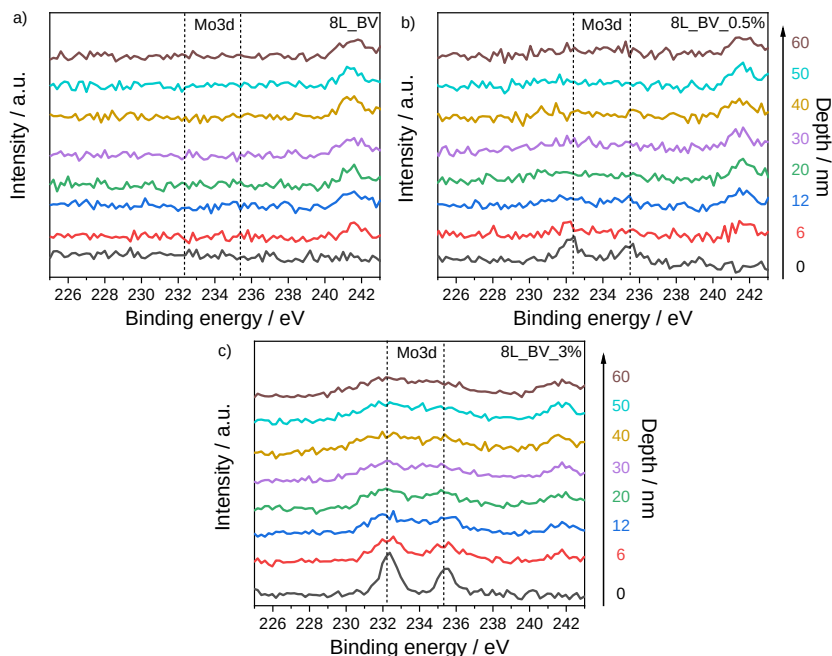


Figure 7.8 XPS spectra in the Mo 3d binding energy region of (a) 8L_BV, (b) 8L_BV_0.5% and (c) 8L_BV_3%, before (black line) and after Ar⁺ ions sputtering with progressively increasing etching depths, in the 6 (red line) to 60 nm (brown line) range.

The relative Mo, V and Bi atomic ratios for 8L films before and after 60 nm-deep etching, calculated based on the corresponding XPS spectra, are reported in Table 7.5.

Table 7.5 Relative atomic ratios from XPS analyses of 8L films before and after etching.

Material	Mo:(Bi+V)		V:Bi	
	Surface	60 nm depth	Surface	60 nm depth
BV	0	0	0.734	2.820
BV_Mo_0.5%	1.4%	0.3%	0.845	2.995
BV_Mo_3%	3.8%	2.1%	0.823	2.879

First of all, the actual Mo:(V+Bi) surface atomic ratios obtained for the 8L_BV_0.5% and 8L_BV_3% electrodes are slightly higher than the nominal ones, as observed elsewhere.^{21,23,35,36} This is a first indication of the attainment of Mo-rich surface photoanodes, which is confirmed by the dramatic Mo:(V+Bi) atomic ratio decrease obtained upon etching. Indeed, in analogy with the trends observed from Figure 7.8, a 5-fold and 2-fold decrease in the effective Mo atomic ratio was detected at the maximum

etching depth, with respect to the top film surface, for the 8L_BV_Mo_0.5% and 8L_BV_Mo_3% doped electrodes, respectively. This phenomenon was attributed to Mo surface segregation at high temperature driven by sublimation of Mo oxides,^{23,35,36,40} according to which the actual dopant level in the bulk of doped BV electrodes may be less than that at their surface.

Furthermore, the V:Bi ratio is always lower than the expected 1:1 value, but it exceeds such value after etching (see Table 7.5). This phenomenon suggests that the investigated BiVO₄-based electrodes are characterized by non-stoichiometric, highly vanadium-deficient and bismuth-rich surfaces, in agreement with previous reports.^{5,40}

7.4.2 Photoelectrochemical performance

7.4.2.1 Multilayer films study

The PEC performance of all multilayer electrodes employed as photoanodes for water oxidation was first checked in a 0.5 M Na₂SO₄ electrolyte solution by performing consecutive linear sweep voltammetry (LSV) scans under AM 1.5 G solar simulating light in both back- (towards the FTO back-contact) and front-side (towards the film/electrolyte interface) irradiation configurations. The photocurrent was found to be stable for at least 5 to 10 scans and reproducible for several months. Figure 7.9 collects the last of each series of scans acquired for all tested materials.

Overall, a maximum photocurrent density of 0.71 and 0.85 mA cm⁻² at 1.23 V vs. RHE under front-side irradiation was recorded with the 0.5 at% and 3 at% doped series electrodes, respectively, to be compared with the 0.16 mA cm⁻² photocurrent density generated with the optimized pure BV electrode. Moreover, while a typical monotonic photocurrent increase with increasing applied potential characterizes the *J-V* curves collected with pure BV, a higher photocurrent in the low applied potential region, resulting in a better fill factor, is achieved with all doped electrodes, also for the lower dopant amount.

In the pure BV multilayer films series, a progressive slight photocurrent increase with rising number of layers was obtained up to 6 layers for both back and front irradiation configurations, with an abrupt increase when passing from the 6L to the 8L electrode. This behaviour can be related to the larger light absorption ability of the thicker (*ca.* 150 nm thick) 8L film, its thickness being pretty similar to the estimated penetration depth (δ) of light at 420 nm (*ca.* 200 nm, as reported in Table 7.3). Moreover, from the morphological point of view, the more regular spherical shape of the nanoparticles composing the 8L film (Figure 7.2d), in comparison to the 4L and 6L electrodes (Figure 7.3a-d), reasonably implies a lower number of grain boundaries responsible for charge recombination and a higher film/electrolyte contact area. The combination of these two factors can explain the steep jump in photocurrent density observed in Figure 7.9a,b when comparing the 6L with the 8L pure BV photoanode.

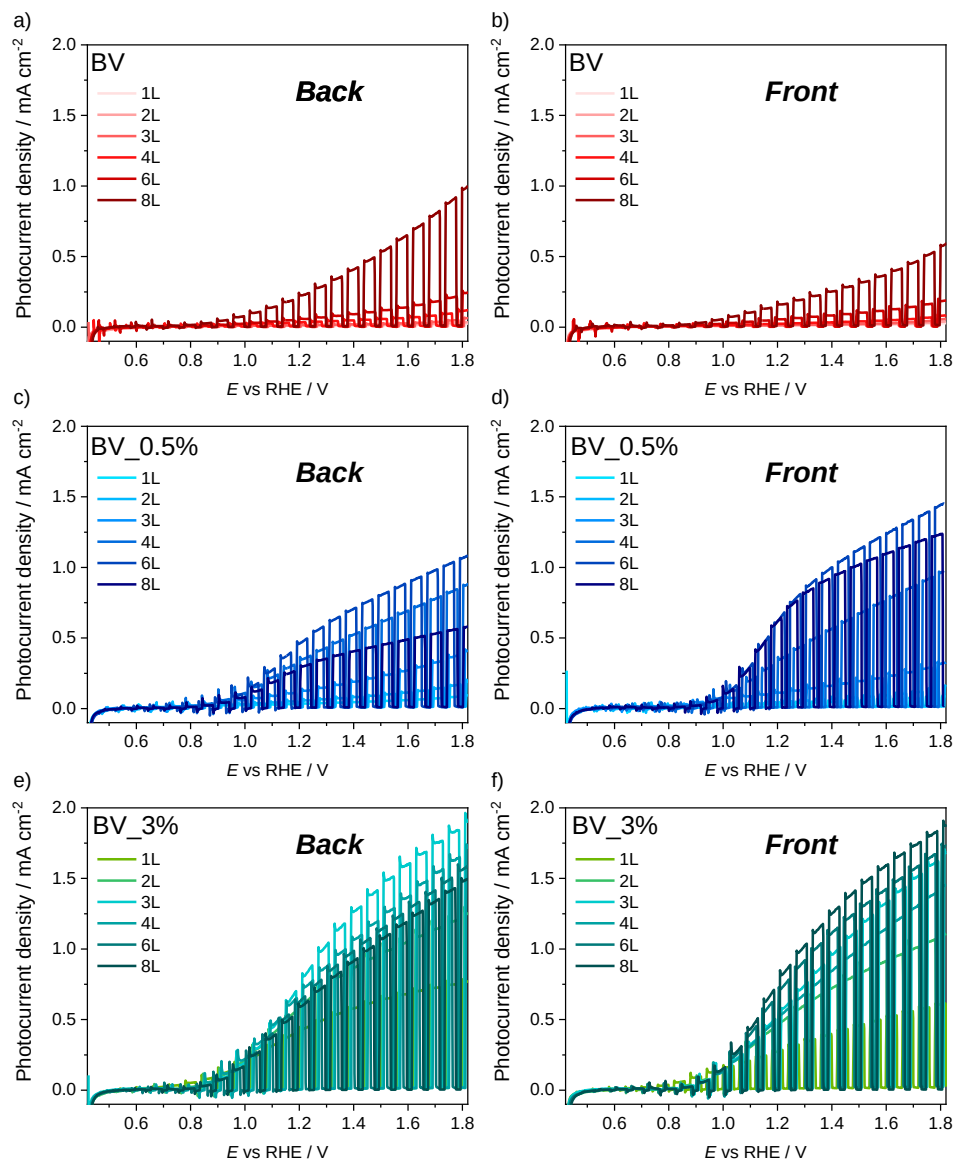


Figure 7.9 Linear sweep voltammetry (LSV) scans of the multilayer films series for (a,b) pure BV, (c,d) BV_{0.5%} and (e,f) BV_{3%}, in a 0.5 M Na_2SO_4 electrolyte solution, recorded under (a,c,e) back- and (b,d,f) front-side irradiation configuration.

Figure 7.9a,b also shows that multilayer pure BV electrodes exhibit comparable back- and front-side irradiation performances except for the 150 nm thick 8L film, showing a considerably higher photocurrent density when irradiated in back- rather than in front-side configuration. Under back-side irradiation electrons are photopromoted close to the FTO back-contact and can be directly injected into the external circuit. This is advantageous in materials suffering from poor electron transport, such as BiVO_4 .^{5,28,41,42}

Therefore, the behaviour observed for the 8L_BV electrode clearly suggests that the performance of pure BV photoanodes is largely limited by severe electron transport issues, especially in the case of photoactive materials thicker than the BiVO_4 charge diffusion length, which is *ca.* 70-100 nm.³⁰ Hence, BV-based photoanodes thicker than 100 nm are expected to exhibit higher efficiencies in back- rather than in front-side irradiation due to the intrinsic limits imposed by electron mobility within the photoactive layer.^{41,42}

An opposite behaviour was obtained with the two series of Mo^{6+} doped multilayer films (Figure 7.9c-f), with front irradiation progressively becoming more advantageous as the number of coating layers increases, ensuring higher photoactivity compared to back illumination. Overall, considerably higher maximum photocurrent values with respect to pure BV were obtained with the two doped materials under both irradiation configurations, even for the lower dopant content. However, it is quite evident that the maximum performances recorded with the thickest 8L_BV_0.5% and 8L_BV_3% electrodes under front-side irradiation (Figure 7.9d and Figure 7.9f), due to their greater absorption ability compared to the thinner electrodes within the corresponding series, underwent a huge drop in efficiency when moving to the back-side illumination, where similar performances were already attained with a lower number of coating layers (Figure 7.9c and Figure 7.9e).

The better performance in front- rather than back-side configuration of the thickest films of the doped series (compare Figure 7.9c,d and Figure 7.9e,f) is very peculiar, BiVO_4 -based materials being generally characterized by inefficient electron transport properties leading to worst performances in front- with respect to back-side configuration. The obtained results provide indication of impressively improved electron transport properties induced by Mo^{6+} incorporation in BiVO_4 , so that photocurrent generation seems to be no longer limited by electron transport,^{8,22,29} in line with the results of previous studies.^{24,36}

Among the undoped BV series, the highest photocurrent was attained with the thickest (150 nm thick) 8L_BV film, under both illumination configurations. In the case of doped BiVO_4 systems, the maximum photocurrent was reached with differently thick electrodes, depending on the irradiation configuration. In particular, under back-side irradiation, the best performance is that of relatively thinner 6L_BV_0.5% and 3L_BV_3% (130 nm and 73 nm thick, respectively). This finding can be related to the larger light absorption ability of doped materials, able to almost fully absorb 420 nm light (83% light absorption) for a thickness exceeding their calculated penetration depths, which is *ca.* 100 and 87 nm for the BV_0.5% and BV_3% series, respectively (see Table 7.4).

The performance trend evidenced in Figure 7.9 can be explained by taking into account multiple morphological and electronic properties of Mo^{6+} -doped BiVO_4 , in relation to the adopted irradiation configuration. Going into more detail, in the 0.5 at% doped series the highest performance was attained with the 6L_BV_0.5% electrode,

followed by the 4L_BV_0.5% and the 8L_BV_0.5% electrodes under back- and front-side configuration, respectively (Figure 7.9c,d). Thus, when charges are photogenerated close to the film/electrolyte interface, 0.5 at% doping is not enough to maximize the efficiency of electron transport within the thickest film. Under back-side irradiation, instead, the main photoactivity determining factor (for films enough thick to ensure enough light absorption) is the distance that photogenerated holes need to travel in order to reach the electrode/electrolyte interface. In this context, as evidenced by the comparison between the SEM images in Figure 7.3b and Figure 7.2e, the 4L_BV_0.5% electrode should provide more available pin-holes for electrolyte diffusion across the film than the 8L_BV_0.5% film, with a consequent larger contact area between the film and the electrolyte, ensuring higher photoactivity under back-side irradiation. This behaviour reflects the fact that, generally, when transport limitations of the majority charge carriers (electrons) are reduced by Mo^{6+} doping, an optimal matching between the photon absorption depth and the minority charge carriers (holes) diffusion length is crucial for maximizing the PEC performance.⁴

On the other hand, a different photoactivity trend was observed for the BV_3% series. In fact, the highest photocurrent generated under front-side irradiation by the 8L_BV_3% electrode suggests that a relatively high dopant concentration enables an effective exploitation of the large light absorption ability of the thickest film. At the same time, the progressive photocurrent increase with increasing number of layers under front-side irradiation demonstrates that the electron transport properties are no longer a limiting factor for the material with the highest Mo^{6+} dopant content.

However, the highly packed structure characterizing the BV_3% series limits an efficient exposition of the material network to the electrolyte, with the films becoming more compact with increasing number of coating layers. This means that hole diffusion towards the film/electrolyte interface in the 3 at% Mo^{6+} doped photoanodes may be hampered with respect to the pure or the less doped BV films, with a consequently larger electron-hole recombination probability. This explains why the performance of this series under back-side irradiation, *i.e.* when the photogenerated holes should travel a relatively longer distance to reach the film/electrolyte interface, achieves its maximum with the 70 nm thick 3L_BV_3% photoanode, in which holes have to travel a distance comparable to their diffusion length in BiVO_4 ,^{25,30} and then it progressively decreases with increasing number of layers. These results support the idea that the PEC performance of BiVO_4 -based electrodes under back-side irradiation is mainly limited by the hole diffusion length rather than by electrode absorption ability.

In order to get a clear overview of the performance enhancement produced by Mo^{6+} doping in relation to the BiVO_4 multilayer electrode structure, the photocurrent densities attained with the three BV photoanodes series in both irradiation configurations at 1.23 V vs. RHE can be directly compared in Figure 7.10, as a function of the number of coating layers.

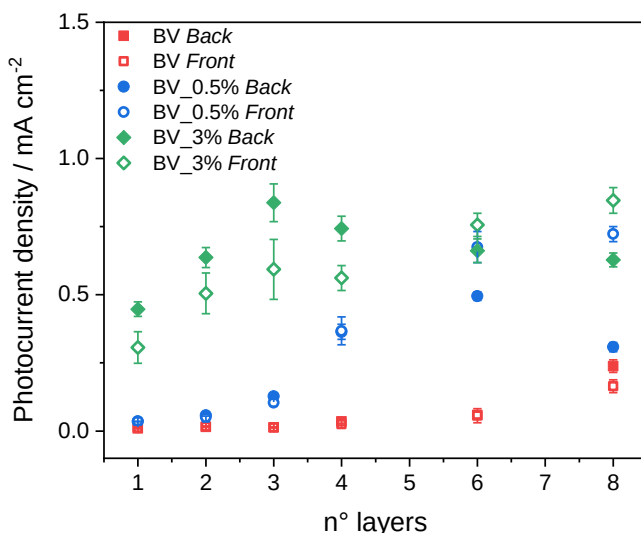


Figure 7.10 Photocurrent density at 1.23 V vs. RHE, with relative error bars, as a function of the number of layers for pure BV (squares) and for the doped BV_0.5% (circles) and BV_3% (diamonds) series, under both back- (full symbols) and front-side (open symbols) irradiation configurations, in a 0.5 M Na_2SO_4 solution. The error bars were calculated as standard deviation of the values extracted from 5 distinct LSV scans.

With pure BV electrodes low photocurrent values, almost independent of the number of layers, were obtained up to 6 layers, with a performance increase for the 8L electrode. An almost linear photocurrent growth with increasing number of layers was achieved in both irradiation configurations with the BV_0.5% doped series, except for the 8L_BV_0.5% electrode, exhibiting a remarkable performance drop when irradiated in back-side configuration.

More interestingly, for a fixed number of coating layers, the electrode of the BV_3% series is always the best performing one, under both sides irradiation, with the thickest 8L_BV_3% film generating 0.85 mA cm^{-2} under front-side irradiation at 1.23 V vs. RHE, corresponding to a 5-fold photocurrent enhancement with respect to 8L pure BiVO_4 .

Furthermore, while among the BV_0.5% series an appreciable photocurrent enhancement with respect to pure BV is attained with at least 4 layers, the same improvement is already attained with the thinnest 1L electrode for the 3 at% dopant series.

More importantly, the data collected in Figure 7.10 show that a progressive increase of the front-side with respect to the back-side irradiation photocurrent is attained with doped electrodes with increasing number of coating layers. In particular, an inversion in the performance obtained in the two irradiation modes occurs with 6L_BV_0.5% and 6L_BV_3%, for the lower and the higher doped electrode series, respectively. Thus, above a certain thickness (ca. 130 nm), the photocurrent generation in doped systems is no longer limited by electron transport. Differently, pure BV electrodes do not exhibit

such behaviour over the entire investigated thickness range, due to the poor electron transport properties intrinsically characterizing BiVO_4 -based photoanodes.

Finally, the 8L_BV_3% electrode shows a significantly higher performance than the equally thick 8L_BV_0.5% electrode, under back-side illumination. This behaviour is quite surprising if we consider the higher degree of film compactness and the higher particles size characterizing the 8L_BV_3% electrode compared to the 8L_BV_0.5% film (Figure 7.2e,f, Table 7.1), since they may cause a longer transit distance for photogenerated holes to travel before reaching the film/electrolyte interface. The obtained data suggest that a relatively high level of Mo^{6+} doping not only promotes electron transport and photon absorption, but also improves the hole diffusion length of BiVO_4 -based materials, as observed elsewhere.^{20,36,43}

Thus, a 3 at% Mo^{6+} content may represent the optimum doping degree for maximizing the photoactivity of BiVO_4 photoanodes towards water oxidation, confirming the results of our study on monolayer Mo^{6+} doped BV films produced employing polyvinylalcohol (PVA) as thickening agent.

7.4.2.2 PEC performance of the thickest electrodes in water oxidation

The complete LSV profiles recorded with the overall best performing 8L photoanodes in the Na_2SO_4 electrolyte solution, under both irradiation modes, are compared in Figure 7.11. Despite a non-negligible photocurrent density can be observed at around 0.6 V vs. RHE in all cases, as observed elsewhere,^{33,36,38,44,45} a better photocurrent onset in the low bias region (referred to as the tangent line to the J - V curve⁴⁶), resulting in a higher fill factor, is achieved upon Mo^{6+} incorporation at any of the employed levels.

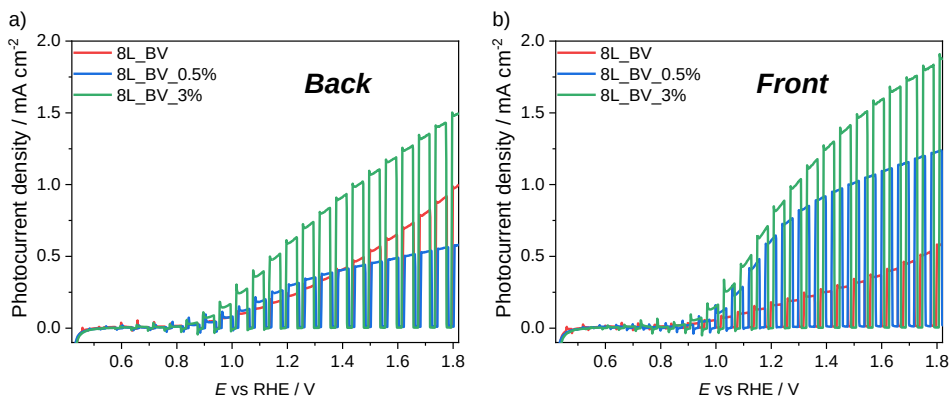


Figure 7.11 LSV plots under (a) back and (b) front irradiation of the 8L_BV (red lines), 6L_BV_0.5% (blue lines) and 6L_BV_3% (green lines) electrodes in a 0.5 M Na_2SO_4 solution.

Looking at the relative performances under back irradiation (Figure 7.11a), a slightly better photocurrent onset in the low 1.0–1.4 V vs. RHE bias region can be observed for the 8L_BV_0.5% electrode with respect to the pure 8L_BV film, at the expense of a lower saturation photocurrent at high potentials. This behaviour in the low potentials regime,

where the performance is limited by the fate of the minority carriers, can be ascribed to inefficient hole transfer to the film/electrolyte interface, originating from either a high surface charge recombination or an inefficient hole transport towards the SCLJ, or both. A higher 3 at% dopant content produces both a better photocurrent onset and a higher saturation photocurrent, supporting the hypothesis of a highly improved hole diffusion length at this higher doping degree.

A quite different picture results from the performances recorded under front-side irradiation (Figure 7.11b), where the beneficial effects induced by Mo^{6+} doping on the electron transport properties can be fully exploited over a 150 nm electrode thickness. In this case, a conspicuous enhancement in performance, in terms of both an improved photocurrent onset and a much higher saturation photocurrent, was indeed attained not only with the 3 at% doping level, providing a photocurrent as high as 1.6 mA cm^{-2} at 1.6 V vs. RHE, but also with the lower 0.5 at% doping level, producing 1.1 mA cm^{-2} photocurrent at the same applied potential. This suggests that, when the charge carrier couples are photogenerated next to the film surface but far from the FTO back-contact, the electron transport across the material bulk is already improved upon 0.5 at% Mo^{6+} doping and further enhanced with the optimal 3 at% dopant addition.

Finally, the LSV profiles relative to the 8L electrodes shown in Figure 7.11 confirm that 3 at% Mo^{6+} doping represents the optimum dopant concentration for enhancing the performance towards water oxidation of our BV films. Under such conditions, the efficiency of BV-based photoanodes is much more limited by the slow water oxidation kinetics than by the poor electron transport in the bulk. Therefore, the remarkably enhanced photoactivity in water oxidation achieved upon Mo^{6+} doping and, in particular, for the 3 at% dopant level in BiVO_4 , can be fully explained only if other factors than the improved electron transport in the material bulk are taken into account. Indeed, hexavalent Mo and W ions acting as BiVO_4 dopants are able to modify not only the bulk but also the surface properties of BiVO_4 , by passivating recombination centres and trap states at both grain boundaries and interfaces.^{5,8,11} In order to shed light onto this aspect, photoelectrochemical impedance spectroscopy (PEIS) analysis was also carried out with the main aim of discerning the effects induced by Mo^{6+} doping on the material bulk from those at the film surface (see Section 7.4.3).

The incident photon to current efficiency (IPCE) analyses carried out at 1.23 V vs. RHE with the 8L_BV, 8L_BV_0.5%, and 8L_BV_3% photoanodes in contact with the 0.5 M Na_2SO_4 solution, under front-side irradiation, are reported in Figure 7.12a.

The attainment of pretty similar IPCE curve onsets at *ca.* 520-530 nm for all tested materials confirms the lack of any significant change in the band gap energy of the photoanodes after Mo^{6+} incorporation, in line with their absorption spectra (Figure 7.5), as verified in other studies.^{18,34}

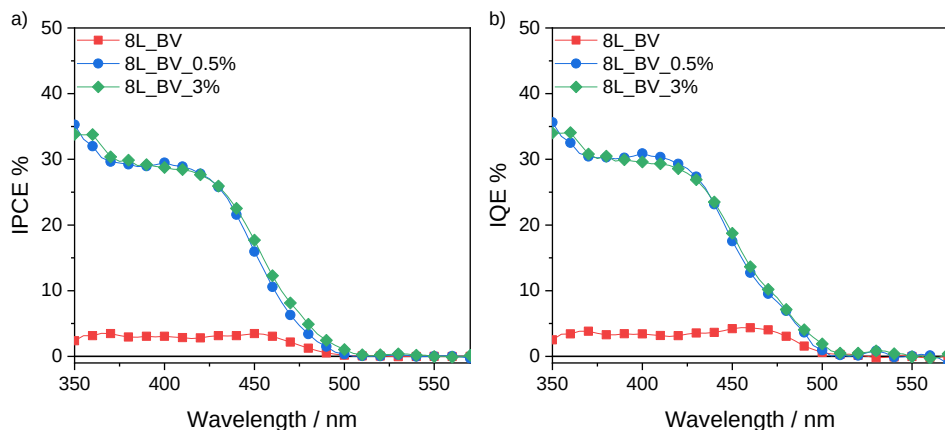


Figure 7.12 (a) Incident photon to current efficiency (IPCE) and (b) internal quantum efficiency (IQE) plots of the 8L photoanodes in a 0.5 M Na_2SO_4 electrolyte solution at 1.23 V vs. RHE, under front-side illumination.

The photoactivity enhancement in terms of IPCE attained upon Mo^{6+} doping is higher than that resulting from AM 1.5 G PEC analyses, with IPCE values 10-fold higher than those obtained with pure BV, regardless of the dopant amount. In fact, a 30% IPCE was recorded at 420 nm with both the 8L_BV_0.5% and 8L_BV_3% films in comparison with the almost negligible 3% IPCE measured with pure 8L_BV. Despite the similarity of the IPCE values recorded with the two doped electrodes in the low wavelength range (for $\lambda < 430$ nm), in line with the comparable photocurrents generated under full-lamp irradiation at this applied potential (Figure 7.11b), the IPCE values recorded for $\lambda > 430$ nm with the 8L_BV_3% film are slightly higher than those acquired with the 8L_BV_0.5% electrode, due to the larger absorption ability of the former in the visible light region (Figure 7.5).

Finally, the internal quantum efficiency (IQE) plots in Figure 7.12b allow a direct comparison between the conversion efficiencies of the investigated electrodes, regardless of their absorption ability, because they are obtained by normalizing the corresponding IPCE plots for the effectively absorbed number of photons. The almost superimposition of the IPCE and IQE curves (Figure 7.12a,b) indicates an almost quantitative absorption of incident photons by the investigated thick films, characterized by a high optical transparency with negligible loss due to undesired light scattering.

The comparison between the IPCE plots recorded in back and front configuration (Figure 7.13) confirms the trends observed under AM 1.5 G irradiation, *i.e.* doped materials exhibit much greater IPCE under front- than under back-side irradiation, while the opposite behaviour is observed with the 8L_BV pure film.

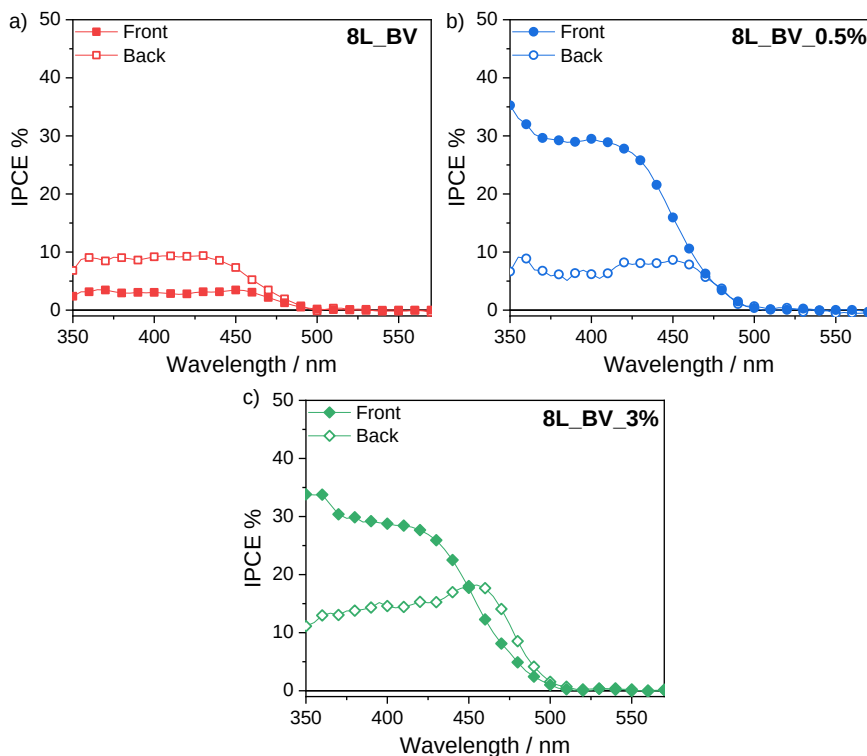


Figure 7.13 Incident photon to current efficiency (IPCE) plots of (a) 8L_BV, (b) 8L_BV_0.5% and (c) 8L_BV_3% photoanodes under back- (void symbols) and front-side (full symbols) illumination in a 0.5 M Na_2SO_4 electrolyte solution at 1.23 V vs. RHE.

Further information can be obtained by comparing for each sample the experimental photocurrent density recorded at 1.23 V vs. RHE under back- and front-side irradiation with that calculated by integrating the product of the corresponding IPCE curve (Figure 7.12a) and the global AM 1.5 G solar spectral irradiation^{41,47,48} over the investigated wavelength range (300–520 nm), as summarized in Table 7.6. Both calculated and experimental photocurrent values obtained for the thickest photoanodes show a progressive increase with increasing Mo^{6+} doping content.

Table 7.6 Photocurrent density values (J) at 1.23 V vs. RHE obtained in LSV scans under AM 1.5 G solar simulated light in a 0.5 M Na_2SO_4 solution and from the integration of the IPCE values recorded in the same electrolyte solution over the solar spectral irradiance. Data refer to measurements performed under both back-side and front-side irradiation.

Material	<i>J</i> from IPCE / mA cm^{-2}		<i>J</i> from AM 1.5 G conditions / mA cm^{-2}	
	Back	Front	Back	Front
8L_BV	0.39	0.16	0.24	0.16
8L_BV_0.5%	0.37	1.14	0.31	0.72
8L_BV_3%	0.84	1.2	0.63	0.85

Predicted photocurrent values are slightly higher than the corresponding AM 1.5 G experimental ones for the two doped electrodes, while a better match occurs for those relative to pure BV (Table 7.6). This behaviour can be explained by considering that different factors may limit the PEC performance of BiVO_4 electrodes in relation to the employed light intensity under different irradiation conditions. In particular, the photoresponse recorded under the relatively high AM 1.5 G light intensity is mainly affected by the slow oxygen evolution kinetics, because the photoanode may acquire a relatively higher electron mobility thanks to the large extent of photogenerated electron-hole couples (photodoping effect).⁴¹ Differently, at the lower light intensity employed in monochromatic IPCE measurements, the performance becomes limited by the BiVO_4 poor electron transport properties. This discrepancy between experimental and predicted values for the doped electrodes is larger under front- than under back-side configuration (see Table 7.6), so it can be reasonably ascribed to the enhanced electron transport properties gained by BiVO_4 upon Mo doping, which are better evidenced by the low light intensity employed in IPCE analyses performed under front-side irradiation.

In comparison with the previously investigated monolayer films of pure and Mo^{6+} doped BiVO_4 (Chapter 6), prepared according to a similar synthesis, but employing PVA as thickening agent (in the following referred as PVA-containing films), a far better performant pure BV material, further improved by doping with Mo, was obtained through the here presented PVA-free multilayer synthesis. In fact, the optimum 8L_BV undoped photoanode belonging to this series produces a relatively high photocurrent density of *ca.* $240 \mu\text{A cm}^{-2}$ at 1.23 V vs. RHE under back-side irradiation, which is far higher than the practically negligible photoresponse obtained with the pure BV electrode of the previously investigated PVA-containing series. Moreover, the employment of the previous synthesis approach excluded any possibility of increasing the light absorption by multilayer films deposition, owing to the severe charge recombination issues occurring at the interface between consecutive layers. Finally, with the best 8L_BV_3% photoanode presented in this chapter, a photocurrent of 0.9 mA cm^{-2} was recorded at 1.23 V vs. RHE under front-side irradiation, while only $80 \mu\text{A cm}^{-2}$ were produced by the corresponding 3 at% Mo^{6+} doped PVA-containing electrode at the same bias. Thus, a strong gain in photoactivity, beyond an improved film quality and light absorption ability, is achieved with the present PVA-free multilayer films.

7.4.2.3 PEC performance of the thickest electrodes in sulfite oxidation

As already mentioned in Chapter 6, sodium sulfite, being both thermodynamically and kinetically easier oxidizable than water, is usually employed as hole scavenger to evaluate the bulk properties of BiVO_4 -based photoanodes, separately from the slow water oxidation occurring at the film/electrolyte interface.^{5,21,33} The PEC performance of Mo^{6+} doped BV towards sulfite oxidation was also tested on the 8L_BV_0.5% and 8L_BV_3% electrodes investigated in this chapter, in comparison with the pure 8L_BV material. This

analysis, reported in Figure 7.14, was carried out with the films in contact with a 0.5 M Na_2SO_3 solution buffered at pH 7 through a 0.5 M potassium phosphate buffer (KPi).

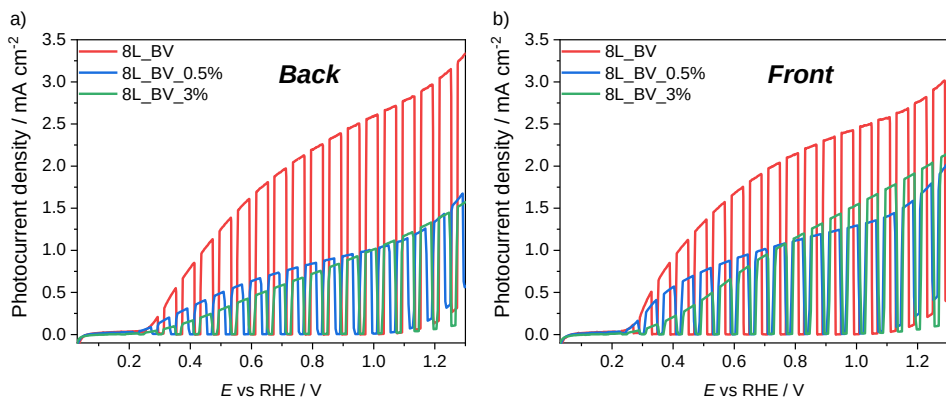


Figure 7.14 Linear sweep voltammetry (LSV) plots recorded under (a) back- and (b) front-side irradiation with the 8L_BV, 8L_BV_0.5% and 8L_BV_3% electrodes in a 0.5 M Na_2SO_3 solution buffered at pH 7 with 0.5 M potassium phosphate (KPi).

First of all, a *ca.* 3-fold photocurrent enhancement and better fill factor were attained with the pure BV electrode in contact with sulfite solution compared to water oxidation conditions. Furthermore, the anticipated photocurrent onset in Figure 7.14, located at around 0.2 V vs. RHE, compared to that that observed in water oxidation (0.6 V vs. RHE, see Figure 7.11), is indicative of a considerably lower overpotential required for sulfite oxidation with respect to water oxidation. Moreover, the *J-V* curves in Figure 7.14 suggest an opposite impact of Mo^{6+} doping on the performance of our BV photoanodes towards sulfite oxidation with respect to water oxidation. Indeed, a lower photocurrent over the entire investigated potential window, resulting in a worse fill factor, characterizes the LSV plots recorded with the two doped photoanodes compared to pure BV in sulfite oxidation, under both irradiation sides.

