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Review

Updates on tracking charge carriers in $BiVO_4$- and $CuWO_4$-based photoanodes

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Semiconductor ternary metal oxides (TMOs) are ideal candidates as photoanode materials for the water oxidation reaction. The dynamics of photogenerated charge carriers dictates the efficiency of photoelectrocatalytic (PEC) systems depending on both internal (inside the photoactive material) and surface (mainly due to reaction kinetics) key issues. This paper presents recent results attained with up-to-date characterization tools to decouple bulk and surface charge recombination in relation to the synthetic strategies implemented to address PEC efficiency losses in TMO photoanodes, with particular focus on $BiVO_4$- and $CuWO_4$-based materials. Key aspects and the perspectives in the field are finally highlighted.

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Requirements for efficient photoelectrodes in photoelectrocatalytic applications

Ternary metal oxide (TMO) semiconductors are ideal candidates as photoactive materials to fabricate photoanodes for the oxygen evolution reaction (OER) in photoelectrocatalytic (PEC) applications. Indeed, ideal PEC materials require that the electron and hole charge carriers produced upon band gap excitation are mobile enough to efficiently reach the semiconductor surface, where they run reductive (e.g. hydrogen evolution) and oxidative (e.g. OER) reactions in competition with recombination processes [1]. TMO semiconductors generally have conduction band (CB) and valence band (VB) edges straddling the water reduction and oxidation potentials, as required in PEC water splitting [2]. Most importantly, their VB is at a potential more positive than the OER potential, which facilitates overcoming the kinetic barriers of this reaction and makes photogenerated holes more prone to oxidize water than the semiconductor metal cations. Consequently, TMO are photostable in aqueous media under the harsh OER conditions. They are composed of inexpensive and abundant elements and may also be synthesized on a large scale through easy solution-based and low-temperature processes, therefore supporting TMOs as a sustainable choice of materials for PEC practical applications.

Early PEC studies mainly focused on binary metal oxides (e.g. TiO_2, WO_3, and ZnO). However, due to their highly ionic character, their band gaps are too large for efficient solar energy exploitation. Band gap narrowing strategies (e.g. doping) proved unsuccessful, mainly because they introduce lattice defects acting as undesired charge carrier recombination centers. On the other hand, the presence of two or three different metal ions in ternary and quaternary semiconductor oxides, respectively, allows tuning their electronic structure, thus impacting on their PEC properties [3].

This review paper focuses on recent studies employing up-to-date time-resolved optical spectroscopic and electrochemical techniques to shed light on the photogenerated charge carrier dynamics (from their formation to internal and interface transfer or recombination) driving PEC processes, in relation to the PEC performance improvement of TMO photoanodes by different synthetic strategies. The main exemplary TMO materials discussed herein are bismuth vanadate ($BiVO_4$) and copper tungstate ($CuWO_4$).

Charge carrier recombination versus photoelectrocatalytic performance

Recombination between photopromoted electrons and holes, occurring either in the bulk or at the surface of photoactive materials, is the main loss of excitation

energy in PEC processes and undermines their efficiency [4] (Figure 1). Bulk recombination is influenced by the semiconductor crystallinity and by the presence of discontinuity sites (e.g. defects and distortion of the crystal lattice or impurities), which facilitate electron–hole annihilation. Surface recombination occurs at sites where the crystal lattice abruptly ends. Lattice truncation, in fact, results in dangling bonds and defects, which can act as charge traps. The extremely slow interface reaction kinetics of the charge carriers (holes, for OER) leads to their accumulation at the surface, and this favors their concurrent surface recombination with photoexcited electrons [5].

In photoelectrocatalysis, the application of an external electrical bias polarizes the photoelectrode inducing the formation of a space charge layer, fostering charge separation. Nevertheless, photoactive materials with good charge carriers' mobility and intrinsically low charge recombination are required. Bulk (internal) recombination can be reduced by minimizing structural defects, increasing the crystallinity degree by using high-purity precursors, and designing nanostructured materials. Doping with heteroatoms, such as Mo in $BiVO_4$, can increase electron transport, leading to higher PEC performances [6], as also predicted by density functional theory (DFT) modeling [7], though a dopant excess may increase the recombination centers.

