Multiple Effects Induced by Mo$^{6+}$ Doping in BiVO$_4$ Photoanodes

Annalisa Polo, Maria Vittoria Dozzi, Ivan Grigioni, Charles Lhermitte, Nukorn Plainpan, Luca Moretti, Giulio Cerullo, Kevin Sivula, and Elena Selli*

Mo$^{6+}$ doping increases the photoelectrochemical performance of BiVO$_4$ photoanodes in water oxidation. Herein, the underlying mechanisms is elucidated through a systematic structural, morphological, and photoelectrochemical investigation on photoelectrodes of pure and Mo$^{6+}$ doped BiVO$_4$ prepared by a novel multistep spin-coating deposition approach, leading to multilayer flat films with high optical transparency. Transient absorption spectroscopy in the nano- to microsecond time scale reveals a longer lifetime of photogenerated holes in the doped films. Besides confirming that Mo$^{6+}$ ions improve the electron transport in the material bulk, impedance spectroscopy also reveals the crucial role of the dopant on the surface properties of BiVO$_4$ photoanodes. The presence of intrabandgap states, acting as traps of photogenerated charge carriers in pure BiVO$_4$, is detected through the build-up of the interfacial surface state capacitance. The limited activity of pure BiVO$_4$ in water oxidation is largely improved upon 3 at% Mo$^{6+}$ incorporation, ensuring a more efficient charge carrier transport with respect to pure BiVO$_4$, together with the beneficial passivation of its trap surface states.

1. Introduction

Solar energy conversion enables to capture the freely available energy from sunlight and turn it into highly valuable and storable chemical fuels such as clean hydrogen from water.[1] Although artificial photosynthesis is the most promising approach to renewable energy for a sustainable society,[2] the development of simultaneously competitive, cost-effective, and efficient systems for storing solar energy in the chemical form on a global scale is still a great challenge.[3,4] The photoelectrochemical (PEC) tandem cell technology allows achieving solar-to-hydrogen conversions above 20% from water splitting by maximizing photon absorption in a two photoelectrode configuration able to harvest complementary portions of the solar spectrum,[5] with the photocathode layered on top of a smaller bandgap photocathode efficiently exploiting the incoming photons and transmitting to the photocathode the photons less energetic than the photocathode material band gap.[6]

Among the semiconducting metal oxides to be employed as photoanodes in this architecture,[7] BiVO$_4$ (BV) emerged for its stabilizing ability on a global scale is still a great challenge.[3,4] The photoelectrochemical (PEC) tandem cell technology allows achieving solar-to-hydrogen conversions above 20% from water splitting by maximizing photon absorption in a two photoelectrode configuration able to harvest complementary portions of the solar spectrum,[5] with the photocathode layered on top of a smaller bandgap photocathode efficiently exploiting the incoming photons and transmitting to the photocathode the photons less energetic than the photocathode material band gap.[6]

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Doping BiVO$_4$ with metal ions higher valent with respect to both Bi$^{3+}$ and V$^{5+}$, such as Mo$^{6+}$ and W$^{6+}$, is the most successful strategy to increase the water oxidation activity of pure BiVO$_4$.[16,17] The observed PEC performance enhancement is usually associated with the alleviation of the intrinsic poor electron transport properties of the material, since the hexavalent ions can act as shallow donors supplying additional free electrons, thus increasing the majority carrier concentration and, consequently, the n-type conductivity in the bulk.[10,18,19] Doping with Mo was found to provide superior conductivity,[20] and therefore higher photocactivity,[16,17,21,22] than doping with W.

Other effects, such as crystal deformation, grain size growth, or the passivation of trap sites, were also invoked to account for the significant improvement in PEC performance observed upon Mo doping of BiVO$_4$.[20,23–28] which was usually found to depend on the dopant content and possibly result from the balance of different effects. In fact, beyond the processes affecting the material bulk, the chemistry at the semiconductor–liquid
Active material thin layers, consisting of either pure BiVO_4 or depositing on conductive glass an increasing number of photo-doping to the PEC performance in water oxidation. Three series, especially when the performance is limited by a sluggish Mo-doped BiVO_4. These were labeled nL_BV and nL_BV_X%, depending on the kind of metal oxide, its synthesis and/or annealing conditions and, eventually, on the nature of the dopant.

This work aims at identifying the mechanisms responsible for the PEC performance enhancement in water oxidation induced by Mo^{6+} doping of BiVO_4 photoanodes, through an in-depth investigation of the role of Mo^{6+} doping in modifying both the bulk properties of the material and the chemistry of surface states. Photoelectrodes of pure and Mo^{6+}-doped BiVO_4 were prepared by means of a novel multistep spin-coating deposition approach, leading to multilayer flat films with high optical transparency, which is an important requirement for their implementation in the dual absorber PEC tandem devices. A systematic investigation was performed, employing a series of complementary structural and PEC investigation strategies, including transient absorption measurements providing information on the dynamics of photogenerated charge carriers in the semiconductor, to correlate the effects of photoactive film thickness and doping to the PEC performance in water oxidation. Three series of photoanodes with increasing thickness were prepared by depositing on conductive glass an increasing number of photo-active material thin layers, consisting of either pure BiVO_4 or Mo-doped BiVO_4. These were labeled nL_BV and nL_BV_X%, respectively, with n referring to the number of coating layers (L) and X standing for the nominal dopant molar ratio (X = 0.5 or 3, corresponding to 0.5 or 3.0 at% Mo).

2. Results and Discussion

2.1. Photoelectrodes Characterization

2.1.1. X-Ray Diffraction and Raman Characterization

The crystal structure and phase composition of the BV-based materials were ascertained by X-Ray diffraction (XRD) and Raman spectroscopy analyses of the thickest 8L electrodes, reported in Figure 1. All XRD traces shown in Figure 1a correspond to the standard pattern of monoclinic BiVO_4 (JCPDS 14-0688), with the main characteristic (110), (121), and (040) diffraction peaks located at ca. 18.9°, 28.9°, and 30.5°, respectively. No patterns belonging to secondary phase impurities can be detected, except for the reflections relative to the fluorine-doped tin oxide (FTO) glass substrate (marked with asterisks in Figure 1a), which excludes the presence of traces of less active tetrahedron and rhombohedron phases.