In this way, the relatively high photocurrent of 3 mA cm^{-2} at 1.23 V vs. RHE attained with the pure BV electrode under back-side irradiation drops to 1.4 mA cm^{-2} with either 0.5 at% or 3 at% Mo-doped BiVO_4 . To the best of our knowledge, these results, together with those presented in Chapter 6, represent one of the first evidences of the detrimental role of the Mo^{6+} dopant in the PEC activity of BiVO_4 in sulfite oxidation, since an overall improved performance upon incorporation of the optimum dopant level has been reported in all studies involving Na_2SO_3 as hole scavenger.^{4-6,18,21,36,49}

With a closer view to the behaviour of the two doped photoanodes in the lower and higher applied potential regions, 0.5 at% Mo doping of BiVO_4 produces a better photocurrent onset than the higher 3 at% Mo doping under both irradiation configurations (Figure 7.14a,b), while a higher photocurrent is provided by the 3 at% doped BV electrode under front illumination at higher potential, when the photocurrent becomes mainly limited by bulk recombination.^{50,51}

The impact of Mo doping of BiVO_4 in sulfite oxidation was also investigated by IPCE analyses in the presence of the hole scavenger, and the results are reported in Figure 7.15.

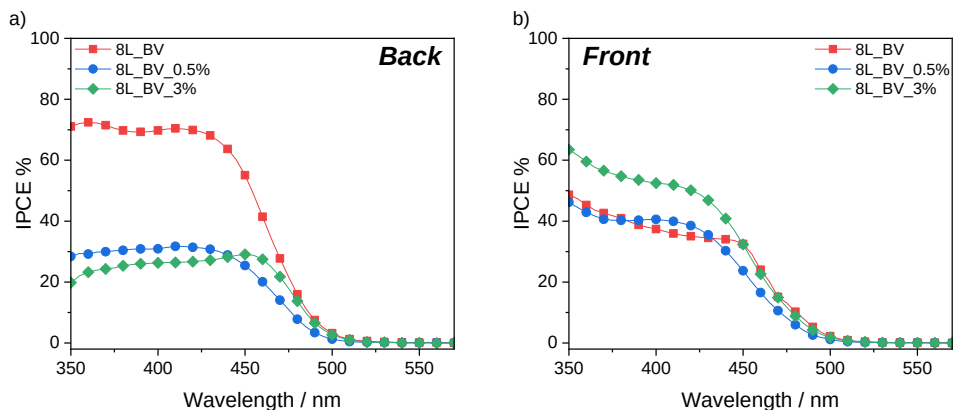


Figure 7.15 Incident photon to current efficiency (IPCE) plots recorded at 1.0 V vs. RHE with the 8L electrodes under (a) back- and (b) front-side irradiation in a 0.5 M Na_2SO_3 solution buffered at pH 7 with 0.5 M potassium phosphate (KPi).

Under back-side irradiation a drop of conversion efficiency occurs upon doping BiVO_4 with Mo^{6+} , to an extent which is almost independent of the dopant amount (Figure 7.15a), with the 70% IPCE recorded with the pure BV electrode at 430 nm dropping to *ca.* 30% with the two doped photoanodes. This means that, when charge carrier couples are generated close to the FTO back-contact through back-side irradiation, the Mo^{6+} dopant, which does not exert its beneficial role in electron transport across the bulk, induces a detrimental effect on hole injection from the film surface towards the SO_3^{2-} hole scavenger. On the contrary, when electron-hole couples are photoproduced close to the film/electrolyte interface under front-side illumination, the electron transport through the material bulk takes advantage of the increased conductivity induced by incorporation of the Mo^{6+} dopant at relatively high concentration, as demonstrated by the slightly enhanced IPCE values recorded in this configuration with the 8L_BV_3% electrode with respect to the pure 8L_BV film (Figure 7.15b).

This result, which is not consistent with the relative trend attained under AM 1.5 G front illumination in the same electrolyte solution (Figure 7.14b), should be ascribed to the different irradiation intensities adopted in the two kinds of analysis. Indeed, as already discussed in Section 7.4.2.2, under the control of electron transport in the bulk when performing IPCE analyses with relatively low (few mW cm^{-2}) light irradiation intensity,⁴¹ the material performance under front-side irradiation can benefit from the largest dopant amount in hampering charge recombination in the bulk of the film.

The here observed PEC performance decrease in sulfite oxidation upon Mo^{6+} dopant incorporation in BiVO_4 can be partly ascribed to the concomitant electrochemical active surface area (ECSA) reduction shown by the doped photoanodes (see Table 7.2). The ratios between the photocurrent density obtained with each thickest doped electrode and

that achieved with pure 8L_BV (at 1.0 V vs. RHE under full lamp front-side irradiation) are compared with the corresponding relative ECSA values in Figure 7.16.

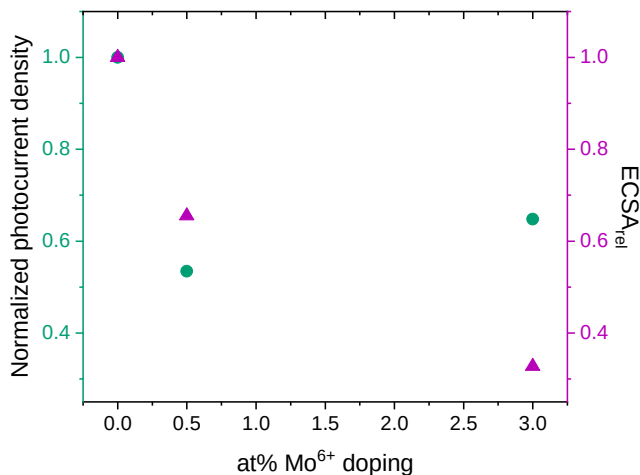


Figure 7.16 Comparison between the ratios of the photocurrent density attained with each 8L doped electrode and that attained with pure 8L_BV at 1.0 V vs. RHE, in sulfite oxidation under full lamp front-side irradiation (green circles) and the corresponding ECSA relative values (purple triangles).

Notably, the relative photocurrent density drop attained with the doped electrodes in sulfite oxidation may be related to the reduction of their ECSA value with respect to the pure 8L_BV electrode. This observation points to the fact that, although the use of a hole scavenger (as sulfite) may help in evaluating the bulk properties induced by doping in BV-based photoanodes, the ECSA effectively exposed by each investigated electrode may play a crucial role on the resultant PEC performance, especially in the case of sacrificial substrate molecules to be oxidized.

By focusing on the data collected in Figure 7.16, a slightly higher photocurrent density ratio respect to the corresponding relative ECSA can be observed only with the 8L_BV_3% photoanode, possibly related to the improved electron conductivity induced by the highest dopant amount incorporated into multilayer BV films, thus being a first proof of the favourable intrinsic impact exerted by Mo^{6+} doping on the bulk properties of BV-based photoanodes.

7.4.3 Photoelectrochemical impedance spectroscopy analysis

Photoelectrochemical impedance spectroscopy (PEIS) is a powerful tool to separately investigate the electrical properties of the electrode in the bulk and at the SCLJ.^{9,52–55} PEIS measurements were carried out under the same conditions as PEC tests, *i.e.* under AM 1.5 G irradiation with the tested 8L_BV and 8L_BV_3% electrodes in contact with either Na_2SO_4 or Na_2SO_3 solutions. The impedance spectra of the two photoanodes acquired during water photooxidation, in the form of Nyquist plots at three representative potentials, are shown in Figure 7.17. Each of the spectra at a specific potential is in

principle composed of two semicircles:^{9,52,53} the semicircle at high frequency corresponds to the electrical response in the space charge region, thus providing information onto the charge transfer from the bulk of the film to the material/electrolyte interface; the low frequency semicircle describes instead the interfacial charge transfer behaviour at the SCLJ.⁵² Therefore, a suitable model considering both the bulk and surface contributions should be employed in fitting the impedance spectra,⁹ to extrapolate information on the electrical properties described by the two semicircles.

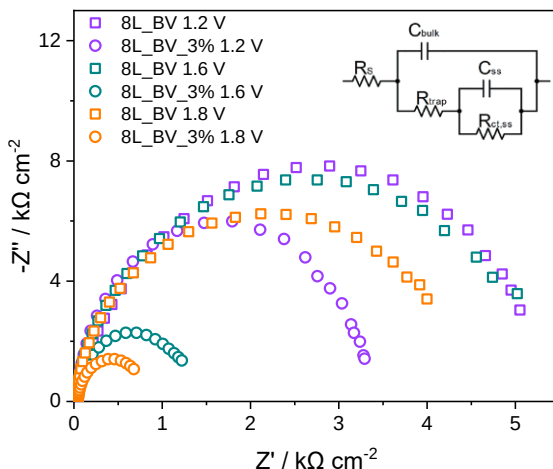


Figure 7.17 Nyquist plots obtained under AM 1.5 G illumination with the 8L_BV electrode (squares) and the 8L_BV_3% film (circles) in a 0.5 M Na₂SO₄ solution, at 1.2 V (violet), 1.6 V (green) and 1.8 V (orange) vs. RHE. The corresponding equivalent circuit is reported in the inset.

Although EIS analyses on similarly Mo⁶⁺ doped BiVO₄ systems as the here examined ones have been already reported, the data interpretation performed so far was mostly based on the simplest Randles circuit model (as in Chapter 6). In this way, only the dielectric capacitance contribution, corresponding to the transfer of charges from the bulk of the absorbing layer to the electrolyte through the SCLJ, was taken into account, while the existence at low frequencies of any chemical capacitance associated with the accumulation or transfer of charges through potential surface states (SS), was neglected.

The here proposed model, shown in the inset of Figure 7.17 and previously employed for other metal oxide systems^{9,52,53} and for W-Ti doped BiVO₄ photoanodes,⁵⁶ consists of the following elements: *i*) a series resistance R_s associated with charge transfer through the external circuit and the semiconductor bulk; *ii*) a bulk capacitance C_{bulk} (with $C_{\text{bulk}}^{-1} = C_{\text{SC}}^{-1} + C_{\text{H}}^{-1}$), which includes C_{SC} referring to the depletion layer inside the semiconductor and C_{H} relative to the Helmholtz layer inside the electrolyte; *iii*) a parallel resistance of hole trapping to surface states R_{trap} ; *iv*) a $C_{\text{ss}}/R_{\text{ct,ss}}$ pair corresponding to surface state capacitance and charge transfer resistance from surface states to oxidize water, respectively. In particular, the presence of the chemical surface state capacitance, associated with the accumulation/transfer of charges through potential surface states,

makes this equivalent circuit an excellent approximation if charge transfer at the SCLJ is affected by the presence of surface states.^{9,54}

The Mott-Schottky (M-S) plots in Figure 7.18a, correlating the C_{SC} values extracted from the impedance spectra to the applied potential, allow to get insight into the electron donor density N_{D} and the flatband potential E_{FB} of the investigated electrodes. First of all, the positive slopes of the well-defined linear region of both plots confirm the n -type character of both the investigated pure and Mo^{6+} doped BV materials.

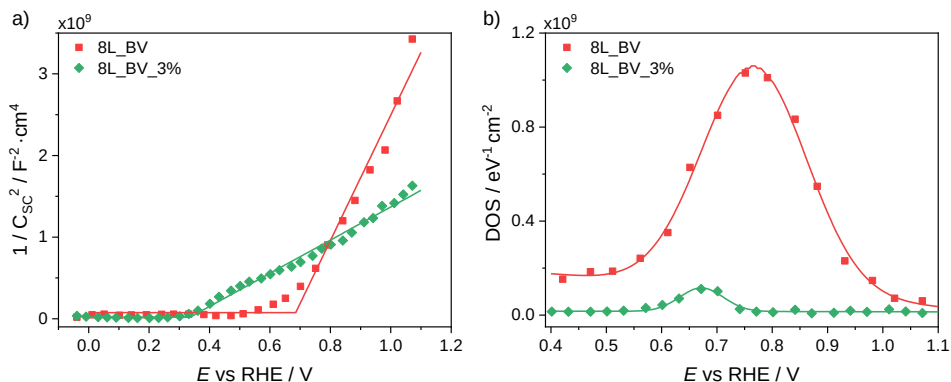


Figure 7.18 (a) Mott-Schottky plots obtained with 8L_BV (red squares) and 8L_BV_3% (green diamonds) in a 0.5 M Na_2SO_4 solution under irradiation, and relative fitting curves. (b) Energetic distribution of density of surface states (DOS) for 8L_BV (red squares) and 8L_BV_3% (green diamonds) fitted with a Gaussian function.

From the slope of the linear fits performed using a dielectric constant¹¹ of 68, N_{D} values of $2.3 \cdot 10^{18}$ and $8.6 \cdot 10^{18} \text{ cm}^{-3}$ were obtained for pure 8L_BV and 8L_BV_3% electrodes, respectively, accounting for a 4-fold enhancement in electron donor density upon a 3 at% Mo^{6+} doping, which is consistent with the supply of additional free electrons in the material bulk due to the n -type character of the chosen dopant element.^{21,26,28,45} Interestingly, the fitting of the linear part of the M-S plots provides a flatband potential values of 0.66 V and 0.32 V vs. RHE for the pure BV_8L and doped 8L_BV_3% electrodes, respectively, with the former value in good agreement with the flatband potential reported for pure BiVO_4 .¹²

The positive shift in E_{FB} found for the pure BV with respect to the doped electrode originates from Fermi level pinning which occurs in the lower potentials range of the M-S plot of the pure material up to 0.7 V vs. RHE, indicating the lack of increase in C_{SC}^{-2} with increasing bias until such potential is applied. This anomalous behaviour reflects the lack of band bending in the depletion region with increasing the applied potential, that typically occurs in the presence of surface states; in such case the Fermi level energy in the material bulk equilibrates with the energy of these states rather than with that of the electrolyte solution.⁵⁷ This causes the so-called Fermi level pinning (FLP),^{58–60} indicating a potential range where any applied voltage results in the charging of surface states rather than in the semiconductor band bending increase, since most of the applied potential

drops should be expected across the Helmholtz layer rather than across the space charge region.^{51,52} Therefore, the observed anodic shift in the flatband potential of pure BV is related to the rigid downward shift of the band edges, caused by holes accumulation at the capacitive layer.¹⁰ On the other hand, the passivation of these surface states, evidently occurring upon Mo^{6+} incorporation, restores the original location of the flatband potential through unpinning of the semiconductor Fermi Level.⁵⁻⁸

To ascertain the presence of surface states causing Fermi level pinning and thus affecting the water oxidation photocurrent onset, we referred to the C_{ss} parameter extracted from the fitting of the PEIS data, whose build-up is an index of charges accumulation at the SCLJ. The C_{ss} contribution can be directly converted into the energetic distribution of the density of surface states (DOS) by:⁹

$$C_{ss} = q \times \text{DOS} \quad (7.1)$$

The so calculated DOS for both the 8L_BV and 8L_BV_3% electrodes are fitted with a Gaussian function and plotted against the applied potential in Figure 7.18b. A very intense and well-defined peak located at *ca.* 0.75 V vs. RHE characterizes the DOS curve relative to 8L_BV, while the 8L_BV_3% electrode exhibits only a much less pronounced peak at lower potential values. The integration of the Gaussian function fitting the DOS of the 8L_BV film provides a total density of surface states N_{ss} of $2.3 \cdot 10^{15} \text{ cm}^{-2}$, which is far above the threshold considered necessary to cause the Fermi level pinning with a bulk donor density of about 10^{18} cm^{-3} .⁵⁸ This is further confirmed by the fact that this DOS falls within the potential range where the FLP was found to occur in the M-S plot of the pure material. A much lower N_{ss} of $9.9 \cdot 10^{13} \text{ cm}^{-2}$ resulted instead from integration of the DOS fit relative to the 8L_BV_3% electrode, corresponding to a two orders of magnitude decrease of the total surface state density at the SCLJ compared to the pure material, as a consequence of the Fermi level unpinning. This phenomenon is also accompanied by a small cathodic shift of the DOS peak, which is strictly connected to the lower potentials shift of the M-S plot in Figure 7.18a, indicating that not only the amount, but also the energy of surface states changes upon Mo^{6+} doping, in such a way that an equal band bending extent would be obtained with a lower applied potential compared to the pure BV film.⁵¹

Thus, as a consequence of Fermi level mitigation upon passivation of the set of surface states located right below the conduction band (CB) edge in pure BV, the material photovoltage would be expected to increase.^{50,61} Correspondingly, a higher photocurrent in the low applied potential region at around 1.0 V vs. RHE can be generated with the 8L_BV_3% electrode with respect to the pure BV_8L film, as a consequence of the fruitful exploitation of the applied potential, which is instead required to compensate the Fermi level pinning in pure BV (Figure 7.11).

The benefits induced by Mo^{6+} doping both in the bulk and at the surface of the BV film, through the N_D increase and the N_{ss} decrease, respectively, greatly overpasses the loss in charge separation eventually caused by a decrease of the depletion width due

increasing electron donor density, in agreement with what previously observed with similar BV-based photoanodes.^{21,28} In fact, the width (W) of the space charge region (out of the region affected by FLP) can be estimated by the following equation:⁵²

$$W = \sqrt{\frac{2 \cdot \varepsilon \cdot \varepsilon_0}{q \cdot N_D} |E - E_{FB}|} \quad (7.2)$$

where ε is the dielectric constant of BiVO₄ (ca. 68¹¹) and ε_0 the vacuum permittivity (8.86 × 10⁻¹² C² J⁻¹ m⁻¹). In this way, a lower W extension, corresponding to ca. 24 nm, can be indeed estimated for the 8L_BV_3% electrode at 1.0 V vs. RHE with respect to the 8L_BV film, where W amounts at ca. 36 nm. Moreover, the calculated widths at the higher applied bias of 1.8 V vs. RHE (amounting at ca. 60 nm and ca. 36 nm in the case of the pure and the doped films, respectively) are sufficiently smaller than the 150 nm film thickness, indicating that both electrodes can sustain at least up to 1.8 V vs. RHE of potential drop within the space charge layer, during PEIS measurements. In other terms, the Mott-Schottky analyses of our BiVO₄-based photoanodes are reasonably valid.

The M-S plots obtained in sacrificial conditions with the 8L_BV, 8L_BV_0.5% and 8L_BV_3% electrodes in contact with the 0.5 M Na₂SO₃ (pH 7) solution (Figure 7.19) reveal a E_{FB} potential location at ca. 0.35-0.27 V vs. RHE, thus lower with respect to that found in water oxidation with the pure BV electrode, and closer to the CB edge.

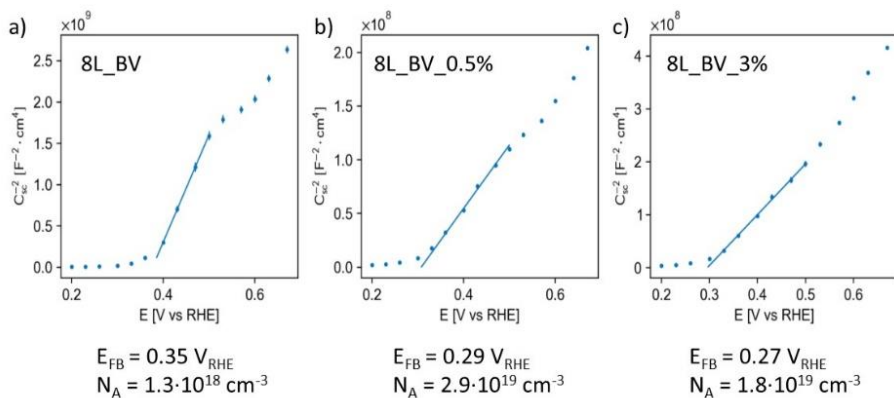


Figure 7.19 Mott-Schottky plots under irradiation for the (a) 8L_BV, (b) 8L_BV_0.5% and (c) 8L_BV_3% photoanodes recorded in a 0.5 M Na₂SO₃ solution buffered at pH 7 with 0.5 M potassium phosphate (KPi).

This finding may indicate the lack of significant Fermi level pinning thanks to the fast hole transfer kinetics characterizing sulfite oxidation, preventing holes accumulation at the SCLJ. Finally, the detected N_D of 2.9 · 10¹⁹ and 1.8 · 10¹⁹ cm⁻³ for the two doped electrodes with respect to the 1.3 · 10¹⁸ cm⁻³ value found with the pure material, confirm that successful doping was achieved through the expected increase of the majority charge carrier density in the material bulk, in line with what observed in non-sacrificial conditions.

7.5 Overall discussion

PEIS analyses revealed that in pure BiVO_4 holes accumulate at the film/electrolyte interface in concentration sufficiently high to act as surface states located at *ca.* 0.75 V vs. RHE, causing Fermi level pinning at the SCLJ during the slow water oxidation reaction. The FLP phenomenon is known to prevent an efficient separation of surface accumulated holes from electrons photopromoted in the CB, due to the absence of beneficial band bending until the surface states are completely passivated. This in turn leads to the significantly lower PEC performance recorded with the pure 8L_BV electrode in water oxidation compared to the more thermodynamically and kinetically favoured sulfite oxidation reaction, for which an anticipated flatband potential, indicative of the lack of FLP, was clearly detected through PEIS analyses.

The passivation of surface states upon Mo^{6+} dopant incorporation, in addition to the increased majority charge carrier concentration in the material bulk, provided the observed great enhancement in PEC performance in water oxidation attained with the doped photoanodes with respect to pure BiVO_4 . This beneficial effect was evidenced in terms of both favoured photocurrent onset and improved saturation photocurrent, which gets progressively higher with increasing dopant level.

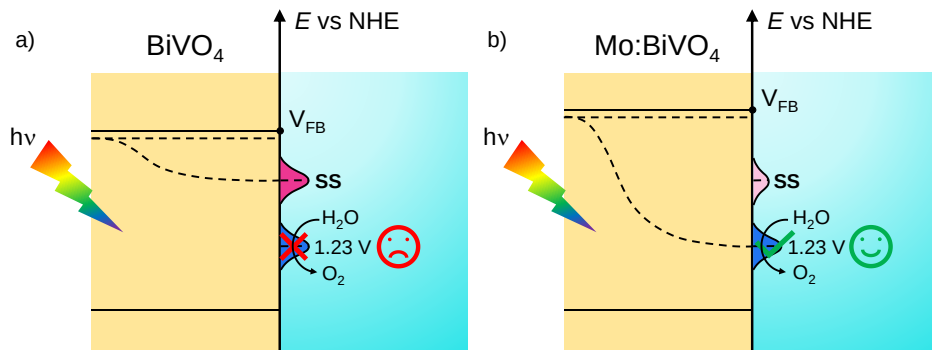
So far, evidence of a surface state capacitance peak at around 0.75 V vs. RHE, associated with accumulated holes at the SCLJ,⁵⁸ was already reported for pure or W^{6+} -doped BV and identified with the $\text{V}^{5+}/\text{V}^{4+}$ redox process,^{10–12} while the hypothesis of surface hole traps passivation upon Mo^{6+} incorporation was also taken into account by a previous transient absorption study.⁸ Moreover, further spectroscopic investigations revealed the presence, in pure BV films, of intra band gap states initially occupied by electrons in the dark, which undergo depopulation under application of an anodic bias, leading to accumulation of trapped holes at the material surface.^{62,63} Recently, Durrant *et al.*¹² disclosed the initial presence of $\text{V}_{\text{OV}}^{4+}$ states, due to oxygen vacancies formation, which can act as detrimental photoinduced VB holes trapping sites, with the consequent formation of $\text{V}_{\text{OV}}^{5+}$ states, which are energetically unable to drive water oxidation (being located at potentials more negative than 1.23 V vs. RHE).

By comparing our results with the above data reported in literature, we propose the mechanism depicted in Figure 7.20 to describe what goes on during either water or sulfite oxidation with pure and Mo^{6+} -doped BV photoanodes.

The surface of pure BV in neutral conditions should be enriched of V^{4+} states (occupied by electrons) formed after localization of the electrons coming from oxygen vacancies formation during the annealing process on neighbouring V^{5+} sites. Upon Fermi level splitting into the quasi-Fermi levels of electrons ($E_{\text{F,n}}$) and holes ($E_{\text{F,p}}$) under illumination, the so generated $E_{\text{F,p}}$ equilibrates with the energy level of the surface states (E_{ss}) rather than with the water oxidation potential (1.23 V vs. RHE), as shown in Figure 7.20a. According to Durrant *et al.*, such surface states, originally corresponding to

defective V^{4+} states, can be progressively converted into photoproducted V^{5+} states, which are energetically unable to promote water oxidation, with the consequent detrimental holes accumulation at the electrode/water interface.

Water oxidation



Sulfite oxidation

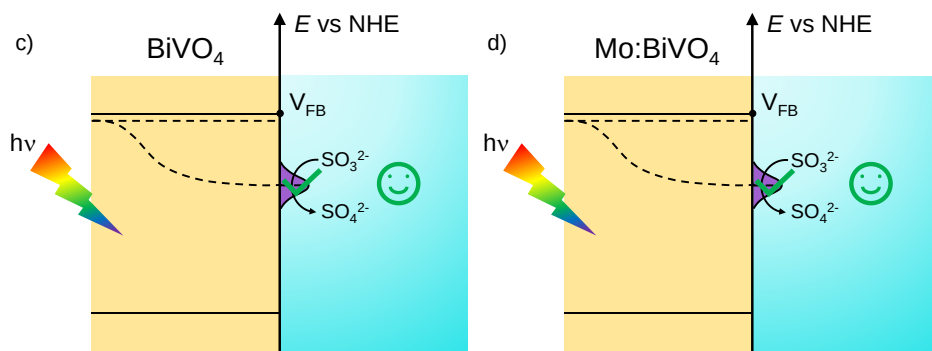


Figure 7.20 Mechanisms of (a,b) water and (c,d) sulphite photoinduced oxidation with (a,c) pure and (b,d) Mo^{6+} doped BiVO_4 . Solid lines indicate the VB and CB of both pristine and doped BV films, while dashed lines indicate the splitting of the Fermi level into quasi Fermi levels of electrons and holes. The purple and blue Gaussian density of states curves are representative of the surface states (SS) and of water oxidation intermediates, respectively.

Since the surface states concentration detected from PEIS measurements is enough to cause Fermi level pinning in pure BV, as suggested by the relative N_{SS} and N_D values, the $E_{F,p}$ stays virtually fixed until the V^{4+} states are completely emptied, leaving unchanged the degree of band bending over the entire potential region affected by this phenomenon, and significantly lowering the photovoltage of the material. Indeed, upon FLP conditions, any additional applied bias is devoted to withdraw electrons from the SS, with potential drop across the Helmholtz layer rather than the space charge region. Consequently, the band edges shift downwards in energy to increase the driving force for charge transfer,

thus causing the observed anodic shift in the flatband potential from its expected value (ca. 0.35 V) to the experimental one at ca. 0.66 V vs. RHE.^{51,52,61}

The above description is in accordance with the build-up of the capacitive peak C_{ss} at 0.75 V vs. RHE inferred from the PEIS measurements (Figure 7.18b) and associated with the accumulated holes at the SCLJ. In line with Durrant *et al.*,¹² since the detected V^{5+} states are energetically close to the CB edge, it is reasonable to rule out their direct involvement in the water oxidation reaction, as instead supported by others.^{9-11,52,62} On the other hand, they may act as shallow traps towards CB electrons, thus behaving as undesired electron-hole couples recombination centres.

When introducing Mo^{6+} in substitution of V^{5+} thanks to the similarity of their ionic radii, the additional free electrons supplied by the higher valent metal result in an increased V^{4+} sites content both in the bulk and at the surface of the BV film.^{1,11,21} This leads not only to a change in the material bulk properties through the donor density N_D increase (see Section 7.4.3) and consequent improvement in electron conductivity,^{24,28,30,35,64,65} but also to the mitigation of the undesired photo-stimulated $\text{V}^{4+}/\text{V}^{5+}$ redox process.¹¹ The strong evidence of this SS passivation process induced by Mo^{6+} doping lies in the reduction of the capacitive peak C_{ss} in Figure 7.18b, supported by a huge decrease in N_{ss} with respect to pure BV, as discussed in Section 7.4.3.

These findings, producing the BV Fermi level unpinning with the consequent restoring of the original E_{FB} location at 0.32 V vs. RHE,¹² as represented in Figure 7.20b, also result in space charge field formation and band bending development, ensuring an effective and beneficial separation of photogenerated charge carriers.^{50-52,61} Moreover, thanks to the increased photovoltage, the so unpinned $E_{F,p}$ can thus equilibrate with the water oxidation potential⁵³ (1.23 V vs. RHE) earlier than in pure BV, thus leading to an appreciable photocurrent onset (see Figure 7.20b).

As a result of the above discussed multiple effects of Mo^{6+} doping, a dramatically improved PEC performance in water oxidation was attained with the investigated doped electrodes compared to pure BV (Figure 7.9-Figure 7.11). Notably, the same surface chemistry detected in our Mo^{6+} doped BV films was also found to be at the basis of the enhanced photocurrent observed after photocharging BV photoanodes in alkaline conditions.^{10,17,61} Therefore, in comparison with the photocharging method, the here presented doping strategy is an effective tool to permanently solve the limitations shown by BiVO_4 -based photoanodes activity towards water oxidation, by operating under safely neutral electrolyte pH conditions.

On the other hand, concerning the mechanism active in sulfite oxidation, no Fermi level pinning was observed for both pure and doped BiVO_4 electrodes, possibly due to the fast and energetically allowed interaction of photogenerated V^{5+} SS states with Na_2SO_3 molecules. Therefore, the quasi-Fermi levels of holes ($E_{F,p}$) under illumination can directly equilibrate with the $\text{SO}_3^{2-}/\text{SO}_4^{2-}$ couple at oxidation potentials corresponding

to ca. 0.93 V vs. NHE^{66} regardless of the presence of the Mo^{6+} dopant, as depicted in Figure 7.20c,d.

In this case the photoproduced V^{5+} states can eventually act as reaction sites rather than surface traps states, thus efficiently driving the kinetically and thermodynamically more favoured sulfite oxidation. This motivates the higher sulfite rather than pure water photooxidation efficiency achieved with all the BV-based photoanodes. At the same time, the slightly higher performance attained with 8L_BV_3% compared to the pure 8L_BV in relation to the corresponding ECSA values, demonstrates the effective but not so relevant electron conductivity improvement in BiVO_4 bulk material upon Mo^{6+} addition.

Therefore, the almost negligible effect induced by Mo^{6+} incorporation on the hole scavenger oxidation reaction indirectly demonstrates that the here reported doping strategy mainly positively impacts on the surface rather than on the bulk properties of the here investigated BV-based films, the former being the main limiting factor of the sluggish water oxidation reaction.

7.6 Conclusions

The heavy impact of Mo^{6+} doping on both the bulk and surface properties of thin BV photoanodes has been effectively demonstrated. Apart from the well-known role of the hexavalent n -type dopant in enhancing the electron conductivity of BiVO_4 through the increase of the majority charge carrier density, we succeeded in identifying the additional effect of surface trap states passivation as primary factor influencing the performance of the investigated photoanodes. While structural XRD and Raman analyses enforced the evidence of the influence of Mo^{6+} at the bulk level in terms of improved electron mobility (through distortion of the VO_4^{3-} tetrahedron upon V^{5+} with Mo^{6+} substitution), XPS measurements also enlightened that most of the introduced dopant is localized at the top surface of the BV film, thus leading to important effects on the surface chemistry of pure BiVO_4 . The performed multilayer films study allowed to ascertain that the improved photoactivity of Mo-doped photoanodes compared to pure BiVO_4 should be ascribed not only to the enhanced electron transport but also to the improved hole diffusion length upon addition of the optimum dopant content. Moreover, in this way, the optimum doping level ensuring good charge transport, while maximizing the absorption capability of the photoanode, was identified. In addition to the far enhanced electron donor density at the highest 3 at% doping degree with respect to pure BiVO_4 films, PEIS analyses allowed to unequivocally identify, for the first time, the mechanism through which the Mo^{6+} dopant passivates the surface states of BiVO_4 . This mechanism is associated with $\text{V}^{5+}/\text{V}^{4+}$ states, acting as detrimental electron-hole pairs recombination centres. Both the outstanding improvement of PEC performance in water oxidation with Mo^{6+} -doped photoanodes and the almost negligible impact produced by the dopant on sulfite oxidation, allowed to recognize the surface chemistry-induced effects as the major factor governing the observed photoactivity.

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Chapter 8

Ultrafast charge carrier dynamics in CuWO₄ photoanodes

8.1 Abstract

CuWO₄ is a ternary metal oxide semiconductor with promising properties for photoelectrochemical (PEC) water splitting and solar light conversion, due to its quite low band gap (2.3 eV) and high stability in alkaline environment. Aiming at understanding the origin of the relatively low PEC efficiency attained with CuWO₄ photoanodes, we here investigate transparent CuWO₄ electrodes prepared by a simple solution-based method through the combination of femtosecond transient absorption spectroscopy with electrochemical, PEC and photochromic characterizations. The very fast recombination dynamics of the charge carriers photogenerated in CuWO₄, which is the reason of its low efficiency, is discussed in relation with its PEC performance and with the recently calculated band structure of this material, also in comparison with the behaviour of other semiconductor oxides employed in PEC applications, in particular Fe₂O₃.

8.2 Introduction

Beyond BiVO₄, Fe₂O₃ and WO₃ as visible light active archetypal candidates for water oxidation, the continuous efforts for circumventing their main drawbacks led to the discovery of novel semiconducting materials.^{1,2}

Indeed, BiVO₄ takes advantage of relatively long-living photogenerated charge carriers, which are compatible with an internal quantum efficiency (IQE) close to unity up to 2.75 eV (450 nm). However, its theoretical solar to hydrogen conversion efficiency is limited to 9% by the 2.4 eV band gap.³⁻⁵

On the other hand, Fe₂O₃, with a band gap of 2.1 eV that is low enough to allow a solar light conversion efficiency higher than 12%,⁶ is characterized by a much faster charge carrier recombination, which seriously limits its PEC performance. This is due to its long-range antiferromagnetic order as typical of first-row transition metals, resulting

in low charge-carrier mobility ($\sim 10^{-2}$ to 10^{-1} cm² V⁻¹ s⁻¹) and in a short hole-diffusion length in the order of 2–20 nm.^{7–9}

WO₃, which is a diamagnetic oxide due to the d^0 configuration, benefits from larger hole mobility and diffusion lengths of 10 cm² V⁻¹ s⁻¹ and 0.15 mm, respectively.¹⁰ Despite these benefits, WO₃ photoanodes exhibit a larger band gap of 2.7 eV, allowing for the harvesting of a limited portion of the visible part of the spectrum (the blue-violet region), and are stable only under acidic conditions (at pH < 5).¹¹

The use of ternary and quaternary oxides has emerged as an attractive alternative for PEC applications to the widely studied binary oxides, thanks to their wider diversity and flexibility in tuning the electronic properties.

CuWO₄, comprised of earth-abundant elements and with a band gap of *ca.* 2.3 eV corresponding to an absorption edge of 550 nm, represents a good candidate photoanode material in this frame.¹² It exhibits a superior visible light harvesting capability than WO₃, in addition to the better stability in prolonged PEC water oxidation experiments under simulated solar irradiation, in both neutral and slightly basic solutions.^{12–15}

Although the exploitation of CuWO₄ as photoanode material dates back to pioneering works of the 80s,^{16,17} and despite it features quantitative selectivity to water oxidation and hole collection at the electrode/electrolyte interface,^{15,18,19} the highest photocurrent obtained with CuWO₄-based electrodes is only of 0.2–0.3 mA cm⁻² at 1.23 V_{RHE},^{20,21} as compared to *e.g.* 6.7 and 6.0 mA cm⁻² obtained with state of the art BiVO₄ and Fe₂O₃ photoanodes.^{22,23} The reasons for such a poor PEC performance are unclear, also because the dynamics of the charge carriers photogenerated in CuWO₄ is still unexplored.

In the work presented in this chapter, we investigate the ultrafast dynamics of the charge carriers photogenerated in transparent CuWO₄ electrodes through femtosecond transient absorption (TA) spectroscopy and discuss it in relation to the recently proposed electronic structure of CuWO₄, which receives full support from the here performed PEC characterization of this ternary oxide.

8.3 Experimental section

8.3.1 Chemicals and materials

The following chemicals, all purchased from Sigma Aldrich, were employed for the work presented in this chapter: copper(II) nitrate trihydrate 99%, citric acid 99%, tetrabutyl ammonium hexafluorophosphate 99%, nitric acid 65%, anhydrous sodium sulfite, boric acid ACS reagent, together with ammonium tungsten oxide hydrate 99% (Fluka). Deionized Millipore water was employed to prepare the solutions.

8.3.2 Photoelectrodes preparation

CuWO₄ photoanodes were prepared by spin coating a 0.5 M precursor solution, prepared as follows, on clean fluorine-doped tin oxide (FTO), followed by annealing of the films. 14 mmol of citric acid were dissolved in 5.3 mL of ethanol and 2.4 mL of

deionized H_2O . Then 5 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.4167 mmol of $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ were sequentially added, under stirring. A film was grown from this solution onto fluorine-doped tin oxide (FTO) glass (Pilkington Glass, TEC-7, thickness 2 mm) by spin coating at 2000 rpm for 20 s. Prior to deposition, the FTO glass was cleaned by 30 min long sonication in a soap solution, then thoroughly rinsed with water, sonicated for 30 min in ethanol and finally dried in air. Before moving the FTO slice to the spin coater, it was soaked in isopropanol for a few seconds. This procedure was found to increase the optical transparency of the final film. After spin coating, the CuWO_4 film was pre-annealed at 250 °C for 10 min and then annealed at 550 °C for 1 h.

