High-Performance BiVO₄ Photoanodes: Elucidating the Combined Effects of Mo-Doping and Surface-Modification with Polyoxometalate Co-catalysts

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Abstract

Doping and surface-modification by co-catalysts are well-established strategies for the performance enhancement of bismuth vanadate (BiVO₄) photoanodes for photoelectrochemical (PEC) water splitting devices. However, our knowledge of the complex effects of doping and surface modification that govern the PEC performance is still underdeveloped, which makes the rational design of high-performance BiVO₄-based photoanodes challenging. Herein, a remarkably effective strategy for enhancing the performance of BiVO₄ photoanodes by combining the bulk doping of BiVO₄ with molybdenum (Mo) and its surface modification with a well-defined molecular cobalt polyoxometalate water oxidation catalyst (CoPOM = Na₁₀[Co₄(H₂O)₂(PW₉O₃₄)₂]) via a simple impregnation protocol without any linkers or binders is reported. The best-performing optimized Mo-BiVO₄/CoPOM photoanode exhibits a photocurrent density of 4.32 mA cm⁻² at 1.23 V vs. RHE under AM 1.5G (1 sun) illumination and an applied-bias photoconversion efficiency (ABPE) of ~0.73%, which is an improvement by the factor of ~24 with respect to pristine BiVO₄. The respective contributions of the Mo-doping and modification with CoPOM to the performance enhancement are disentangled based on detailed mechanistic investigations. The positive effect of Mo-doping is shown to be related to enhanced electronic conductivity and passivation of surface states, whereby these beneficial effects are operative only at relatively high
applied bias potentials (> 0.9 V vs. RHE), and at lower bias potentials (< 0.7 V vs. RHE) they are counterbalanced by strongly detrimental effects related to increased concentration of electron polaronic states induced by the Mo-doping. The highly beneficial effect of CoPOM deposition is unambiguously demonstrated to be related to the enhancement of water oxidation catalysis. Notably, the molecular CoPOM acts as a pre-catalyst, as it undergoes (at least partially) conversion to cobalt oxide under the PEC operating conditions. Our work thus establishes CoPOM-derived catalysts as effective water oxidation catalysts at BiVO₄ photoanodes, and suggests that further progress in BiVO₄ photoanode development depends critically on devising alternative strategies for conductivity enhancement that would avoid the negative polaronic effects associated with the conventional bulk doping of BiVO₄.

**Keywords:** Photoelectrochemistry, Water splitting, Bismuth vanadate, Polyoxometalate, Polaronic effects, Photovoltage, Photocurrent

1. Introduction

Hydrogen generation via photoelectrochemical (PEC) water splitting represents one of the promising strategies to secure the future supply of free (low-entropy) energy in an environmentally sustainable manner.¹⁻⁴ Compared to the hydrogen evolution reaction (HER), which is a proton-coupled two-electron process, the oxygen evolution reaction (OER) is a typical kinetic bottleneck of PEC devices since the mechanism of oxygen generation is much more complex, involving concerted transfer of four electrons and four protons.⁵⁻⁶ Accordingly, the development of efficient, stable and low-cost photoanodes for water oxidation is of paramount importance for the realization of economically viable PEC water splitting devices.⁷ Some of the most intensely investigated photoanodes are based on passivated high-quality semiconductors (e.g., Si or III–V compounds),⁸⁻¹⁰ hybrid inorganic-organic architectures,¹¹⁻¹⁴ or on low-cost metal oxides, such as Fe₂O₃,¹⁵,¹⁶ CuWO₄,¹⁷,¹⁸ or BiVO₄.³,¹⁹⁻二十五 In particular, BiVO₄ is an attractive material owing to its bandgap energy of ~2.4–2.6 eV, which translates to the maximum theoretically achievable photocurrents of 6.4–8.9 mA cm⁻² and the solar-to-hydrogen (STH) efficiencies of 8–11% under AM 1.5G (1 sun) illumination. However, the PEC performance of pristine BiVO₄ photoanodes is typically far below the theoretical limit, both in terms of maximum photocurrents and achievable photovoltages, the latter manifested by rather positive photocurrent onset potentials.
(with respect to the reversible hydrogen electrode, RHE) and generally poor fill-factors of the *photocurrent density-potential* (*J-V*) curves. The reasons for this suboptimal performance have been identified as (i) poor bulk electronic conductivity of BiVO₄ and the presence of surface intragap states, both of which result in severe electron-hole recombination,²²,²⁶,²⁷ and (ii) ineffective hole extraction and slow rate of water oxidation at pristine BiVO₄ surfaces.²³ Concerning the former, significant improvements in performance have been demonstrated, for example, by doping BiVO₄ with molybdenum,²⁸–³² whereby the beneficial effect of Mo doping has been ascribed to increased electronic conductivity and/or passivation of surface recombination centers.²⁶,³³–³⁵ In addition, further improvements have been reported after modification of BiVO₄ with various additional hole extractors and/or OER catalysts, such as rhodium oxide,²⁸ vanadium oxide,³⁶ iron oxyhydroxide,²⁹ cobalt oxide,³¹,³⁷,³⁸ cobalt hexacyanoferrate,³⁹ iron/nickel oxide,³,²¹,³⁵,⁴⁰,⁴¹ or cobalt/nickel sulfide,⁴² whereby the question of whether the improvement should be ascribed to enhanced water oxidation kinetics or to other factors (*e.g.*, enhanced charge extraction or passivation of surface recombination centers) is still a source of intense debates and seems to depend on specific catalysts and photoanode architectures.³⁹,⁴³–⁴⁷