Thus, Mo^{6+} incorporation does not induce any phase change in monoclinic BV up to 3.0 at% Mo doping, in line with previous reports. Moreover, no peaks relative to crystalline MoO_3 are detectable in the XRD patterns, suggesting the formation of a solid solution of Mo^{6+}-doped BV. All XRD patterns exhibit sharp, relatively high-intensity peaks, indicating the high crystallinity of the films. A slight (ca. 0.1°) shift of the (040) peak is observed for highly doped 8L_BV_3%, which can be ascribed to the compressive lattice strain induced by substitution of Mo^{6+} ions for relatively smaller V^{5+} ions (having 0.41 and 0.35 Å ionic radius, respectively), causing the partial distortion of the VO_4\(^{3-}\) tetrahedron space lattice. This should enhance the electron mobility of BiVO_4 and suggests the successful incorporation of Mo into the BiVO_4 lattice.

Furthermore, the progressive intensity increase of the XRD reflection at 2θ = 18.9° with increasing Mo dopant content (Figure 1a) is in line with a progressive preferential growth along the (110) and (010) directions.

The Raman spectra of both pure and doped BV (Figure 1b) exhibit the typical modes of the monoclinic phase of BiVO_4, consistently with XRD analysis results. The dominant Raman band at ca. 827 cm\(^{-1}\) is assigned to the symmetric δ_0(V–O) stretching mode of the VO_4\(^{3-}\) units and the weak shoulder at ca. 710 cm\(^{-1}\) to the corresponding δ_0a (V–O) asymmetric mode. The weak bands at around 325 and 360 cm\(^{-1}\) are identified as the asymmetric δ_0a(VO_4\(^{3-}\)) and symmetric δ_0s(VO_4\(^{3-}\)) deformation modes of VO_4\(^{3-}\), respectively, while the band at around 210 cm\(^{-1}\) is ascribed to external (rotational or translational) modes. The progressive red shift of the δ_0(V–O) stretching mode with increasing Mo^{6+} dopant amount, passing from 827 cm\(^{-1}\) for pure 8L_BV to 820 cm\(^{-1}\) for 8L_BV_3%, also results from the Mo^{6+} for V^{5+} replacement in the BiVO_4.

Figure 1. a) X-Ray diffraction (XRD) patterns and b) Raman spectra of 8L_BV, 8L_BV_0.5%, and 8L_BV_3%. The reflections relative to the fluorine-doped tin oxide (FTO) substrate are marked with an asterisk. The Raman spectrum of MoO_3 (gray trace) is also reported for comparison.
causing elongation of the V–O bond in the VO₄ unit due to the larger ionic radius of Mo⁶⁺ compared to V⁵⁺. Also, the small shoulder appearing at 890 cm⁻¹ in the Raman spectrum of 8L_BV_3%, coinciding with the Mo–O–Mo stretching mode in the Raman spectrum of pure MoO₃ also reported in Figure 1b, is an indication of Mo⁶⁺ for V⁵⁺ substitution.

### 2.1.2. Morphological Characterization

The top-down low magnification scanning electron microscope (SEM) images of the 8L_BV, 8L_BV_0.5%, and 8L_BV_3% electrodes (Figure S1, Supporting Information) account for a flat surface with uniform texture, composed of densely packed, ~100–200 nm sized grains, indicating a homogeneous and compact coverage of the rough FTO surface.

The high magnification images relative to the 4, 6, and 8L films with different Mo dopant contents (0, 0.5, and 3 at%) are compared in Figure 2. A worm-like structure typical of BV films is detected for the pure and 0.5 at% Mo⁶⁺-doped films up to 6L, which progressively turns into a spherical shape morphology with increasing dopant amount and/or number of coating layers.

As evidenced by the estimated nanoparticles size in the films reported in Table 1, for a fixed number of coating layers a progressive increase in grain size is observed with increasing dopant amount, possibly consequent to a Mo⁶⁺-induced particles agglomeration process, especially when present in relatively high amount (i.e., 3 at%), leading to a denser film structure with a reduced number of free pin-holes between the sintered particles compared to pure BV. Moreover, a relatively high (3 at%) Mo⁶⁺ dopant content can also promote nanoparticles sintering between adjacent layers, as reflected by the abrupt increase in grain size observed when passing from 6 to 8 layers (Table 1).

Notably, the feature sizes reported in Table 1 are comparable with the typical 70–100 nm charge diffusion length reported for BiVO₄-based electrodes, with only the 3 at% Mo⁶⁺-doped series (4L_BV_3%, 6L_BV_3%, and 8L_BV_3% electrodes) having grain sizes far above this threshold value.

The trend in grain size is reflected by the change in the real surface area of the electrodes, in terms of electrochemical active surface area (ECSA) determined, as detailed in the Supporting Information, through cyclic voltammetry measurements such as those shown in Figure S2, Supporting Information. Relative ECSA values, i.e., normalized with respect to that of the thinnest 4L_BV electrode, are collected in Table S1, Supporting Information. An ECSA decrease is observed with increasing Mo⁶⁺ dopant content for a fixed number of layers, the highest variation being attained with the 8L films, while only a slight decrease in ECSA occurs when increasing the number of layers, this trend becoming progressively more evident with increasing Mo⁶⁺ dopant content.
The average film thickness of the thickest 8-layered photoanodes, evaluated by means of SEM cross-section images (Figure 3), is ca. 150 ± 15 nm, independent of the dopant amount, i.e., slightly lower than the average particles sizes detected for the 8L_BV_3% film, suggesting a preferential film growth parallel to the FTO substrate.