For electrochromic measurements, one side of a 5 x 5 cm² FTO electrode was protected with a 0.4 mm x 5 cm scotch tape stripe and then coated by the same spin coating procedure adopted for photoanodes preparation. The scotch tape was removed before annealing.

8.3.3 Physical characterization methods

The here reported absorption spectrum for CuWO_4 , referring to a double layered film electrode to minimize the presence of interference fringes, was recorded in the transmission mode with a Jasco V-650 spectrophotometer. The crystalline phase of the material was determined through X-ray diffraction (XRD) analysis using a Philips PW 1830/40 instrument, equipped with a Cu sealed tube at 40 kV and 40 mA. A model LEO 1430 scanning electron microscope operating at a 10 kV accelerating voltage and at 8 mm working distance was used to acquire the top view and cross-sectional images of the CuWO_4 film.

8.3.4 Photochromism

The photochromic experiments were performed by irradiating a 25 x 9 mm² CuWO_4 electrode, sealed inside a N_2 filled glovebox in a 10 mm-thick cuvette modified to allow the insertion of the 9 mm wide electrode and containing 3 mL of ethanol previously stored overnight in the glovebox, in order to attain a completely oxygen free environment. The film was irradiated with a 300 W Xe arc lamp (Lot Oriel, LSH302), with a light intensity of ca. 150 mW cm⁻², measured with a PM100A Thorlabs power meter equipped with a S302C thermal power sensor. The photochromic effect was monitored by recording the absorption spectra at fixed irradiation times. The irradiated cuvette was cooled by means of a flux of compressed air.

At the end of the photoreduction experiment, the CuWO_4 electrode was moved from the air-tight cuvette to a Shimadzu UV-Vis-IR spectrophotometer (model 3600) and the spectral changes due to progressive back oxidation to the pristine condition were measured every hour for 10 hours. The absorbance difference plotted in Figure 8.2b is obtained by subtracting the spectrum recorded after 11 h exposure to air from the spectra

recorded at different times. After 11 h long contact with air almost complete back oxidation to the pristine conditions was attained.

8.3.5 Electrochemical methods

Cyclovoltammetry experiments were performed by polarizing a 9 x 50 mm² electrode within the same cuvette employed in the photochromic experiments. The ohmic contact was obtained by soldering with indium a copper wire to the uncovered FTO edge; the contact was then glued with an epoxy resin (Araldite) for insulation. Two platinum wires were used as counter and quasi-reference electrodes, respectively, and the cuvette was closed with a rubber septum. The potential was modulated with an Autolab PGSTAT 12 (EcoChemie, Utrecht, The Netherlands) instrument controlled by the NOVA software. The potential of the Pt pseudo-reference electrode was calibrated with respect to RHE using the ferrocene/ferrocinium redox couple (+400 mV_{RHE}) as standard.²⁴ The electrolyte was a 0.1 M tetrabutyl ammonium hexafluorophosphate solution in acetonitrile, which was deaerated through N₂ bubbling for 5 min prior to the electrochemical experiments.

Mott-Schottky measurements were performed by acquiring a series of potentiostatic electrochemical impedance spectroscopy (EIS) spectra with a Parstat potentiostat, with a sinusoid of peak-to-peak amplitude 10 mV in the 10⁵ – 0.1 Hz frequency range. The electrolyte employed was a 0.3 M Na₂SO₄ solution at pH 7. The bias range was between –0.2 and 0.6 V vs. Ag/AgCl (V_{Ag/AgCl}) and the potentials were scanned in the cathodic direction, to avoid possible irreversibility due to reduction of the metallic components. Capacitance values were extracted by a non-linear least squares fitting with an equivalent-circuit model featuring the parallel of a faradaic resistance and a double-layer capacitance, in series with an ohmic resistance (Randle's model).¹⁸ As customary in EIS modelling, morphological heterogeneities of the film were accounted for by replacing the double-layer capacitance with a Constant Phase Element (CPE). Fitting was carried out with a Matlab-based program written by the authors, allowing better control over the regression statistics than the commonly used commercial packages. The CPE exponent estimates ranged in the 0.86–0.98 interval and did not exhibit any measurable potential dependence.

The extrapolation to zero of the linear part of the Mott-Schottky plot, and the subsequent correction of the intercept for $kT/q \approx 25$ mV at room temperature, provided a value of 0.51 V_{RHE}, which was attributed to the energy level of intra-gap trap states, as described in Section 8.4.3.

8.3.6 Photoelectrochemical methods

PEC measurements were performed in the three-electrode glass cell described in Section 4.3.2.1. The FTO/CuWO₄ electrode was used as working electrode, a Pt wire as counter electrode and a Ag/AgCl electrode as reference electrode. The photoanodes were tested under back (from the FTO side) irradiation. The light source was an Oriel, Model 81172 solar simulator equipped with a AM 1.5 G filter. The light intensity, measured by

means of a Thorlabs PM200 power meter equipped with a S130VC power head with Si detector, was 100 W cm^{-2} . PEC measurements were carried out with the electrode in contact with a 0.1 M buffer borate (KBi) solution at pH 9 or with 0.1 M pH 9 KBi containing 0.5 M Na₂SO₃.

The KBi solution was prepared by dropwise adding a 1.0 M KOH solution to aqueous boric acid up to pH 9, followed by dilution to 0.1 M. Prior to performing the linear scans, the open circuit potential (OCP) of the electrode was measured for 10 min under irradiation. Then the scan started from the so determined OCP with a 10 mV s^{-1} sweep rate. The potential vs. Ag/AgCl was converted to the RHE scale at pH 0 (corresponding to NHE) using Eq. 4.19.

Incident photon to current efficiency (IPCE) scans were recorded under a 1.23 V vs. RHE bias and the current was measured with a 10 nm step, within the 300 to 550 nm wavelength range. A 300 W Lot-Oriel Xe lamp was employed as irradiation source, equipped with a Lot-Oriel Omni- λ 150 monochromator and a Thorlabs SC10 automatic shutter. The incident light power was measured at each irradiation wavelength and the IPCE was calculated according to Eq. 4.30. The internal quantum efficiency (IQE) was calculated by combining the IPCE curve with the absorption (A) spectrum of the photoanode using Eq. 4.31.

8.3.7 Transient absorption spectroscopy

Femtosecond transient absorption (TA) experiments were performed using an amplified Ti:sapphire laser system (Libra, Coherent) delivering 4 mJ, 100 fs pulses at wavelength $\lambda = 800 \text{ nm}$ with 1 kHz repetition rate. A 400- μJ fraction of the laser energy was used for the experiment, 95% of which was frequency doubled to $\lambda = 400 \text{ nm}$ and used as pump, while the remaining 5% was focused on a CaF₂ crystal to generate the white light continuum probe, covering the 380-680 nm wavelength range. TA spectra were measured with an Acton Sp2150 spectrometer (Princeton Instruments) equipped with a CCD camera (Entwicklungsbros Stresing) detecting data at the full 1 kHz repetition rate of the laser. The photoexcited spot area was $6 \times 10^{-4} \text{ cm}^2$ with a pump energy ranging from 16 to 500 nJ, corresponding to a fluence from ≈ 27 to $830 \mu\text{J cm}^{-2}$.

8.4 Results

8.4.1 Photoelectrodes characterization

As shown in Figure 8.1a reporting the absorption spectrum of a CuWO₄ double layer film, the investigated CuWO₄ electrodes are optically transparent at wavelengths longer than the absorption edge of the material. The absorbance drops above 350 nm, due to the indirect band gap and the low absorption coefficient of CuWO₄;¹³ the broad and weak feature above 700 nm can be identified with the tail of the infrared Cu d-d transition.²⁵

The X-ray diffraction (XRD) pattern of a polycrystalline CuWO₄ film, shown in Figure 8.1b, coincides with the set of Bragg reflections reported in reference JCPDF 72-

0616, without reflections typical of WO_3 , CuO and Cu_2O , indicating that CuWO_4 is in pure triclinic form.^{13,17,18} The scanning electron microscopy (SEM) image presented in Figure 8.1c confirms that the CuWO_4 layer completely covers the conductive FTO substrate and is composed of small grains with *ca.* 50 nm average diameter. The CuWO_4 film in the here investigated electrodes is *ca.* 80 nm thick, as estimated from cross section SEM images reported in Figure 8.1d.

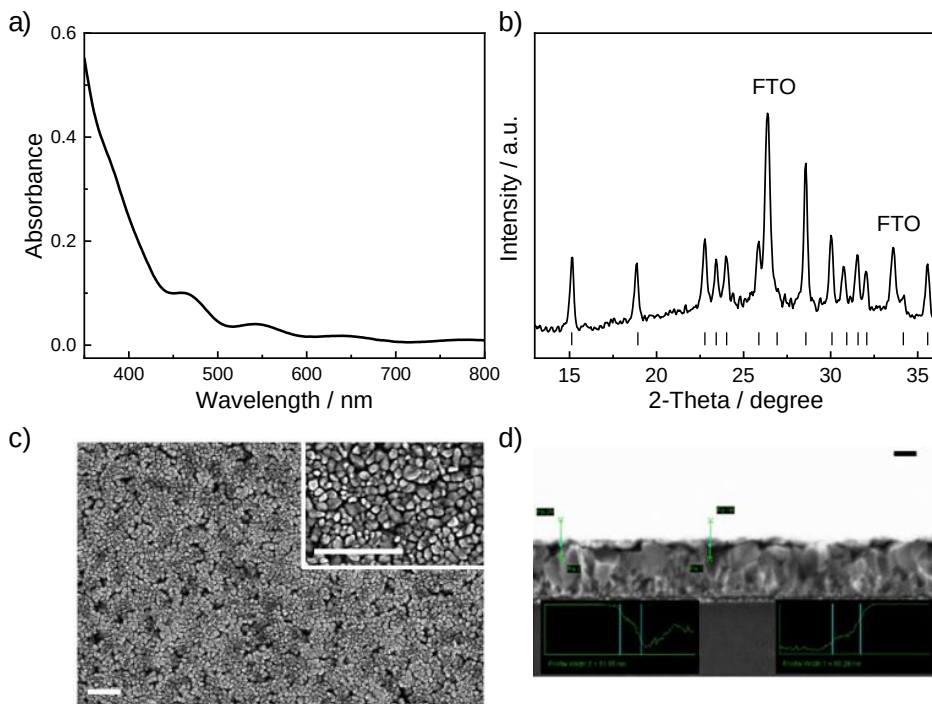


Figure 8.1 (a) Absorption spectrum of a CuWO_4 photoelectrode. (b) X-ray diffraction pattern of the CuWO_4 thin film coated on FTO glass. The grey bars are the reference Bragg reflections of CuWO_4 from JCPDF 72-0616. The FTO reflections are marked separately. (c) SEM top-view images (scale bars: 500 nm) and (d) cross section image (scale bar: 200 nm) of the CuWO_4 film accounting for a thickness of *ca.* 80 nm.

8.4.2 Photochromic characterization

Photochromic experiments are typically employed to reveal the electronic structure of semiconductor oxides. The observation of a photochromic behavior can indicate the presence of electron or hole trap sites causing accumulation of photogenerated charge carriers which are responsible for the arising of optical transitions.^{26,27} The induced spectral changes are evidenced under irradiation of the semiconductor in the presence of electron donors able to fill photogenerated holes, thus stabilizing trapped electrons. For example, the irradiation of TiO_2 or WO_3 under anaerobic conditions in the presence of organic hole scavengers, progressively induces a characteristic blue colour associated

with the electronic transitions from the filled intra band gap trap states (Ti³⁺ or W⁵⁺ sites) to the conduction band (CB).^{28–31}

The photochromic behavior of CuWO₄ was investigated by irradiating a film in deaerated ethanol with the aim of ascertaining the presence of trap states and related optical transitions, by monitoring the absorption spectrum changes by spectrophotometric analysis. Figure 8.2a shows that a positive absorption variation ΔA , extending over the visible spectrum with a shoulder at ca. 600 nm, linearly increases under irradiation. This signal can be assigned to electrons trapped in CuWO₄, in line with the ΔA signal decrease with time observed when, after 2 h-long irradiation, the film was exposed to air, as shown in Figure 8.2b. Thus, evidence is obtained that electron trapping in CuWO₄ is reversible and that metastable trapped states can be back oxidized by atmospheric oxygen.

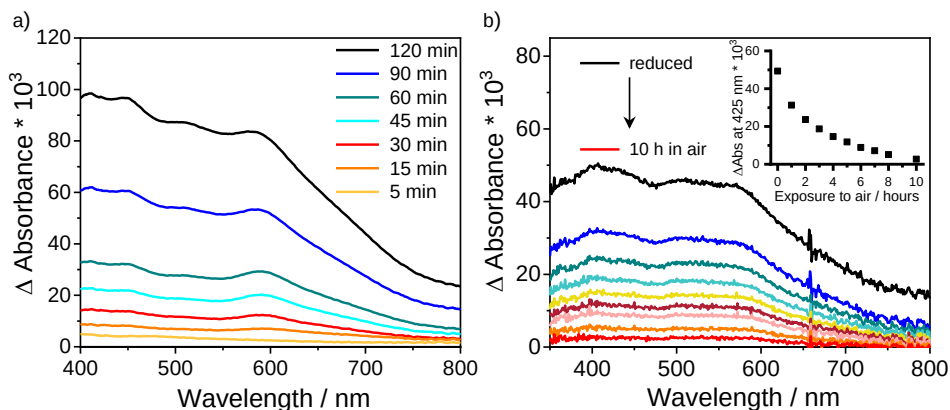


Figure 8.2 (a) Photochromic measurements of a CuWO₄ electrode recorded in deaerated ethanol at increasing time under irradiation with a 300 W Xe arc lam. (b) Recovery, under exposure to air, of the spectral changes induced by CuWO₄ photoreduction; the inset shows the decay of the signal at 425 nm.

8.4.3 Electrochemical characterization

A cyclic voltammetry (CV) test was employed to investigate and localize redox states within the band gap of CuWO₄. As shown in Figure 8.3a, a Butler-Volmer type current rise (marked with a blue arrow), starting at ca. 2.0 V_{RHE}, indicates the oxidation of the highest occupied states of the valence band (VB) of CuWO₄. At the lowest investigated potential range, a quasi-reversible redox process centered at ca. 0 V_{RHE} (cathodic and anodic peaks marked with grey arrows) is found, that might be related to the reduction and oxidation of the narrow band composed of localized Cu 3d states, as first proposed by Pyper *et al.*¹⁸ and confirmed by recent calculations.³²

The voltammetric features found in the potential range between the VB oxidation threshold (ca. 2.0–2.4 V_{RHE}) and the Cu 3d states (ca. 0 V_{RHE}), consisting in two relatively weak oxidation peaks (marked with green arrows in Figure 8.3a) and a broad cathodic feature (marked with a red arrow), can be thus interpreted as the redox response of intra-

gap states, possibly located in the 0.5–1.0 V_{RHE} range, although the presence of surface adsorbed species cannot be discarded.

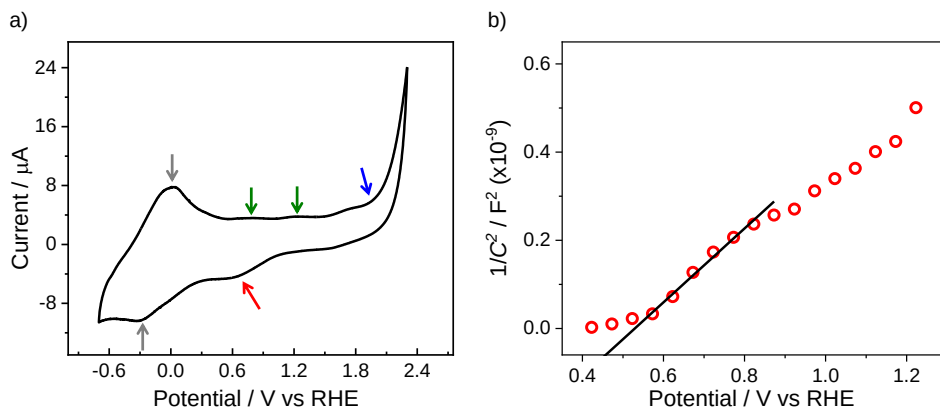


Figure 8.3 (a) Cyclic voltammogram recorded in 0.1 M tetrabutylammonium hexafluorophosphate, with a scan rate of 100 mV s⁻¹. (b) Mott-Schottky plot of the CuWO₄ photoanode in a 0.3 M Na₂SO₄ solution at pH 7.

The Mott-Schottky plot recorded with the CuWO₄ photoanode in a 0.3 M Na₂SO₄ solution at pH 7 (Figure 8.3b) presents a change in slope that suggests the occurrence of Fermi level pinning.³³ This can be related to the presence of mid-gap states, energetically located at 0.51 V_{RHE} minimum potential, as calculated from the intercept of the linear part of the Mott-Schottky plot on the abscissa axis, and perfectly in line with CV results.

8.4.4 Photoelectrochemical performance

Figure 8.4a reports the linear sweep voltammetry (LSV) recorded with the CuWO₄ electrode in contact with a 0.1 M potassium borate aqueous solution buffered at pH 9, both in the presence and in the absence of 0.5 M Na₂SO₃ as hole scavenger. The significant contribution of the dark current arising in the presence of the electron donor was subtracted from the overall value measured under irradiation,³⁴ while only a negligible current in the dark, as shown in Figure 8.4a, was recorded with the CuWO₄ electrode in contact with the pure KBi solution (in the absence of the hole scavenger) in the whole investigated potential window.¹⁸

The photocurrent values obtained at 1.23 V_{RHE} in the presence or absence of sulfite, *i.e.* 0.40 and 0.15 mA cm⁻², respectively, are compatible with those recorded with electrodes prepared through other routes, in light of the relatively thinner photoactive layer here employed.^{13,18,21} As expected, in the presence of an electron donor the photocurrent onset potential shifts to more negative values.³⁵ However, only a *ca.* 3-fold photocurrent density increase was observed at 1.23 V_{RHE} upon addition of Na₂SO₃, which is two orders of magnitude smaller than that measured, for instance, with BiVO₄ at 1.23 V_{RHE} in the presence of the same hole scavenger.³⁶ This supports the view that surface water oxidation is almost quantitative on CuWO₄, as recently outlined by Gao *et al.*,³⁴

and implies that the overall efficiency of this material is limited by poor internal charge transport or fast bulk charge carrier recombination, hampering efficient hole diffusion from the excitation site to the oxide surface.

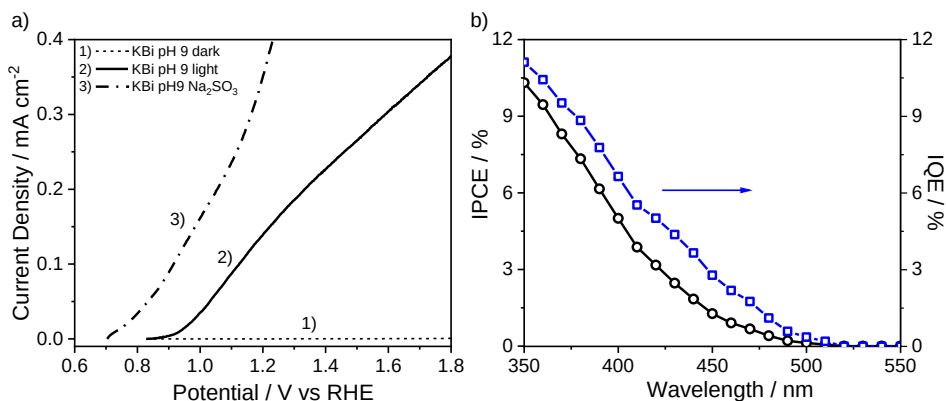


Figure 8.4 (a) Linear sweep voltammetry under AM 1.5 G simulated solar light for the CuWO₄ film in contact with 0.1 M potassium borate (KBi) aqueous solutions at pH 9, 1) in the presence of 0.5 M Na₂SO₃ (dash dot line), 2) in the absence of Na₂SO₃ (continuous line) and 3) in the absence of irradiation and of Na₂SO₃ (short dash line). (b) Incident photon to current efficiency (IPCE, black circles) and internal quantum efficiency (IQE, blue squares) of the CuWO₄ photoanode at 1.23 V_{RHE} in KBi at pH 9.

The incident photon to current efficiency (IPCE) curve shown in Figure 8.4b reflects the absorption spectrum of CuWO₄ (see Figure 8.1a), decreasing with increasing wavelength, and the IQE curve, obtained by normalizing the photocurrent for the intensity of absorbed light, has a similar wavelength dependence. The photocurrent onset is at *ca.* 510 nm, in line with that reported for bulk CuWO₄^{18,37} and slightly red-shifted with respect to that of an optimized 1 μ m thick film of WO₃ exhibiting photocurrent onset at *ca.* 480 nm, thus confirming the narrower band gap of CuWO₄.³⁸

8.4.5 Transient absorption analysis

The ultrafast charge carrier dynamics in CuWO₄ was here investigated through femtosecond TA spectroscopy. Previously, only a time-resolved microwave conductivity investigation was reported on the long-lived charge carriers in CuWO₄.³⁹ In order to investigate how transient decay processes depend on the density of photogenerated charges, TA experiments were performed at different excitation fluences of the 400 nm-centered pump pulse, ranging from 27 to 830 μ J cm⁻². As shown in Figure 8.5, the ΔA values monitored at different wavelengths increase linearly with the pump fluence, indicating that multiphoton absorption of the pump and nonlinear carrier interactions are not significantly contributing to the observed signal.

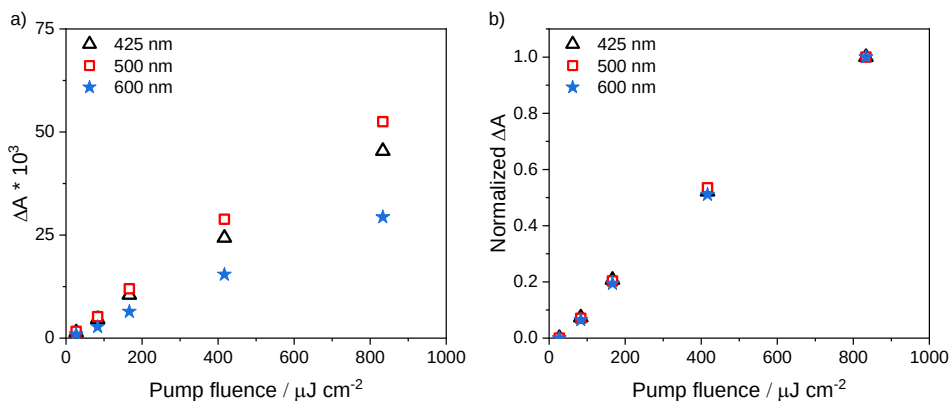


Figure 8.5 (a) Dependence of the ΔA values at 425, 500 and 600 nm on the intensity of the pump fluence; (b) normalized ΔA values reported in panel a).

Upon excitation at 400 nm, promoting electrons from the VB of CuWO₄ into the localized Cu 3d-based band, the film exhibits a broad transient absorption increase ($\Delta A > 0$) extending over the entire visible spectral range (Figure 8.6a), similar to the ΔA feature recorded in photochromic measurements (Figure 8.2), which is thus ascribed to trapped electrons. The results are similar to those obtained with Fe₂O₃ oxide in the same timescale.^{40,41} In the case of CuWO₄, the transient spectrum does not present any photobleaching ($\Delta A < 0$), expected at wavelengths shorter than the band gap absorption onset (detected at ca. 510 nm from IPCE measurements), and which would be diagnostic of a ground state absorption blocking due to promotion of charge carriers in the CB.

The decays of ΔA signal obtained with different pump fluences and monitored at 500 nm are reported in Figure 8.6b. No significant change in the dynamics upon varying the pump fluence can be appreciated, within the investigated fluence range. This indicates that higher order kinetics, like a carrier-carrier annihilation (Auger recombination) decay mechanism, does not play any relevant role in the material response at least within the here employed pump fluences.⁴⁰ A detailed analysis, reported in Appendix B, aiming at identifying the best model fitting for the TA decay curves, definitely rules out the presence of nonlinear processes correlated to multiple-exciton generation under high pump excitation energies,⁴² and responsible for the fast decay dynamics recorded for CuWO₄.

The TA signal in CuWO₄ decays much faster than in other semiconductor oxides such as the well-studied BiVO₄ material,⁴³ with a behavior similar to that observed in Fe₂O₃.⁴⁰ This can be visualized from the plot of the normalized ΔA time traces at different probe wavelengths shown in Figure 8.6c, where the signal halves in ca. 1 ps, with only a slight dependence on the detection wavelength. The ΔA decay becomes slightly faster by moving the monitoring wavelength from 425 nm to 600 nm, without any appreciable difference at wavelengths above 600 nm. The lack of a strong dependence of the dynamics on the probe wavelength suggests that the carriers are trapped in the Cu 3d band or in

lower energy mid-gap states within the pump laser pulse, in a way similar to that reported in pioneering ultrafast TA studies on hematite.⁴⁰

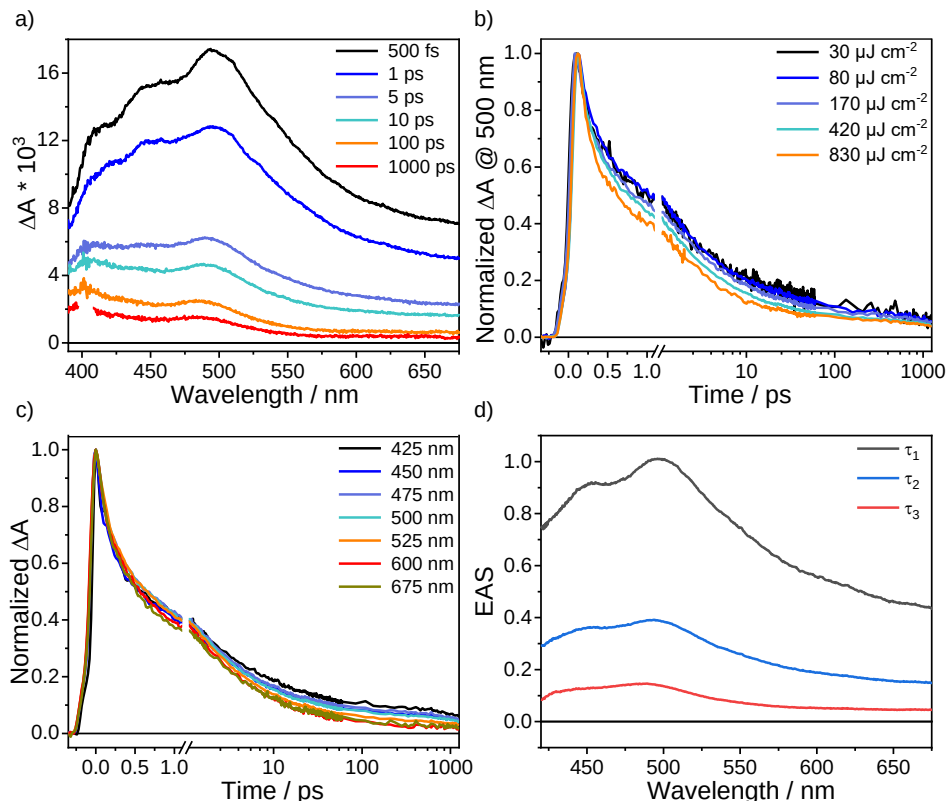


Figure 8.6 (a) Femtosecond TA spectra recorded at different times after photoexcitation of CuWO_4 at 400 nm under vacuum; ΔA decay traces (b) at 500 nm upon excitation with different pump fluences and (c) at different wavelengths upon excitation with a 420 $\mu\text{J cm}^{-2}$ fluence. (d) Evolution Associated Spectra (EAS) obtained from global analysis of the $\Delta A(\lambda, \Delta t)$ data recorded upon photoexcitation at 400 nm with a 170 $\mu\text{J cm}^{-2}$ fluence.

In order to shed light on the overall evolution of the ΔA signal as a function of wavelength and delay and to better visualize individual spectral contributions over the entire probe wavelength range, global analysis^{44,45} was carried out on the data set acquired with a representative pump fluence of 170 $\mu\text{J cm}^{-2}$. The time-dependent TA spectra reported in form of evolution-associated spectra (EAS) in Figure 8.6d consist of three kinetic components with different time constants, which span over the entire investigated 400–700 nm wavelength region. The analysis of their relative amplitudes indicates that the fastest component, with a time constant $\tau_1 = 780 \pm 10$ fs, dominates over the entire spectral range. The rest of the ΔA signal decays with a time constant $\tau_2 = 9.4 \pm 0.1$ ps, with only a small contribution from the longest time constant $\tau_3 = 1.18 \pm 0.02$ ns.

In agreement with the single decay traces reported in Figure 8.6c, the results of global analysis are in line with a slight dependence of the signal decay on the monitoring wavelength, with both EAS relative to the first two time constants τ_1 and τ_2 exhibiting a maximum around 500 nm and that associated with the slowest component τ_3 being slightly blue-shifted and peaking at 480 nm.

Our interpretation of TA data well reflects the CuWO₄ band structure recently calculated by Thang *et al.*,³² by treating the material as a Mott-Hubbard magnetic insulator, a feature common to both CuWO₄ and Fe₂O₃ oxides. According to this model, shown in Figure 8.7, the VB of CuWO₄ consists of O 2p states partly mixed with Cu 3d states, that is separated by *ca.* 2.1 eV from a narrow band consisting of very localized, Cu empty 3d levels, while a wider band dominated by W 5d and Cu 3d states is located at higher energy, corresponding to a gap of about 5 eV from the top of the VB. Similarly, the recently calculated electronic structure of hematite consists of two energetically well separated conduction bands, both primarily of Fe 3d character, accounting for the detected positive TA signal in the ultrafast regime.⁴¹

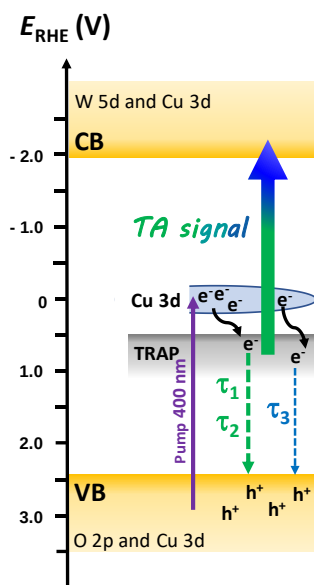


Figure 8.7 Ultrafast relaxation and recombination pathways of electrons photopromoted in CuWO₄ upon 400 nm excitation.

In this picture the optical absorption in CuWO₄ associated with the 2.3 eV experimental band gap implies the transition from a not fully localized mixed O 2p–Cu 3d state within the VB to localized Cu 3d states. The localized nature of these Cu 3d states is responsible for the low charge carrier mobility in excited CuWO₄, while the forbidden character of this d–d transition results in a low absorption coefficient in the visible region.⁴⁶ Furthermore, on the basis of the here collected results by means of different

techniques, trap states experimentally detected in the 0.5–1.0 V_{RHE} range are located just below the Cu 3d band edge, which is positioned at ca. 0 V_{RHE}.

According to Figure 8.7, upon ultrafast photoexcitation at 400 nm (3.1 eV), corresponding to an energy just higher than the first localized (Cu 3d in character) band, electrons are promoted from the VB to high energy states of the Cu 3d band, from which they quickly relax within the laser pulse to its bottom or towards mid-gap states (located just below the Cu 3d band edge).^{40,47} The observed TA signal is thus ascribed to the photoinduced absorption ($\Delta A > 0$) of electrons trapped in such states, which are promoted to the W 5d-based high energy conduction band (CB) (Figure 8.7).

The above attribution is in agreement with that recently reported for Fe₂O₃ investigated in the same ultrafast timescale⁴¹ and matches well with the maximum absorption energy of the involved transition, located at around 500 nm (≈ 2.5 eV, see TA spectra in Figure 8.6a), corresponding to the energy difference between the mid-gap trap states at around 0.5–1.0 V_{RHE} and the highest empty CB located at ca. -2 V_{RHE} (i.e. 4–5 eV higher than the top of the VB).³² Moreover, the ultrafast TA spectra are similar to those recorded in photochromic tests in the presence of a hole scavenger, which is able to fill the holes photogenerated in the VB, thus stabilizing the electrons trapped in mid-gap states. This rules out any contribution to the TA signal originated by the holes photogenerated in the VB.⁴¹

The fastest time constants τ_1 and τ_2 are associated with the recombination with VB holes of electrons located at the high-energy levels of the mid-gap states, while the longest time constant τ_3 is associated with the recombination of electrons trapped more in depth in these mid-gap states, from which the promotion to the highest W 5d CB requires higher photon energy. This is reflected by the slight blue-shift of the EAS spectrum associated to the τ_3 time constant compared to that of the other two components (Figure 8.6d). This relatively longer-lived, though minority, decay component, associated to deeply trapped electrons, may significantly reduce electron/hole recombination losses, thus favoring hole transfer in water oxidation at the electrode surface.

8.5 Overall discussion and conclusions

Although the performance achieved with the here investigated transparent CuWO₄ electrodes is in line with literature data for this material,^{12,13,15,18,33,37,39,48,49} the photocurrent produced under 1 sun illumination is much lower than the photocurrent limit of 9 mA cm⁻², calculated¹⁵ by taking into account the overlap between the absorption spectrum of CuWO₄ and the solar spectrum. Furthermore, the photocurrent generated by CuWO₄ photoanodes is only moderately affected by the presence of a hole scavenger. In fact, we found that the current density recorded at 1.23 V vs. RHE with the electrode in contact with Na₂SO₃-containing KBi buffer is only 3-fold higher than that measured in pure KBi (see Figure 8.4a). This behaviour differs from that found with oxides like BiVO₄, which suffer from sluggish surface oxidation kinetics, whose performance is

extremely improved upon addition of a hole scavengers or an oxygen evolution catalysts allowing almost complete surface accumulated holes consumption.^{36,50–53}

On the other hand, the typically low PEC activity shown by Fe₂O₃ photoanodes (band gap of 2.1 eV) relatively to the theoretical photocurrent limit^{6,54} of 12 mA cm⁻², is only moderately improved upon addition of H₂O₂ hole scavenger (similarly to what here observed with CuWO₄ electrode),³⁵ suggesting that a severe internal charge recombination rather than surface holes accumulation mainly limits the PEC performances of Fe₂O₃ electrodes.⁵⁵

Massive internal recombination thus appears to be common to both CuWO₄ and Fe₂O₃.^{32,56} Indeed, for both CuWO₄ and Fe₂O₃ the TA spectrum initially decays very fast, compared to other oxides such as TiO₂ or BiVO₄.^{57–59} In CuWO₄, the TA signal halves in *ca.* 1 ps and only a small fraction of the photogenerated charges survives for more than 1 ns, to take part to the PEC reaction.

In early femtosecond-TA studies on Fe₂O₃, the photoinduced TA signal was found to disappear within 300 ps,⁴⁰ and the lack of long-lived components in Fe₂O₃ was reflected by the extremely low photocurrent values (10 μA cm⁻²) reported in pioneering studies on this material.⁶⁰ However, recently investigated nanostructured and doped Fe₂O₃-based electrodes exhibit longer-living components and higher efficiencies.^{58,61–63}

On the basis of the large similarity between CuWO₄ and Fe₂O₃, the use of strategies such as doping, nanostructuring and the combination with proper oxygen evolution catalysts,^{13,34} which largely contributed to increase the performance of hematite photoanodes,⁶⁴ might lead to similar improvements also in the case of CuWO₄ photoanodes. Encouraging photocurrent values have been already observed with nanostructured⁶⁵ or doped CuWO₄ electrodes, for instance upon Mo⁶⁺ for W⁶⁺ ions substitution.^{66,67}

Therefore, CuWO₄ and related cuprates deserve further attention as material for efficient photoelectrochemical water splitting and other photocatalytic applications, although several limitations need to be carefully addressed in order to enhance their efficiency.

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Appendix B (Chapter 8)

B1 Fitting of TA decay curves

Aiming at checking the occurrence of nonlinear decay processes on the sub-picosecond to few picoseconds timescale, the absorbance difference ΔA signals generated at different pump fluences and monitored at 500 nm were first fitted according to kinetic models alternative to the tri-exponential decay model employed in the global analysis reported in Chapter 8.

For example, a single-exponential model was used to fit the transient absorption decay curve generated upon excitation with the minimum pump fluence of $30 \mu\text{J cm}^{-2}$, in the 0–2 ps range. As shown in Figure B1, this model provided a reasonable, though not perfect, fitting of the ΔA decay curve.