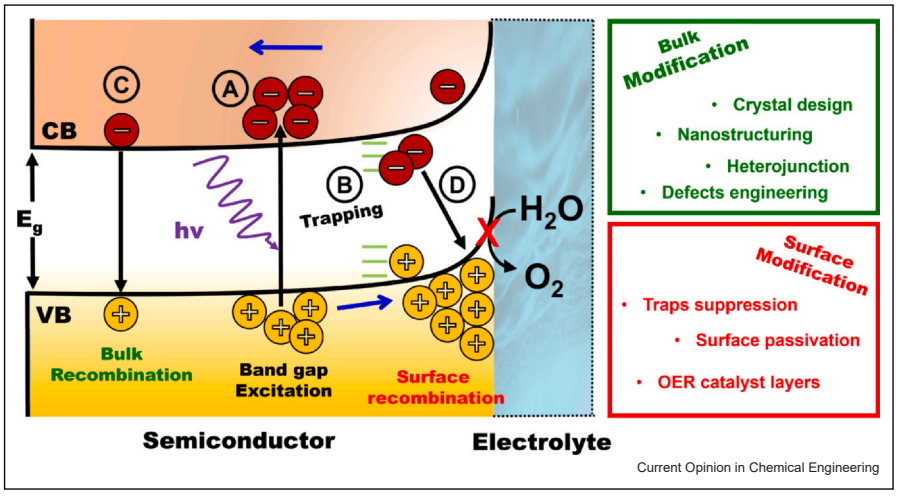
Deposition of passivation layers (e.g. TiO_2 and Al_2O_3) reduces surface trap states and surface charge recombination. The use of Co, Fe, Ni–based OER catalyst coatings, recently reviewed in Ref. [8], boosts the OER kinetics and dramatically increases the PEC performance of $BiVO_4$-based systems [5]. However, the deposition of co-catalysts on other semiconductor oxides (e.g. $CuWO_4$ and Fe_2O_3) is less effective [9]. Heterojunctions of semiconductor oxides with suitable band gap offsets (e.g. $WO_3/BiVO_4$ or $CuWO_4/BiVO_4$ photoanodes) allow better spatial charge separation and PEC activity [10–13].

PEC results attained with $BiVO_4$ materials prepared by several techniques, also in relation to efficiencies exhibited by emerging/alternative materials, can be compared in ref. [14]. Recent progress on metal oxides and other relevant materials, their scalability, and potential application in state-of-the-art PEC systems are overviewed in Ref. [15].

Monitoring the photoproduced charge dynamics by transient absorption and emission spectroscopies

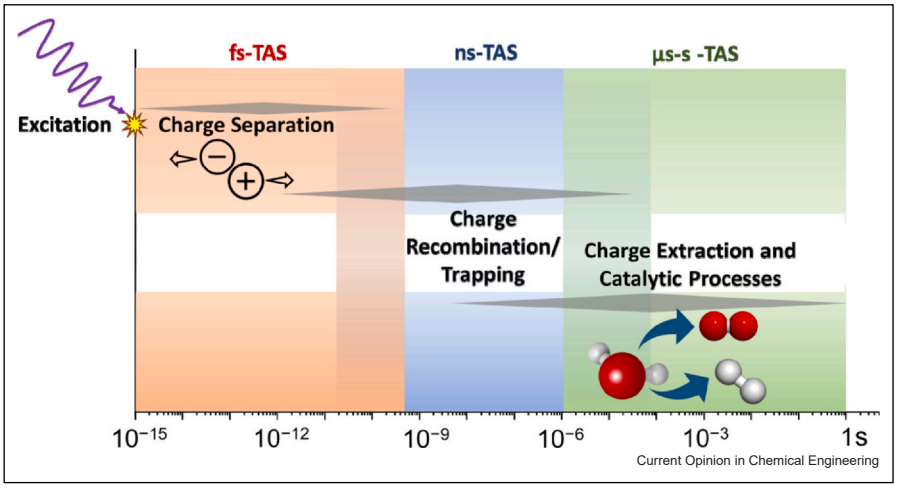
Advanced spectroscopic techniques such as time-resolved transient absorption (TAS) and photoluminescence (PL) spectroscopy provide valuable information on charge carriers' dynamics in semiconductor materials after photon absorption. Ultrafast TAS (Figure 2) in the fs regime allows to follow the early evolution of photogenerated charge carriers, leading to electron–hole recombination and trapping, while TAS signals acquisition at longer time scales (up to 10^{-6}–1 s time window) explores interface electron transfer.