Well-defined polyoxometalates (POMs) – molecular metal oxide clusters – comprising redox-active transition metals, *e.g.* Co or Mn, are known as effective catalysts in various (photo)electrocatalytic systems.⁴⁸–⁵¹ A prototypical example is the complex CoPOM (Na₁₀[Co₄(H₂O)₂(PW₉O₃₄)₂] with a Co₄O₄ core stabilized by oxidatively resistant polytungstate ligands.⁵¹ Notably, this CoPOM has been reported to be an efficient *homogeneous* water oxidation catalyst,⁵¹–⁵³ though there is also some evidence that – depending on specific experimental conditions (*e.g.*, pH and composition of electrolyte, catalyst concentration, applied electrode potential) – this CoPOM can also undergo conversion to cobalt oxide, and thus behave rather as a *pre*-catalyst for the formation of a *heterogeneous* water oxidation catalyst (CoOₓ) which then often accounts for the major part of activity in water oxidation.⁵⁴,⁵⁵ Very recently, there have been several reports of successful immobilization of CoPOM onto various photoanodes (*e.g.*, TiO₂, Fe₂O₃, BiVO₄,⁵⁶ or TiO₂/carbon nitride hybrids⁵⁷), typically using diverse cationic polyelectrolytes (*e.g.*, polyethyleneimine) or N-doped carbon⁵⁸ as an interlayer or linker. However, the scope of CoPOM-modified photoanodes investigated so far is rather limited, and our knowledge of the factors governing the PEC performance of CoPOM-containing photoelectrochemical
architectures is still underdeveloped, which makes the rational design of high-performance Co-POM-based photoanodes very challenging.

In the present work, we report significant improvements of the PEC performance of mesoporous BiVO$_4$ photoanodes using a combined strategy of Mo-doping and direct deposition of CoPOM via a simple impregnation protocol without any linkers or binders. The best-performing optimized Mo-BiVO$_4$/CoPOM photoanode exhibits a photocurrent density of 4.32 mA cm$^{-2}$ at 1.23 V vs. RHE under AM 1.5G (1 sun) irradiation and an applied-bias photoconversion efficiency (ABPE) of $\sim$0.73%, which is an improvement by the factor of 24 and 2.5 compared to pristine BiVO$_4$ ($\sim$0.03%) and Mo-BiVO$_4$ ($\sim$0.29%), respectively. Furthermore, we disentangle the respective contributions of the Mo-doping and modification with CoPOM to the performance enhancement and show compelling evidence that the beneficial role of CoPOM is related to enhanced kinetics of water oxidation. Finally, we provide several unprecedented insights into the effects of both Mo-doping (e.g., Mo-induced limitation of photovoltage) and CoPOM modification (e.g., compositional changes under operating conditions and significant electrolyte effects), which are of great importance for the further design and development of efficient photoanodes for water splitting.