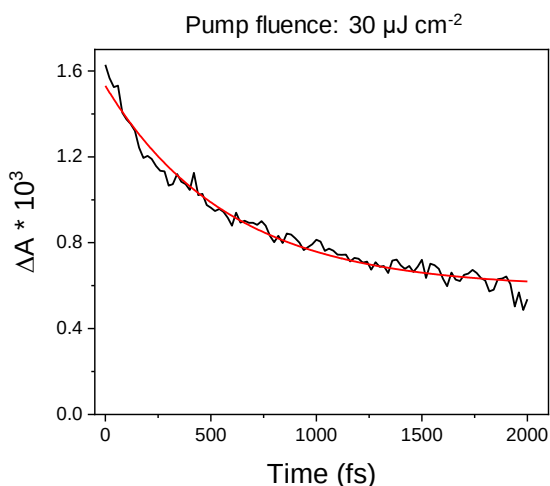


Figure B1 Single exponential decay fitting of the ΔA dynamics generated with $30 \mu\text{J cm}^{-2}$ pump fluence and monitored at 500 nm.

Aiming at ascertaining if the observed dynamics results from multiple exciton interactions or higher order interactions with the pump, the decay traces acquired at the maximum pump fluence of $830 \mu\text{J cm}^{-2}$ were then fitted according to a second order decay to check the possibility of bimolecular (exciton-exciton) recombination, where the decay channel for exciton population decreases quadratically with the exciton density N , according to the following equation:

$$-\frac{dN}{dt} = k_A N^2 \quad (\text{B1})$$

The $N(t)$ solution to this model (Eq. B2) was found to adequately fit transient signals resulting from exciton–exciton annihilation (EEA) processes generated by high pump fluences in systems of reduced dimensionality, such as metal dichalcogenides monolayer MoS_2 .¹

$$N(t) = \frac{N_0}{1 + k_A N_0 t} \quad (\text{B2})$$

However, as shown in Figure B2, this model did not provide an adequate fitting of the ΔA decay curve recorded upon excitation at the maximum pump fluence employed in the work presented in Chapter 8.

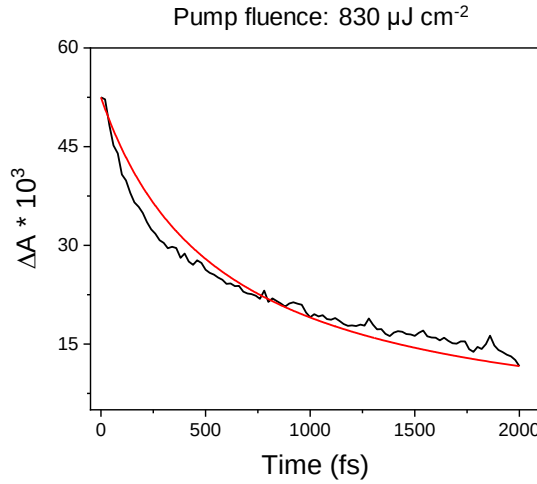


Figure B2 Second order decay fitting of the ΔA dynamics generated with $830 \mu\text{J cm}^{-2}$ pump fluence and monitored at 500 nm .

The possible existence of EEA channels, parallel to monoexponential decay, in the TA dynamics recorded with our CuWO_4 films for intermediate pump fluences of *ca.* 170 and $420 \mu\text{J cm}^{-2}$, was also checked by employing the hybrid first order–second order decay model expressed by Eq. B3, which has recently been adopted for the identification of EEA process in hematite thin films.²

$$-\frac{dN}{dt} = \frac{N}{\tau} + \gamma_{\text{EEA}} N^2 \quad (\text{B3})$$

The quadratic term appearing in both the second order (Eq. B1) and the hybrid first order–second order (Eq. B3) models is representative of interactions between excitons that are responsible for a faster decay of the generated population at high excitation densities. The analytical solution of Eq. B3 can be written as Eq. B4.

$$N(t) = \frac{N_0 e^{-\frac{t}{\tau}}}{1 + \gamma_{\text{EEA}} \tau N_0 \left[1 - e^{-\frac{t}{\tau}} \right]} \quad (\text{B4})$$

The obtained fittings of the decay signals generated upon pumping at the two intermediate fluence values are shown in Figure B3.

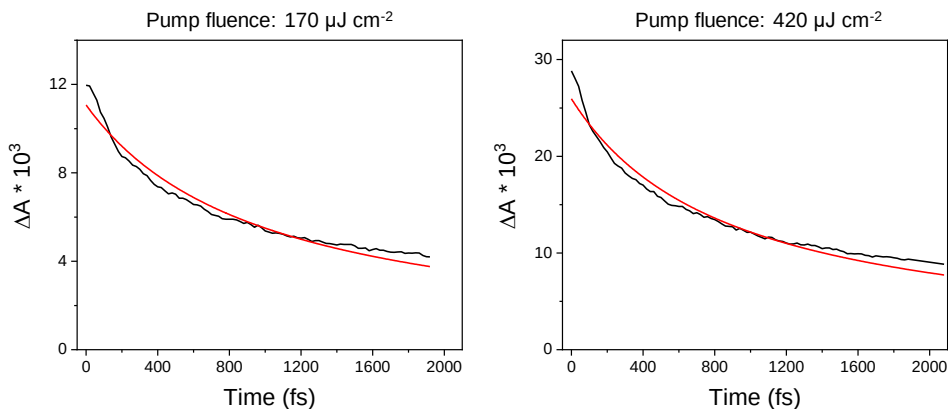


Figure B3 Hybrid first order–second order EEA model fitting applied to the early decay dynamics generated with $170 \mu\text{J cm}^{-2}$ and $420 \mu\text{J cm}^{-2}$ pump fluences and monitored at 500 nm.

Figures B2 and B3 indicate that both the bimolecular and the hybrid fitting models are not suited for fitting the here obtained ΔA decay traces, even in the case of high pump fluence. This, together with the observation of a pump fluence-independent dynamics (Figure 8.6b) and of the linear increase of the generated ΔA signal with increasing pump fluence (Figure 8.5), allows us to definitely rule out the presence of nonlinear processes in the fast decay dynamics monitored for the investigated CuWO_4 films, at least within the range of the here employed pump fluences.

Instead, we found that the entire set of TA decay curves generated with all tested pump fluences adequately fits a tri-exponential decay model in the whole explored timescale. For example, Figure B4 reports the tri-exponential decay fits of the decay traces recorded with the intermediate pump fluences of 170 and $420 \mu\text{J cm}^{-2}$. Thus, we performed a global analysis^{3,4} of the whole TA decay based on this model, as reported in Chapter 8.

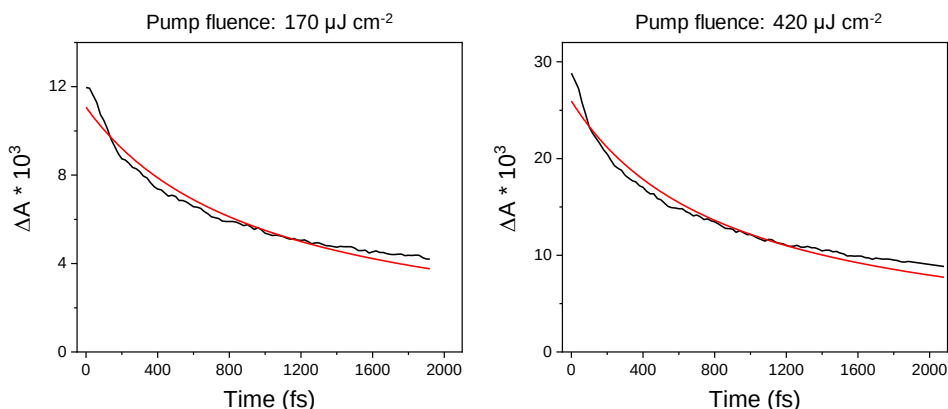


Figure B4 Tri-exponential decay fitting applied to the dynamics generated with $170 \mu\text{J cm}^{-2}$ and $420 \mu\text{J cm}^{-2}$ pump fluences and monitored at 500 nm.

Global analysis of the TA data sets was performed using the Glotaran program.^{3,4} In this program the spectral shapes are meant to be characteristic of electronic structures that either interconvert sequentially (Evolution-Associated Spectra), or decay in parallel (Decay-Associated Spectra). The time constants extrapolated with both these approaches are the same, and an example of their temporal evolution recorded in case of the CuWO_4 electrodes is shown in Figure B5.

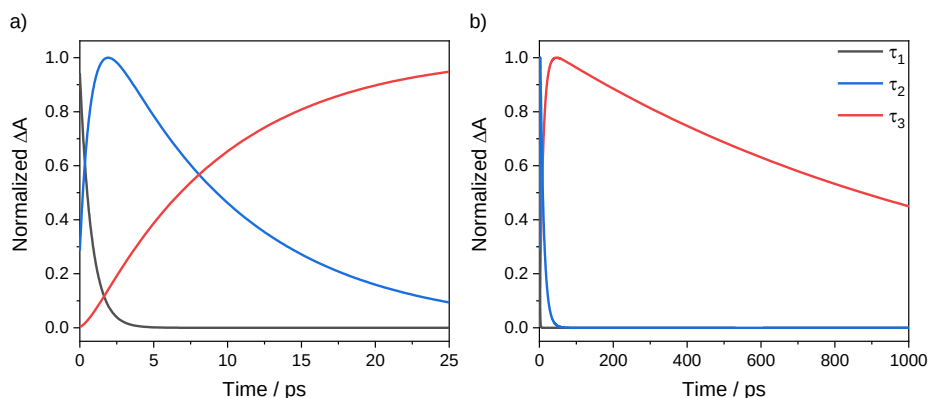


Figure B5 Normalized ΔA decay traces in the (a) 0–25 ps and (b) 0–1000 ps range obtained from global analysis of the $\Delta A(\lambda, \Delta t)$ data recorded upon photoexcitation at 400 nm with a $170 \mu\text{J cm}^{-2}$ fluence.

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Chapter 9

Effective visible light exploitation by copper molybdo-tungstate photoanodes

9.1 Abstract

The need for stable oxide-based semiconductors with narrow band gap, able to maximize the exploitation of the visible light portion of the solar spectrum, is a challenging issue for photoelectrocatalytic (PEC) applications. In this chapter $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ ($E_g = 2.0$ eV for $x = 0.5$), exhibiting a significantly reduced optical band gap E_g compared to isostructural CuWO_4 ($E_g = 2.3$ eV), was investigated as photoactive material for the preparation of photoanodes. $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes with different thickness (80 – 530 nm), prepared by a simple solution-based process in the form of multilayer films, effectively exhibit visible light photoactivity up to 650 nm, *i.e.*, extended compared to CuWO_4 photoanodes prepared by the same way. Furthermore, the systematic investigation on the effects on photoactivity of the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ layer thickness evidences that long wavelength photons can better be exploited by thicker electrodes. PEC measurements in the presence of NaNO_2 , acting as a suitable hole scavenger ensuring enhanced photocurrent generation compared to that of water oxidation while minimizing dark currents, allowed us to elucidate the role that molybdenum incorporation plays on the charge separation efficiency in the bulk and on the charge injection efficiency at the photoanode surface. The adopted Mo for W substitution increases the visible light photoactivity of copper tungstate towards improved exploitation and storage of visible light into chemical energy *via* photoelectrocatalysis.

9.2 Introduction

An efficient use of CuWO_4 requires the overcoming of the poor charge transport and inefficient charge separation of this material.^{1,2} Doping a semiconductor with foreign atoms has proved an efficient strategy not only to alter its charge carrier density and thus the related charge transport properties, but also in tuning the energy band structure. Attempts of doping ternary metal oxides with elements such as Ni,³ N,⁴ Cr,⁴⁻⁶ and Mo^{7,8} resulted in the increase of their visible light absorption capability. To date, there are only

few reports on the doping of CuWO_4 for improved photoactivity.^{2,8-11} For example, among these few successful attempts, the doping with Fe has led to a 1.5-fold improvement in photocurrent density and to a 50% increase in charge separation efficiency at 1.23 V vs. RHE, compared to the undoped CuWO_4 material. This result has been attributed to the increase in charge carrier density upon Cu^{2+} with Fe^{3+} substitution in the material lattice, resulting in improved electron conductivity.²

In particular, partial substitution of W^{6+} with Mo^{6+} in the CuWO_4 structure has resulted in a further band gap reduction of *ca.* 0.3 eV (from 2.3 to 2.0 eV)⁷ corresponding to an increased photon absorption in the visible light region of the ternary oxide material.^{7,8,11} First principles calculations identified in the shift of the CB edge toward lower energy the cause of the observed band gap narrowing.¹⁰

In the work presented in this chapter, we aim at ascertaining the role that molybdenum for tungsten substitution has in increasing the PEC performance of intrinsically poorly performing CuWO_4 , in relation to the transport properties of the charge carriers photogenerated in differently thick photoactive layers and to the charge transfer efficiency at the film/electrolyte interface. We focused on $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ semiconductor oxide obtained by 50% Mo^{6+} for W^{6+} substitution, which is quite easy to achieve, the two ions having very similar radii.¹² This material was prepared by a facile solution-based synthetic route and proved to be pure in phase. Its thorough PEC characterization allowed us to demonstrate that the attained reduction in band gap energy directly results in a more efficient exploitation of longer wavelength photons compared to pure CuWO_4 photoanodes. The role that molybdenum incorporation has on the efficiencies of photoproduced charge separation in the bulk and charge injection at the electrode/electrolyte interface has been clarified in addition to that of the thickness of the photoactive layer in affecting the photoanodes wavelength-dependent PEC performance, also in the presence of a suitable hole scavenger.

9.3 Experimental section

9.3.1 Chemicals and materials

The following chemicals, all purchased from Sigma Aldrich, were employed as supplied: copper(II) nitrate trihydrate (99%, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), ammonium metatungstate hydrate (99%, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$), citric acid (99%), boric acid (99%) and ethanol (99%). Molybdenum(VI) oxide bis(2,4-pentanedionate) (99%, $\text{C}_{10}\text{H}_{14}\text{MoO}_6$) was an Alfa Aesar product. Fluorine-doped 2 mm thick tin oxide (FTO) glass was purchased from Pilkington Glass (TEC-7).

9.3.2 Photoelectrodes preparation

A 0.5 M solution of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ was prepared as follows. 0.270 g of citric acid, 0.122 g of copper nitrate, 0.062 g of ammonium metatungstate and 0.082 g of molybdenum oxide bis-pentanedionate were added to 1.0 mL of an ethanol-water 2:1

solution. Complete dissolution of the metal precursors, corresponding to a 1:1 W:Mo molar ratio, was ensured in the chosen solvent composition and any phase segregation was excluded in the resulting film. The precursors were dissolved by keeping the solution under constant stirring for 45 min at 80 °C. The so obtained green paste is stable for several weeks. The photoelectrodes were prepared by spin coating it onto a $2.5 \times 2.5 \text{ cm}^2$ FTO glass at 4000 rpm for 30 s. Prior to deposition, the FTO glass was cleaned by 30 min-long sonication in a soap solution, followed by careful washing, sonication in ethanol for 30 min and drying in air. The clean glass slices then underwent a 15 min-long UV-cleaner ozone treatment to remove any organic species deposited onto the FTO surface. They were finally soaked in isopropanol for a few seconds right before the spin coating deposition, to increase the FTO affinity for the metal oxide precursor solution and reduce the light scattering of the resulting films in the long wavelengths spectral region.

After deposition, the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ films were dried at 250 °C for 10 min, followed by annealing at 550 °C for 1 h. Pure CuWO_4 films were prepared by a similar procedure without adding the molybdenum precursor to the initial solution. Multilayer films (up to 5 layers), labeled as nL ($n = 1\text{--}5$) $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$, were prepared by coating the so deposited films with the same precursor solution, followed by annealing at 550 °C after each deposition step.

9.3.3 Physical and photoelectrochemical methods

UV–visible absorption spectra were recorded in the transmission mode using a Jasco V-670 spectrophotometer. The crystalline phase of the materials was investigated through X-ray powder diffraction (XRPD) analysis using a Philips PW1820 diffractometer, equipped with a Cu sealed tube that provided $K\alpha$ radiation at 40 mA and 40 kV. A model LEO 1430 scanning electron microscope operating at a 10 kV accelerating voltage and at 8 mm working distance was used to acquire the top view and cross-section images of the films, up to three deposited layers. A Dektak XT Bruker profilometer was employed to measure the thickness of the thicker 4L and 5L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ films.

Linear Sweep Voltammetry (LSV) measurements were carried out using the three-electrode glass cell described in Section 4.3.2.1. The FTO/ $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ film was used as working electrode, an Ag/AgCl (3.0 M NaCl) as reference electrode and a platinum gauze as counter electrode. The electrical bias was swept at 10 mV s^{-1} using an Autolab PGSTAT 12, controlled by the NOVA software. The light source was an Oriel, Model 81172 solar simulator equipped with an AM 1.5 G filter. The light intensity, measured by means of a Thorlabs PM200 power meter equipped with a S130VC power head with Si detector, was 100 mW cm^{-2} . During a typical LSV test, 5 consecutive J - V scans were performed with each electrode, preceded by Fermi level equilibrium under irradiation up to open circuit potential (OCP). Identical OCP values were recorded prior to the beginning of each scan with each mono- or multi-layer electrode and all of them provided stable and reproducible photocurrent from the first to the last scan.

The investigated films were tested as photoanodes under both back (through the FTO side) and front (through the deposited film side) irradiation configuration, in contact with a 0.1 M K_3BO_3 aqueous solution at pH 9.¹³ The buffer borate solution was prepared by adding KOH to aqueous boric acid up to the desired pH. Furthermore, a series of different sacrificial agents, acting as electron donor species, was employed in LSV measurements. 0.1 M aqueous solutions of either H_2O_2 , NH_3 or NaNO_2 were buffered at pH 9 in a K_3BO_3 solution, while the 0.1 M Na_2SO_3 aqueous solution did not contain K_3BO_3 as it is naturally at pH 9. The potential values vs. Ag/AgCl were converted into the RHE scale using Eq. 4.19.

Incident photon to current efficiency (IPCE) measurements were carried out at 1.23, 1.5 and 1.7 V vs. RHE under irradiation with a 300 W Lot-Oriel Xe lamp equipped with a Lot-Oriel Omni- λ 150 monochromator and a Thorlabs SC10 automatic shutter, in the same above mentioned three-electrode cell glass containing the K_3BO_3 buffered solution, to which the NaNO_2 hole scavenger was eventually added. The IPCE values were calculated using Eq. 4.30. Chopped chronoamperometric scans at different wavelengths were recorded in back-side configuration at 1.23 V vs. RHE within the 300-650 nm wavelength range, with a 10 nm step. A 420 nm filter was employed at $\lambda > 500$ nm, to avoid any contribution from the high-order harmonics originated from the monochromator.

9.4 Results and discussion

9.4.1 Photoelectrodes characterization

As shown in Figure 9.1a, the multilayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes exhibit an absorption increasing with increasing number of deposited layers, with an absorption tail due to light scattering observed with the thickest films. The gradual colour increase can be appreciated also from their pictures shown in the inset of Figure 9.1a. The absorption onset of the material is at *ca.* 650 nm, corresponding to a band gap of *ca.* 1.9 eV, as confirmed by the Tauc plot analysis reported in Figure C2 – Appendix C and in agreement with the *ca.* 2.0 eV estimated band gap reported for a 50% degree of Mo for W substitution.⁷ Thus, the absorption onset of pure copper tungstate, having a band gap energy of 2.3 eV,¹⁰ is effectively extended towards the visible light region upon 50% Mo for W substitution.

From the film thickness values (Table 9.1), determined as described in the following, together with the absorption spectrum of the films, the absorption coefficients of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ at different wavelengths were calculated according to the Lambert Beer law, as the slopes of the lines obtained by plotting the absorbance of the film at a selected wavelength against the film thickness of multilayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes (see Figure C1 – Appendix C). The best fitting reported in Figure 9.1b was obtained for $\lambda = 430$ nm, the corresponding absorption coefficient being $\alpha_{430\text{nm}} = (3.41 \pm 0.10) \times 10^4 \text{ cm}^{-1}$.

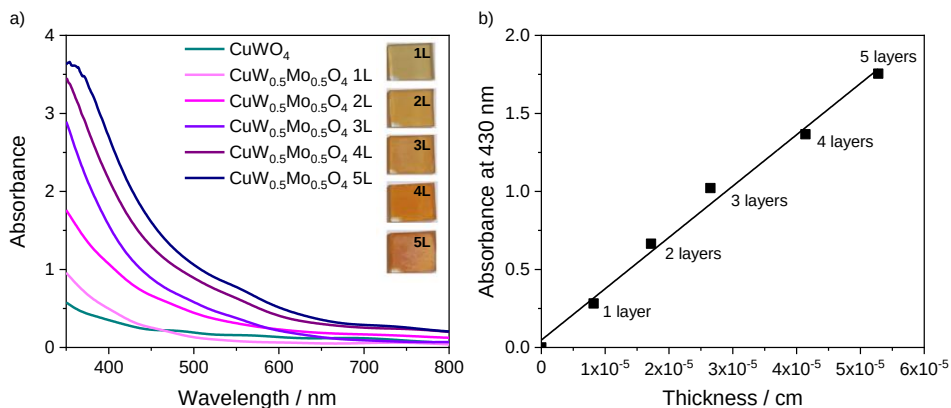


Figure 9.1 (a) Absorption spectra of multilayer (1L–5L) $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ photoelectrodes. Inset: picture of the photoelectrodes. (b) Absorption at 430 nm of multilayer photoanodes vs. their thickness.

The XRPD patterns relative to the 1L, 2L and 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ films, reported in Figure 9.2a, show the reflections characteristic of pure wolframite,^{7,8} which become more intense with increasing the material thickness. Thus, 50% Mo for W substitution has no effects on the crystalline phase formation, within the detection limits of the XRPD technique. The presence of Mo is confirmed by the change of lattice constants and the consequent peak shifts observed in the XRPD patterns of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ in comparison with CuWO_4 (see the detailed view in Figure 9.2b), which are almost identical to those recently reported²⁶ for a $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ sample with the same nominal Mo:W molar ratio.

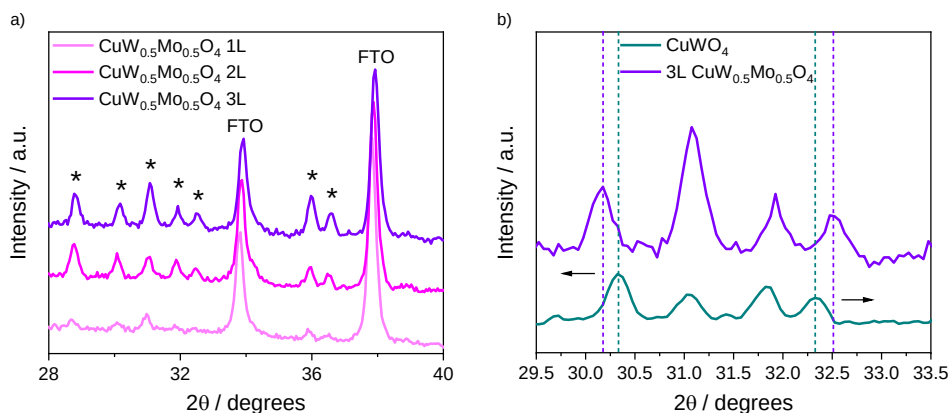


Figure 9.2 (a) X-ray powder diffraction (XRPD) patterns of 1L, 2L and 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes, in the 28 – 40 degrees 2θ range. The asterisks mark the reflections typical of wolframite. (b) Detailed view of the XRPD pattern in the 29.5° – 33.5° 2θ range of CuWO_4 (green) and 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ (violet), to be compared with Figure 1b of ref. 8 of this chapter.

The thickness values of the multilayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes, evaluated either by means of SEM cross section images in Figure 9.3a–c or by profilometry, are reported in Table 9.1 and indicate that the average increase in film thickness is *ca.* 110 nm upon each

deposited layer. The top view scanning electron microscopy (SEM) images of 1L, 2L and 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes (Figure 9.3d–f) reveal a structure composed of densely aggregated crystallites, which may facilitate the electrolyte diffusion across the film by increasing the contact area between the electrolyte solution and the photoactive material. In the case of the thickest film a decrease in the agglomerates size can be observed in the top view SEM images acquired with the same electrode after PEC tests (see Figure 9.3g,h), resulting from an extended contact between the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ film and the electrolyte.

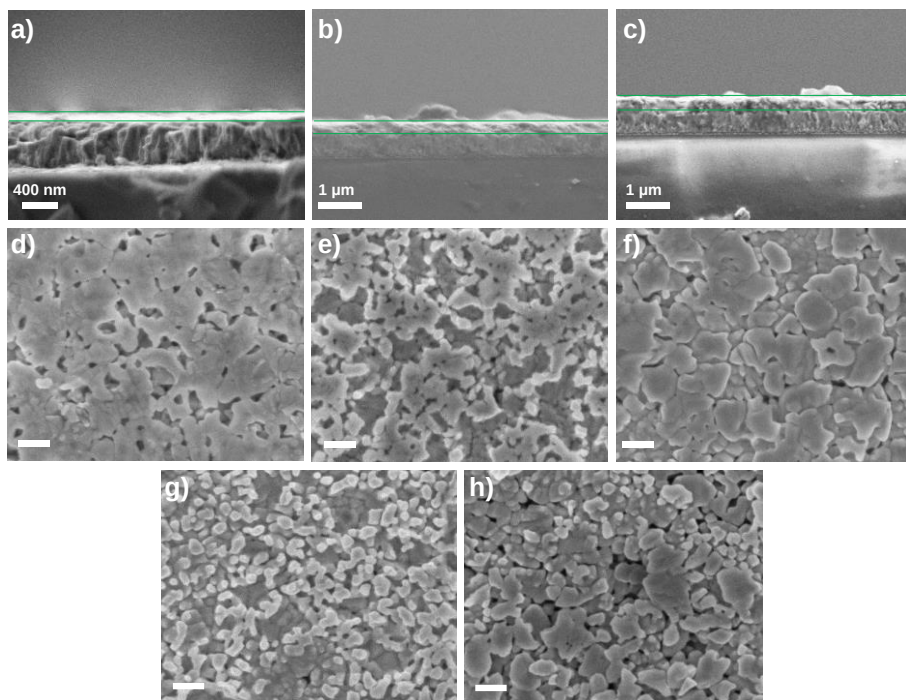


Figure 9.3 Cross-section SEM images of (a) 1L, (b) 2L and (c) 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes. Top-view SEM images of (d) 1L, (e) 2L and (f) 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes. Top-view SEM images recorded after PEC tests of (g) 2L and (h) 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes. The scalebar is 200 nm.

Table 9.1 Thickness of multilayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes estimated from SEM cross-section images and by profilometry.

Sample	Thickness / nm
1L	80 ± 20
2L	170 ± 10
3L	270 ± 10
4L	410 ± 20
5L	530 ± 30

9.4.2 Photoelectrochemical performance

During a typical LSV test under simulated solar light irradiation, 5 consecutive photocurrent density vs. applied potential (J - V) scans were performed with each electrode. The J - V curves reported in Figure 9.4 correspond to the fifth scan performed with each electrode. Each mono- or multi-layer electrode provided stable and reproducible photocurrent from the first to the last scan, with no difference in photocurrent. Thus, high repeatability was obtained with all films, in line with the high photostability of CuWO_4 -based materials.

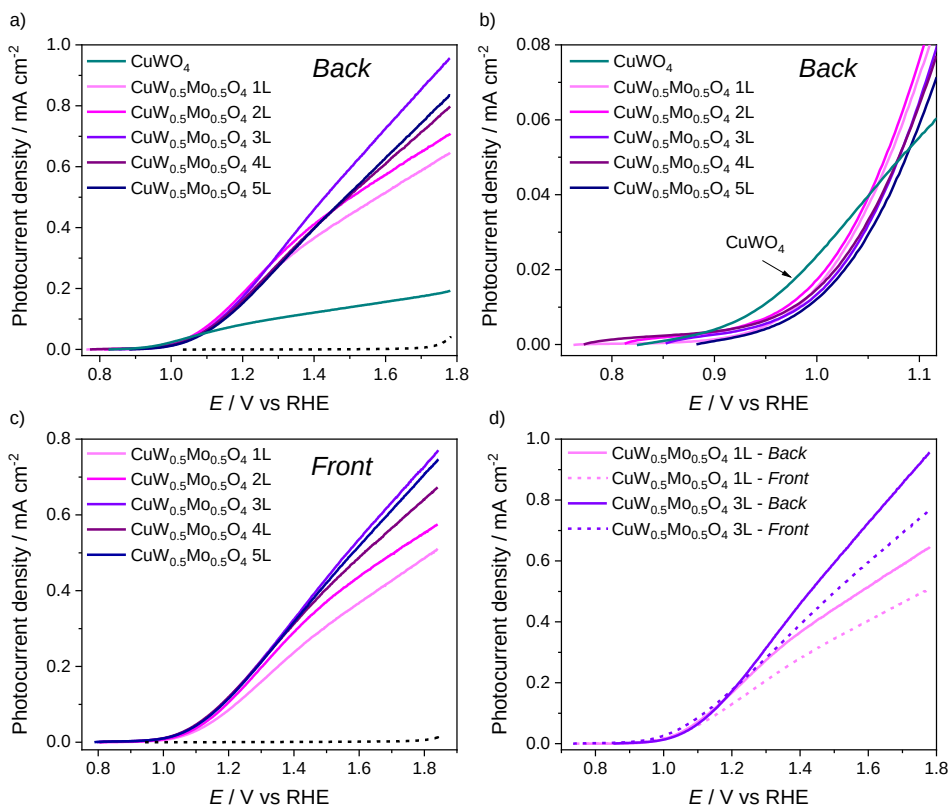


Figure 9.4 Linear Sweep Voltammetry (LSV) of (a) 1L–5L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ and CuWO_4 electrodes in back configuration and (b) magnification at low potentials, evidencing the delay in photocurrent onset recorded with $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ with respect to CuWO_4 photoanodes. c) LSV plots of 1L–5L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes in front configuration and d) back and front LSV comparison for 1L and 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ films. The current in the absence of irradiation is also shown in panels (a) and (c) (black dashed lines).

Figure 9.4a shows the J - V plots recorded with the multilayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes and a monolayer CuWO_4 electrode under back-side solar simulated light (i.e. the electrodes were irradiated through the FTO glass), in contact with a 0.1 M K_3BO_3 solution at pH 9. First of all, the introduction of Mo into CuWO_4 produces a more than 3-

fold improvement in photocurrent density at 1.7 V vs. RHE. Moreover, no significant difference in the LSV curves of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ films could be noted up to an applied potential of *ca.* 1.3 V vs. RHE, while progressively higher photocurrent density values were recorded at higher applied potentials with increasing number of deposited layers up to the 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrode, which was found to be the most active one. Despite this, molybdenum incorporation induces a modest delay in the photocurrent onset with respect to the benchmark CuWO_4 electrode, as well-underlined by the magnification of the analyzed LSV plots shown in Figure 9.4b.

Consequently, the highest photocurrent density of *ca.* 1 mA cm^{-2} was recorded at 1.7 V vs. RHE for the 3L film, while lower performances were obtained with thicker 4L and 5L electrodes, despite they practically absorb 100% of the incident light, also at long wavelengths. This provides a first indication of electron mobility issues occurring in films composed of more than three layers, *i.e.* thicker than *ca.* 270 nm. On the other hand, the slightly higher activity resulting for the 5L film compared to the 4L film could be related to the contribution to photocurrent of the longest wavelength photons, the exploitation of which increases with increasing film thickness, *i.e.* with increasing absorption of long wavelengths radiation (as discussed in more detail in the following, in relation to the magnification of IPCE profiles, Figure 9.5b).

The *J-V* curves recorded under back-side irradiation were compared with the results of LSV analyses performed under front-side illumination (Figure 9.4c), *i.e.* by irradiating the material through the electrode/electrolyte interface. This allows to get more insight into the charge carriers mobility within the material and to assess if the internal charge transport is limited by either the minority or the majority charge carriers,¹⁴ *i.e.*, by the holes or the electrons, respectively, in a *n*-type semiconductor material.¹⁵ The LSV plots recorded with the 1L and 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes (*ca.* 80 and 270 nm thick, respectively) under back- and front-side irradiation are compared in Figure 9.4d. Since for both selected films the photocurrent recorded under front-side irradiation is lower than that recorded under back-side irradiation, poor electron transport appears to be the limiting factor for this material. Moreover, the 3L electrode exhibits the best PEC performance among the tested films either under front or back irradiation. Thus a *ca.* 270 nm film thickness seems to correspond to the best balance between photon absorption in the photoactive layer and electron transport efficiency within it.

The IPCE plots recorded under back-side irradiation at 1.23 V vs. RHE are reported in Figure 9.5 for the complete series of multilayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes and for a single layer CuWO_4 photoanode. By comparing the curves obtained with the two monolayer CuWO_4 and $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ photoanodes evidence is obtained of the higher efficiency of the composite molybdenum-containing material with respect to pure CuWO_4 , over the entire investigated wavelengths range. This demonstrates that the increased visible light absorption capability (see Figure 9.1a) consequent to Mo for W substitution results in a higher number of photogenerated charge couples, which are

effectively responsible for the higher visible light activity of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ with respect to CuWO_4 .

Furthermore, by comparing the IPCE curves obtained with multilayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes (Figure 9.5a), the thinnest 1L and 2L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ films are most efficient in the UV region up to 390 nm, whereas thicker films exhibit the best photoactivity in the visible light region. The high absorption coefficient value of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ in the UV region (the extinction coefficient at 400 nm is three times greater than at 500 nm, see Figure C2 – Appendix C) implies that UV radiation is absorbed almost quantitatively even by the thinner films, which results in high photocurrent values. On the other hand, in thicker electrodes (thicker than 2L) and under back-side irradiation, most of the UV photogenerated holes need to travel across the whole film to reach their extraction sites at the film/electrolyte interface. The probability that they recombine with photopromoted electrons increases with increasing film thickness leading to lower IPCE values in the UV region with respect to thinner films. Concerning the relatively higher IPCE values of the thicker films in the visible region (Figure 9.5b), owing to the lower absorption capability of the material at longer wavelengths (Figure C2 – Appendix C), quantitative light harvesting can be attained only in thicker films, which are consequently able to better exploit visible light. The best compromise between efficient hole transport across the film and maximum visible light exploitation under back-side irradiation is attained with the ca. 270 nm thick film (3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrode).

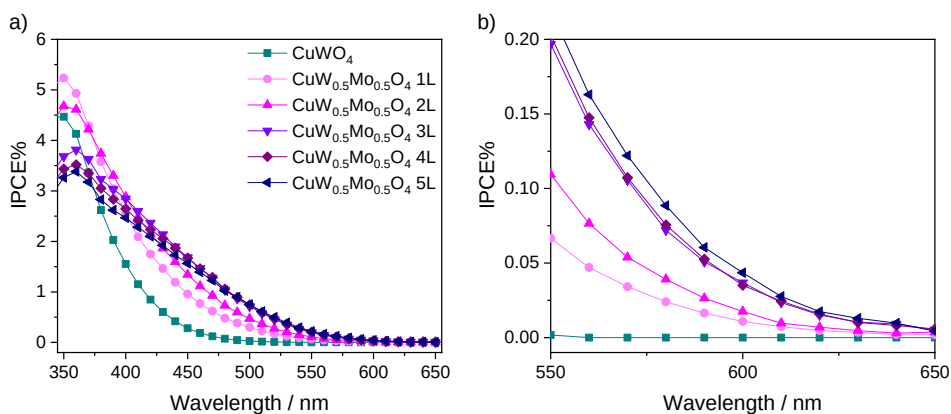


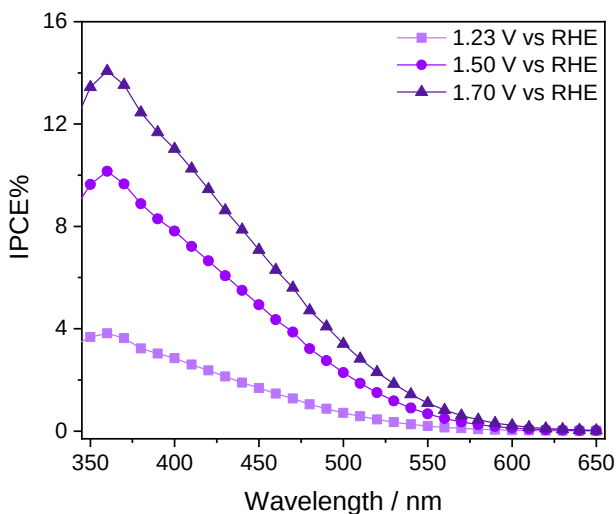
Figure 9.5 (a) Incident photon to current efficiency (IPCE) of CuWO_4 monolayer and 1L–5L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes at 1.23 V vs. RHE and (b) magnification at the longest wavelengths region of the IPCE profiles in panel a).

The recorded IPCE values are also in good agreement with the performances under full lamp irradiation recorded in LSV scans. In fact, as shown in Table 9.2, there is a good matching between the photocurrent density values at 1.23 V vs. RHE in J - V curves and the photocurrent density calculated by integrating the product between the IPCE curves and the standard AM 1.5 G solar spectrum¹⁶ over the whole investigated wavelengths range (300–650 nm for the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ multilayer films).