The atomic force microscope (AFM) images shown in Figure S3, Supporting Information, confirm the spherical shape of the nanoparticles composing 8L films, as well as the grain coalescence with increasing dopant amount, while the 3D surface topography images, also reported in Figure S3, Supporting Information, reveal the presence of distinctive reliefs on the surface, becoming progressively more extended and sharper as the particles dimension increases with increasing dopant amount. In parallel, the surface roughness, estimated through the root mean square (RMS) factor reported in Figure S3, Supporting Information, also increases with increasing dopant amount.

2.1.3. Optical Characterization

The absorption coefficients (α) at 420 nm of pure BV and of 0.5 at%- and 3 at%-doped BV were estimated on the basis of the Lambert–Beer law[43,44] from the absorbance at 420 nm of the thickest 8L electrode of each series (see Figure S4, Supporting Information) and their thickness evaluated from the cross-section images shown in Figure 3. The so determined α_{420nm} values are 0.015, 0.020, and 0.023 nm^{-1} for pure BV, 0.5 at%, and 3 at% Mo⁶⁺ doped films, respectively. The thickness of all investigated photoanodes, estimated from the α_{420nm} values and the absorbance of the photoactive films at 420 nm, are collected in Table S2, Supporting Information.

From the estimated absorption coefficients at 420 nm, the light penetration depth values were calculated, corresponding to film thicknesses ensuring 96%, 83%, and 63% absorption of the incident 420 nm radiation, as δ_{96%} = 3 α⁻¹, δ_{83%} = 2 α⁻¹ and δ_{63%} = α⁻¹, respectively.[44] The obtained values for 8L films are reported in Table S3, Supporting Information. The δ value accounting for 96% absorption of incident 420 nm photons, ca. 200 nm for the 8L_BV electrode, in perfect agreement with literature values,[42,44,45] decreases to ca. 150 and 130 nm in the case of the 8L_BV_0.5%, and 8L_BV_3% doped systems, respectively.

The above reported α_{420nm} values indicate that Mo doping decreases the fraction of light transmitted through our BV films. Indeed, the absorption spectra of the 8L electrodes shown in Figure S4, Supporting Information evidence that the absorbance of Mo-containing films at wavelengths shorter than the BiVO₄ absorption edge (ca. 520 nm for a 2.4 eV bandgap) is higher than that of the undoped BV film, though without any change in spectral shape. Thus, the apparent absorbance increase with increasing Mo⁶⁺ content should be correlated to the grain size enlargement in the films, causing scattering effects, reflected by a slightly higher opacity of 3 at% Mo⁶⁺-doped films, rather than to band gap energy narrowing of the material.

2.1.4. X-Ray Photoelectron Spectroscopy Characterization

The elemental surface composition of 8L films was finally investigated by X-Ray photoelectron spectroscopy (XPS). Survey spectra confirmed the presence of Bi, V, O, and Mo, and no other elements, apart from adventitious carbon. The XPS spectra in the binding energy (BE) regions of Bi 4f, V 2p, O 1s, and Mo 3d are shown in Figure 4. The characteristic spin–orbit doublet separation of the Bi 4f (Bi4f₇/₂ and Bi4f₅/₂) and V 2p (V2p₁/₂ and V2p₃/₂) signals typical of monoclinic scheelite BiVO₄[23,25,46,47] can be observed in Figure 4a,b, with the Bi 4f₇/₂ and Bi 4f₅/₂ core level peaks at BE 158.9 and 164.3 eV, respectively (Figure 4a), confirming the presence of Bi⁴⁺ cations, and the V 2p₁/₂ and V 2p₃/₂ core level peaks at BE 516.7 and 524.3 eV, respectively (Figure 4b), allowing unambiguous assignment to V⁵⁺.

The O 1s signal (Figure 4c) at ca. 529.7 eV is assigned to lattice oxygen (V–O) and the shoulder at around 532 eV to oxygen vacancies and hydroxyl groups (–OH) on the BiVO₄ film surface[39,48,49] which can act as surface hole trapping sites or intermediates of the oxygen evolution reaction.[48,49] This shoulder is most evident in the XPS spectrum of 8L_BV and almost disappears in the XPS signal of 8L_BV_3% (Figure 4c), indicating a lower concentration of oxygen vacancies and surface –OH groups upon 3 at% Mo⁶⁺ incorporation.

Definite evidence of successful Mo⁶⁺ doping is provided by the presence of the two characteristic Mo 3d₅/₂ and 3d₃/₂ peaks, located at 232.1 and 235.1 eV, respectively, only in the XPS spectra of the two doped photoanodes (Figure 4d), with intensity increasing with increasing nominal doping degree.[23,34,40,46,47,50]
The composition of the 8L films was also investigated at different depths from the surface, by acquiring the XPS spectra after etching with $\text{Ar}^+$ ions sputtering. The so recorded spectra of the doped electrodes in the Mo 3d binding energy region are collected in Figure 5, while those in the Bi 4f, V 2p, C 1s, and O 1s BE regions are reported in Figure S5–S7, Supporting Information.

Notably, for both 8L_BV_0.5% (Figure 5a) and 8L_BV_3% (Figure 5b), the intensity of the Mo 3d XPS signal decreases with increasing etching depth, the Mo content in the bulk being below the detection limit of XPS analysis. Gradient doping is thus evidenced, with Mo$^{4+}$ ions being confined at the top of the film surface, especially in the case of 0.5 at% Mo doping.