Figure 1



Pathways involving charges photoproduced **(A)** in a semiconductor with band gap energy E_g, including trapping **(B)**, bulk **(C)**, and surface recombination **(D)**, in competition to diffusion (blue arrows) to their extraction sites. In photoanodes for OER, guided by the favorable band bending, electrons diffuse to the external circuit (left blue arrow) and holes diffuse to the electrode/electrolyte interface (right blue arrow). Because of the relatively slow four-hole process to oxygen evolution, surface hole accumulation is in competition with surface recombination. Bulk and surface modification strategies (right boxes) alleviate charge recombination.

Figure 2



Time domains of the processes involving photogenerated charge carriers in PEC systems. After photoexcitation, charge separation occurs in 10^{-15}–10^{-9} s, followed by charge trapping and recombination (10^{-12}–10^{-4} s), in competition with catalytic processes (10^{-6}–1 s).

By monitoring the absorption changes, from the UV–VIS to the near and mid-IR range occurring after pump excitation, the dynamics of different transient species can be studied, as long as their spectral signatures are carefully assigned in dedicated experiments. For example, photoproduced trapped holes in $BiVO_4$ mainly absorb up to 700 nm (with a maximum at 470 nm), while trapped electrons absorb above 900 nm [16]. TAS spectra of $CuWO_4$ are dominated by trapped electrons throughout the visible region [17]. Transient spectra can be deconvoluted into different components by global analysis [10,17].

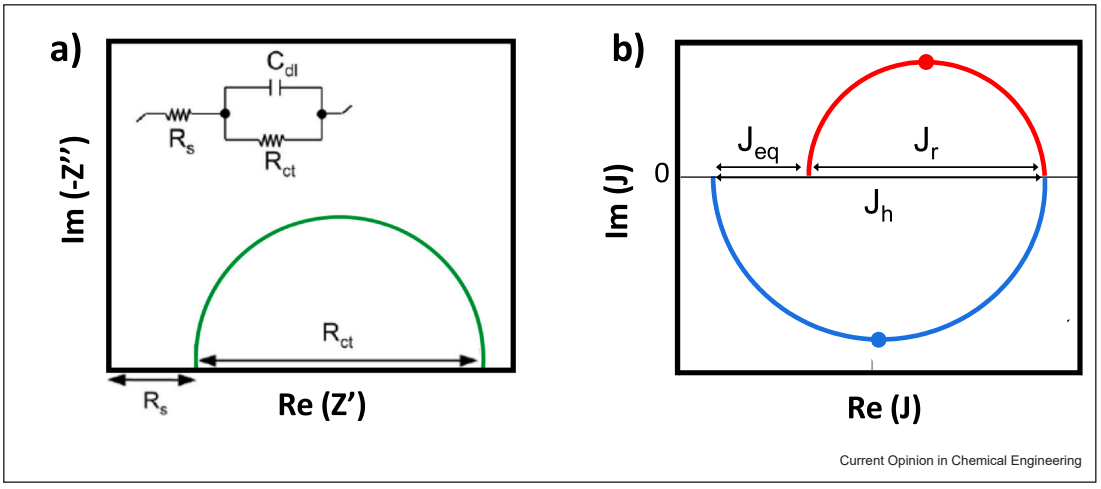
The charge carrier dynamics in metal oxide photoanodes from photoinduced charge generation (polaron formation and charge trapping, bulk and surface recombination, charge separation) to their extraction at the semiconductor/electrolyte interface, in relation to light-driven photocatalytic reactions, has been recently reviewed [18,19]. Information complementary to TAS is provided by PL and time-resolved PL, probing radiative electron–hole recombination [20].