Table 9.2 Photocurrent density measured at 1.23 V vs. RHE and integrated photocurrent values calculated from IPCE analyses at the same applied potential for $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ multilayer electrodes.

Sample	Measured photocurrent / mA cm^{-2}	Integrated photocurrent / mA cm^{-2}
1L	0.107	0.104
2L	0.132	0.119
3L	0.145	0.127
4L	0.147	0.123
5L	0.143	0.118

Besides at 1.23 V vs. RHE, the IPCE curve for the best performing 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrode was recorded in back-side configuration also at 1.50 and 1.70 V vs. RHE (Figure 9.6), in order to evaluate the conversion efficiency of the material upon increasing charge separation. As shown in Figure 9.6, the conversion efficiency gets higher with increasing applied potential over the whole investigated wavelengths, with the IPCE value recorded at 400 nm showing a 2.5-fold and 3.5-fold enhancement as the potential increases from 1.23 to 1.5 and to 1.7 V vs. RHE, respectively. The observed behavior is in line with the photocurrent density enhancement recorded in LSV scans under simulated solar light irradiation. In particular, the IPCE almost linearly increases with increasing applied potential (see Figure 9.6), because the holes generated by high energy photons, which are mainly confined in the proximity of the FTO back-contact, benefit of the enhanced charge carrier separation due to the progressively higher external bias and have larger probability to reach the film/electrolyte interface where O_2 evolution occurs.

**Figure 9.6** Incident photon to current efficiency (IPCE) of the 3L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrode at different applied potentials.

Finally, the chopped photocurrent measurements under monochromatic irradiation at different wavelengths performed with our photoanodes at 1.23 V vs. RHE provide uncontroversial evidence that all $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ -based photoanodes absorb light and exhibit photoactivity up to 650 nm, while CuWO_4 is photoactive only below 550 nm. In fact, as shown in Figure 9.7, whereas all tested photoanodes, including the CuWO_4 -based one, originate a photocurrent signal under irradiation at 450 nm (Figure 9.7, bottom panel), the photocurrent signal is zero for CuWO_4 under irradiation at 550 nm (Figure 9.7, mid panel), while all 1L–5L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ photoanodes remain photoactive at this wavelength and maintain their photoactivity up to 650 nm (Figure 9.7, top panel). This demonstrates that Mo for W substitution in CuWO_4 largely extends the photoactivity of this material into the visible region, at least up to 650 nm.

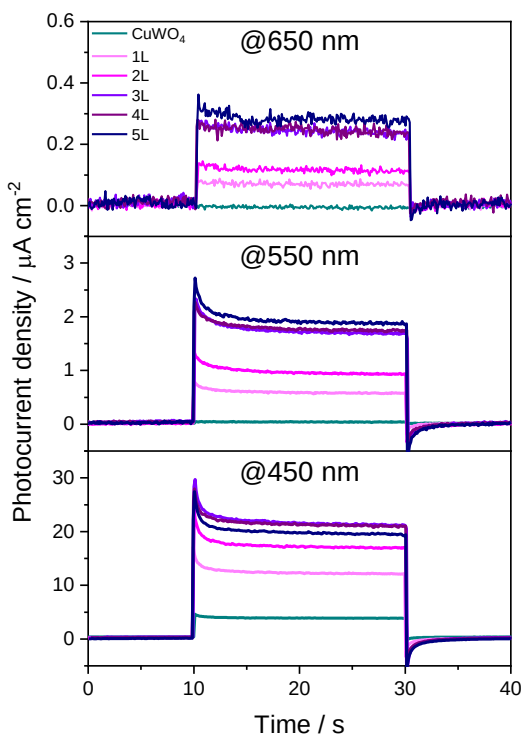


Figure 9.7 Chopped chronoamperometry at 1.23 V vs. RHE of the 1L–5L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes and of the CuWO_4 electrode under irradiation at 650 nm (top panel), 550 nm (mid panel) and 450 nm (bottom panel).

9.4.3 Sacrificial agents' tests

Two are the main limiting factors for PEC water oxidation performed by semiconductor-based photoanodes, *i.e.*, *i*) the transport of photopromoted electrons and photogenerated holes through the bulk material to the FTO back-contact and to the film/electrolyte interface, respectively, and *ii*) the interfacial hole injection kinetics, determining the oxygen evolution efficiency. Decoupling these two contributions is

therefore required in order to shed light on the intrinsic properties of the investigated photoactive material. In particular, the use of a suitable hole scavenger-containing electrolyte, acting as electron donor, allows one to study the intrinsic properties of the bulk material, under the assumption that hole injection at the material/electrolyte interface is not rate limiting under such conditions.¹⁷

Previous studies pointed out that significant dark current is observed if CuWO_4 electrodes are in contact with Na_2SO_3 - and H_2O_2 -containing solutions.¹⁸ Therefore, the performance of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ photoanodes was investigated in the presence of various hole scavengers, *i.e.* Na_2SO_3 , H_2O_2 , NaNO_2 and NH_3 , to check the existence of dark currents and verify if and how the response of this material is affected by the redox potential of the donor species. The concentration of all sacrificial agents was kept constant at 0.1 M within 0.1 M K_3BO_3 buffer solutions at pH 9, except for the 0.1 M Na_2SO_3 solution, which was at pH 9 in the absence of buffer.

The dark current onset in the presence of different sacrificial agents was measured first using both the 1L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ film and a glassy carbon as working electrode, in order to attain an apparent redox scale for the employed species (Figure 9.8a). For the electrode immersed in 0.1 M K_3BO_3 in the absence of any hole scavenger, the dark current potential onset is the highest, *i.e.*, around 1.8 V vs. RHE. On the other hand, the most easily oxidizable species is H_2O_2 , immediately followed by Na_2SO_3 , with a dark current onset located at *ca.* 1.0 V vs. RHE. More positive onset potentials, *i.e.*, *ca.* 1.4 and 1.6 V vs. RHE, were found for NaNO_2 and NH_3 , respectively. Thus, moving from the most stable to the most oxidizable species, the following scale results: H_2O (*i.e.* K_3BO_3 aqueous solution) > NH_3 > NaNO_2 >> Na_2SO_3 > H_2O_2 .

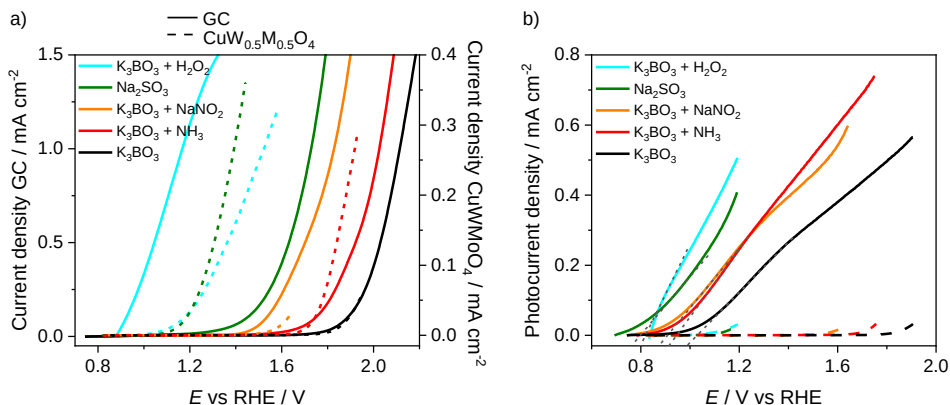


Figure 9.8 (a) Dark current recorded using a glassy carbon (GC, continuous lines) or our 1L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ sample (dashed lines) as working electrode in contact with a 0.1 M K_3BO_3 solution, 0.1 M K_3BO_3 solutions containing different hole scavengers at a 0.1 M concentration or 0.1 M Na_2SO_3 . (b) LSV curves recorded in the presence of the employed sacrificial agents with the monolayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrode, under dark (dashed lines) or back-side AM 1.5 G irradiation conditions (continuous lines). All solutions were at pH 9. The photocurrent onset potential was calculated by extrapolation of the tangent line of each LSV plot (black dashed lines in panel b).

The LSV curves obtained with a monolayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrode in contact with the hole scavenger-containing solutions under back-side simulated solar irradiation are shown in Figure 9.8b. The LSV curve obtained with the 0.1 M K_3BO_3 aqueous solution is also reported, as reference. In the absence of any electron donor species the photocurrent onset potential was *ca.* 1.0 V vs. RHE, *i.e.*, 800 mV lower than under dark conditions. The photocurrent onset potentials in the presence of the hole scavengers, extrapolated from the curves shown in Figure 9.8b, are reported in Table 9.3. Compared to the pure K_3BO_3 electrolyte solution, the use of Na_2SO_3 and H_2O_2 as hole scavengers led to the largest decrease of photocurrent onset potential, which was around 0.8 V vs. RHE in both cases, in good agreement with the conduction band edge value of *ca.* 0.7 V vs. RHE.⁷ However, owing to the significant dark current generated in the presence of these sacrificial agents at a potential as low as 1.2 V vs. RHE, Na_2SO_3 and H_2O_2 were discarded as hole scavengers in our PEC investigation.

Table 9.3 Photocurrent onset potential values extrapolated from LSV plots recorded in different solutions (Figure 9.8b).

Electrolyte solution	Photocurrent onset potential / eV
K_3BO_3	1.03
NH_3	0.95
NaNO_2	0.91
H_2O_2	0.82
Na_2SO_3	0.79

On the other hand, in the presence of NH_3 and NaNO_2 hole scavengers, a lower negative shift of the photocurrent onset potential (located at *ca.* 0.9 V vs. RHE) was observed and negligible dark current up to 1.75 and 1.6 V vs. RHE, respectively. This allows the exploitation of a wider applied potential window in PEC measurements. Because of the high volatility of NH_3 , which may result in uncontrollable concentration variation of its aqueous solutions, we finally selected NaNO_2 as the most suitable sacrificial agent for our PEC tests. In its presence the photocurrent density at 1.23 V vs. RHE is double compared to that measured in pure K_3BO_3 (0.30 vs. 0.15 mA cm^{-2} , see Figure 9.8b), with negligible dark current at such applied bias. Anyway, regardless of the employed electron donor, the photocurrent just moderately increased with respect to water oxidation (in K_3BO_3). This is in contrast with the considerable increase typically observed with semiconductors the PEC performance of which is limited by surface holes accumulation and slow water oxidation kinetics. For instance, BiVO_4 photoanodes generate up to 100 times higher current in contact with a hole scavenger containing solution,¹⁹ whereas Fe_2O_3 electrodes in contact with H_2O_2 allow the complete consumption of surface holes.^{20,21} This suggests that the transfer of surface holes to water or electron donor species has minor limiting effects on PEC efficiency of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$.

The IPCE curves obtained at 1.23 V vs. RHE with the 1L and 5L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes in the presence of the NaNO_2 hole scavenger (Figure 9.9) evidence the extended visible light photoactivity of the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ material, which is maximum for the thickest 5L photoanode.

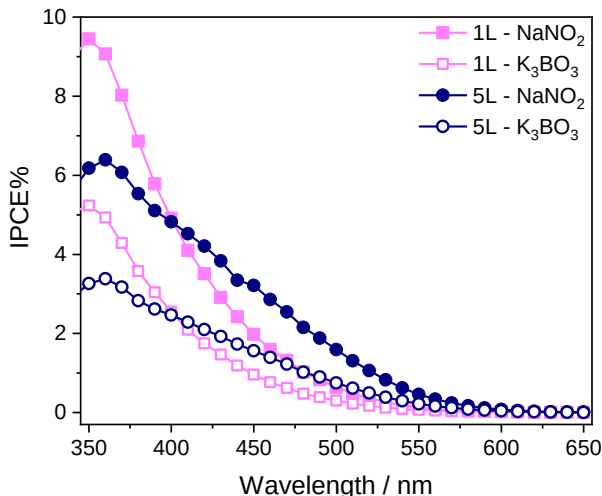


Figure 9.9 Incident photon to current efficiency (IPCE) of 1L and 5L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes at 1.23 V vs. RHE in K_3BO_3 both in the absence (void symbols) and in the presence (full symbols) of NaNO_2 .

9.4.4 Charge separation and charge injection efficiencies

PEC measurements in the presence of NaNO_2 as hole scavenger allowed us to evaluate the charge separation and charge injection efficiencies and thus assess if the performance of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ photoanodes is limited by either the material bulk properties or the surface hole injection kinetics.

The photocurrent density J can be expressed as the combination of different contributions, according to:^{20,21}

$$J = J_{\text{abs}} \eta_{\text{sep}} \eta_{\text{inj}} \quad (9.1)$$

where J_{abs} is the theoretical maximum photocurrent density obtained if all absorbed photons are converted into electricity, which was estimated by converting into current the integral of the product between the standard AM 1.5 G solar spectrum and the absorption spectrum of the photoelectrode over the 300–650 nm range (4.39 mA cm^{-2} for our 1L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ material),²² η_{sep} is the charge separation efficiency and η_{inj} is the interfacial charge injection efficiency. From this equation the charge separation and charge injection efficiencies can be easily calculated by taking into account the photocurrent densities recorded in the presence (J_{NaNO_2}) and absence ($J_{\text{K}_3\text{BO}_3}$) of the hole scavenger, as follows:

$$\eta_{\text{inj}} = J_{\text{K}_3\text{BO}_3} / J_{\text{NaNO}_2} \quad (9.2)$$

$$\eta_{\text{sep}} = J_{\text{NaNO}_2} / J_{\text{abs}} \quad (9.3)$$

The calculated η_{inj} and η_{sep} values for the 1L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrode and for the CuWO_4 electrode are shown in Figure 9.10 as a function of the applied potential. At 1.23 V vs. RHE η_{inj} and η_{sep} are 52% and 6%, respectively, for 1L $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$, which clearly indicate that charge separation in the bulk material is the main limiting factor for the PEC performance of our investigated material, in line with the limited photoactivity improvement attained in the presence of electron donor species.

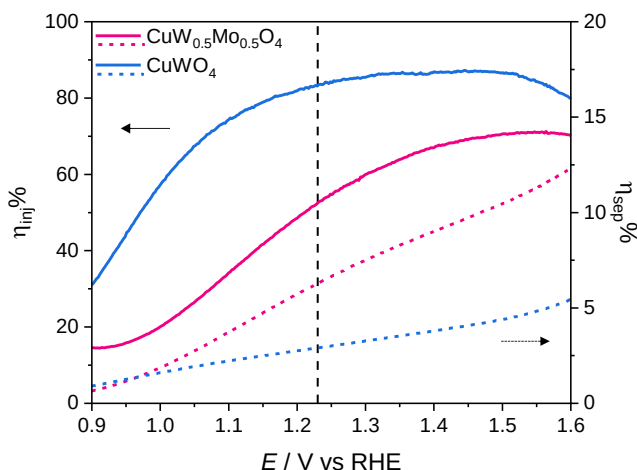


Figure 9.10 Charge injection efficiency η_{inj} (continuous lines) and charge separation efficiency η_{sep} (dashed lines) calculated for the monolayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ (fuchsia) and CuWO_4 (light blue) electrodes vs. the applied potential.

For our CuWO_4 photoanode (with J_{abs} amounting to 3.60 mA cm^{-2} in the 300–550 nm range) $\eta_{\text{inj}} = 83\%$ and $\eta_{\text{sep}} = 3\%$ at 1.23 V vs. RHE. This implies that Mo incorporation into CuWO_4 induces a two-fold increase of the charge separation properties in the bulk, in line with recent reports,¹¹ while it negatively affects the hole injection efficiency at the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ film/electrolyte interface, with a η_{inj} decrease.

The increased charge separation efficiency can result from the increased majority carrier (*i.e.*, electron) concentration in Mo-doped CuWO_4 with respect to CuWO_4 evidenced through Mott-Schottky plots in previous studies on Mo-doped CuWO_4 .^{25–27} This would improve the material conductivity and thus reduce charge recombination in $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ films. On the other hand, the reduction in charge injection efficiency may be ascribed to a Mo-induced increase of the surface trap states of CuWO_4 ,^{9,13,18,23,24} which would decrease the efficiency of water oxidation especially at relatively low applied potentials, by inducing Fermi level pinning at the semiconductor–liquid junction. An indirect evidence of the increase of surface trap states in $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ films is the modest delay in photocurrent onset of the LSV curves recorded with $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ -based photoanodes with respect to the CuWO_4 evidenced in the enlargement of Figure 9.4a at low potentials shown in Figure 9.4b. As recently outlined,²⁷ such delay is compatible with an increase in surface trap states upon Mo incorporation, which hampers

the photocurrent onset at low overpotentials, *i.e.*, when the driving force to separate photoproducted electron-hole couples is small. Taken together, the two-fold improvement in charge separation and the decrease in charge injection efficiency result in the overall enhanced PEC activity of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ with respect to CuWO_4 .

9.5 Conclusions

Substitution of Mo for W into the CuWO_4 structure is responsible for the conduction band edge energy lowering and consequent band gap narrowing. Thus, the increased PEC performance of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ with respect to CuWO_4 mainly results from the extended visible light absorption ability and photoactivity of the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ material up to 650 nm. This effect is maximum for the highest film thickness explored in this study ensuring the exploitation of long wavelength photons in the visible region, which are efficiently harvested for longer optical paths within the photoactive films. However, Mo for W substitution also increases the efficiency of photoproducted charge separation, due to an increased conductivity of the material, while the lower charge injection efficiency of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ with respect to pure CuWO_4 may result from an increased amount of surface trap states. With its 2.0 eV band gap, copper molybdo-tungstate shows promise as photoanode material for practical water splitting. Further improvements are needed and might be attained through nanostructuring, the development of efficient oxygen evolution co-catalysts for this class of materials and the fine modification of the electronic structure by doping with other elements.

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Appendix C (Chapter 9)

C1 Calculation of the absorption coefficient α

The absorption coefficient α of the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ material at different wavelengths was calculated according to the Lambert-Beer law, as the slope of the lines obtained by plotting the absorbance at a selected wavelength against the film thickness of the multilayer $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ electrodes, as shown in Figure C1.

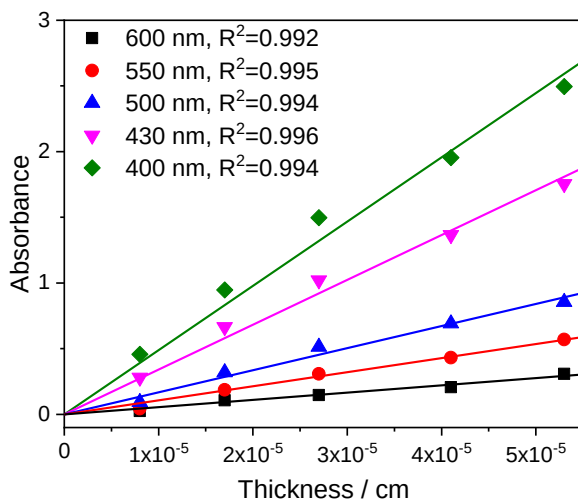


Figure C1 Absorbance of the multilayer (1L–5L) $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ photoanodes at various wavelengths vs. their thickness, and R^2 values for each regression line. The calculated absorption coefficients are $\alpha_{400\text{nm}} = (4.89 \pm 0.16) \cdot 10^4 \text{ cm}^{-1}$, $\alpha_{430\text{nm}} = (3.41 \pm 0.10) \cdot 10^4 \text{ cm}^{-1}$, $\alpha_{500\text{nm}} = (1.68 \pm 0.06) \cdot 10^4 \text{ cm}^{-1}$, $\alpha_{550\text{nm}} = (1.07 \pm 0.03) \cdot 10^4 \text{ cm}^{-1}$, $\alpha_{600\text{nm}} = (0.55 \pm 0.02) \cdot 10^4 \text{ cm}^{-1}$.

The best fitting was obtained for $\lambda = 430 \text{ nm}$, the corresponding absorption coefficient being $\alpha_{430\text{nm}} = (3.41 \pm 0.10) \times 10^4 \text{ cm}^{-1}$.

C2 Tauc plot analysis

From the absorption coefficient profile for the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ material (Figure C2a), determined from the above-described procedure applied on the 1L–5L multilayer electrodes at all wavelengths in the 350–800 nm range, the Tauc plot analysis for an indirect band gap semiconductor was also performed, as reported in Figure C2b.

From this analysis, a band gap value for our $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ material of *ca.* 2.0 eV was extrapolated from the linear portion of the Tauc plot, which is in line with the absorption onset at *ca.* 650 nm resulting from the absorption spectra of the multilayer (1L–5L) films in Figure 9.1a.

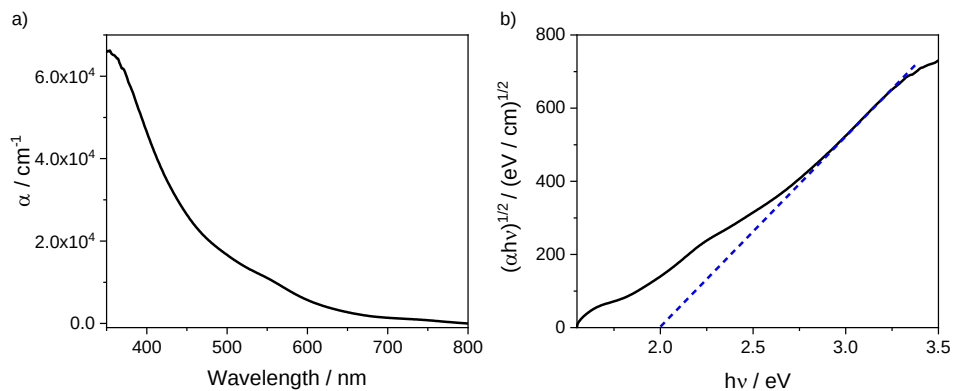


Figure C2 (a) Absorption coefficient of $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ in the 350–800 nm wavelength range and (b) corresponding Tauc plot analysis.

Chapter 10

Synthesis temperature effects on the hydrogenation efficiency of ZnFe_2O_4 flat films as photoanodes for water oxidation

10.1 Abstract

The effects induced by post-synthesis hydrogenation on ZnFe_2O_4 flat films in terms of photoelectrochemical (PEC) performance of photoanodes for water oxidation have been deeply investigated as a function of the annealing temperature of the materials. The structure and morphology of the films greatly affect the efficacy of the post synthesis treatment. In fact, highly compact films are obtained upon annealing at high temperatures, and this limits the exposure of the material bulk to the reductive H_2 atmosphere, making the treatment largely ineffective. On the other hand, a mild hydrogen treatment greatly enhances the separation of photoproduct charges in films annealed at lower temperatures, as a result of the introduction of oxygen vacancies with n -type character. A comparison between present results and those obtained with ZnFe_2O_4 nanorods clearly demonstrates that specific structural and/or surface properties, together with the initial film morphology, differently affect the overall contribution of post-synthesis hydrogenation on the efficiency of zinc ferrite-based photoanodes.

10.2 Introduction

Despite the numerous binary and ternary transition metal oxides which have been extensively studied, such as TiO_2 , WO_3 , BiVO_4 , Fe_2O_3 , and CuWO_4 , their relatively wide band gap and/or poor semiconducting properties compromise the efficient utilization of solar energy.^{1–3} Therefore, the search for new ternary and multinary oxides capable of absorbing a larger fraction of the solar spectrum and efficiently driving the oxygen evolution reaction (OER) remains an important need.

In this regard, the spinel ferrite phases formed by ternary oxide compounds of iron(III) and a divalent metal (MFe_2O_4), have recently gained increasing interest thanks to the possibility to tune the band gap energy (1.4–2.1 eV) in order to get suitable light

harvesting in the visible range, by selecting the divalent M cation ($M = \text{Zn, Mg, Cu, Ca, etc.}$), in addition to their excellent thermal and chemical stabilities.^{1,2,4-7} Specifically, ZnFe_2O_4 (ZFO) with a 2.0 eV band gap has become a model system of this class of materials in different studies, as it shares many advantages of the pioneer binary metal oxide Fe_2O_3 , together with a 200 mV more negative photocurrent onset potential, which in principle allows water splitting to proceed with a smaller photocathode photopotential compared to hematite photoanodes.^{2,8} However, despite the various improvement strategies adopted,⁸⁻¹³ the performances of ZFO as a main photoanode component remain far below that of the benchmark Fe_2O_3 .^{14,15} Among the different factors responsible for the low performances, a strong bulk recombination associated with a poor electronic conductivity has emerged as a main issue.^{6,16,17} This limitation may be linked to the extremely high temperatures required for the crystallization of this class of materials.^{9,10,18}

Post-synthesis thermal annealing under mild reductive conditions (under H_2 gas at 200 °C) was shown to improve the conductivity of ZFO photoelectrodes through the introduction of oxygen vacancies acting as n -type dopants, thus increasing the majority carriers density of the material.^{6,10,11,17,19,20} This should occur through the interaction of hydrogen with oxygen in the ZFO lattice, leading to the removal of a water molecule and to the consequent formation of an oxygen vacancy, where the two electrons left behind this reaction are localized.¹⁰ Hydrogen annealing treatment carried out on nanostructured ZFO films with nanorod (NR) morphology,¹⁹ has led to the benchmark photocurrent for solar water oxidation with ZFO photoanodes used as single photon absorbers. In that study the likely role of cation disorder with respect to film crystallinity in enhancing the majority carrier transport of ZFO NR electrodes was also pointed out, with a resulting superior separation of photogenerated charges.

Optimizing this aspect was linked to the observed PEC performance for the hydrogenated films as a function of the film annealing temperature. However, the understanding of how the effects induced by the adopted reductive treatment itself depend on the intrinsic properties of the as prepared materials, and in particular on the electrode annealing temperature, is still lacking.

In the work presented in this chapter, the effects induced by this post-synthesis hydrogenation (performed under mild heating conditions) on the PEC performance of ZnFe_2O_4 photoanodes are systematically studied in relation to the annealing temperature employed in their synthesis. We focused on ZnFe_2O_4 flat films as ideal models to investigate the effects produced by reductive hydrogen atmosphere on the intrinsic electronic properties of the material.^{6,10,21,22} In addition, we demonstrate that the particular temperature adopted during the synthetic thermal treatment of ZnFe_2O_4 not only affects the final performance of unmodified flat films, but also ensures different PEC efficiency increases upon the application of the hydrogen treatment under the same conditions. The multiple factors which may be at the origin of the different trends in PEC performance, in relation to the annealing temperature, detected for pristine and hydrogenated ZnFe_2O_4

films, are here investigated and deeply discussed. In particular, to rule out film thickness as additional parameter affecting the poor charge transport properties of ZFO electrodes, in this chapter we focused on the investigation of films with a moderate thickness of *ca.* 100 nm, prepared according to a generalized approach for ternary metal oxides,²³ which offers a facile processable green route to obtain optically transparent films suitable to be employed as photoanodes in dual absorber tandem PEC cells.

The study presented in this chapter has been carried out in the Laboratory of Prof. Sivula during my visiting period at the EPFL of Lausanne.

10.3 Experimental section

10.3.1 Chemicals and materials

The following chemicals were employed. Zn(NO₃)₂·6H₂O was purchased from ABCR, Fe(NO₃)₃·9H₂O was supplied by Acros Organics, HNO₃ and NH₄OH (25%) were purchased from VWR and NaOH was provided by Reactolab SA. Ethylenediaminetetraacetic acid (EDTA) was purchased from (Fluka, Buchs). The used substrate was FTO coated aluminoborosilicate glass (Solaronix).

10.3.2 Photoelectrodes preparation

The ZnFe₂O₄ photoanodes were synthesized via spin coating and subsequent annealing. In order to prepare the ZnFe₂O₄ precursor solution, 10.959 g (1.5 eq.) EDTA was initially dissolved into 50 mL of 18.2 MΩ resistance Millipore water upon addition of 5 mL of fresh 25% NH₄OH solution. To allow the complete dissolution of EDTA, the solution mixture was maintained under continuous stirring for about 30 min. Then, 10.1 g (1 eq.) of Fe(NO₃)₃·9H₂O was added, causing the formation of a white precipitate which was suspected to be EDTA that precipitated from solution due to the decrease in pH upon adding the acidic Fe(NO₃). The precipitate was dissolved upon addition of 5 mL of the 25% NH₄OH solution. Finally, 3.786 g (1 eq.) of Zn(NO₃)₂·6H₂O was dissolved into the mixture by adding the 25% NH₄OH solution until the solution pH was 5. The solution was then heated at 60 °C under stirring for 1 h until all the solids had dissolved and no precipitate was visibly detected. Once cooled to room temperature, the final solution pH was brought back to 5 by adding diluted HNO₃ or NH₄OH solutions and the final volume was adjusted to 100 mL by water addition. The final solution was 0.25 M in Fe³⁺, 0.125 M in Zn²⁺ and 0.375 M in EDTA, and was stable for several months. Prior to deposition, the FTO substrates were cleaned thoroughly with four 15 min long sonication cycles in a soap/water mixture, acetone, ethanol, and finally in distilled water. The cleaned substrates then underwent plasma cleaning for 15 min.

The Fe³⁺- and Zn²⁺-containing solution was deposited onto the clean FTO coated glass substrate through spin coating using a dynamic technique where the substrate was first spun at 4500 rpm. Once the substrate was at this speed, 0.75 mL of the previously

prepared solution was deposited on top while keeping the electrode spinning for 45 s to allow the solution to homogeneously distribute over the FTO substrate.

The thin films were then calcined at 400 °C in air to burn off all organic materials. The deposition and calcination procedures were repeated 20 times in order to obtain electrodes of the desired thickness. The films were then annealed for 20 min in a preheated tubular furnace at different temperatures, *i.e.*, at 500 °C, 600 °C, 700 °C, and 800 °C, followed by cooling down to room temperature with the furnace off. The obtained samples were labelled as 20L_X, where X refers to the annealing temperature in Celsius.

To increase the film conductivity, the prepared electrodes underwent a post synthesis hydrogen treatment in a tubular furnace at 200 °C for 60 min under H₂ atmosphere. These samples were named 20L_X_H₂.

A series of thinner films was also prepared by the same way, starting from a 0.50 M in Fe³⁺, 0.25 M in Zn²⁺ and 0.75 M in EDTA precursor solution. The deposition of the so obtained “doubly concentrated ZFO precursor solution” (DC) onto clean FTO was repeated 5 times by maintaining the same pre-annealing treatment at 400 °C between each deposition step and the same final thermal treatment for 20 min at 500 °C or 800 °C. These films were also subjected to the previously described post synthesis hydrogen treatment. These two series of films were referred to as DC_5L_X and DC_5L_X_H₂, with X referring to the annealing temperature in Celsius.

10.3.3 Physical characterization methods

The crystal structure and phase composition of all synthesized 20L ZFO films was assessed by means of X-ray diffraction (XRD) and Raman spectroscopy analyses. For investigating the crystalline phase of the materials, a Panalytical Empyrean system (Theta-Theta, 240 mm) was employed, equipped with a PIXcel-1D detector, Bragg-Brentano beam optics (including a hybrid monochromator), and parallel beam optics. Raman spectra were collected with a LabRam spectrometer (Jobin Yvon Horiba). SEM images were acquired using a Zeiss Gemini 300 scanning electron microscope in the HV mode. The excitation line was provided by an Ar laser (532.19 nm). UV-visible absorption spectra were recorded in the transmission mode in a UV-3600 Shimadzu spectrometer.

10.3.4 Photoelectrochemical methods

PEC experiments were carried out using the three-electrode cappuccino cell²⁴ described in Section 4.3.2.2, connected to a BioLogic SP-500 potentiostat. The ZnFe₂O₄ films were used as working electrode, while an Ag/AgCl (3.0 M NaCl) electrode and a Pt wire were used as reference and counter electrode, respectively. The light source was a 1000 W Xe arc lamp (Newport Oriel) calibrated using a Si photodiode to provide a 100 mW cm⁻² light intensity and a photon flux corresponding to the AM 1.5 G spectrum for energy larger than the band gap of the tested material.²⁵ The investigated electrodes were

tested as photoanodes in Linear Sweep Voltammetry (LSV) measurements under both back (through the FTO glass substrate side) and front (through the deposited film side) irradiation configurations, in contact with a 1.0 M NaOH aqueous solution (pH 14). The acquired potential vs. Ag/AgCl values were converted into the RHE scale using Eq. 4.19.

10.4 Results and discussion

10.4.1 Photoelectrodes characterization

The XRD patterns and Raman spectra recorded for all investigated 20L_X samples are shown in Figure 10.1. The diffractograms shown in Figure 10.1a display only the (220), (311), and (511) reflections associated to the spinel ferrite cubic structure (Fd3m space group) and to the FTO substrate, indicating that no signals related to any segregated (binary oxide) phases are detectable.¹⁹ The crystallinity of the ZFO films appears to be strongly correlated to the synthesis temperature, as demonstrated by the peak intensity increase with increasing annealing temperature, particularly evident for the (311) reflection, in agreement with previous results obtained with NR films.¹⁹

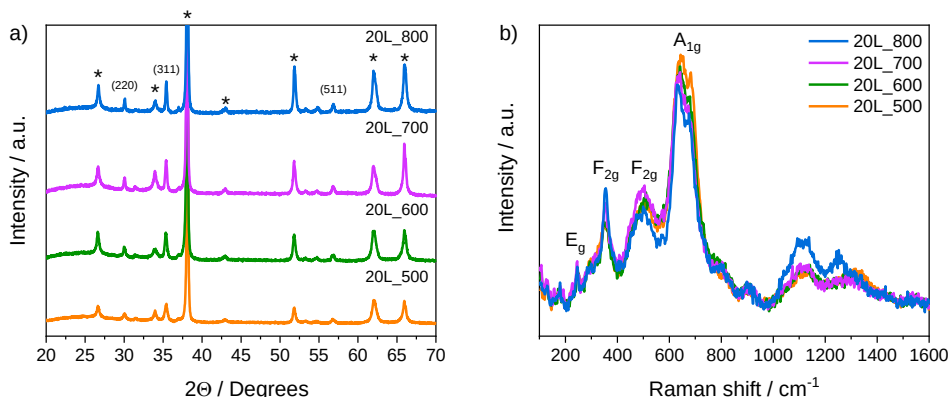


Figure 10.1 (a) X-ray diffraction (XRD) patterns and (b) Raman spectra of the 20L films annealed at different temperatures. Reflections originated from the FTO substrate are indicated by asterisks.

The Raman spectra of the same films (Figure 10.1b) were also collected in order to confirm the formation of a crystal phase without the presence of secondary phases. All Raman spectra exhibit the characteristic Raman modes of ZFO,²⁶ i.e., E_g at 245 cm^{-1} , F_{2g} at 355 cm^{-1} and 505 cm^{-1} and A_{1g} centred at 650 cm^{-1} . The lack of the intense 1320 cm^{-1} centered band typical of hematite ($\alpha\text{-Fe}_2\text{O}_3$)²⁷ and of the broad feature at 1400 cm^{-1} relative to maghemite ($\gamma\text{-Fe}_2\text{O}_3$)²⁸ corroborates the absence of these impurity phases in the synthesized spinel ferrite electrodes, while the presence of traces of magnetite (Fe_3O_4), with bands at 500 cm^{-1} and 679 cm^{-1} ,²⁹ superimposed to the ZFO Raman features, cannot be completely excluded. The same phase composition and purity was identified in the Raman spectra relative to the thinner DC_5L films (not shown for the sake of brevity) indicating the growth of a monophasic spinel ferrite also in this case.

The scanning electron microscopy analysis of the 20L_800 sample, shown in Figure 10.2, demonstrates a flat film morphology, composed of densely packed, interconnected nanoparticles (Figure 10.2a). Cross sectional SEM images (Figure 10.2b) indicate that the films are approximately 100 nm thick.

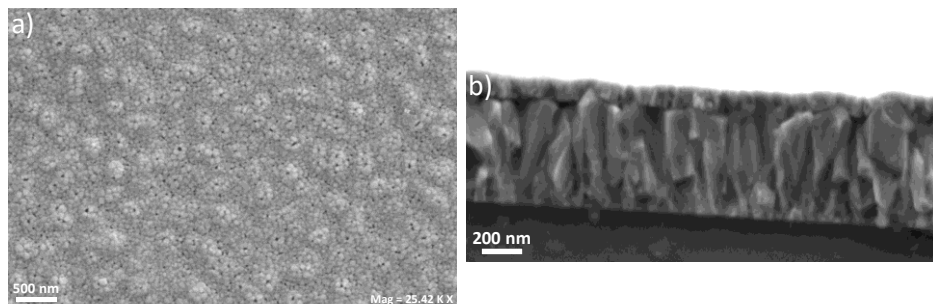


Figure 10.2 (a) Top down and (b) cross section SEM images of the 20L_800 film.

The absorbance spectra of both 20L_X and DC_5L_X film series are reported in Figure 10.3. Both electrode series exhibit high optical transparency in the wavelength range above the absorption onset of the material (*ca.* 620 nm in agreement with a band gap energy of 2.0 eV), which is characterized by the presence of interference fringes due to the flatness of the investigated thin films. The high level of film transparency can be also appreciated in the inset of Figure 10.3. The 20L samples exhibit a *ca.* 1.7-fold higher absorbance with respect to that observed with DC_5L films, thus confirming their relatively higher thickness. Within each series the change of film annealing temperature does not produce any significant variation in terms of either UV-vis absorption capability or ZFO nanoparticles interconnection.