The actual Mo:(V + Bi) surface atomic ratios obtained for the 8L_BV_0.5% and 8L_BV_3% electrodes (Table 2) are slightly higher than the nominal ones, as observed elsewhere,[21,37,46,47] which is the first indication of Mo-rich surface photoanodes, confirmed by the dramatic Mo:(V + Bi) atomic ratio decrease obtained upon etching. This phenomenon was attributed to Mo surface segregation at high temperatures driven by sublimation of Mo oxides.[21,46,47,51]

**Figure 4.** X-Ray photoelectron spectroscopy (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.

**Figure 5.** XPS spectra in the Mo 3d binding energy region of: a) 8L_BV_0.5% and b) 8L_BV_3%, before (black line) and after $\text{Ar}^+$ ions sputtering at progressively increasing etching depth, in the 6 (red line) to 60 nm (brown line) range.
2.2. Transient Absorption Spectroscopy (TAS)

The charge carrier dynamics of the BiVO$_4$-based multilayer photoanodes was investigated through TAS in the nanosecond to microsecond time scale,[22,52] by recording the differential absorption ($\Delta A$) signal evolution for pure BV and for the doped materials. In particular, in the present work, we monitored the photinduced absorption feature of BiVO$_4$ at 470 nm, attributed to photoproduced holes trapped in BiVO$_4$ intra-bandgap (IBG) states. Their trapping occurs within 5 ps after excitation, which is beyond the lower limit of the here employed time window.[22,52-56]

The normalized $\Delta A$ decay traces probed at 470 nm for each of the multilayer electrode series are compared in Figure S8, Supporting Information as a function of the film thickness on the 100 $\mu$s time scale. In all cases the $\Delta A$ signal completely decays on this time scale, allowing a direct comparison of the dynamics of photoproduced holes in different electrodes.

Figure 6 shows the magnification of the $\Delta A$ signals at 470 nm on a 200 ns time scale, which was successfully fitted using a biexponential decay model, according to Equation (1)

$$\Delta A = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + \Delta A_0$$  \hspace{1cm} (1)

where $\tau_1$ and $\tau_2$ are the time constants of the faster and slower decay processes, respectively, $A_1$ and $A_2$ are the weighted amplitudes of the contribution of each of the two processes to the overall decay, and $\Delta A_0$ is the signal offset. The $\Delta A$ signal almost totally decays on the 200 ns time scale, although zero $\Delta A_0$ values were reached only in the case of pure BV. The corresponding fitting parameters are reported in Table 3.

Direct comparison of the obtained fitting parameters within each film series with constant doping degree and different thickness is allowed by the almost unchanged grain size with an increasing thickness (see Table 1). In contrast, due to the non-negligible increase in particle size occurring with increasing Mo$^{6+}$ dopant content at constant film thickness, morphological features may affect the charge carrier dynamics in electrodes with different doping degrees.

Upon photoexcitation with the here employed 240 $\mu$J cm$^{-2}$ fluence, most trapped holes recombine within 5–20 ns, regardless of the film thickness and doping degree, as indicated by the much larger $A_1$ values (in the 76–86% range) compared to the $A_2$ values (14–24%) reported in Table 3. While the relative weights of the two decay processes are almost unaffected by the film thickness, a progressive increase of both $\tau_1$ and $\tau_2$ is observed with an increasing number of photoactive layers (Table 3). Thus, IBG-trapped holes recombination with both thermalized ($\tau_1$) or longer lived trapped electrons ($\tau_2$) occurs faster in thinner films, where a lower fraction of holes are photogenerated in the material bulk. An analogous behavior was recently observed for zinc ferrite photoanodes with a similar planar morphology.[57]

As for the effect of Mo$^{6+}$ doping on the charge carrier dynamics, in doped materials both $\tau_1$ and $\tau_2$ are longer than...
in pure BV for a fixed number of coating layers, indicating an increased charge separation efficiency. The $\tau_1$ and $\tau_2$ values obtained for 0.5%-doped BV are longer than those obtained for 3%-doped BV. However, also the relative weights of the two time constants should be taken into account, in the light of the different average grain sizes and morphology attained in the presence of different dopant amounts. In fact, as shown in Table 3, the average weight of the fast decay component, $A_1$, increases in the order 0, 0.5%, and 3% Mo doping, i.e., with increasing average particle size in the material (see Table 1), indicating that the fast decay component should be associated to hole recombination in the bulk material. Thus, increased charge separation (longest $\tau_1$ and $\tau_2$ values) results from an optimal balance between doping effects and film morphology, grain size, etc. being maximum in the thickest 0.5% Mo-doped BV_8L_0.5% electrode, having a much smaller grain size than the corresponding thickest 3 at% Mo-doped BV_8L_3% electrode (see Table 1).

2.3. Photoelectrochemical Performance of Multilayer Films

2.3.1. Linear Sweep Voltammetry

The PEC performance of all investigated multilayer films employed as photoanodes for water oxidation was checked in a 0.5 M Na$_2$SO$_4$ electrolyte solution by performing consecutive linear sweep voltammetry (LSV) scans under AM 1.5 G solar simulating light under both back- (through the FTO back-contact) and front-side (through the film/electrolyte interface) irradiation configurations. The photocurrent was stable for at least 10 scans and reproducible for several months. The last scans acquired with intermittent illumination for all investigated electrodes are collected in Figure S9, Supporting Information (up to 3 layers), and in Figure 7 (4, 6, and 8L electrodes).

In pure BV electrodes, a progressive slight photocurrent increase is observed with an increasing number of coating layers up to 6L, under both back- and front-side irradiation, followed by an abrupt increase when passing from the 6L to the 8L electrode. This behavior can be related to the almost complete light absorption of the thickest ($\approx$ 150 nm thick) 8L film (see Table S3, Supporting Information), though other factors may come into play. In fact, at low thickness the PEC performance may be limited by poor photon absorption, while with increasing photovoltaic film thickness, a significant increase in photocurrent occurs, once the film thickness exceeds an inactive layer depth, which is a signature of the so-called “dead-layer effect” observed for both thin BiVO$_4$ (thickness $\leq$ 125 nm)\cite{58} and hematite films\cite{59,60}. This phenomenon, arising from lattice mismatch at the film/FTO interface, results from the formation of amorphous, rich in trap states, material near the interface, which can be mitigated by SnO$_2$\cite{61,62} or WO$_3$ underlayers\cite{58}.