However, TAS and PL experiments are unable to discern between bulk and surface charge carriers' recombination, unless well-designed experiments are put in place. For example, coupling $BiVO_4$ with WO_3 enabled to highlight the effect of the built-in electric field at the interface via *operando*-TAS and revealed that the heterojunction depopulates intra-bandgap states in $BiVO_4$ and enhances charge separation [10]. Similarly, the suppression of surface recombination by adopting suitable post-synthesis procedures enables to isolate bulk recombination processes, which can be selectively investigated by TAS and PL analyses [16,20].

Up-to-date photoelectrochemical techniques for tracking charge carrier recombination

The PEC performance of photoelectrodes is generally probed by linear sweep voltammetry in terms of photocurrent J versus applied potential V curves. PEC measurements in the presence of hole scavengers more easily oxidizable than water (e.g. H_2O_2 or Na_2SO_3) may allow decoupling the contributions of the electrodes' bulk and surface processes on the overall PEC performance and the calculation of the photogenerated charge separation efficiency (η_{sep}) in the bulk and the minority charge carrier (i.e. holes) injection efficiency at the electrode/electrolyte interface (η_{inj}) [21]. However, the so-calculated η_{sep} and η_{inj} values may not strictly reflect water oxidation conditions because the sacrificial redox agents involved in the electrochemical reaction at the film/electrolyte interface can affect the semiconductor band bending and charge accumulation. More reliable information is provided by intensity-modulated photocurrent spectroscopy (IMPS), a powerful tool operating in the frequency domain, allowing to unequivocally decouple *operando* the bulk and surface contributions in photoanodes by their respective time constants and in the absence of sacrificial species. At difference to electrochemical impedance spectroscopy (EIS), widely employed in semiconductor materials characterization [22], which probes the complex response of an electrode to a sinusoidal modulation of the applied potential over a wide frequency range, IMPS takes advantage of the modulation of the light intensity to modulate the surface concentration of the photogenerated carriers. Moreover, EIS data fitting is based on the identification of suitable equivalent electrical circuits reproducing the basic electronic processes occurring inside the electrode under

Figure 3



(a) EIS data fitted by the Randles equivalent circuit, simulating the elements related to charge accumulation (capacitance, C) and charge recombination and transfer (resistances, R) inside the electrode. **(b)** IMPS data represented as a Nyquist plot of the complex photocurrent at a given applied potential. The negative semicircle (blue line) is associated to the charge transport in the bulk, and its diameter indicates the magnitude of the bulk photocurrent J_h in the absence of surface recombination. The positive semicircle (red line) is representative of surface recombination; its amplitude indicates the photocurrent loss J_r due to surface charge recombination. J_{eq} is the diferrence between J_h and J_r.