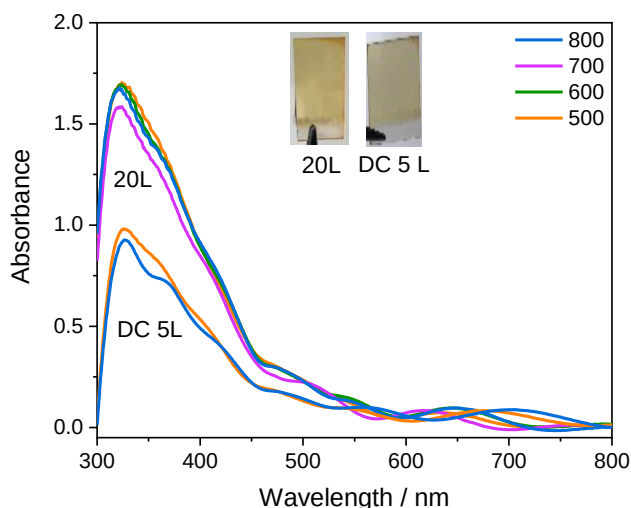


Figure 10.3 Absorption spectra of the 20L and DC_5L films series annealed at different temperatures (in Celsius).

The 20L and DC_5L films annealed at 800 °C showed significantly different surface topography, as evidenced by the AFM analyses reported in Figure 10.4. In the case of 20L films, the higher number of layer depositions, requiring a 400 °C treatment at each intermediate step, caused the formation of a quite smooth surface consisting of densely aggregated small grains (Figure 10.4b). On the other hand, the fewer deposition steps used for producing the thinner DC_5L_800 sample drastically change the film topography, which appears mainly composed of sharper grains with a ridge shape (Figure 10.4a) possibly resulting from the underlying FTO substrate. Indeed, the DC_5L film is characterized by a higher surface roughness with respect to the corresponding 20L electrode, as demonstrated by the relative root mean square (RMS) roughness factors reported in Figure 10.4 for each film.

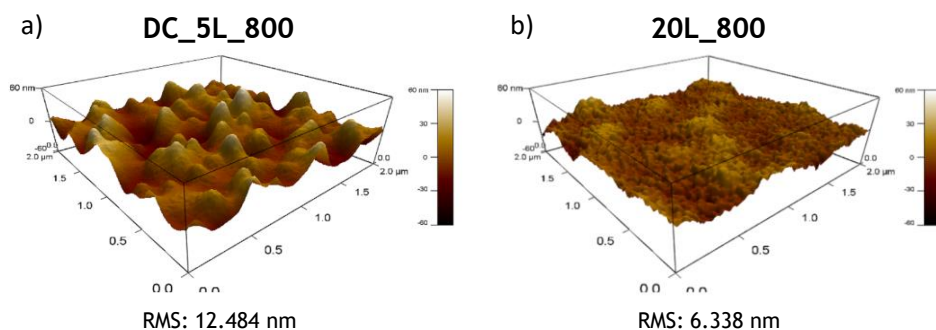


Figure 10.4 AFM images and root mean square (RMS) factors for the (a) DC_5L_800 and (b) 20L_800 films.

10.4.2 Photoelectrochemical performance

The PEC performance of all synthesized 20L and DC_5L films was checked in a 1.0 M NaOH solution. The results of the tests performed with the pristine 20L_800 are reported as an example in Figure 10.5a. The comparison of the photocurrent vs. voltage (*J-V*) curves recorded in Linear Sweep Voltammetry (LSV) scans under irradiation through the ZFO/water interface of the film (front-side irradiation) or through the glass substrate side (back-side irradiation) indicates a progressively higher photocurrent density for back-side illumination rather than front-side illumination. Thus, the photogenerated charge separation in the bulk is more efficient when the majority charge carriers, electrons in the case of a *n*-type semiconductors³⁰ as ZFO, are generated close to the back FTO contact where they can be directly transferred to the conductive substrate. This supports the notion that electron transport through the bulk of the film towards the FTO substrate is more limiting than hole transport towards the film/electrolyte interface.

The need for a hydrogen treatment, aiming to improve the majority charge carrier transport through the introduction of oxygen vacancies, was assessed by calculating the charge separation and charge injection efficiencies.^{6,10,21,22} To this aim, the PEC

performance of the 20L_800 film was also investigated in the presence of H_2O_2 as hole scavenger in the 1.0 M NaOH electrolyte.

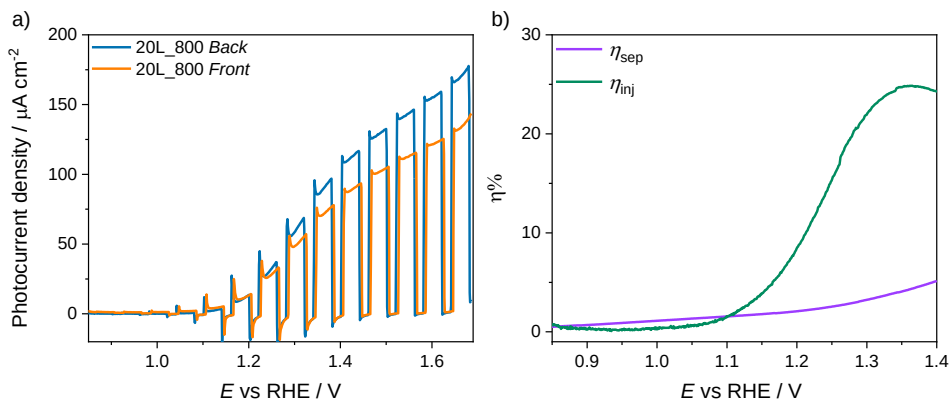


Figure 10.5 (a) Linear Sweep Voltammetry (LSV) plots relative to the 20L_800 film in 1.0 M NaOH under both back- and front-side irradiation configurations. (b) Charge separation (η_{sep}) and charge injection efficiencies (η_{inj}) calculated for the same film.

The photocurrent density produced during water oxidation can be expressed as $J_{H_2O} = J_{abs} \cdot \eta_{sep} \cdot \eta_{inj}$, where J_{abs} is the theoretical maximum photocurrent density calculated by converting the absorbed photons into current, η_{sep} the charge separation yield of the photogenerated carriers, and η_{inj} the minority charge carriers injection yield at the film/electrolyte interface.³¹ J_{abs} was calculated as $7.38\ mA\ cm^{-2}$, by integrating the absorption spectrum of the investigated film on the AM 1.5 G solar spectrum. Using a hole scavenger such as H_2O_2 , for which a 100% charge injection yield can be assumed (i.e., $\eta_{inj} = 1$),^{31,32} the charge separation efficiency η_{sep} was calculated from the photocurrent density measured in the presence of H_2O_2 under such conditions $J_{H_2O_2} = J_{abs} \cdot \eta_{sep}$. Moreover, the hole injection efficiency for pure water oxidation was finally obtained as the ratio between J_{H_2O} and $J_{H_2O_2}$.

As shown in Figure 10.5b, a very low η_{sep} (below 10%) was obtained, while higher η_{inj} values were recorded above 1.1 V vs. RHE up to 25% charge injection efficiency attained around 1.35 V vs. RHE. This means that the material performance is mainly limited by an inefficient charge separation in the bulk, which could be improved by a reductive treatment under H_2 atmosphere.

Figure 10.6 shows the J - V curves recorded in 1.0 M NaOH under back-side irradiation and the corresponding dark scans relative to the 20L_X and 20L_X- H_2 samples thermally treated at the lowest (500 °C, Figure 10.6a) or at the highest (800 °C, Figure 10.6b) temperature. First, no detectable contribution from the dark scan to the recorded photoactivity can be observed for all electrodes in the whole investigated potential window. By comparing the performance relative to the two different pristine films, a better fill factor resulting in a 2.4-fold enhancement of photocurrent density recorded at

1.5 V vs. RHE was attained by increasing the ZFO film annealing temperature from 500 °C to 800 °C. This should be clearly related to the higher crystallinity degree attained by annealing at higher temperature. On the contrary, the gain in performance upon reduction by hydrogen treatment is incredibly higher in the case of the ZFO film annealed at 500 °C. In fact, 20L_500_H₂ shows either a better fill factor or a better photocurrent onset compared to the corresponding untreated 20L_500 electrode, resulting in a five-fold higher photocurrent density of 230 $\mu\text{A cm}^{-2}$ at 1.5 V vs. RHE for the so optimized photoanode (Figure 10.6a).

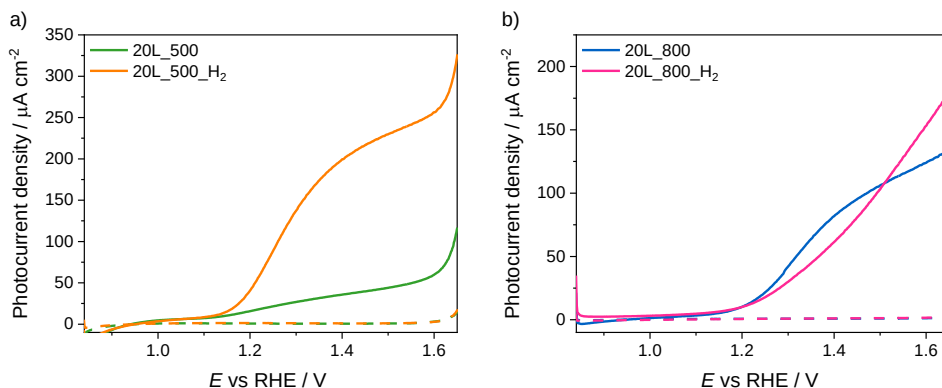


Figure 10.6 Linear Sweep Voltammetry (LSV) plots of the films annealed at (a) 500 °C and (b) 800 °C, before and after the hydrogen treatment. Dashed lines refer to the recorded dark currents.

However, hydrogenation does not produce the same effect when performed on the 20L_800 film. As shown in Figure 10.6b, only a slight photocurrent density enhancement was recorded above 1.5 V vs. RHE upon hydrogenation of the pristine 20L_800 film. Moreover, a worse photocurrent onset, accompanied by a lower fill factor, was induced by the reductive treatment.

The effects of the hydrogen treatment vs. the adopted annealing temperature, enduring for several months, can be appreciated in Figure 10.7, reporting the photocurrent density values recorded at the fixed applied potential of 1.5 V vs. RHE for all investigated electrodes as a function of their annealing temperature. Two opposite trends can be observed for the films in their pure and hydrogenated forms. While in the case of pristine electrodes an increase in photocurrent density occurs with increasing annealing temperature, a progressive drop in performance with increasing annealing temperature characterizes the materials after hydrogenation. For the two films series, the photocurrent density is almost constantly moving from 500 °C to 600 °C, while it sharply changes when raising the annealing temperature from 700 °C to 800 °C. The observed photoactivity increase for the pristine electrodes can be reasonably correlated to the increase in the material crystallinity with increasing annealing temperature.¹⁹ In fact, in highly crystalline materials trapping of photogenerated charge carriers on lattice disorder sites is prevented,³³ resulting in a relatively low charge transfer resistance in the bulk and

consequently enhanced charge separation.⁹ For the untreated pristine films, this resulted in a photocurrent enhancement with increasing annealing temperature so that no detectable improvement was observed upon hydrogenation of highly crystalline films already endowed with excellent charge separation properties.

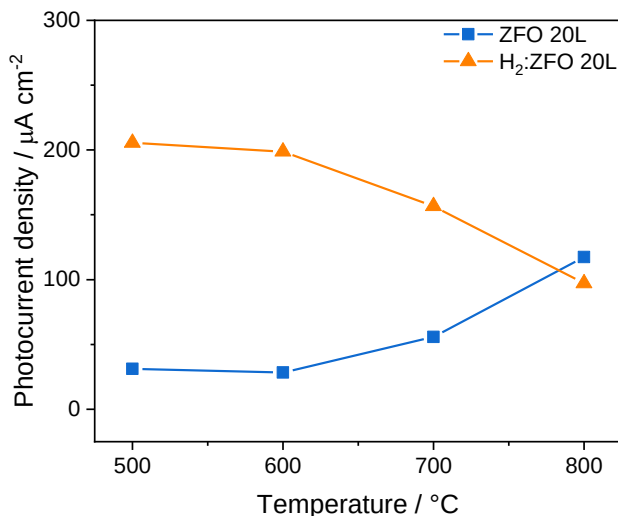


Figure 10.7 Photocurrent density measured with the 20L films at 1.5 V vs. RHE as a function of the annealing temperature.

However, other factors could also account for the photoactivity drop with increasing annealing temperature observed for the hydrogenated films. For example, the *ca.* 100 nm thickness of the 20L film series should not be sufficient to appreciate the beneficial effect of the reduction treatment when the material conductivity is good enough due to the significant crystallinity degree imparted by the high annealing temperature. Moreover, the 20L structure combined with annealing at 800 °C also produces highly compact films as shown by the AFM image in Figure 10.4b, which may hamper efficient exposure of the bulk material to hydrogen, especially when the film surface has a flat morphology.

To identify the main reason of the ineffectiveness of hydrogenation in combination with the high annealing temperature of 20L films, we also tested the performance of thinner DC_5L films annealed at 500 °C and 800 °C. Figure 10.8 reports the *J-V* curves acquired with these materials under back-side AM 1.5 G irradiation. As shown, the beneficial effect induced on the PEC performance of the pristine films by the higher crystallinity of the materials annealed at 800 °C was confirmed in the case of the thinner DC_5L_800 electrode vs. the DC_5L_500 film. However, a different photoactivity improvement trend occurred upon hydrogenation of thinner DC_5L films with respect to the 20L electrode series. In fact, the DC_5L_800 electrode exhibits higher photocurrent density compared to the DC_5L_500 film even after the hydrogen treatment, in addition to the six-fold photocurrent enhancement at 1.5 V vs. RHE with respect to the pristine DC_5L_800 photoanode.

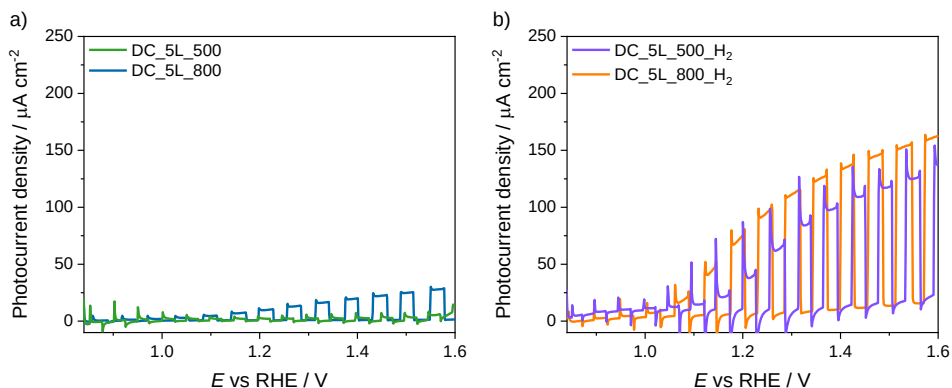


Figure 10.8 Linear Sweep Voltammetry (LSV) plots of DC_5L_500 and DC_5L_800 films (a) before and (b) after hydrogenation.

This means that the beneficial effect induced by hydrogenation in favouring bulk charge transport properties can be attained also for a highly crystalline and performant starting material (annealed at 800 °C) with a thickness below 100 nm. Thus, the higher thickness of 20L films is not the main reason for the lack of PEC performance improvement of 20L_800 upon hydrogenation. In fact, post-synthesis mild hydrogenation promotes even the PEC performance of an efficient material, such as DC_5L_800, the performance of which is not expected to be affected by charge transportation limitations due to its low thickness and high crystallinity. The highly compact structure of the 20L_800 film may instead be at the origin of its ineffective exposition to H₂ with a consequently limited bulk oxygen vacancies production.

Thus, in order to maximize the PEC performance of ZFO flat materials by exploiting both the intrinsic charge carrier separation capability of a highly crystalline structure and the further enhanced charge conductivity induced by oxygen vacancy introduction, the starting ZFO flat film has to be annealed at a relatively high temperature and expose a high surface area together with a less compact structure, able to promote H₂ penetration into its bulk structure. In fact, the hydrogenation efficiency itself strongly depends on the annealing temperature, which in turn affects the compactness of the film structure and its permeability towards hydrogenation.

In particular, we propose a synthetic strategy aiming at promoting the PEC properties of ZFO films with flat morphology. In order to maximize their efficiency as photoanodes it is thus recommended to apply a hydrogen treatment to films prepared in a multilayer structure of at least 100 nm thickness (20L series), previously annealed at low temperature (500 °C). At the same time, to approach such maximum performance by following a much more time-saving synthetic route, the same H₂ treatment should be performed for thinner ZFO films (DC_5L series) annealed at high temperatures (800 °C).

Potential synergistic effects induced by combining hydrogenation and multiple synthetic parameters (*i.e.*, annealing temperature, number of deposited layers, and

structure compactness) have been systematically studied, thus paving out a way for designing more efficient ZFO-based flat films to be employed as photoanodes for O₂ production from water oxidation.

10.5 Conclusions

The efficiency of hydrogenation of ZFO photoanodes in terms of enhanced PEC performance strongly depends on the annealing temperature of the starting material, being maximum for 20L films annealed at relatively low temperature (500 °C), while an increasing drop in performance occurs with increasing annealing temperature. We ascribed the enhanced photocurrent upon hydrogen treatment of films previously annealed at low temperatures (500 °C–600 °C) to the improved charge separation properties thanks to the *n*-type character of the induced oxygen vacancies. On the other hand, the decrease in hydrogenation efficiency with the rise in temperature can be due to the inefficient exposure of the material bulk to the reductive H₂ flux when the film presents a compact structure, as a consequence of the combined high annealing temperature and multilayer structure, and a low surface area because of its flat morphology. These insights point to the effectiveness of films with high surface areas as in the case of the NR morphology, which is known to perform the best for this material. Thus, future efforts at enhancing the performance of the ZFO material in flat form should focus on films with a less compact structure and higher surface area, to fully exploit the efficacy of the H₂ treatment.

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Chapter 11

Key factors boosting the performance of ZnFe_2O_4 flat photoanodes for solar water oxidation

11.1 Abstract

The investigation on the combined effects of the synthesis temperature and hydrogenation efficiency on the PEC performance of ZnFe_2O_4 flat films treated in Chapter 10 has been here extended to a comprehensive range of film thickness, thanks to an optimized sol-gel synthesis approach. This made possible the detection of a synergistic effect between a high material crystallinity, induced by the use of a high annealing temperature, and the efficiency of hydrogenation as *n*-type doping treatment, which proved to be maximum for the thickest photoactive layers. The specific roles of the annealing temperature and hydrogen reduction, in relation to the film thickness, were identified by decoupling their effects onto the bulk charge separation and surface charge injection processes, by means of Intensity Modulated Photocurrent Spectroscopy (IMPS), performed *in operando* conditions. The key role of the film morphology (planar vs. nanostructured architectures) in establishing the impact that the investigated structural parameters, *i.e.* the film crystallinity and the spinel inversion degree, have on the PEC performance of ZnFe_2O_4 photoanodes, was also successfully elucidated.

11.2 Introduction

Despite the many advantages of nanostructured architectures such as the NR morphology (*e.g.* the channelized electron transport and the reduced distance for minority charge carriers to reach the semiconductor/electrolyte interface), resulting in a high charge collection efficiency, the severe light scattering as side-effect of nanostructuring can compromise their utilization as top-layer photoanodes in PEC tandem devices.¹⁻³

In Chapter 10 the attention was turned to the development and optimization of optically transparent ZFO films with planar geometry, suitable to be employed as photoanodes in tandem cells, by means of a versatile organic ligand (EDTA)-based sol-

gel synthesis approach for ternary metal oxides.^{1,4} However, despite its effectiveness in producing pure-phase materials, this method did not produce high-performance ZFO photoanodes even after hydrogen annealing. In fact, hydrogenation applied on these compact electrodes proved to be ineffective in further improving the performance of the more crystalline films annealed at 800 °C, while only inducing appreciable activity enhancement in the case of the poorly crystalline films synthesized at lower temperature (500 °C–600 °C).⁴

The observed behaviour raises important fundamental questions regarding the combined influence of the annealing temperature and hydrogen reduction treatment on the carrier transport and overall PEC performance of ZFO photoanodes for water oxidation, which have yet to be addressed in the literature. While the flat (non-nanostructured) films provide a convenient platform for studying these aspects since the thickness can be carefully controlled without the convoluting effects of a nanostructure, our previously-used EDTA-based deposition method is limited in preparing thick films (>100nm) given the low solubility of the precursors.

Accordingly, in the present work this limitation was addressed by using a modified EDTA-free sol-gel synthesis with an increased precursor concentration to prepare ZFO flat films of widely different thickness (up to *ca.* 300 nm in one single spin-coating deposition step) to conduct a thorough investigation of the PEC performance over a comprehensive range of film thickness. Together with *in operando* (during the water oxidation reaction) evaluation by the Intensity Modulated Photocurrent Spectroscopy (IMPS) technique, the planar ZFO electrodes have proved to be an ideal model system to gain more insight into the influence that the hydrogen annealing treatment has on the fate of the photogenerated charges as a function of both the annealing temperature and film thickness in the absence of any morphological factor dictated by a nanostructured architecture.

The study presented in this chapter has been carried out in the Laboratory of Prof. Sivula during my visiting period at the EPFL in Lausanne.

11.3 Experimental section

11.3.1 Chemicals and materials

The following chemicals were employed: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ABCR), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Acros Organics), NaOH (Reactolab SA) and Na_2SO_3 (Sigma-Aldrich). F-doped Tin oxide (FTO) coated aluminoborosilicate glass Solaronix was used as conducting substrate.

11.3.2 Photoelectrodes preparation

Thin ZnFe_2O_4 films with different thicknesses were prepared through single step spin-coating deposition of aqueous precursor solutions with varying concentration, followed

by a two-step annealing procedure. The employed concentrations of the two metal nitrate precursors were determined from preliminary solubility tests conducted with the aim to maximize the precursor concentration while employing a suitable stoichiometry to give the desired phase. In this way, nominal precursor concentrations were obtained up to 40-fold higher than those used in our previously reported EDTA-based synthesis approach (which was 0.25 M in Fe and 0.125 M in Zn).¹ The solutions were prepared in Millipore water (18.2 M Ω resistance). Prior to deposition, the employed FTO coated glass substrates were thoroughly cleaned by three 15 min each subsequent sonication cycles in a soap/water mixture, acetone, ethanol, and finally in distilled water before plasma cleaning for 15 min.

ZFO flat films of various thicknesses were synthesized through a single step deposition of the aqueous precursor solution onto the clean FTO substrates, using a static spin coating technique. For this, an equal volume (150 μ L) of each precursor solution was dispensed on the substrate which was then spun at 500 rpm for 45 s.

After spin coating and air drying at room temperature, the films were first annealed at 400 $^{\circ}$ C in air and subsequently for 20 min in a tubular furnace preheated at 600 $^{\circ}$ C or 800 $^{\circ}$ C, followed by natural cooling to room temperature after switching the furnace off. Finally, the so-prepared electrodes underwent a post-synthesis reductive treatment at 200 $^{\circ}$ C under a H₂ atmosphere for 1 h or 4 h, to increase the photoactive film conductivity.

Powder samples for XRPD analysis and Rietveld refinements (see next section) were prepared by calcining the precursor solutions at different temperatures (600 $^{\circ}$ C, 700 $^{\circ}$ C and 800 $^{\circ}$ C) for two hours.

11.3.3 Physical characterization methods

XRD data were collected using a Panalytical Empyrean system (Theta-Theta, 240 mm) equipped with a PIXcel-1D detector, Bragg-Brentano beam optics (including a hybrid monochromator) and parallel beam optics. Raman spectra were recorded with a LabRam confocal Raman spectrometer (HORIBA Jobin Yvon XploRA PLUS) using a 532 nm wavelength laser for excitation. X-ray powder diffraction (XRPD) analysis on the powder samples was conducted through a Bruker D8 Discover diffractometer using a non-monochromatized Cu-source, a Nickel filter and a LYNXEYE-XE energy-dispersive detector, which was set to filter Fe fluorescence. Presented results were extracted from Rietveld refinements. SEM data were collected using a Zeiss Gemini 300 scanning electron microscope in HV mode. Transmittance and reflectance data were collected using a UV-3600 (Shimadzu) spectrometer equipped with an integrating sphere.

11.3.4 Photoelectrochemical methods

PEC measurements were carried out with a BioLogic SP-500 potentiostat connected to a cappuccino-type PEC cell (active geometric area of 0.25 cm² for the working electrode) described in Section 4.3.2.2, in a three-electrode configuration where a

Ag/AgCl KCl (sat.) electrode and a Pt wire were used as reference and counter electrode, respectively. The light source was a 1000 W Xe arc lamp (Newport Oriel) calibrated using a Si photodiode to provide a photon flux corresponding to the AM 1.5 G spectrum, considering the photons with an energy higher than a band gap of 2.0 eV. Chopped linear sweep voltammetry (LSV) scans were acquired with a 20 mV s⁻¹ scan rate by irradiating the electrode in both back (through the substrate-side) and front (through electrolyte side) configurations. The applied potentials acquired vs. Ag/AgCl in all measurements were converted to the reversible hydrogen electrode (RHE) using Eq. 4.19. LSV measurements were performed in both water and sacrificial oxidation conditions, *i.e.* in a 1.0 M NaOH aqueous electrolyte solution at pH 14, or in a 1.0 M NaOH solution containing also 0.5 M Na₂SO₃, respectively.

Photoelectrochemical impedance (PEIS) measurements were carried out in 1.0 M NaOH electrolyte solution (pH 14) using a Bio-Logic SP-500 potentiostat coupled with the EC-Lab (V11.12) electrochemical platform. During each PEIS scan, the potential modulation frequency was scanned between 160 Hz and 50 mHz. A custom program written with the Python programming language by Dr. F. Boudoire was used to process and fit the PEIS data.

11.3.5 Intensity modulated photocurrent spectroscopy

Intensity modulated photocurrent spectroscopy (IMPS) was performed using a blue LED light generated by a customized light modulation system with 4 Cree XLamp MC-E LEDs. The sinusoidal modulation of the light intensity was controlled by an arbitrary/function generator (Tektronix AFG3021C), with a modulation depth of 10% and a frequency range from 80 kHz to 0.5 Hz. A three-electrode cappuccino-type cell was used, similar to that employed in the other PEC measurements. A Thompson Electrochem potentiostat (model 251) was used to control the applied potential on the working electrode and the photocurrent response was recorded by a digital oscilloscope (Tektronix DPO7254C) via a 50 Ω resistor (Velleman E6/E12) in series with a platinum counter electrode. IMPS data were processed and fitted by Yongpeng Liu using a custom program written with the Python programming language by Dr. Florent Boudoire. The lmfit package for Python was used to perform curve fitting with nonlinear regression.

11.4 Results

To gain insight into the effect of the annealing temperature and the reductive hydrogen treatment on the carrier transport and transfer, a series of flat, non-nanostructured ZFO electrodes were prepared using 8 different precursor concentrations as reported in Table 11.1 with the label nX (with n ranging from 2 to 40) indicating the concentration factor of each solution compared to that employed in the previous chapter. Each of the 8 films obtained by spin coating the different precursor concentration solutions were annealed at 600 °C or at 800 °C. Thickness measurements of the as prepared ZFO films by UV-vis

absorption (see Section 11.4.1) gave similar values for both annealing temperatures as shown in Table 11.1. Electrodes annealed at 600 °C or 800 °C were directly employed in PEC measurements (coded as “pristine” samples) or underwent a further hydrogen treatment for 1 h or 4 h at 200 °C to increase their carrier conductivity. For the sake of clarity, we will indicate the two main series of electrodes (including the pristine, the 1 h- and 4 h-hydrogenated samples) differing in the annealing temperature simply as the two investigated electrodes series. All investigated ZFO electrodes are labelled as ZFO_X@Y, where X indicates the film thickness in nm, while Y stands for the employed annealing temperature. The post-synthesis hydrogen treatment is indicated, whenever necessary, in full or with the labels 1 h H₂ or 4 h H₂, depending on the treatment duration. Moreover, unless specified, all employed hydrogenation labels refer to the 1 h-long treatment.

Table 11.1 Adopted precursor solution concentrations and corresponding films thickness at each annealing temperature.

Concentration factor	[Fe ³⁺] / M	[Zn ²⁺] / M	Thickness @ 600 °C / nm	Thickness @ 800 °C / nm
2x	0.5	0.25	60	50
4x	1.0	0.5	70	70
6x	1.5	0.75	80	90
8x	2.0	1.0	100	100
10x	2.5	1.25	140	120
20x	5.0	2.5	160	160
30x	7.5	3.75	220	240
40x	10	5.0	240	310

11.4.1 Photoelectrodes characterization

The phase composition and crystal structure of the as-prepared ZFO films were evaluated through X-ray diffraction (XRD) and Raman spectroscopy analyses. Results obtained for the 160 nm thick films annealed at 600 °C or 800 °C, as representative samples of the two electrodes series, are reported in Figure 11.1. The XRD patterns in Figure 11.1a only display the reflections typical of cubic spinel ZnFe₂O₄ (JCPDS: 01-089-1010) and the diffraction peaks of SnO₂ associated to the FTO substrate (marked by asterisks). No signals for other segregated phases can be discerned. The peaks at about $2\theta = 30^\circ$, 35.2° and 56.6° are indicative of the (220), (311) and (511) crystal planes, respectively, of the pure ZnFe₂O₄ phase, which crystallizes with a *Fd3m* space group.^{5–7} The intensity of these reflections increases when the annealing temperature passes from

600 °C to 800 °C, which is a first indication of the enhanced crystallinity of the films with rising the annealing temperature, in line with previous results on ZFO NR films.⁸ On the other hand, the mild post-annealing hydrogen treatment does not change the crystal structure of ZFO films, as already found for NR electrodes.^{5,7,9}

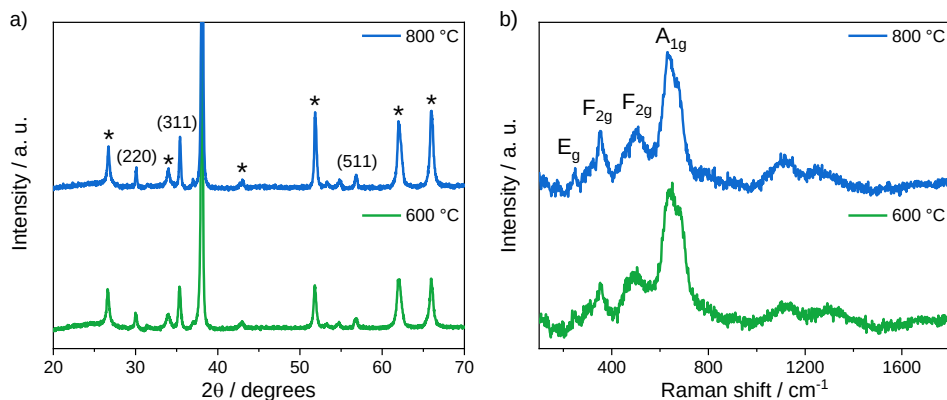


Figure 11.1 (a) XRD patterns and (b) Raman spectra of representative films annealed at 600 °C or 800 °C.

The Raman spectra over a wide 100–1800 cm⁻¹ range reported in Figure 11.1b further confirm the crystal phase and the absence of parasitic phases in the as-prepared thin films annealed at 600 °C or 800 °C. In both cases, the weak feature appearing at 245 cm⁻¹ and the three bands centred at 352, 506 and 629 cm⁻¹ can be identified with the E_g, F_{2g} (two modes) and A_{1g} first-order Raman active modes typical of ZFO.¹⁰ Also the broad weak feature at around 1120 cm⁻¹ can be assigned to ZFO on the basis of literature reports,¹¹ despite its similarity with the Raman signature of magnetite (Fe₃O₄).^{12,13} More importantly, the absence of the characteristic intense signal of α-Fe₂O₃ at 1320 cm⁻¹ and of the broad band above 1400 cm⁻¹ typical of γ-Fe₂O₃ confirm the absence of undesired hematite^{14,15} or maghemite,¹⁶ respectively, thus corroborating the formation of the spinel ferrites without any other parasitic phase. According to Thota *et al.*,¹⁷ the A_{1g} mode, which is representative of the symmetric stretch of tetrahedral units, may split into two separate peaks associated with the lattice vibrations in the tetrahedral positions of both Zn and Fe cations, in the presence of an inversion degree (later defined in the discussion). Based on this, the only slightly A_{1g} mode split detectable in both Raman spectra, in the peaks located at 648 and 680 cm⁻¹, may indicate a partial inversion degree in the synthesized films.

The trends in the estimated crystalline domain size and cation disorder as a function of the synthesis temperature were investigated through a detailed structural analysis performed by means of the Rietveld refinement of the XRPD patterns of the ZFO samples synthesized at 600 °C, 700 °C and 800 °C by a similar procedure (Figure 11.2a), without the employment of the FTO substrate. ZnFe₂O₄ possesses an almost normal spinel crystal structure composed of a cubic closed-packed array of oxygen atoms with the Zn²⁺ and Fe³⁺ ions located at the tetrahedral and octahedral sites, respectively.¹⁸ The degree of

inversion (δ) is defined as the fraction of tetrahedral sites occupied by Fe^{3+} ions and is mainly known to affect the magnetic behaviour of spinel ferrites,^{19,20} although it has been proved to play also a crucial role on the PEC properties of ZFO samples with NR morphology,⁸ more important than their crystallinity degree. The trends in the spinel inversion degree, δ , and crystalline domain size (estimated by the integral breadth), d , attained at the different annealing temperatures are compared in Figure 11.2b. Despite the same inverse behaviour for δ and d with increasing annealing temperature is observed as for ZFO NR samples,⁸ the relative variation degree of these two parameters is significantly different with respect to the previous study.

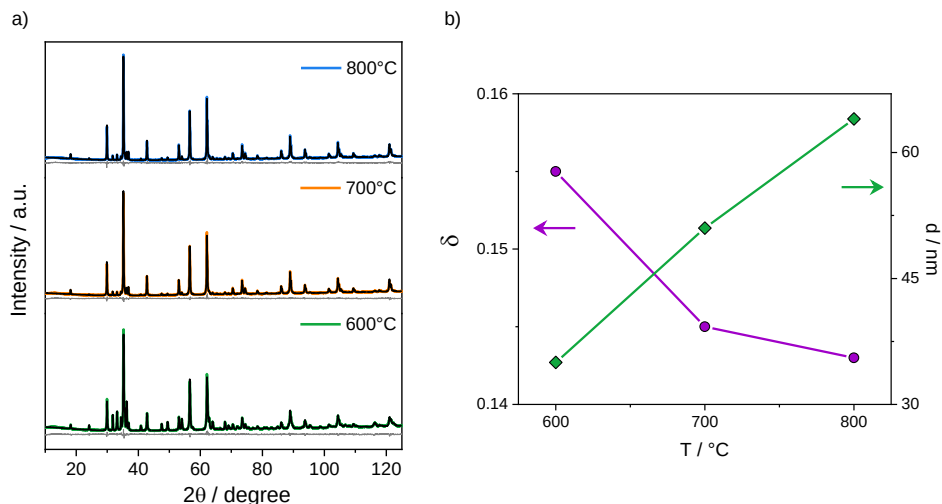


Figure 11.2 (a) Rietveld refinement of the XRPD pattern of ZFO samples annealed at different temperatures, with the coloured trace referring to the experimental data, the superimposed black trace referring to the fit Rietveld refinement and the grey trace below each pattern being the corresponding residual. (b) Trends in the spinel inversion degree δ (purple circles) and in the estimated crystalline domain size d (green diamonds) in ZFO films as a function of the annealing temperature.

In particular, a steep monotonic *ca.* 50% increase of d results from Figure 11.2b when rising the annealing temperature from 600 °C to 800 °C, while the cation disorder δ exhibits only a minor decrease, from 0.15 to 0.14, for an annealing temperature increase from 600 °C to 800 °C. This is in stark contrast with the much higher (*ca.* 60%) decrease in cation disorder found for the ZFO NR electrodes within the same temperatures range, with δ dropping from 0.30 to 0.13.⁸ Moreover, the relatively low maximum value of $\delta = 0.15$ achieved in the case of ZFO flat films, which is far below $\delta = 1$ expected for a totally inverted spinel structure, supports the view that our as-prepared ZFO flat films primarily exhibit the normal spinel phase. On the other hand, the remarkable increase (*ca.* 50%) of the crystalline domain size from 35 to 65 nm (Figure 11.2b), which is comparable with the *ca.* 70% increase observed in NR films,⁸ should correspond to a significant enhancement in the material crystallinity upon rising the synthesis temperature, in

agreement with other reports.¹¹ These considerations imply that any major difference in the charge transport properties in the here investigated ZFO film electrodes arises from differences in crystallinity rather than in cation disorder, in contrast to the behaviour shown by ZFO NR films.⁸

Figure 11.3 shows representative cross-sectional SEM images of films prepared starting from the 7.5 M in $[\text{Fe}^{3+}]$ and 3.75 M in $[\text{Zn}^{2+}]$ ZFO precursor solution and annealed either at 600 °C (Figure 11.3a) or 800 °C (Figure 11.3b). The typical planar film geometry is afforded by the simple spin-coating technique, regardless of the adopted annealing temperature. Both images exhibit dense and compact layers composed of interconnected nanoparticles, with comparable thickness in the 220–240 range regardless of the thermal treatment. This points to the lack of any change in morphological factors (such as surface roughness and, consequently, surface area of the film) with varying the annealing temperature, which rules out any possible influence of morphological factors on the PEC performance of the two films series.