As to morphology effects, the more regular spherical shape of the nanoparticles composing the 8L film (Figure 2g), in comparison to 4 and 6L electrodes (Figure 2a,d), implies a lower number of grain boundaries responsible for charge recombination, which can explain the steep photocurrent density jump observed in Figure 7 when passing from the 6L_BV to the thickest 8L_BV electrode, which exhibits the highest photocurrent among the undoped BV electrodes under both illumination configurations. Mo$^{6+}$-doped BV electrodes produce considerably higher photocurrent with respect to pure BV under both irradiation configurations, indicating that molybdenum doping helps overcoming the “dead-layer effect” impacting pure BV. Moreover, while a typical monotonic photocurrent increase with increasing

![Figure 7. Linear sweep voltammetry (LSV) scans of the: a,d) 4L, b,e) 6L, and c,f) 8L electrodes under a–c) back- and d–f) front-side irradiation in a 0.5 M Na$_2$SO$_4$ electrolyte solution.](image-url)
applied potential characterizes the $J-V$ curves collected with pure 
BV, a better fill factor with a steeper photocurrent onset in the 
low applied potential region is obtained with doped electrodes, 
regardless of the dopant amount (Figure 7).

The dependence of photocurrent on the irradiation side 
of the electrodes is diagnostic of electron or hole transport 
limitations in the bulk of the material. Figure 8 shows the 
photocurrent densities recorded under either front- or back-side 
irradiation at the reference potential of 1.23 V versus reversible 
hydrogen electrode (RHE) as a function of the number of coating 
layers in the three photoanodes series. Pure BV photoanodes pro-
duce relatively low photocurrent values, monotonically increas-
ing with an increasing number of coating layers under both 
irradiation configurations, with comparable values under back-
and front-side irradiation up to a 150 nm thickness, while the 
8L_BV electrode generates a considerably higher photocurrent 
density when irradiated in back- rather than in front-side 
configuration.

Under back-side irradiation, a high density of charge carriers 
is photoproduced close to the FTO back-contact and electrons can 
be directly injected into the external circuit, which is an 
advantage in the case of materials suffering from poor electron 
transport, such as BiVO$_4$.[9,11,25,61] Therefore, the behavior 
observed with the thickest 8L_BV electrode reflects the bulk 
electron transport issues limiting the performance of pure BV 
when the thickness of the photoactive layer exceeds the ca. 70–100 nm 
typical BiVO$_4$ charge diffusion length.[42] For this reason, the 
photocurrent produced under back-side irradiation in pure BV 
photoanodes thicker than 100 nm (i.e., the 8L_BV electrode) 
exceeds that produced under front-side irradiation, reflecting 
the intrinsic limitations imposed by electron mobility within 
the photoactive layer.[11,61]

Conversely, for the two series of Mo$^{6+}$-doped multilayer films 
the photocurrent density under front-side irradiation progressively 
increases with an increasing number of coating layers 
(Figure 8) and 6 and 8L films produce higher photocurrent under 
front- than under back-side irradiation. Indeed, 
under front-side irradiation a large density of charge carriers 
is photogenerated near the SCLJ and electrons have to travel a 
longer distance across the material bulk before reaching the 
FTO back-contact to the external circuit. Therefore, the better 
performance under front- rather than back-side configuration 
characterizing the thickest films of the two doped series 
(compare, for instance, Figure 7c with 7f) provides a clear 
indication of the largely improved electron transport produced 
by Mo$^{5+}$ incorporation in BiVO$_4$, poor electron transport in 
the material bulk being no longer limiting for photocurrent 
production.[22,38,41]

The performance trend outlined for the Mo$^{6+}$-doped photoan-
odes in Figure 7 and S9, Supporting Information, thus results 
from morphological, optical, and electronic effects produced 
by doping. When the transport of the majority charge carriers 
electrons in n-type semiconductors) in the bulk is no longer lim-
iting due to the presence of the Mo dopant, the PEC performance 
of BiVO$_4$ is maximized by an optimal compromise between 
photon absorption depth and minority charge carriers (holes 
in n-type semiconductors) diffusion length.[24] In fact, 
Figure 8 evidences that under front-side irradiation BV$_{3\%}$ 
 electrodes show a progressive photocurrent increase with 
increasing number of layers, attaining a maximum value 
with the thickest 8L_BV$_{3\%}$ electrode, which ensures almost 
complete light absorption. On the other side, these electrodes 
have a highly packed structure and they become more 
compact with increasing number of coating layers, which limits 
the exposition of the material to the electrolyte 
(see ECSA values in Table S1, Supporting Information). 
Thus, hole diffusion toward the film/electrolyte interface 
becomes progressively more hampered with increasing film 
thickness, with the consequent increase of electron–hole 
recombination probability. For this reason, the performance 
of the BV$_{3\%}$ electrodes under back-side irradiation is maxi-
mum for 70–90 nm thick films, i.e., for 3L_BV$_{3\%}$ 
(Figure 8), in which the distance that photogenerated holes 
need to travel to reach the film/electrolyte interface is compa-
rable to their diffusion length in BiVO$_4$.[19,42] Thicker electrodes 
become relatively less performing under back-side irradiation. 
This highlights that under such conditions the PEC perform-
ance of Mo$^{6+}$-doped BiVO$_4$ photoanodes is mainly limited 
by the hole diffusion length.

2.3.2. Incident Photon to Current Efficiency

The incident photon to current efficiency (IPCE) analyses 
recorded under front-side irradiation at 1.23 V versus RHE with 
the 8L_BV, 8L_BV$_{0.5\%}$, and 8L_BV$_{3\%}$ photoanodes 
(Figure S10a) show pretty similar IPCE curve onsets at ca. 
520–530 nm for all tested materials, confirming that Mo doping 
does not affect the bandgap energy of BV.[19,61] in line with 
the absorption spectra reported in Figure S4, Supporting 
Information. The IPCE values attained upon Mo$^{6+}$ doping are
The remarkably enhanced photoactivity in water oxidation achieved upon Mo\(^{6+}\) doping cannot be fully explained only in terms of improved electron transport in the material bulk. Indeed, hexavalent Mo\(^{6+}\) ions modify not only the bulk but also the surface properties of BiVO\(_4\). Aiming at evidencing the effects induced by Mo\(^{6+}\) doping on the material surface,\(^{[29,66-69]}\) we performed an electrochemical impedance spectroscopy (EIS) analysis with the 8L\(_{\text{BV}}\) and 8L\(_{\text{BV}}-3\%\) electrodes in contact with a Na\(_2\)SO\(_4\) solution, either in the dark (EIS), or under the same conditions as LSV tests, i.e., under AM 1.5 G irradiation (photoelectrochemical impedance spectroscopy, PEIS).