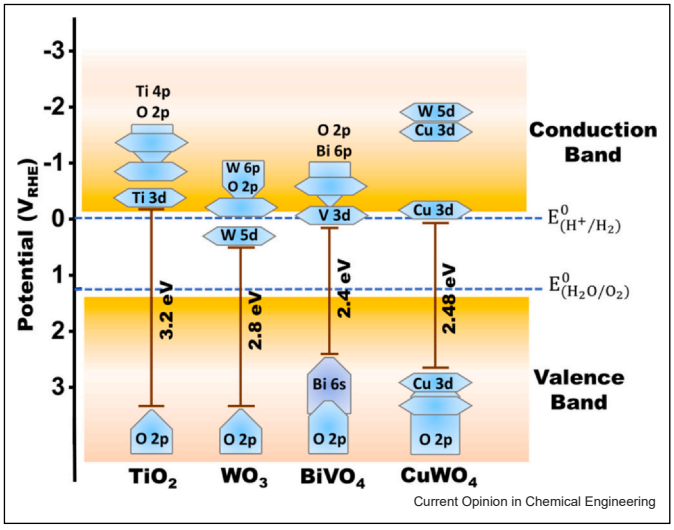
operating conditions (see Figure 3a). Otherwise, IMPS data are generally represented as a Nyquist plot of the complex photocurrent response at a certain applied potential, typically composed of two semicircles (see Figure 3b) [23]. By combining the parameters calculated from IMPS profiles (J_h and J_r) in relation to the maximum theoretical current density J_{abs} of the material, both charge separation and charge injection efficiencies can be calculated under true operation conditions [24,25].

Finally, recent progress in advanced atomic force microscopy–based techniques, such as the spatially resolved surface photovoltage (SRSPV) technique [26], allows to address the challenges arising from low concentration of surface charges and spatial heterogeneity. Employing a nanosized conducting tip to measure the local surface photovoltage by extracting charges in the photoinduced surface potential, the photogenerated charge distribution on a single micrometric particle can be directly mapped, and the driving force of charge separation at the nanoscale can be quantitatively determined. This type of analysis is particularly suitable to investigate charge distribution in faceted materials and has been successfully employed to visualize photogenerated electron and hole separation in faceted $BiVO_4$ crystals [27,28].

Recent advances in $BiVO_4$-based photoanodes

Bismuth vanadate is an extremely promising TMO for PEC water splitting due to its suitable band edge positions and a theoretical solar-to-hydrogen (STH) conversion of 9% (maximum photocurrent density of 7.5 mA cm^{-2}) [29]. Its most photoactive crystal structure (monoclinic scheelite) has a band gap of 2.4 eV due to the presence of a larger lattice distortion and a beneficial overlap between Bi 6 s and O 2p orbitals leading to a reduced band gap compared to the tetragonal scheelite structure (Figure 4). However, the indirect band gap of monoclinic scheelite $BiVO_4$ results in a low electron–hole separation due to poor carrier mobility and relatively short hole diffusion length. The slow

Figure 4



Band structure and location of selected binary and ternary metal oxide semiconductors compared to the water splitting redox potentials.

water oxidation kinetics favors $BiVO_4$ surface hole accumulation, which is followed by charge recombination and anodic photocorrosion with loss of vanadium ions, affecting the photoanode stability [30].

A series of effective strategies (see Figure 1) led to increasing the PEC performance of $BiVO_4$ [30] by enhancing light absorption, facilitating charge separation and transport, accelerating surface reactions, and improving its long-term stability [1,20,31]. Recent successful methods involve tailoring surface oxygen vacancies [32], surface passivation with atomic layer deposition oxide coatings (like HfO_2, leading to 800-hour stable PEC) [33], doping and coupling with other oxides [34].

Few performance-focused articles supplemented PEC results with advanced optical and electrochemical in-depth characterizations. Most reports build on the consolidated synthesis of worm-like nanostructured $BiVO_4$ through BiOI precursor films [35–37]. For example, the reduced surface charge trapping achieved with borate adsorption on BiOI-derived electrodes allows achieving a current density of 4.6 $mA{\cdot}cm^{-2}$ at 1.23 V_{RHE}. EIS supports the idea that boron surface doping enhances interfacial charge transfer [35], while IMPS analysis confirms the decrease of surface recombination kinetics due to surface modifications and provides information on the hole transfer process. Moreover, incorporating P-O interfacial bonds between $BiVO_4$ and the OER co-catalyst boosts the PEC performance to 6.73 $mA{\cdot}cm^{-2}$ at 1.23 V_{RHE} [36]. The drop of steady-state PL upon surface modification with OER catalyst reveals decreased radiative charge recombination, while ns-TAS indicates an increase in charge carriers lifetime.