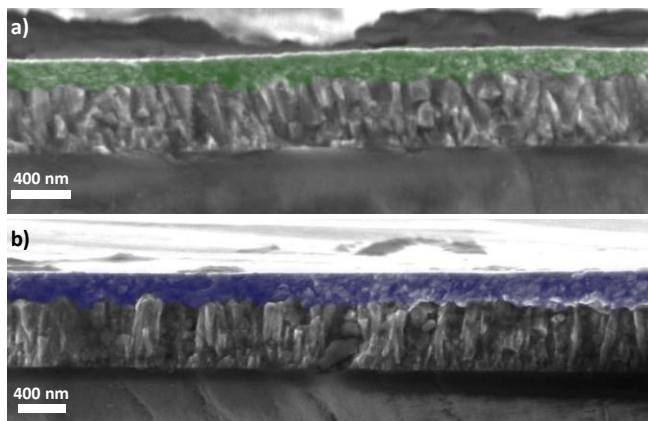


Figure 11.3 Cross sectional SEM images of the (a) ca. 220 nm and (b) ca. 240 nm thick films annealed at 600 °C (Mag = 25.62 K X) and 800 °C (Mag = 20.55 K X), respectively.

The thickness of all synthesized films (reported in Table 11.1) was estimated from the absorption coefficient α at the corresponding annealing temperature (see Table 11.2). The α calculation was based on the following equation:^{21,22}

$$\alpha = -\frac{1}{h} \ln \left(\frac{T\%}{100 - R\%} \right) \quad (11.1)$$

where h is the thickness of the reference sample for each annealing temperature estimated from the cross-sectional SEM images in Figure 11.3, T% and R% are the percentage transmittance and reflectance data, respectively, of the same electrodes at a selected wavelength.

The most suitable wavelength for α estimation was identified by comparing the absorbance at selected wavelengths vs. thickness linear regression plots (see Figure 11.4). The linearity requirement of the Lambert-Beer law was better satisfied at $\lambda = 400$ nm.

The corresponding $\alpha(\lambda)$ values for the two annealing temperatures are $\alpha_{600}(400 \text{ nm}) = 0.0085 \text{ nm}^{-1}$ and $\alpha_{800}(400 \text{ nm}) = 0.0093 \text{ nm}^{-1}$.

Table 11.2 Calculated absorption coefficients at different wavelengths for each annealing temperature.

Selected wavelength / nm	α_{λ} @ 600 °C / nm^{-1}	α_{λ} @ 800 °C / nm^{-1}
350	0.0156	0.0164
400	0.0085	0.0093
450	0.0033	0.0039
500	0.0019	0.0020

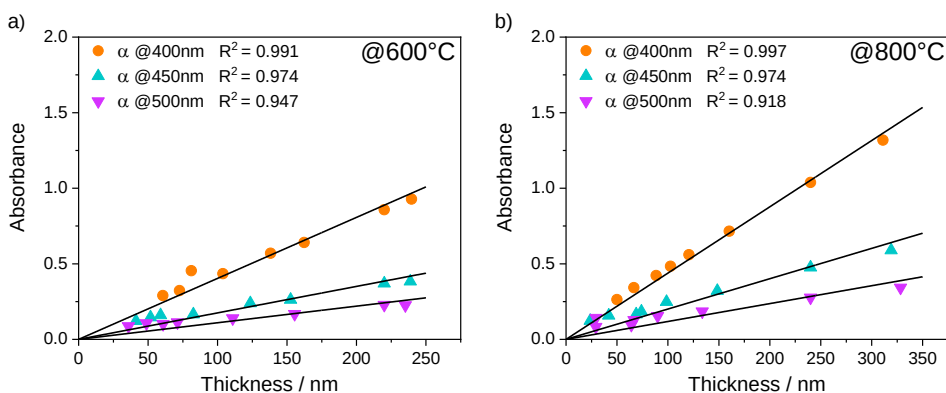


Figure 11.4 Absorbance at different wavelengths vs. film thickness for both (a) the 600 °C and (b) the 800 °C films series. The best linearity was found for $\lambda = 400 \text{ nm}$ in both cases, with absorption coefficient values $\alpha_{600} = 0.0085 \text{ nm}^{-1}$ and $\alpha_{800} = 0.0093 \text{ nm}^{-1}$.

11.4.2 Photoelectrochemical performance

Typical current density vs. applied potential (J - V) curves were collected under standard water oxidation conditions (intermittent 1-Sun chopped-light illumination, 1.0 M NaOH electrolyte) without any added co-catalyst overlayer, aiming at ascertaining how the investigated parameters, *i.e.* the annealing temperature, the film thickness and the reduction treatment with hydrogen, as well as their interplay, may affect the PEC performance of ZFO electrodes. Figure 11.5 reports the overall photocurrent trends recorded at 1.5 V vs. RHE for each of the two electrodes series synthesized at different annealing temperature (either pristine or hydrogenated electrodes), under both back (substrate side) and front (electrolyte side) illumination, as a function of the film thickness. The J values with relative error bar reported in Figure 11.5 correspond to the average photocurrent measured with electrodes of each type, evidencing a good reproducibility of the obtained results as well as of the adopted synthesis method and post-synthesis hydrogen treatment.

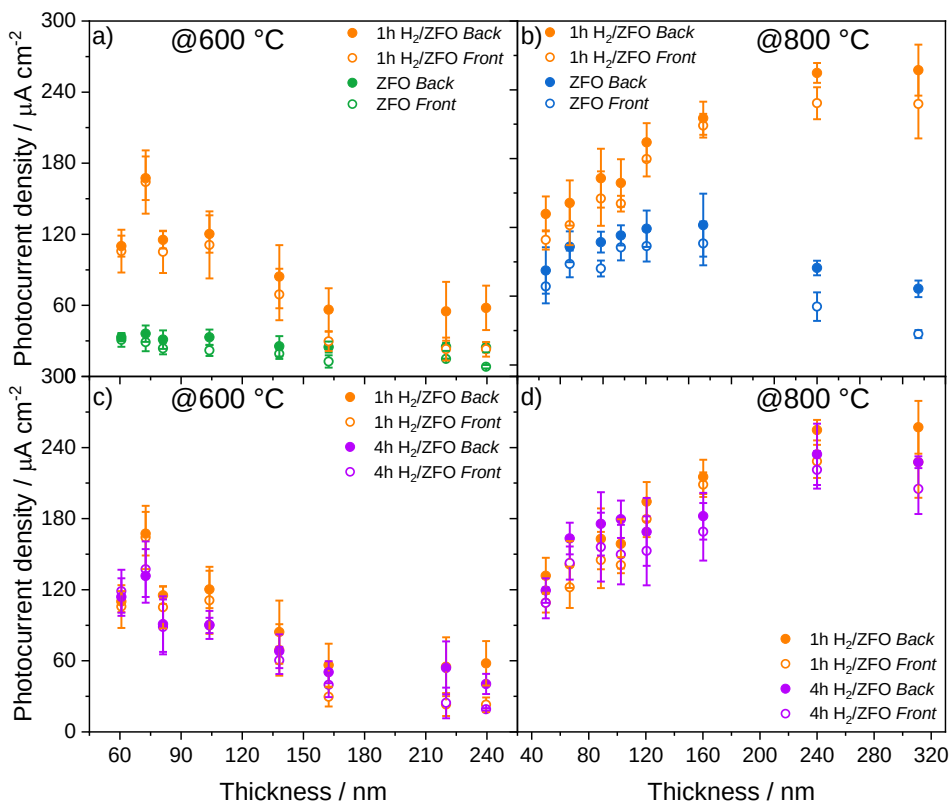


Figure 11.5 Comparison of the photocurrent density (J) values at 1.5 V vs. RHE as a function of the film thickness of the pristine and the 1 h hydrogenated electrodes annealed at (a) 600 °C and (b) 800 °C, or of the 1 h and 4 h hydrogenated samples annealed at (c) 600 °C and (d) 800 °C. All J values were obtained as the average of linear sweep voltammetry measurements carried out with multiple samples in a 1.0 M aqueous NaOH solution under both back- and front-side irradiation.

First of all, by comparing the performance attained after 1 h- or 4 h-long hydrogen treatment (Figure 11.5c,d), it is evident that no further improvement was induced by extending the reductive treatment up to 4 h. Thus, the film composition equilibrium in terms of oxygen vacancies was already reached after 1 h-long reductive treatment. For this reason, the following discussion will be focused on the comparison between the pristine and the 1 h-long hydrogenated electrodes (Figure 11.5a,b).

Overall, from the analysis of the results in Figure 11.5a,b, a different behaviour is observed for the pristine and the H_2 treated electrodes depending on the annealing temperature. Focusing first on the pristine films, the electrodes annealed at 600 °C exhibit a very poor and flat performance (the photocurrent density always remaining below 40 $\mu A\ cm^{-2}$) regardless of the film thickness (Figure 11.5a), as a consequence of their relatively low crystallinity, according to the results of XRPD analysis (Figure 11.2b). In contrast, the higher crystallinity of the films annealed at 800 °C ensures higher activity already in the pristine electrodes, exhibiting a bell-shape trend vs. thickness of the

photocurrent values with a maximum of $130 \mu\text{A cm}^{-2}$ at around 160 nm, followed by a rapid decrease when moving towards thicker films (Figure 11.5b).

After hydrogenation, the overall performance was improved but to a very different extent depending on the film thickness and on the annealing temperature. Indeed, while the maximum photocurrent increase among the hydrogenated less crystalline electrodes was recorded at a low thickness (70 nm), followed by a steep drop with increasing thickness values (Figure 11.5a), the same reductive treatment applied on the more crystalline films induced a progressive enhancement in performance with increasing film thickness, up to a plateau, reached at 240 nm (Figure 11.5b). Despite a maximum 4-fold enhancement in photocurrent was obtained upon hydrogenation for both films series, largely different absolute photocurrent values were attained in the two cases. In fact, a maximum average photocurrent density of only $160 \mu\text{A cm}^{-2}$ was achieved with the hydrogenated electrodes annealed at 600°C , while the combination of the higher annealing temperature with the subsequent hydrogen treatment boosted the performance of the thicker photoactive layers up to an average photocurrent density of $260 \mu\text{A cm}^{-2}$, which is the maximum value recorded in the frame of this study.

The above described trends reflect the performance obtained in both irradiation configurations, with the front illumination photocurrent being lower than the back photocurrent in almost all cases. This suggests that the bulk transport properties of our ZFO photoanodes are mainly limited by electrons which have to reach the back FTO contact.

In order to reveal the effects of hydrogenation on films of different thickness depending on the annealing temperature, we will now focus on the comparison of the results obtained with the 70 nm and the 240 nm thick films of each series, as limit cases within the investigated thickness range. Figure 11.6 compares the complete *J-V* curves for these electrodes, before and after hydrogenation, collected under back-side irradiation.

The reported photocurrent-voltage curves exhibit typical anodic behaviour, with a photocurrent onset at around 0.8 V vs. RHE, in agreement with previous studies,^{1,4,5,8,17} and sharp transient photocurrent spikes, which are indicative of a relatively high recombination at low bias until the space charge layer is sufficiently large to prevent recombination. The transient spikes are more pronounced in the case of the less crystalline samples annealed at 600°C . The comparison over the entire applied potential range confirms that the higher annealing temperature leads to higher photocurrent values in the case of the pristine samples. Moreover, the different impact of hydrogen treatment on the two limit thicknesses, depending on the annealing temperature, is even more evident from the complete *J-V* profiles. Not only a higher saturation photocurrent (at high bias, *e.g.* 1.5 V vs. RHE), but also an improved photocurrent onset in the low applied potential region, leading to a greatly enhanced fill factor, were achieved upon hydrogenation of the optimal ZFO_70@600 (Figure 11.6a) and ZFO_240@800 (Figure 11.6d) electrodes. In stark contrast, only a minor increase in performance is noted upon hydrogen treatment of the

ZFO_240@600 sample (Figure 11.6b), and a decrease in performance with a later photocurrent onset potential and a lower fill factor were induced by hydrogenation of the ZFO_70@800 electrode, compared to the pristine film (Figure 11.6c).

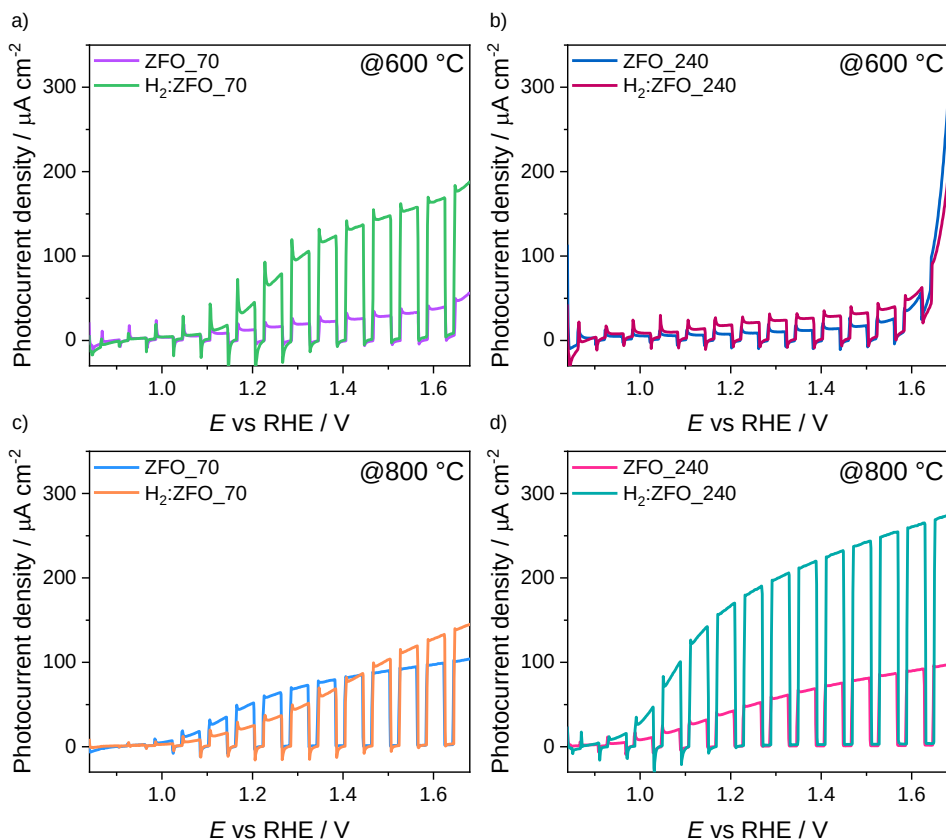


Figure 11.6 Linear Sweep Voltammetry (LSV) plots recorded with the (a,c) 70 nm and (b,d) 240 nm thick films annealed at (a,b) 600 °C or (c,d) 800 °C, before and after 1 h hydrogenation, in 1.0 M NaOH electrolyte solution under back-side irradiation.

It is well known that the photocurrent onset potential for water oxidation is usually subjected to a severe surface recombination, due to the narrow width of the space charge layer in the low applied potential region,²³ which may be reflected in a delay of the photocurrent onset potential with respect to the flatband potential, as previously observed in ZFO films.^{5,11} In light of this, the later photocurrent onset potential exhibited by the hydrogenated form of the ZFO_70@800 electrode compared to the pristine one may be a first indication of the detrimental role of the hydrogen treatment towards the surface properties of this sample, for example through the introduction of oxygen vacancies acting as surface trap states.^{9,24}

To shed light onto the origin of the different impact of the hydrogen treatment onto the PEC performance of ZFO films, depending on both their thickness and annealing

temperature, the bulk charge separation and the surface charge injection contributions to the overall photocurrent were decoupled first by means of the analyses conducted under sacrificial conditions,²⁵ i.e. upon addition of Na₂SO₃ as hole scavenger to the NaOH electrolyte solution.

According to this approach, the photogenerated charge separation efficiency (η_{sep}) and minority charge carrier injection efficiency (η_{inj}) were estimated from the J - V curves recorded under non-sacrificial and sacrificial conditions. Indeed, the water oxidation photocurrent density can be expressed as $J_{\text{H}_2\text{O}} = J_{\text{abs}} \eta_{\text{sep}} \eta_{\text{inj}}$, where J_{abs} is the theoretical maximum photocurrent density considering the measured light absorption of each film, calculated from the integration of the product between the standard AM 1.5 G solar spectrum and the absorption spectrum of each electrode, over the proper absorption wavelength range.

Analogously, by assuming a 100% charge injection efficiency for Na₂SO₃ oxidation ($\eta_{\text{inj}} = 1$),²⁵ the photocurrent of sulfite oxidation ($J_{\text{Na}_2\text{SO}_3}$) is such that $J_{\text{Na}_2\text{SO}_3} = J_{\text{abs}} \eta_{\text{sep}}$, from which η_{sep} can be simply obtained by dividing the photocurrent measured in the presence of the Na₂SO₃ hole scavenger by J_{abs} .

From the combination of the two photocurrent expressions (in the presence and absence of hole scavenger) one can finally calculate η_{inj} , which is equal to the ratio between $J_{\text{H}_2\text{O}}$ and $J_{\text{Na}_2\text{SO}_3}$. The so-calculated efficiencies for the thinnest and thickest films of the two investigated electrodes series are reported as a function of the applied potential in Figure 11.7.

In all cases, η_{sep} values are much lower than η_{inj} values, indicating that the photocurrent response of our flat ZFO photoanodes is ultimately governed by a severe bulk recombination, probably due to either a very low mobility and diffusion length of the carriers or a high density of bulk defects. The bulk charge separation efficiencies relative to the pristine samples exhibit a typical gradual amelioration with increasing bias thanks to the progressive widening of the depletion region adjacent to the electrode/electrolyte interface,²⁵ although remaining below the 4% in all cases. These low η_{sep} values are in line with those reported for nanostructured ZFO samples^{5,7,9,26,27} and further decrease when moving from the thinner (Figure 11.7a,c) to the thicker film (Figure 11.7b,d) within each electrodes series, likely due to the increasing probability of charge recombination as the thickness increases.

No influence of the annealing temperature on the resulting η_{sep} values can be detected at any of the examined film thickness (compare Figure 11.7a and c, Figure 11.7b and d). On the other hand, hydrogen treatment induces a conspicuous improvement in charge separation efficiency compared to the pristine films up to a maximum 3-fold enhancement at 1.5 V vs. RHE (Figure 11.7c). This occurs in almost all cases except for the low crystalline thicker film, exhibiting an intrinsically poor η_{sep} which remains low also after hydrogenation (Figure 11.7b).

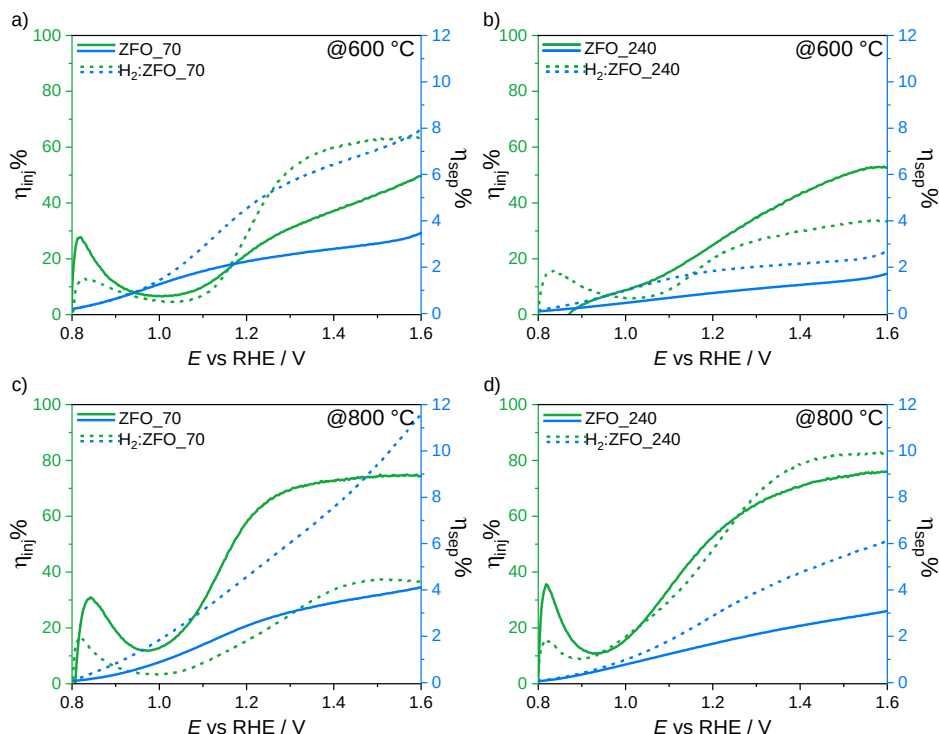


Figure 11.7 Charge injection (η_{inj} , green lines) and charge separation (η_{sep} , blue lines) efficiencies calculated from LSV measurements under sacrificial conditions with the (a,c) 70 nm and (b,d) 240 nm thick films annealed at (a,b) 600 °C or (c,d) 800 °C, before (continuous lines) and after (dashed lines) 1 h hydrogenation.

In contrast with its minor role onto the bulk charge separation efficiencies, the annealing temperature has a great impact on the charge transfer efficiencies at the semiconductor–liquid junction (SCLJ) interface. In fact, focusing the attention on the pristine samples of both series, the more crystalline films annealed at 800 °C (Figure 11.7c,d) exhibit a η_{inj} close to 80% already at 1.4 V vs. RHE, which is double than that shown by the less crystalline electrodes annealed at 600 °C (Figure 11.7a,b). Moreover, the achievement of this plateau value in the case of the electrodes annealed at 800 °C occurs with a steeper increase in η_{inj} at the photocurrent onset potential compared to that observed with the electrodes annealed at 600 °C, which is indicative of an efficient mitigation of surface recombination with increasing band bending.^{5,25} The η_{inj} behaviour observed with electrodes annealed at the two temperatures, independent of the film thickness, is in perfect agreement with that found for ZFO electrodes with NR morphology.^{7,8}

On the other hand, the impact that the hydrogen treatment has on surface injection is strictly correlated to both the film thickness and the annealing temperature. In fact, while inducing a slight improvement of η_{inj} for the best performing ZFO_70@600 and

ZFO_240@800 electrodes in the high potential region, hydrogenation of the ZFO_240@600 and ZFO_70@800 films led to a decrease of η_{inj} over the entire applied potential range. This is in line with the worse photocurrent onset for water oxidation observed with the ZFO_70@800 electrode after hydrogenation (see *J-V* curves in Figure 11.6c) and indicates that the hydrogen treatment has a negative impact on the surface injection properties of this ZFO sample.

11.4.3 Intensity modulated photocurrent spectroscopy analysis

PEC analyses conducted in the presence of sacrificial agents would be not representative of the true water oxidation conditions since either the space charge properties (*e.g.* band-bending) or the charge accumulation at the photoanode surface can be influenced by the nature of the redox species involved in the electrochemical reaction at the film/electrolyte interface.²⁸ Therefore, care must be taken in estimating the η_{sep} and η_{inj} for water oxidation, which is affected by a large surface kinetics bottleneck, from measurements carried out under sacrificial conditions, *i.e.* under the assumption that no charge accumulation occurs at the SCLJ. In fact, especially in the presence of a significant charge accumulation at the SCLJ under sluggish oxidation conditions, the η_{sep} and η_{inj} values estimated from sacrificial measurements may considerably differ from those effectively sought. For this reason and aiming at validating the results obtained from PEC measurements in the presence of Na₂SO₃, η_{sep} and η_{inj} were also evaluated *in operando* conditions by means of Intensity Modulated Photocurrent Spectroscopy (IMPS) measurements, conducted under water photooxidation conditions (in 1.0 M NaOH electrolyte). IMPS has indeed proved to be a powerful frequency domain tool to unequivocally decouple the bulk and surface contributions of photoanodes by their respective time constants.^{29,30}

The IMPS response for the 8 selected electrodes is shown in Figure 11.8 as Nyquist plots of the complex photocurrent at 1.5 V vs. RHE, which can be directly compared to the *J* at the same bias reported in Figure 11.5. All Nyquist plots are composed of two semicircles: the negative semicircle located in the lower quadrant and representative of the higher frequency process (shorter time constants), corresponding to charge generation and transport in the bulk, and the positive semicircle located in the upper quadrant and associated with surface recombination occurring at lower frequencies (longer time constant).³¹

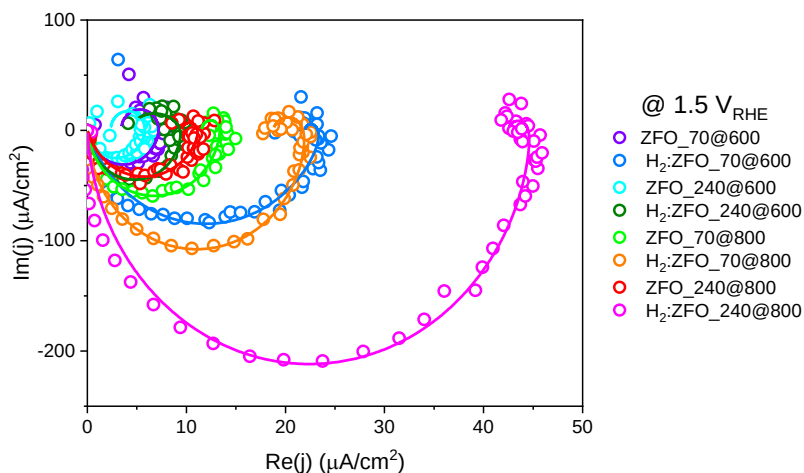


Figure 11.8 Intensity modulated photocurrent spectroscopy (IMPS) analyses at 1.5 V vs. RHE for the 70 nm and 240 nm thick films annealed at either 600 °C or 800 °C. The represented raw data (circles) and fitted model (lines) were obtained upon normalization to the electron current recorded at the IMPS setup.

Specifically, the amplitudes of the negative and positive semicircles are directly indicative of the bulk photocurrent available for water oxidation (J_h) and of the photocurrent losses due to surface recombination (J_r), respectively. Therefore, the significantly smaller surface recombination semicircle in comparison with the bulk transport semicircle observable in all reported cases (Figure 11.8) indicates that a large steady-state photocurrent is available for water oxidation at the surface of our ZFO photoanodes, in analogy with other metal oxide photoanodes.^{32,33}

Information on the aforementioned J_h and J_r parameters, as well as on the corresponding time constants for photocurrent generation in the photoanode bulk (bulk hole current), τ_h , and for the surface recombination losses, τ_r , were extracted from the fit of the IMPS response to a phenomenological model with two resistor–capacitor (RC) responses,^{28,30} described by the following equation:³¹

$$j(\omega) = \frac{j_h}{1 + (i\omega\tau_h)^{\alpha_1}} + \frac{j_r}{1 + (i\omega\tau_r)^{\alpha_2}} \quad (11.2)$$

where the non-ideality factors α_1 and α_2 , which can be used to describe the deformation of the semicircles due to frequency dependence effects, were selected to be close to 1. All the extracted parameters at 1.5 V vs. RHE, for each of the 8 films, are shown in Figure 11.9.

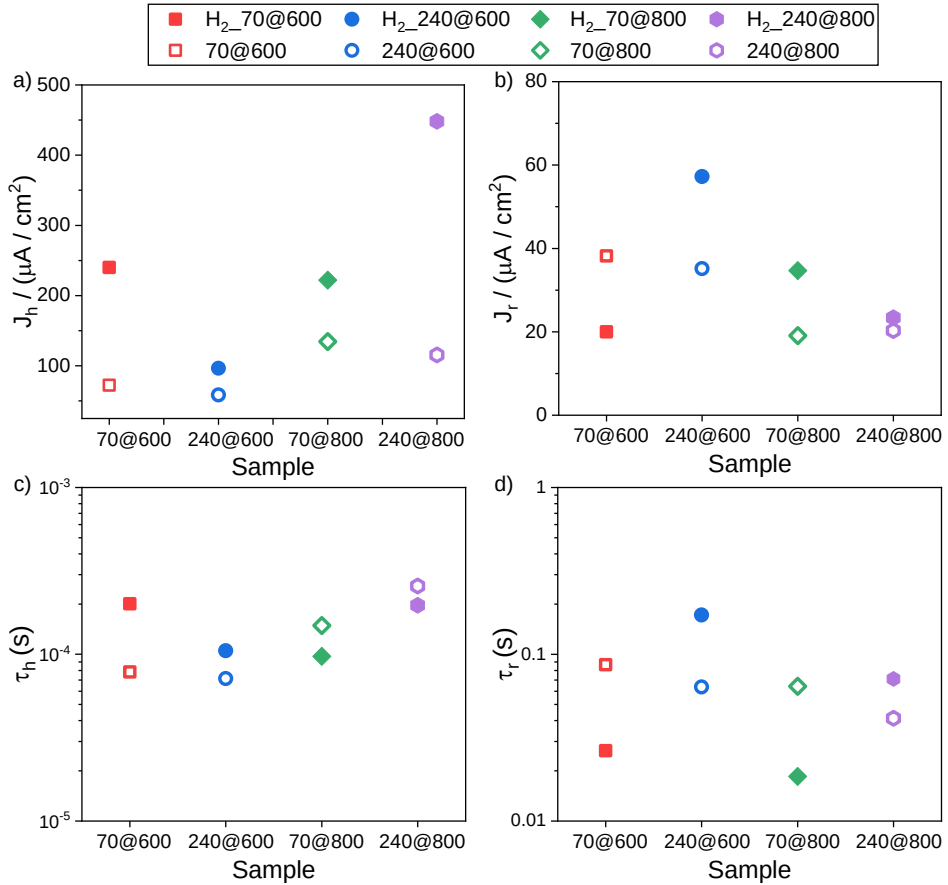


Figure 11.9 Parameters at 1.5 V vs. RHE extracted from the IMPS fit model for the 70 nm and 240 nm thick films annealed at 600 °C or 800 °C: (a) bulk hole photocurrent (J_h), (b) surface recombination losses (J_r) and corresponding time constants (c) τ_h and (d) τ_r , respectively.

From the employed model,³¹ an accurate estimation of the η_{sep} and η_{inj} parameters *in operando* can be pursued by simply calculating them as $\eta_{\text{sep}} = J_h/J_{\text{abs}}$ (where J_{abs} is the maximum photocurrent expected for each ZFO film based on its absorbance spectrum) and $\eta_{\text{inj}} = (J_h - J_r)/J_h$. Figure 11.10 shows the comparison of these quantities extracted at 1.5 V vs. RHE for all investigated electrodes.

The huge discrepancy between the surface injection and the bulk separation efficiencies is even more marked in this case, with maximum values of 95% (η_{inj}) and 5% (η_{sep}), respectively, and accounts for bulk charge separation as main limiting issue for the performance of the material. The already-assessed effects of both annealing temperature and hydrogen treatment on the two decoupled contributions, in relation to the film thickness, are confirmed, as discussed in the following.

While the charge injection efficiency doubles from *ca.* 40% to *ca.* 80% in pristine samples annealed at higher temperature, regardless of the film thickness, hydrogenation

does not markedly influence the charge transfer efficiency at the photoanode surface, except for one main case (Figure 11.10a). In fact, beyond the highest increase in η_{inj} detected for the hydrogenated thinner film annealed at 600 °C compared to its pristine form, a slight improvement of the surface injection properties occurs after hydrogenation for the thicker electrode annealed at 800 °C.

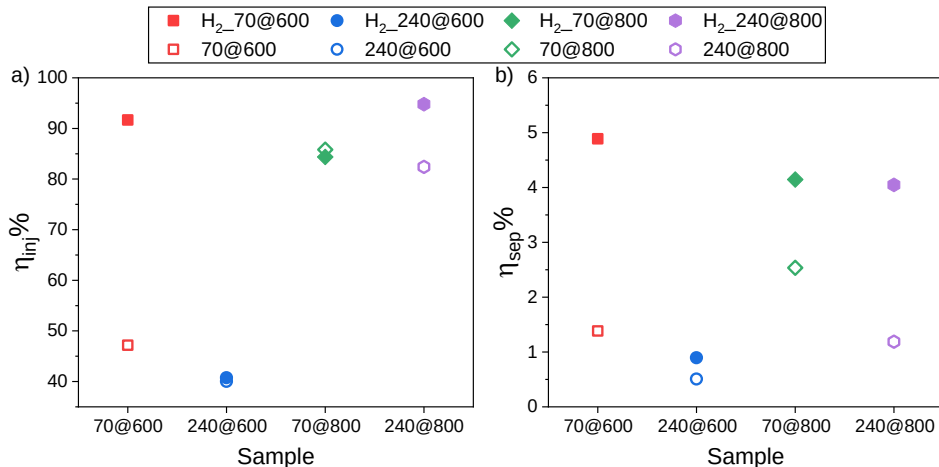


Figure 11.10 (a) Charge injection (η_{inj}) and (b) charge separation (η_{sep}) efficiencies calculated from IMPS data at 1.5 V vs. RHE, for the 70 nm and 240 nm thick films annealed at 600 °C or 800 °C, before and after 1 h-long hydrogenation.

On the other hand, the calculated charge separation efficiencies (Figure 11.10b) appear very sensitive to both the film thickness and the reductive treatment. In agreement with the results obtained under sacrificial conditions, the η_{sep} values of the pristine films decrease with increasing film thickness, for both annealing temperatures. The modest improvement in charge separation induced by the higher annealing temperature can be appreciated only for the thinner film of the series.

In this picture, hydrogen treatment plays a crucial role by inducing a remarkable improvement of the bulk charge separation in almost all cases, up to a maximum 4-fold enhancement observed with the best performing ZFO_70@600 and ZFO_240@800 films. Moreover, as a result of the higher hydrogenation efficiency observed with the thicker film within the 800 °C series, its η_{sep} attains the same value as the reduced form of the thinner film, despite the two electrodes exhibit significantly different efficiencies prior to hydrogenation. This suggests that hydrogen treatment performed on the more crystalline films annealed at 800 °C enhances their bulk charge separation up to a maximum value regardless of the film thickness, beyond which the performance of the electrodes is ultimately governed by their photon absorption capability. A different behaviour is observed for the less crystalline samples annealed at 600 °C, with an increase in η_{sep} upon hydrogenation for the thinner film of the series only.

11.4.4 Electrochemical impedance spectroscopy analysis

Electrochemical impedance spectroscopy experiments were conducted under standard water oxidation conditions (1-Sun illumination, 1.0 M NaOH electrolyte) in back-side configuration, on the ZFO_70@600 and ZFO_160@800 films, in both pristine and hydrogenated forms. The EIS data were fitted to a modified Randles circuit, already described in Chapter 4, and consisting of a series resistance R_s , a bulk capacitance C_{bulk} such that $C_{\text{bulk}}^{-1} = C_{\text{SC}}^{-1} + C_{\text{H}}^{-1}$, where C_{SC} is the space charge layer capacitance and C_{H} the Helmholtz capacitance, a parallel resistance of hole trapping to surface states R_{trap} , a surface state capacitance C_{SS} and a charge transfer resistance from surface states to oxidize water $R_{\text{ct,ss}}$. The Mott-Schottky (M-S) plots for the investigated electrodes, constructed with the values of C_{SC} plotted as a function of the applied potential, are shown in Figure 11.11.