The impedance spectra recorded with the two photoanodes at three representative applied potentials in the dark and under irradiation are shown in Figure S11a.b, Supporting Information, respectively, in the form of Nyquist plots. EIS spectra recorded in the dark display a single semicircle and their interpretation can be based on the Randles circuit model, by taking into account only the dielectric capacitance contribution, corresponding to the transfer of charges from the bulk of the semiconductor layer to the photoanode/electrolyte interface through the SCLJ. In contrast, each spectrum recorded under irradiation at a specific potential is in principle composed of two semicircles,\(^{[29,66-67]}\) the semicircle at high frequency corresponding to the electrical response in the space charge region, which provides information on the charge transfer from the film bulk to the material/electrolyte interface, the low-frequency semicircle describing instead the interfacial charge transfer behavior at the SCLJ.\(^{[66]}\) Therefore, a model considering both bulk and surface contributions is required to fit the impedance spectra under irradiation\(^{[29]}\) and extract information on the electric properties described by the two semicircles.

The here employed circuit model is shown in the inset of Figure 10a. It was already employed for other metal oxide systems\(^ {^{[29,66,67]}}\) including W-Ti-doped BiVO\(_4\) photoanodes\(^ {^{[70]}}\) and consists of: i) a series resistance \(R_0\) associated with charge transfer through the external circuit and the semiconductor bulk; ii) a bulk capacitance \(C_{\text{bulk}}\) (with \(C_{\text{bulk}}^{-1} = C_{\text{SC}}^{-1} + C_{\text{H}}^{-1}\)), with \(C_{\text{SC}}\) referring to the depletion layer inside the semiconductor and \(C_{\text{H}}\)

![Figure 9](https://www.advancedsciencenews.com/sol_rrl_2200349/fig9.png)

**Figure 9.** Incident photon to current efficiency (IPCE) plots of: a) 8L\(_{\text{BV}}\), b) 8L\(_{\text{BV}}-0.5\%\), and c) 8L\(_{\text{BV}}-3\%\) photoanodes under back- (void symbols) and front-side (full symbols) irradiation in a 0.5 M Na\(_2\)SO\(_4\) electrolyte solution at 1.23 V versus RHE.
to the Helmholtz layer inside the electrolyte; iii) a parallel resistance of hole trapping to surface states \( R_{\text{ct,ss}} \); iv) a \( C_R/R_{\text{ct,ss}} \) pair corresponding to surface state capacitance \( C_R \) and charge transfer resistance \( R_{\text{ct,ss}} \) from surface states to oxidize water, respectively. The presence of the chemical surface state capacitance, associated with the accumulation/transfer of charges through potential surface states, makes this equivalent circuit a good approximation if charge transfer at the SCLJ is affected by the presence of surface states.[29,68]

From the Mott–Schottky (M–S) plots reported in Figure S12, Supporting Information, correlating the \( C_{\text{SC}} \) values extracted from impedance spectra recorded in the dark to the applied potential, the electron donor density \( N_D \) and flatband potential \( E_{\text{FB}} \) of the investigated electrodes were evaluated, according to the Randles model (inset of Figure S12, Supporting Information). The positive slopes of the well-defined linear region of both plots confirm the n-type character of pure and Mo\textsuperscript{6+}-doped BV materials. Extrapolation of the linear part of the M–S plots provides \( E_{\text{FB}} \) values of 0.59 and 0.74 V versus RHE for the pure BV, 8L and doped 8L_BV_3% electrodes, respectively, as shown in Figure S12, Supporting Information, the former value being in good agreement with the \( E_{\text{FB}} \) reported for pure BiVO\textsubscript{4}.[71] From the slope of the linear fits, \( N_D \) values of 4.79·10\textsuperscript{19} and 1.97·10\textsuperscript{20} cm\textsuperscript{-3} are obtained for pure 8L_BV and 8L_BV_3% electrodes, respectively, using a dielectric constant of 68[39] (Table 4). The linear portion of the \( C_{\text{SC}}^{-2} \) versus applied potential plot at higher potential was employed in the case of undoped BV. A fourfold enhancement in donor density is thus attained upon a 3 at% Mo\textsuperscript{6+} doping, consistent with the additional free electrons in the material bulk provided by the n-type dopant.[19,47,40,72]

The flat region in the M–S plot of pure BV recorded in the dark (Figure S12, Supporting Information), i.e., the lack of increase in \( C_{\text{SC}}^{-2} \) in the 0.6–0.9 V versus RHE region, may originate from Fermi-level pinning (FLP).[73–75] occurring when an increase of applied voltage results in the charging of surface states rather than in the increase of the semiconductor band bending.[76] In this case, most of the applied potential drop should occur across the Helmholtz layer rather than across the space charge region.[66,77] No FLP appears instead for the 8L_BV_3% electrode (Figure S12, Supporting Information).