Finally, Fe-N co-doping introduces N and Fe states in shallow bands at energies close to $BiVO_4$ VB and CB, respectively, without substantial changes in their positions. On the other hand, individual doping leads to deep states (at energies far from the VB and CB) acting as traps and recombination centers. ns-TAS indicates that both hole concentration and lifetime increase with Fe-N co-doping. EIS reveals a decrease in bulk charge resistance, while OER catalyst deposition decreases surface charge transfer resistance. These modifications lead to an impressive current density of 7.01 $mA{\cdot}cm^{-2}$ at 1.23 V versus RHE [37], highlighting the pivotal role of band and doping engineering in enhancing PEC properties of $BiVO_4$. Oxygen vacancies engineering is a further tool to boost the PEC activity; electron paramagnetic resonance is valuable to detect low-concentration ionized oxygen vacancies in oxides and can be combined with X-ray photoelectron spectroscopy, which is informative on surface defects [38].

Employing five complementary techniques to modulate the electronic occupancy of states associated with oxygen vacancies in $BiVO_4$ (at ca. 0.6 below the CB), a thermally activated electron detrapping process from these states was recently evidenced [39]. This band determines the kinetics of electron extraction from the oxide. Due to its low energy barrier, IR irradiation can excite bulk-trapped electrons, otherwise fated to recombine, thus improving $BiVO_4$ PEC performance at higher temperatures.

Crystal and morphology design of TMO is crucial to regulate defects, density of charge carriers and traps, and conductivity. Mo-doped $BiVO_4$ nanocrystals were recently reported to achieve optimal electron mobility supported by high charge carrier density and low charge transport resistance (revealed by EIS measurements). The outstanding PEC performance of 2.52 $mA{\cdot}cm^{-2}$ (comparable to BiOI-based $BiVO_4$) increased to 4.4 $mA{\cdot}cm^{-2}$ upon OER catalyst deposition [40]. A systematic structural, morphological, and PEC investigation outlined the multiple effects induced by Mo^{6+} doping in $BiVO_4$ photoanodes. TAS analysis (in the nano- to micro-second time scale) revealed a longer lifetime of photogenerated holes in optimized 3 atom % Mo-doped films [41].

Recent results provided evidence that $BiVO_4$ PEC performance increases also through coupling with other semiconductor oxides in a heterojunction and nanostructuring. The electric field build-in the $WO_3/BiVO_4$ heterojunctions due to the proper band alignment of the two oxides enhances charge separation, as demonstrated by recent ultrafast TAS investigations [10]. The advantage of this heterojunction can be fully exploited under front-side (i.e. through the $BiVO_4$ layer) irradiation, while direct photoexcitation of WO_3 leads to undesired charge recombination undermining the $WO_3/BiVO_4$ PEC performance [42]. This can be overcome by nanostructuring the WO_3 scaffold, thus ensuring a faster electron extraction from the heterojunction with an overall increase of the PEC performance [43].

A very recent *operando* photoinduced absorption spectroscopy and TAS study on faceted $BiVO_4$ indicates a 30-fold enhancement in the density of accumulated long-lived reactive holes and a fivefold increase in their lifetime in facet-engineered $BiVO_4$ photocatalyst particles with respect to unfaceted ones, which align well with the 70-fold enhancement observed in OER performance with faceting [44].

The comparison between the kinetics of electrochemical and PEC water oxidation on $BiVO_4$ photoanodes evidenced that current density versus the surface hole density plots obtained from *operando* optical absorption

analyses under electrochemical and PEC conditions are indistinguishable [45]. This points to the accumulation of a sufficient density of surface holes as the key step for both PEC and electrochemical water oxidation, which proceed through the same chemical-driven rate-determining step.