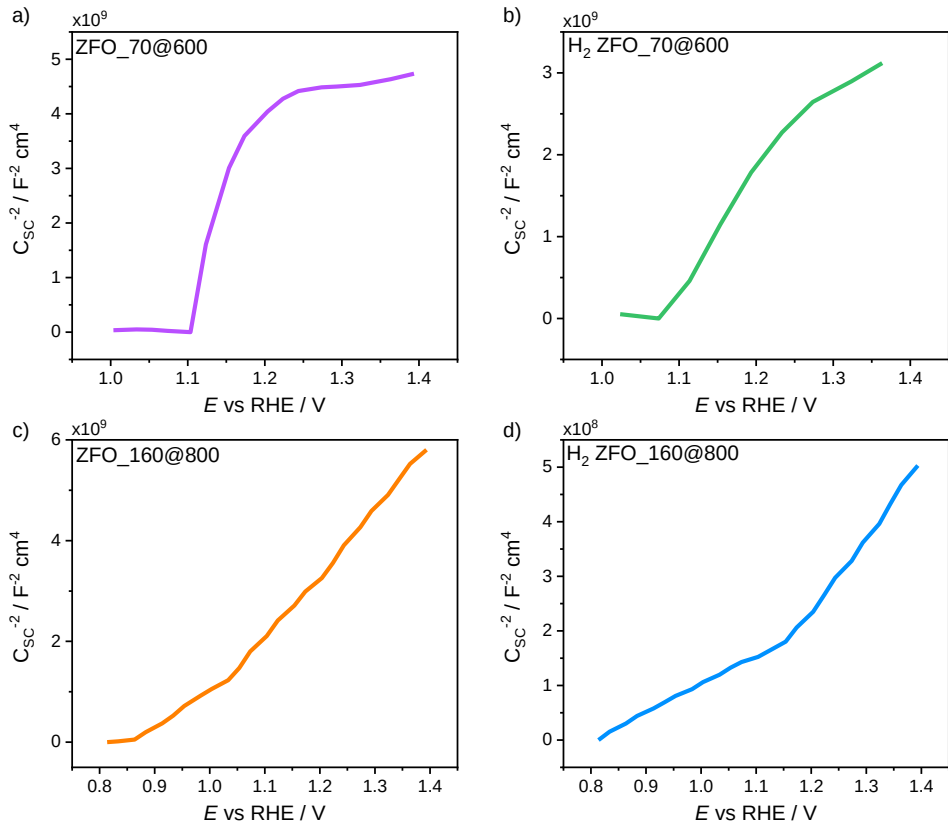


Figure 11.11 Mott-Schottky plots obtained for the (a,b) ZFO_70@600 and (c,d) ZFO_160@800 films in their (a,c) pure and (b,d) hydrogenated forms, from EIS measurements carried out in 1.0 M NaOH under AM 1.5 G solar simulated irradiation.

The fitting parameters, *i.e.* the donor density values N_D and the flatband potential E_{FB} extrapolated from the slope and the abscissa-intercept of each M-S plot, respectively, are

reported in Table 11.3, together with the space charge layer width (W) at 1.5 V vs. RHE, calculated according to the following equation:³⁴

$$W = \sqrt{\frac{2\epsilon\epsilon_0}{qN_D}|E - E_{FB}|} \quad (11.3)$$

where ϵ is the dielectric constant of ZFO and ϵ_0 is vacuum permittivity.

Table 11.3 EIS fitting parameters and calculated space charge width.

Sample	E_{FB} / V_{RHE}	N_D / cm^{-3}	$W @ 1.5 V_{RHE} / \text{nm}$
ZFO_70@600	1.10	$1.9 \cdot 10^{16}$	500
H ₂ ZFO_70@600	1.05	$1.0 \cdot 10^{18}$	70
ZFO_160@800	0.80	$1.7 \cdot 10^{18}$	70
H ₂ ZFO_160@800	0.80	$2.7 \cdot 10^{19}$	17

The results of the M-S analysis show that both E_{FB} and N_D of the films are affected by the annealing temperature. Specifically, the effect of surface states passivation increasing with the annealing temperature is supported by the *ca.* 0.8 V vs. RHE more negative E_{FB} value of the films annealed at 800 °C, in both the pristine and hydrogenated forms, in comparison with the less crystalline samples annealed at 600 °C. The extrapolated flatband potential is in good accordance with the photocurrent onset potentials of the J - V plots reported in Figure 11.6. Moreover, the very low N_D value of $1.9 \cdot 10^{16} \text{ cm}^{-3}$ of pristine ZFO_70@600 film undergoes a two order magnitude enhancement upon rising the annealing temperature, reaching a value of $1.7 \cdot 10^{18} \text{ cm}^{-3}$ for pristine ZFO_160@800.

For both annealing temperatures a further increase in donor density is provided by hydrogenation, demonstrating its n -type character able to enhance the electron conductivity of the films. A two orders and one order magnitude donor density increase was attained upon hydrogenation of the ZFO_70@600 and ZFO_160@800 films, respectively, up to N_D values of $1.0 \cdot 10^{18} \text{ cm}^{-3}$ and $2.7 \cdot 10^{19} \text{ cm}^{-3}$.

From the detected donor density values, a reduction of the space charge layer width upon hydrogenation of the two pristine samples can be observed, according to Eq. 11.3. While a reasonable decrease in W from 70 to 17 nm can be attained for ZFO_160@800 after hydrogenation, a much less reliable W value of 500 nm was found for ZFO_70@600 in comparison with the 70 nm thick W estimated for the corresponding hydrogenated form, owing to the extraordinarily low N_D value detected for the pristine ZFO_70@600 sample. Despite the uncertain estimation of W for the pristine 600 °C annealed film due to the experimental limits encountered in the detection of N_D , it is reasonably to guess that a decrease in W , at least to the same extent as for the 800 °C films couple, occurs also upon hydrogenation of the less crystalline sample.

11.5 Overall discussion

The results of IMPS measurements conducted *in operando* confirm the trends of η_{sep} and η_{inj} obtained from PEC measurements in the presence of a sacrificial agent. The main points inferred from both analyses can be summarized as follows.

The thermal treatment performed at the higher temperature (800 °C) mainly improves the charge injection properties at the surface of the ZFO photoanodes, likely through the deactivation of surface trapping states at the film/electrolyte interface.²³ While the same behaviour was observed for the η_{inj} of the ZFO NR electrodes,⁸ the charge separation properties of the here-investigated ZFO flat films are affected by the annealing temperature in a significantly different way compared to nanostructured electrodes. The present study indeed reveals that the higher annealing temperature in ZFO flat films is correlated to the enhancement of their charge transport properties as a result of the increased film crystallinity,³⁵ ultimately leading to the observed improved charge separation with respect to the less crystalline samples, at least at the lower film thickness (Figure 11.10b). This suggests that charge transport in ZFO flat films should be primarily governed by the crystallinity of the material rather than by cation disorder, unlike what was found with ZFO NR.⁸

Hydrogen treatment plays a crucial role in improving charge separation at the various film thicknesses to a largely different extent depending on the annealing temperature. This reflects the well-established doping effect of hydrogenation, known to enhance the performance of metal oxide photoanodes through the introduction of oxygen vacancies acting as electron donors.^{5,9,24,36} In this way, charge separation across the bulk of the film can benefit from the so-enhanced majority carrier density, through either the increase of the electric field in the space charge region³⁷ or the enhanced film conductivity, which should, in turn, lead to an improved electron transport.^{9,24,36}

A higher hydrogenation efficiency in terms of a larger improvement in η_{sep} is attained, among the more crystalline electrodes, when moving towards the thicker film of the series (Figure 11.10b). The different behaviour in η_{sep} observed within the 800 °C electrodes series, before and after hydrogenation, can be explained by considering the different strength of the electric field resulting from polarizing the two samples (especially at a potential as high as 1.5 V vs. RHE), depending on their thickness and doping density, which in turn influence the width of the space charge region. In fact, a larger potential drop, responsible for the better charge separation observed among the pristine electrodes, is expected in the thinner with respect to the thicker electrode, due to the much stronger electric field at 1.5 V vs. RHE polarization. On the other hand, after hydrogenation any relevant further gain in electric field under polarization of the thinner ZFO_70@800 film is prevented by the narrowing of the depletion region caused by the increase in donor density, according to EIS analyses (Section 11.4.4). This explains why the originally higher η_{sep} of the thinner pristine electrode does not increase, after hydrogenation, to the

same extent as for the thicker film, rather reaching the same value as the reduced form of the ZFO₂₄₀@800 electrode.

The hydrogen treatment has a different effect on the charge separation properties of the electrodes annealed at 600 °C, depending on the film thickness. In fact, the reductive treatment applied on the poorly crystalline films induces a significant η_{sep} increase in the thinner electrode only, while a negligible improvement is observed with the hydrogenated thicker film compared to its pristine form. This anomalous behaviour can be ascribed to the very poor crystallinity imparted by the lower annealing temperature, which should hamper charge transport over thick films.

Minor effects, strongly dependent on both film thickness and annealing temperature, were produced by hydrogenation on the charge injection properties at the photoanode surface. Merging the results obtained through PEC measurements in the presence of the sacrificial agent with those of IMPS analyses leads to the conclusion that, while an almost unchanged or slightly improved η_{inj} is induced by hydrogenation on the thicker films annealed at 600 °C or 800 °C, respectively, the surface of the thinner films was influenced by the hydrogen treatment in opposite ways depending on the annealing temperature. Specifically, an amelioration of the surface injection properties is observed upon hydrogenation of ZFO₇₀@600, likely induced by the passivation of surface states affecting the performance of the pristine sample. On the contrary, the η_{inj} obtained for reduced ZFO₇₀@800 is even worse than in its pristine form, possibly due to hydrogenation-induced surface states, *e.g.* oxygen vacancies leading to charge accumulation at the SCLJ interface.^{5,7,9,24,38} However, in almost any case (except for the thinner film annealed at 600 °C) the influence of hydrogen treatment on the surface charge transfer efficiency is far less significant than that exerted on the charge separation efficiency, for which a maximum 4-fold enhancement is reached with the best performing ZFO₂₄₀@800 electrode after hydrogenation.

Bearing the above considerations in mind, we can go back to the photocurrent trends at 1.5 V vs. RHE reported in Figure 11.5 and deal with the discussion on how the observed PEC performance of ZFO photoanodes is affected by all investigated parameters. A first conclusion is that the poor crystallinity induced by the lower annealing temperature results in the very low bulk charge separation and surface charge injection efficiencies for all electrodes annealed at 600 °C, leading to the almost flat photocurrent as a function of the film thickness (Figure 11.5a). This is reasonably due to the presence of a huge amount of both bulk and surface defects in the less crystalline electrodes.

Annealing at higher temperature (800 °C) induces defects passivation as a consequence of the gain in film crystallinity according to XRPD analysis (Figure 11.2b), which results in a considerable improvement in charge injection efficiency at the SCLJ interface, for any film thickness, and in a minor enhancement in charge separation observable at low thickness only. Indeed, the lack of increase in η_{sep} with rising the annealing temperature, at high thickness, is also the reason for the photocurrent drop

observed among the pristine electrodes annealed at 800 °C, after the maximum value recorded at an intermediate thickness (Figure 11.5b). This behaviour can be reasonably ascribed to the progressive increase in bulk resistance to charge transport and/or to the decrease of the electric field in the space charge region with increasing thickness.³⁹ Despite this, an overall higher performance is shown by the more crystalline samples compared to the films series annealed at 600 °C, as a result of the enhancement primarily in η_{inj} and secondly in η_{sep} , with rising the annealing temperature.

Different results were obtained with ZFO NR photoanodes, for which the relatively lower 600 °C annealing temperature led to an optimized performance. Indeed, while high annealing temperatures proved effective in improving the surface charge injection properties of ZFO films regardless of their morphology, a higher cation disorder induced by low annealing temperatures, instead of a high film crystallinity, was found to optimize the charge transport properties of ZFO NR electrodes. The comparison of the current results with those on ZFO NR films allows therefore to shed light onto the relative weight of the spinel inversion degree and of the film crystallinity onto the PEC performance of ZFO photoanodes, depending on the film morphology. In the case of a planar morphology, not only the surface charge injection, but also the charge separation efficiency is promoted by a higher film crystallinity. This suggests that, upon varying the annealing temperature, the crystalline domain size exerts a dominant role over the cation disorder in determining the charge transport properties of ZFO flat films, in stark contrast with the case of ZFO NR electrodes.

Hydrogenation of the films annealed at 600 °C does not provide any significant advantage to the final performance, due to the very low thickness exploitable in this case because of the poor crystallinity, which strongly limits photocurrent generation. In fact, an increase of both the charge separation and charge injection efficiencies was induced at a very low thickness only. On the other hand, the larger amount of charge carriers that should be in principle released by a thicker film, and which further increases after hydrogenation, may in turn lead to enhanced charge accumulation at the SCLJ, which can be responsible for the lack of improvement in both η_{sep} and η_{inj} , rather than to a higher photocurrent production.

Conversely, much more beneficial is the application of hydrogen treatment to the more crystalline films annealed at 800 °C, where the optimization of the charge separation in the thicker photoactive layer allows to take advantage of its superior absorption capability for the actual exploitation of a larger amount of photogenerated couples. Therefore, the combined use of the higher 800 °C annealing temperature for effective surface charge injection and of hydrogen doping for an improved bulk charge transport is essential to maximize the performance of ZFO compact films with flat morphology.

11.6 Conclusions

The first systematic investigation is here reported on the effects of the interplay between annealing temperature, film thickness and hydrogen reducing treatment onto the PEC performance of ZFO flat films as photoanodes for water oxidation, where the nanostructure does not play any role. Optically transparent electrodes with a planar morphology were easily synthesized through a rapid synthesis method allowing to obtain films of a wide thickness range in a one-step spin-coating deposition. The prepared films were ideal model to shed light onto the correlation between each of the investigated parameters and the final photoactivity, without the influence of any morphological factor specific of 1D nanostructures (such as channelized electron transport, relatively shorter radial distance for minority charge carriers to the SCLJ and larger surface area).

IMPS measurements performed *in operando* allowed to identify the peculiar role of the annealing temperature and hydrogen treatment separately onto the bulk charge separation and surface charge injection processes, as a function of the film thickness. Moreover, a comparison with the results obtained with ZFO nanorod electrodes revealed that the correlation between structural parameters, *i.e.* the film crystallinity and the spinel inversion degree, and the resulting PEC performance is controlled by the film morphology.

We found that, unlike for ZFO NR films exhibiting superior charge transport properties in the presence of a high cation disorder, a high film crystallinity is favourable for the performance of ZFO flat films in pristine form, as well as for effectively enhanced bulk charge separation upon hydrogenation. The verified highest synergism between the superior material crystallinity at high temperature and hydrogenation efficiency allowed to exploit the thickest photoactive layers for maximized photocurrent generation.

The complementarity of the roles played by the here optimized synthetic parameters should be exploited in the construction of efficient ZFO photoanodes to be implemented in PEC tandem cells, where planar geometry is an important requirement for a high optical film transparency.

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Chapter 12

Final remarks

The work presented in this PhD thesis aimed at investigating the photoelectrochemical (PEC) properties of three main classes of ternary metal oxides as promising photoanodes for direct solar water splitting in tandem cell devices. As extensively described in Chapter 3, multinary, *e.g.* ternary and quaternary, oxides have emerged as attractive alternatives to the well-established binary oxides (*e.g.* TiO_2 , ZnO , WO_3),¹ since they offer a wider tunability of the electronic structures thanks to the much larger variability of the composition when two or more *d*-block transition metals are involved.

Aiming at increasing the theoretical conversion efficiency of the final tandem PEC device, where two complementary photoelectrodes are stacked to maximize solar photons absorption, optically transparent photoanodes of the examined materials were preferred to nanostructured films.² Indeed, the nanostructuring strategy, although proves effective in overcoming charge carrier transport limitations, shows strong limitations in guaranteeing an efficient transmission of the photons not absorbed by the top photoanode to the bottom photocathode, due to severe light scattering effects.^{3,4}

To address this issue, a simple and easily processable synthetic approach was adopted here, based on the spin coating technique, allowing to prepare the different metal oxide electrodes with minimum light scattering, thanks to the planar structure and optical transparency in the wavelength region outside of the material band gap. Moreover, the use of flat (*i.e.*, non-nanostructured) films provided a convenient platform for a thorough study of the intrinsic limitations of each of the examined materials in the absence of any morphological factor dictated by nanostructured architectures (such as channelized electron transport and/or reduced distance for minority charge carriers to reach the semiconductor/electrolyte interface), under a careful control of the film thickness.

However, this choice implies quite a few issues not only to the bulk charge transport efficiency but also to the yield of charge transfer at the electrode/electrolyte interface, likely due to the relatively low surface area of planar electrodes, which need to be overcome for the engineering of high-performing overall PEC devices.

In this thesis, different optimization strategies have been adopted in order to mitigate several of these intrinsic bottlenecks to the PEC activity of the photoanode components under study.

Sensitizing effects of BiVO₄ in the TiO₂/BiVO₄ heterojunction

Firstly focusing on BiVO₄ (band gap of *ca.* 2.4 eV), which is currently one of the most promising photoanode materials¹ being efficient, stable and visible light active, Chapter 5 provides an intriguing example of its exploitation as visible light sensitizer towards wide band gap materials, such as pioneering TiO₂. The coupling of the two materials offers the chance to combine the appealing properties of each of them, namely the excellent photoactivity of BiVO₄ under visible solar irradiation and the more negative conduction band (CB) potential of TiO₂ (-0.16 V vs. NHE),⁵ suitable for proton reduction.

Combined photoelectrochemical and photocatalytic reduction test studies demonstrated the effectiveness of this system in producing highly reductive electrons through TiO₂ sensitization towards visible light, despite the unfavourable relative band edge alignment of the two isolated oxides. Indeed, the observed photoactivity under visible light can be explained by the occurrence either of a counterintuitive up-hill electron injection mechanism or of a Type II band alignment.

Linear sweep voltammetry analyses carried out under selective excitation of BiVO₄ with visible light ($\lambda > 420$ nm) evidenced that TiO₂ is photoactive in this spectral region only in the combined system, while a negligible photocurrent response characterizes its pure form (without BiVO₄). Evidence for the hot electron injection mechanism was gathered through incident photon to current efficiency (IPCE) measurements showing that TiO₂, which is active up to 410 nm consistently with its 3.2 eV band gap, is successfully sensitized to visible light up to 490 nm after being coupled with BiVO₄, which is instead active up to 520 nm as an isolate component. This suggests that visible light excited electrons in BiVO₄ need a small extra amount of energy to be injected into the more negative TiO₂ CB.

Photocatalytic reduction tests of methyl viologen as molecular probe revealed the visible light-induced superior photocatalytic activity of the TiO₂/BiVO₄ heterojunction with respect to the individual components as well as to different semiconductor systems tested in the same conditions such as the well-established WO₃/BiVO₄ heterojunction, known for ensuring an excellent charge separation. Thus, both photocatalytic and PEC tests account for the effective occurrence of a visible light-induced electron injection process from the CB of BiVO₄ to the CB of TiO₂, resulting in TiO₂ sensitization and production of highly reductive electrons under visible light irradiation.

Further efforts in this direction would concern the increase of the electron transfer yield occurring in the whole system for exploitation of the TiO₂/BiVO₄ heterojunction in overall water splitting under visible light, without the application of any external bias.⁶

Role of Mo⁶⁺ doping on the bulk and interfacial properties of BiVO₄ photoanodes

The role of molybdenum doping onto the bulk and interfacial charge transfer properties of BiVO₄ photoanodes was investigated through two different synthetic approaches, by varying the dopant content and changing the species undergoing oxidation.

Hexavalent metal ions (*e.g.*, Mo⁶⁺ and W⁶⁺) as dopants for BiVO₄ have been often reported to act as shallow donors able to increase the majority charge carrier density and, consequently, the electron conductivity in the material bulk, thus providing an effective strategy to mitigate the poor electron transport properties of this oxide material. However, recent evidences of surface states-related issues in BiVO₄, identified with the V⁵⁺/V⁴⁺ reductive process and consequent creation of sites acting as traps for the photogenerated carriers,⁷ have been accompanied by findings reporting doping with W⁶⁺ ions as an effective surface states passivation strategy for BiVO₄-based materials.⁸

The work presented in Chapter 6 concerns a preliminary screening of several Mo⁶⁺ doping contents in BiVO₄ electrodes prepared as monolayer films by means of an advantageous and time saving synthetic approach, employing polyvinyl alcohol (PVA) as thickening agent of the oxide precursor solutions.

The results of photocurrent measurements under simulated AM 1.5 G light and IPCE tests under monochromatic irradiation account for a *ca.* two order magnitude enhancement of the performance in water oxidation attained with the optimum 3 at% dopant concentration with respect to pure BiVO₄ electrodes. On the other hand, the same analyses carried out in the presence of the sulfite hole scavenger revealed an opposite trend of performance as a function of the doping degree. In this case, the much lower increase in activity observed upon the optimal 0.5 at% Mo⁶⁺ incorporation compared to the previous case should be entirely ascribed to the comparable gain in electrochemical active surface area (ECSA) of the doped films with respect to the undoped one, rather than to effectively improved electronic properties of the material.

The observed behaviour was elucidated by electrochemical impedance spectroscopy and Mott-Schottky analysis. While, in pure water oxidation, the doped electrodes can benefit from both an increased donor density in the bulk and a progressive decrease in interfacial charge transfer resistance with increasing Mo⁶⁺ doping, the oxidation reaction of sulfite is hampered by a progressively higher resistance to interfacial charge transfer induced by an increasing dopant incorporation, which suggests the occurrence of specific interactions between the dopant and the electron donor species in solution.

On the other hand, the coupling of the investigated photoanodes with a NiFeO_x co-catalyst pointed out the beneficial effects, in terms of enhanced electron conductivity, induced by an increasing Mo⁶⁺ incorporation into the bulk charge transport properties of the BiVO₄ material.

The study presented in Chapter 7 provides more insight into the observed peculiar behaviour depending on the oxidizable substrate in solution. In this case, a multilayer

films study with two main representative Mo^{6+} doping contents (0.5 at% and 3 at%) was performed. The electrodes were prepared through a multistep spin coating deposition of different oxide precursor solutions not containing PVA. Unexpectedly, this proved greatly advantageous in terms of both film transparency and performance, compared to the previously employed synthetic approach. Indeed, the major light harvesting capability attained with the multilayer strategy also resulted in an up to 5-fold increase in PEC performance compared to the previous PVA-containing monolayer films, thus overcoming the limits of charge transport across thicker photoactive layers. The higher 3 at% dopant content proved to be again the best performing one for pure water oxidation, ensuring a *ca.* 5-fold improvement in photocurrent at 1.23 V vs. RHE when employed in the optimum 8 layers electrode, with respect to the corresponding (PVA free) pure film.

The well-established effect of the hexavalent *n*-type dopant in improving the bulk electron transport properties of BiVO_4 was definitely demonstrated by the attainment of higher photocurrent densities in the less favourable front- compared to back-side irradiation configuration, thanks to the increased donor density attained upon rising the dopant content. Moreover, photoelectrochemical impedance spectroscopy (PEIS) analysis allowed to identify the additional role of Mo^{6+} , *i.e.* concerning the passivation of detrimental $\text{V}^{5+}/\text{V}^{4+}$ surface traps, as primary function of the dopant in favouring water oxidation.

Evidence of this phenomenon was provided by the suppression of the build-up of the surface state capacitance upon Mo^{6+} incorporation. On the other hand, this primary role of the adopted doping strategy on the surface chemistry of BiVO_4 has an almost negligible impact on the much easier oxidation of the sulfite hole scavenger, when the detrimental accumulation of surface holes at the photoanode/electrolyte interface can be ruled out. This study proved thus successful in ascertaining the important role of Mo^{6+} dopant onto the surface-related issues of BiVO_4 photoanodes for water oxidation, in addition to the well-known effect on the bulk charge transport properties.

Future work on this topic would consist in the deposition of a suitable co-catalyst acting as passivation layer,⁹ *i.e.* capable of further suppressing surface recombination, to be combined with the effects of Mo doping on both the bulk and surface properties of BiVO_4 .

Copper tungstate-based photoanode materials

In Chapter 8 the ultrafast charge carrier recombination limiting the performance of CuWO_4 (band gap of *ca.* 2.3 eV) photoanode, which emerged as visible light active and more stable oxide alternative to the wide band gap WO_3 , has been investigated for the first time by means of transient absorption (TA) spectroscopy. The results of this analysis, in combination with those of a both electrochemical and photochromic characterization, pointed out the presence of intra-gap states, acting as electron traps and thus responsible for a severe internal charge recombination which strongly limits the observed

performance. These trap states, detected by cyclovoltammetry analysis to be located *ca.* 0.5–1.0 V_{RHE} below the empty Cu 3d band edge, upon ultrafast photoexcitation at 400 nm are responsible for a broad 500 nm-centered photoinduced absorption band extending over the entire visible spectral range and corresponding to electron promotion to an energetically higher W 5d-based CB. However, this TA signal was found to halve in *ca.* 1 ps so that the amount of the photogenerated charge carriers that survive for more than 1 ns, thus able to take part to the PEC reaction, represents only a small fraction.

Global analysis^{10,11} of the ΔA transient signal evolution, carried out over the entire probe wavelength range, allowed to deconvolve the overall signal into three individual spectral contributions and corresponding kinetic components, which are associated with the recombination of electrons in the mid-gap states with valence band holes, and characterized by different time constants. Only a small contribution is associated to the longest time constant of *ca.* 1 ns.

Finally, a band energy model for CuWO_4 was built in the light of the results of the here reported electrochemical and TA analysis, which corroborates the band structure of CuWO_4 recently calculated¹² by treating this material as a Mott–Hubbard magnetic insulator, analogously to hematite.

In Chapter 9 a 50% Mo for W substitution strategy in CuWO_4 was adopted with the aim to further increase the long-wavelength photons exploitation capability of the copper tungstate photoanode material. According to previous calculations, a narrowing of the band gap should be induced by Mo incorporation, due to a shift to lower energy of the CB edge with respect to that of the pure CuWO_4 material.¹³

The impact of molybdenum for tungsten substitution in CuWO_4 photoanodes was investigated in relation to the thickness of the photoactive layer in multilayer films. The effectively enhanced visible light-induced photoactivity, as a result of the extended absorption capability compared to pure CuWO_4 electrodes, was demonstrated by a thorough PEC characterization. Specifically, the systematic investigation on the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ multilayer films evidenced a wavelength-dependent performance trend, where long-wavelength photons in the visible region are better exploited for longer optical paths within the thicker photoactive films. Consequently, an extended visible light photoactivity was observed, compared to that of the pure CuWO_4 material, up to 650 nm, *i.e.* corresponding to a 2.0 eV band gap in agreement with theoretical predictions.

Furthermore, the identification of NaNO_2 as a suitable hole scavenger, able to ensure enhanced photocurrent generation compared to pure water oxidation while minimizing dark currents, allowed to elucidate the role of Mo for W substitution also on the charge separation in the bulk and charge injection efficiencies at the film/electrolyte interface. An increased efficiency of the photoproduced charge separation, representing the main limiting factor to the performance of copper tungstate-based materials, was found as additional benefit of the adopted doping strategy that contributed to the enhanced photoactivity observed with the $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ material. However, a lower charge

injection efficiency was recorded for the quaternary oxide with respect to pure copper tungstate, as side-effect of the employed metal ions substitution, possibly due to the introduction of new surface trap states.

Future work will be devoted in mitigating this adverse effect to further enhance the gain in photoactivity achievable with $\text{CuW}_{0.5}\text{Mo}_{0.5}\text{O}_4$ with respect to pure CuWO_4 . Moreover, the integration of CuWO_4 -based electrodes with a suitable electrocatalyst¹⁴ to bypass the charge carrier recombination at mid-gap surface states, thus improving the overall PEC water oxidation efficiency, will be part of further research work.

Key factors boosting the performance of ZnFe_2O_4 flat films

Finally, Chapter 10 and 11 report about the optimization of ZnFe_2O_4 (ZFO) flat films photoanodes prepared through two different sol-gel synthetic approaches, as ideal models to investigate the effects induced by a post-synthesis reductive treatment under hydrogen atmosphere, on the intrinsic electronic properties of this material.

ZFO, belonging to the class of spinel ferrites, has emerged as photoactive material thanks to its narrow band gap of 2.0 eV, as well as for its remarkable thermal and chemical stability.¹⁵ In a previous study, the leading role of spinel inversion degree, instead of film crystallinity, in improving the photogenerated charge transport and separation, was detected in H_2 treated-ZFO photoanodes with a nanorod (NR) morphology.¹⁶ However, the relationship between the synthesis annealing temperature, which is in turn strictly correlated to the above-cited structural parameters, and the effectiveness of hydrogen treatment was not investigated.

For this reason, one of the goals of this PhD thesis was to study the intrinsic influence of the hydrogen treatment on the fate of the photogenerated charges as a function of both the annealing temperature and the film thickness, in the absence of any morphological factor dictated by a nanostructured architecture.

In the preliminary study presented in Chapter 10, the effect of the synthesis temperature on the PEC performance of both pristine and H_2 treated ZFO films was examined. The analysis was carried out by keeping the film thickness constant to focus on the effect of four different annealing temperatures (in the 500–800 °C range) on a multilayer compact structure synthesized by means of an EDTA-based sol gel approach.³ However, the EDTA-based synthetic strategy, while allowing to synthesize pure-phase materials, proved unsuccessful in producing highly performant ZFO photoanodes.

Indeed, although the use of the higher annealing temperature was advantageous in terms of activity among the pristine films, hydrogenation applied to these compact electrodes proved ineffective in further improving the performance of such highly crystalline films, while only inducing appreciable photocurrent enhancement on the poorly crystalline electrodes synthesized at the lower temperatures.¹⁷ Moreover, this study resulted to be somehow limited by the possibility to investigate the combined effects of the annealing temperature and the hydrogen treatment on the PEC performance

of only relatively thin (*ca.* 100 nm thick) ZFO electrodes, due to solubility issues of the precursors.

Therefore, a modified EDTA-free sol-gel synthesis with a higher precursor concentration of the spin-coated solutions was later adopted, which allowed us to conduct a thorough investigation over a wide range of thickness of ZFO flat films, prepared in a single spin-coating deposition step.

As reported in Chapter 11, a quite different picture in terms of PEC performance enhancement upon hydrogenation, as a function of the annealing temperature (600 °C or 800 °C), was observed compared to the study on EDTA-containing films. In fact, the already higher photocurrent values recorded with the more crystalline films annealed at 800 °C, likely due to a lower charge transfer resistance, were further enhanced by the hydrogen treatment, at a larger extent with increasing film thickness.

The origin of this remarkable result, accounting for a better exploited synergism between the material crystallinity and the beneficial effect of hydrogenation in the case of thicker electrodes, was elucidated by decoupling the effects of each of the investigated parameters on the charge separation in the bulk and charge injection efficiency at the film surface.

In this regard, analyses were conducted either by employing a suitable hole scavenger or in pure water oxidation conditions by means of intensity modulated photocurrent spectroscopy (IMPS). The so-obtained results evidence that, while the use of a higher annealing temperature exerts a major impact on the charge injection properties at the ZFO film surface, likely through defects passivation induced by the increased film crystallinity, the hydrogen treatment plays its main role in improving the bulk charge separation, to a largely different extent depending on the film thickness. The latter behaviour well reflects the *n*-type character of H₂ doping, which is supposed to enhance the majority carrier density of the film through the introduction of oxygen vacancies.¹⁸ The verified synergism between the material crystallinity and the hydrogenation efficiency allows to take advantage of a superior charge separation in thicker photoactive layers, which are in principle capable of a larger photoinduced charge carrier generation, to maximize the performance of ZFO films with flat morphology.

The leading role of crystallinity in ZFO flat films, both in promoting charge separation upon hydrogenation and in the passivation of surface defects, is different from what observed with ZFO NR electrodes, where cation disorder was found to play a dominant part. Overall, the different behaviour observed in these two cases of study shed light on the peculiar impact on PEC performance of the investigated structural parameters (*i.e.* film crystallinity and cation disorder) depending on the ZFO film morphology.

Further optimization of ZFO compact flat films could be achieved by exploring new strategies of doping in line with the research efforts made on hematite photoanodes,¹⁹ and through a fine control of oxygen vacancies, with the final aim of further reducing the bulk recombination losses which severely limit the recorded photocurrent. Moreover, the

loading of a carefully selected co-catalyst overlayer may help in further mitigating surface recombination, in addition to reducing the water oxidation overpotential.¹⁵

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List of scientific contributions

Publications

1. I. Grigioni,[‡] A. Polo,[‡] M. V. Dozzi, L. Ganzer, B. Bozzini, G. Cerullo, Elena Selli, “Ultrafast Charge Carrier Dynamics in CuWO₄ Photoanodes”, *J. Phys. Chem. C* **2021**, 125, 5692–5699.
2. A. Polo, C. Nomellini, I. Grigioni, M. V. Dozzi, E. Selli, “Effective Visible Light Exploitation by Copper Molybdo-tungstate Photoanodes”, *ACS Appl. Energy Mater.* **2020**, 3, 6956–6964.
3. A. Polo*, C. R. Lhermitte, M. V. Dozzi, E. Selli, K. Sivula, “Hydrogenation of ZnFe₂O₄ Flat Films: Effects of the Pre-Annealing Temperature on the Photoanodes Efficiency for Water Oxidation”, *Surfaces* **2020**, 3, 93–104.
4. C. R. Lhermitte, A. Polo, L. Yao, F. A. Boudoire, N. Guijarro, K. Sivula, “Generalized Synthesis to Produce Transparent Thin Films of Ternary Metal Oxide Photoelectrodes”, *ChemSusChem* **2020**, 13, 3645–3653.
5. A. Polo, I. Grigioni, M. V. Dozzi, E. Selli, “Sensitizing effects of BiVO₄ and visible light induced production of highly reductive electrons in the TiO₂/BiVO₄ heterojunction”, *Catalysis Today* **2020**, 340, 19–25.
6. L. Bolzonello, A. Polo, A. Volpato, E. Meneghin, M. Cordaro, M. Trapani, M. Fortino, A. Pedone, M. A. Castriciano, E. Collini, “Two-Dimensional Electronic Spectroscopy Reveals Dynamics and Mechanisms of Solvent-Driven Inertial Relaxation in Polar BODIPY Dyes”, *J. Phys. Chem. Lett.* **2018**, 9, 1079–1085.
7. A. Polo, I. Grigioni, M. Magni, A. Facibeni, M. V. Dozzi, E. Selli, “Unravelling the bulk and interfacial charge transfer effects of molybdenum doping in BiVO₄ photoanodes”, *submitted*.
8. A. Polo, F. A. Boudoire, C. R. Lhermitte, Y. Liu, N. Guijarro, M. V. Dozzi, E. Selli, K. Sivula, “Key factors boosting the performance of ZnFe₂O₄ flat photoanodes for solar water oxidation”, *to be submitted*.

9. A. Polo, I. Grigioni, F. Boudoire, C. R. Lhermitte, K. Sivula, M. V. Dozzi, E. Selli, “Mo⁶⁺ doping-induced effects in BiVO₄ multilayer films photoanodes”, *in preparation*.

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Communications

1. A. Polo, F. A. Boudoire, C. R. J. Lhermitte, N. Guijarro, P. A. Schouwink, M. V. Dozzi, K. Sivula, “Engineering of performance-boosting hydrogenation on ZnFe_2O_4 photoanodes: effects of thickness and thermal annealing temperature”, 2nd Enerchem Congress Oral presentation, Padova (Italy), 12–14 February 2020. **Oral presentation.**
2. A. Polo, C. Nomellini, I. Grigioni, M. V. Dozzi, E. Selli, “Novel ternary metal oxide-based materials for extended visible-light photoactivity: the case of molybdenum doped copper tungstate”, 7th International Conference on Semiconductor Photochemistry (SP7), Milan (Italy), 11–14 September 2019. **Short oral and poster presentations.**
3. A. Polo, C. Nomellini, I. Grigioni, M. V. Dozzi, E. Selli, “ $\text{CuW}_{1-x}\text{Mo}_x\text{O}_4$ as efficient visible light harvester for photoelectrochemical water oxidation”, UK-Italian joint meeting on Photochemistry 2019, Lipari (Italy), 24–26 June 2019. **Poster presentation.**
4. A. Polo, I. Grigioni, M. V. Dozzi, E. Selli, “Photo(electro)catalytic characterization of Molybdenum Doped BiVO_4 -based Photoanodes for Oxygen Evolution”, 10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA 10), Almeria (Spain), 8–14 June 2018. **Short oral and poster presentations.**
5. A. Polo, I. Grigioni, M. V. Dozzi, E. Selli, “Molybdenum Doped BiVO_4 Photoanodes for Oxygen Evolution”, 1st EnerChem School of the Italian Chemical Society (SCI), Firenze (Italy), 20–24 February 2018. **Poster presentation.**
6. A. Polo, I. Grigioni, M. V. Dozzi, E. Selli, “ $\text{TiO}_2/\text{BiVO}_4$ Heterojunction for Photoelectrochemical Water Splitting”, Italian Photochemistry Meeting (IPM) 2017, Perugia (Italy), 14–16 December 2017. **Oral presentation.**
7. A. Polo, I. Grigioni, M. V. Dozzi, E. Selli, “ $\text{TiO}_2/\text{BiVO}_4$ Heterojunction for Photoelectrochemical Water Splitting”, XXVI National Congress of the Italian Chemical Society (SCI), Paestum (Italy), 10–14 September 2017. **Poster presentation.** Winner of the “Young Physico-Chemist Award 2017”.

Research activity abroad

FEBRUARY 2019 – SEPTEMBER 2019

Laboratory for Molecular Engineering of Optoelectronic Nanomaterials (LIMNO), Prof. Kevin Sivula, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland.

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