The elaboration according to the EC model (inset of Figure 10a) of PEIS data collected with the two electrodes under irradiation allows extraction of the \( C_{\text{SS}} \) contribution, arising from charge accumulation at the SCLJ, which can be directly converted into the energy distribution density of surface states (DOS) under irradiation[29] by \( C_{\text{SS}} = q \times \text{DOS} \), \( q \) being the elementary charge. The so calculated DOS for both 8L_BV and 8L_BV_3% electrodes are plotted in Figure 10b against the applied potential and fitted with a Gaussian function. A very intense and well-defined peak located at ca. 0.75 V versus RHE, which falls within the potential range of FLP in the dark (Figure S12, Supporting Information), characterizes the DOS curve relative to 8L_BV, while the 8L_BV_3% electrode exhibits only a much less pronounced peak at lower potential. A total density of surface states \( N_{SS} = 2.87\times10^{15} \text{ cm}^{-2} \) is obtained from the integration of the DOS versus potential curve of the 8L_BV film, while a much lower \( N_{SS} = 1.41\times10^{14} \text{ cm}^{-2} \) results from the integration of the DOS curve relative to the 8L_BV_3% electrode (Table 4).

The presence of charge accumulation in the undoped BV might be related to the shift of the relative M–S plot, recorded under irradiation, toward higher potential values compared to doped BV (Figure 10a), which should reflect a rigid downward shift of the band edges, caused by holes accumulation at the capacitive layer of pure 8L_BV.[78] Moreover, a high photovoltage is developed in the doped photoanode, as suggested by the large \( E_{\text{FB}} \) shift toward less positive potential evidenced in the doped electrode under irradiation compared to dark conditions (Figure S13b, Supporting Information), while no shift is observed in the case of the pure BV photoanode (Figure S13a, Supporting Information).

### Table 4. Flatband potential \( E_{\text{FB}} \) and donor density \( N_D \) obtained from EIS and total density of surface states \( N_{SS} \) under irradiation.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>( E_{\text{FB}} ) vs. RHE [V]</th>
<th>( N_D ) [cm\textsuperscript{-3}]</th>
<th>( N_{SS} ) [cm\textsuperscript{-2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8L_BV</td>
<td>0.59</td>
<td>4.79·10\textsuperscript{19}</td>
<td>2.87·10\textsuperscript{15}</td>
</tr>
<tr>
<td>8L_BV_3%</td>
<td>0.74</td>
<td>1.97·10\textsuperscript{20}</td>
<td>1.41·10\textsuperscript{14}</td>
</tr>
</tbody>
</table>
The suppression of this charge accumulation upon a 3 at% Mo$^{6+}$ incorporation may be a consequence of Fermi-level unpinning in 8L_BV_3% with respect to 8L_BV. However, also a favorable hole extraction promoted by the observed gradient doping$^{[79]}$ in 8L_BV_3%, with a higher concentration of Mo$^{6+}$ ions at the top of the film surface, or an accelerated oxygen evolution reaction by Mo segregation at the electrode surface, may not be discarded to be at the basis of the observed decrease in $C_{SS}$ in doped BV with respect to pure BV.

Furthermore, Figure 10b shows that the DOS peak in doped BV appears at lower potential with respect to pure BV, in line with the relative trend in the M–S plots in Figure 10a, indicating that Mo$^{6+}$ doping induces a charge not only in the amount, but also in the energy level of surface states, so that an equal band bending extent would be obtained with a lower applied potential compared to pure BV.$^{[77]}$ This is also evidenced by the large gain in photovoltage observed for the doped electrode (Figure S13, Supporting Information)$^{[80,81]}$ as a consequence of the successful suppression of charge accumulation consequent to Mo$^{6+}$ incorporation.

2.5. Mo Doping-Induced Surface Effects

PEIS analysis reveals that holes accumulate at the film/electrolyte interface in pure BiVO$_4$ in a concentration sufficiently high to act as surface states located at ca. 0.75 V versus RHE. Evidence of a surface state capacitance peak around 0.75 V versus RHE, associated with accumulated holes at the SCLJ$^{[78]}$ was reported for pure or W$^{6+}$-doped BV and identified with the V$^{5+}$/V$^{4+}$ redox process,$^{[39,71,78]}$ as well as the presence of IBG states in pure BV films, which are occupied by electrons in the dark and undergo depopulation upon application of an anodic bias, leading to accumulation of trapped holes at the material surface.$^{[52,82]}$ Surface V$^{4+}$ states, due to oxygen vacancies formation, were also recently evidenced,$^{[83]}$ which can act as trapping sites of photoproduced holes located at an energetically unfavorable potential to drive water oxidation.

The surface state passivation upon Mo$^{6+}$ dopant incorporation, in addition to the increased majority charge carrier concentration in the material bulk, results in the observed great enhancement in PEC performance in water oxidation attained with the 8L_BV_3% electrode with respect to pure BiVO$_4$. Thus, by taking into account present results together with recent literature reports, the mechanism shown in Figure 11 is proposed to describe water oxidation at pure and Mo$^{6+}$-doped BV photoanodes.

The surface of pure BV in neutral conditions should be rich in V$^{4+}$ states (occupied by electrons) formed after the localization of electrons from oxygen vacancies formation during the annealing process on neighboring V$^{5+}$ sites. That is, the Fermi level in the dark $E_F$ stays virtually fixed under increasing bias application until V$^{4+}$ states are completely emptied, leaving unchanged the band bending degree and significantly lowering the photovoltage of the pure material. Upon irradiation, Fermi level splitting occurs into the quasi-Fermi levels of electrons ($E_{F,n}$) and holes ($E_{F,p}$), represented by the dashed lines in Figure 11, and such surface states can be progressively converted into photoproduced V$^{5+}$ states, which are energetically unable to promote water oxidation, with the consequent detrimental accumulation of holes at the pure BV/water interface (Figure 11a).

When Mo$^{6+}$ is introduced in BV, the additional free electrons supplied by the higher valent metal not only change the properties of the material bulk through the donor density $N_D$ increase and consequent improvement in electron conductivity,$^{[9,16–18,42,46]}$ but also mitigates holes accumulation, as ascertained by the reduction of the capacitive peak $C_{SS}$ in Figure 10b, with a huge decrease in $N_{SS}$ with respect to pure BV. These findings result in an increased photovoltage for the doped material, so that $E_{F,p}$ can equilibrate with the water oxidation potential$^{[70]}$ at a lower potential than in pure BV,$^{[83]}$ leading to the conspicuous enhancement in water oxidation photocurrent (Figure 11b).