Recent advances in $CuWO_4$-based photoanodes

$CuWO_4$ has a relatively small band gap of 2.2 eV, which makes it suitable for light harvesting in the visible region with STH > 10%. Its reduced band gap compared to WO_3 (2.7 eV) is ascribed to an upward shift of the VB due to hybridization between the O 2p and Cu 3d orbitals (Figure 4). $CuWO_4$ has a triclinic crystal structure like monoclinic wolframite [46] and is more chemically stable at moderately basic pH compared to $BiVO_4$. Indeed, $CuWO_4$ electrodes exhibit PEC stability tests of several hours.

The composition of its CB is still under debate. Recent calculations evidence a narrow band originating from empty 3d levels at an energy gap of 2.1 eV from the VB, and a higher energy CB dominated by W 5d and Cu 3d states, ca. 5 eV above the VB edge [47]. Moreover, $CuWO_4$ is a Mott-Hubbard antiferromagnetic insulator-like Fe_2O_3; they are both characterized by low charge carriers' mobility, high charge-phonon coupling for holes, and short hole drift length. This translates into the poor photoproduced charge separation and PEC efficiency achieved so far with $CuWO_4$ electrodes, which can generate only 0.5 mA cm^{-2} at 1.23 V_{RHE} compared to the theoretical value (10 mA·cm^{-2}) and a photocurrent onset potential largely positive with respect to its flat band potential [9,48–50]. This is perfectly in line with the very fast (less than 1 ns) recombination dynamics of the charge carriers photogenerated in $CuWO_4$, recently acquired by fs-TAS analysis on transparent electrodes [17].

Recent progress in $CuWO_4$-based photoanodes are reviewed in Ref. [46]. The modest increase in PEC activity attained by either $CuWO_4$ faceting [49] or oxygen vacancies introduced by N_2 treatment [51] were attributed to increased charge separation, while yttrium doping produces a higher current density and, according to DFT calculations, a higher density of electronic states in the first CB [52]. N-doping of $CuWO_4$ in the presence of proper structure-directing agent was recently found to guarantee an extended visible light activation toward OER (up to ca. 540 nm), accompanied by a larger exposure of highly reactive (100) facets, thus affording noteworthy material stability and efficiency among the state-of-the-art $CuWO_4$-based photoanodes [53].

A recent IMPS analysis, in full agreement with the results attained with PEC measurements in the presence of hole scavenger, unequivocally demonstrates that the $CuWO_4$ performance is mainly limited by poor charge carrier separation efficiency η_{sep} within the material bulk, which undergoes a fourfold increase upon the 50 at % of molybdenum for tungsten substitution, without producing any significant change in the η_{inj} of the unmodified materials [11]. The attained η_{sep} enhancement has been related to the increased electrons concentration in 50 at% Mo-substituted $CuWO_4$ with respect to pure $CuWO_4$, with a consequent improved material conductivity, also evidenced by Mott–Schottky analyses reported in other studies on similar systems [54].

Conclusions and critical perspectives

The recently developed up-to-date techniques, together with classical analyses, provide valuable information on the intrinsic properties of PEC materials and crucial indications on the routes to follow for improving their PEC performance. The main critical issue for relatively well-performing $BiVO_4$ photoanodes consists in hole accumulation at the semiconductor/electrolyte solution interface, with accumulated holes undergoing severe recombination with photoexcited electrons in competition with interface electron transfer initiating PEC reactions. On the other hand, in the case of $CuWO_4$ photoanodes, both TAS and IMPS analyses point to the very short lifetime of photoproduced bulk charge carriers as the main limitation.

Thus, while state-of-the-art surface modified-$BiVO_4$ photoanodes already perform close to the theoretical limit of the material, bulk modification strategies applied to $CuWO_4$ systems merit to be further explored and optimized. In general, we strongly encourage to provide reports on TMO-based photoactive materials supported by in-depth characterization (preferably under *operando* conditions), aiming at clearly unveiling the peculiar effects produced by different synthetic strategies on the bulk and/or surface properties of the materials, in relation to their PEC performance, thus also providing essential data to be further processed by machine learning methodologies [55].

Data Availability

No data were used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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