3. Conclusions

Mo$^{6+}$ doping of BiVO$_4$ strongly impacts both bulk and surface properties of thin BV photoanodes. Besides the well-known role of the hexavalent n-type dopants in enhancing the electron conductivity of BiVO$_4$ by increasing the majority charge carrier density, and an elongation of the lifetime of photoproduced holes in the nano- to the microsecond time scale, here evidenced through TAS for the first time, a decrease in charge accumulation, induced by Mo doping, at the interface under irradiation is identified as a primary factor increasing the PEC performance of BiVO$_4$-based photoanodes. Multiple factors, including morphological, bulk and surface chemistry-induced effects, thus govern the photocactivity of Mo$^{6+}$-doped BiVO$_4$ photoanodes, which are at the basis of the outstanding improvement in their PEC performance upon doping.

4. Experimental Section

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-pentanediol) ($\geq 99\%$), citric acid ($99\%$), nitric acid 23.3%, sodium sulfate ($\geq 99\%$), acetone. FTO glass, 2 mm thick, was purchased from Pilkington Glass (TEC-7).
**Photoelectrodes Preparation:** Pure BV electrodes were prepared according to a previously described procedure.[1] 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 μL of the so-obtained solution onto clean FTO at 8000 rpm for 30 s with an acceleration rate of 6000 rpm s⁻¹. The films were then dried at 80 °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 was then cut into 2.5 cm² slices that underwent a 15 min-long UV-cleaner ozone treatment to remove any organic species deposited onto the FTO surface. Prior to deposition, the FTO slices were soaked in acetone for a few seconds to increase the quality of the resulting film. 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, to obtain nominal molar dopant contents of 0.5 at% or 3.0 at% (i.e., mol (Mo)/mol (Bi) + mol (V)) = 0.005 or 0.03, respectively). The obtained precursor solutions were employed to prepare multilayer films of 0.5 at% or 3 at% Mo-doped BV with different thicknesses, by repeating the same spin coating procedure and an annealing treatment adopted for pure BV up to 8 times. In all cases, films of both pure and doped BV with a high optical transparency were obtained regardless of the film thickness and the dopant content.

**Characterization Methods:** The crystalline phase of the materials was determined by collecting their XRD patterns using a Panalytical Empyrean system (Theta-Theta, 240 mm) 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. Grain size was estimated employing the ImageJ software. UV–visible absorption spectra of the multilayer films were recorded in transmittance mode with a Jasco V-670 spectrophotometer. AFM images were measured using a Cypher S AFM from Asylum Research. XPS analyses were performed with PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany) with a monochromatic Al Kα 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 SiO₂) of ~5.8 nm min⁻¹ with a sampling depth of ~60 nm.

**Transient Absorption Spectroscopy:** Two electronically synchronized lasers were used in TAS measurements. An amplified femtosecond laser (Light Conversion Pharos) at 2 kHz repetition rate, with a central wavelength of 1024 nm and pulse duration of about 280 fs, was used for the generation of the probe pulses. The second harmonic at 512 nm was focused into a 3 mm sapphire plate to generate a broadband white light continuum spanning 380 to 490 nm. The third harmonic of a femtosecond laser via an electronic delay, was used as a pump. Repetition rate, 355 nm central wavelength, and pulse duration of 100 ps, electronically triggered at 1 kHz and synchronized with respect to the femtosecond laser via an electronic delay, was used as a pump. It was focused on a 500 μm diameter spot at a fluence of 240 μJ cm⁻². The spectrum of the transmitted probe beam was measured by a high-speed spectrometer (Entwicklungsbuero EB Streising) working at the full 2 kHz femtosecond laser repetition rate. Thanks to the electronic modulation of the pump pulse, two consecutive probe pulses measure the excited and unexcited sample, respectively.

**Photoelectrochemical Characterization:** PEC experiments were carried out using a three-electrode cappuccino-type electrochemical cell, where each of the BV-based photoanodes was setup as a working electrode with an active geometric area of 0.25 cm², a Pt wire as a counter electrode and a (Metrohm) Ag/AgCl (KCl sat’d) as the reference electrode. The cell was connected to a computer-controlled (EC-LAB V11.12) BioLogic SP-500 potentiostat to perform PEC measurements. Simulated AM 1.5 G solar irradiation was provided by a 1000 W Xe arc lamp (Newport Oriel), calibrated to the AM 1.5 G spectrum using a Si photodiode sensor (S120VC, Thorlabs). 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 Na₂SO₄ aqueous solution (pH 7). All measurements, the applied potential, measured with respect to the Ag/AgCl reference electrode, was converted into the RHE scale based on the Nernst equation $E_{\text{RHE}} = E_{\text{AgCl}} + E_{\text{AgCl}} + 0.059 \times \text{pH}$. LSV measurements were performed at a scan rate of 20 mV s⁻¹. Ten consecutive LSV scans were recorded for all tested electrodes in each irradiation configuration, without ever observing any decay in photocurrent. IPCE measurements were collected using the same three-electrode configuration cappuccino-type cell at a fixed applied potential of 1.23 V versus RHE. 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 a S120VC (Thorlabs) photodiode power sensor. The IPCE curves were calculated as $\text{IPCE} = \frac{\mu}{C_0} \times 100$. The 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 $\text{IQE} = \frac{\mu A}{C_0}$. EIS measurements were carried out using a BioLogic SP-500 potentiostat coupled with the EC-Lab (V11.12) electrochemical platform, either in the dark or under AM 1.5 G simulated solar light provided by a 1000 W Xe arc lamp (Newport Oriel). During each PEIS scan, a voltage perturbation within a frequency range from 1 Hz 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.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

bismuth vanadate, bulk charge transport, impedance spectroscopy, molybdenum doping, photoelectrochemistry, surface states passivation, water oxidation

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