2. Results and discussion

The detailed descriptions for the fabrication of BiVO$_4$ and Mo-BiVO$_4$/CoPOM films are given in the ESI†. The fabrication protocols (incl. doping concentration and co-catalyst loading) were optimized by screening for the highest photoelectrocatalytic activity in each case. In short, the BiVO$_4$ and Mo-BiVO$_4$ films were prepared via spin coating onto FTO glass substrates, followed by drying and calcination. The CoPOM complex was synthesized according to a previously reported method,$^{51}$ and deposited via impregnation to obtain Mo-BiVO$_4$/CoPOM photoelectrodes. The X-ray diffraction (XRD) patterns of all BiVO$_4$-based photoanodes exhibit the typical diffraction peaks of monoclinic scheelite BiVO$_4$ (Fig. S1a†), indicating that the crystal structure of BiVO$_4$ is not significantly altered upon Mo-doping or deposition of CoPOM. No shifts of diffraction peaks or new reflexes related to molybdenum oxide were detected, which suggests that Mo is present in low amount as a homogenously distributed dopant without affecting the structure of BiVO$_4$. As expected, as the amount of deposited CoPOM was very low, it could be detected neither in XRD nor by Fourier-transform infrared spectroscopy (FT-IR) (Fig. S1b†). However, the presence of CoPOM in Mo-
BiVO$_4$/CoPOM was verified by transmission electron microscopy, energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) (see below).

The morphology and film thickness of as-prepared BiVO$_4$, Mo-BiVO$_4$ and Mo-BiVO$_4$/CoPOM photoanodes were investigated by field emission scanning electron microscopy (FESEM). As shown in Fig. 1a, all of the films are composed of uniform and homogeneous worm-like nanoparticles with an average diameter of ~100-200 nm, forming a three-dimensional mesoporous structure with pore sizes in the range of tens of nanometers. The introduction of F-108 as a structural agent during the synthesis is responsible for inducing this porous architecture, which serves as the foundation for all subsequent surface-modified photoanodes. Notably, both Mo doping shown in Fig. 1b and surface modification with CoPOM shown in Fig. 1c have no appreciable effect on the morphology of BiVO$_4$, retaining the typical porous structure. Fig. S2a-S2c† shows the cross-section SEM images of all three photoanodes, showing that the material layers have a comparable thickness of 600 ± 20 nm. Since the structure of the Mo-BiVO$_4$ material is porous and the CoPOM was deposited via the impregnation method, a homogenous distribution of the co-catalyst throughout the porous layer is expected. To investigate the distribution of CoPOM, EDX elemental mapping was carried out. For both in the cross-section and the surface of Mo-BiVO$_4$/CoPOM, the elements Mo, Bi, V and O (representing Mo-BiVO$_4$) and Co, W (representing CoPOM) have been detected. These EDX mapping results demonstrate a very dense and uniform distribution of CoPOM within the mesoporous Mo-BiVO$_4$ structure (Fig. S2d and S2e†). A closer look with the help of high-resolution transmission electron microscopy (HRTEM) revealed that Mo-BiVO$_4$/CoPOM contains uniformly distributed nanospheres with a diameter of less than 10 nm (Fig. 1f and 1g). Since these nanospheres are completely absent in the (CoPOM-free) Mo-BiVO$_4$ photoanode (Fig. 1d and 1e), we assume the nanospheres to be CoPOM nanoparticles. These CoPOM nanospheres are closely spaced and homogeneously distributed on the surface of the Mo-BiVO$_4$ porous support (Fig. 1f and 1g). Furthermore, Fig. 1h shows the scanning transmission electron microscopy (STEM) image of Mo-BiVO$_4$/CoPOM with EDX
mapping images of Bi, V, O, Mo, Co, and W, which again confirms the uniform distribution of the Mo dopant and of the CoPOM co-catalyst.

Fig. 1. FESEM images of (a) BiVO_4, (b) Mo-BiVO_4 and (c) Mo-BiVO_4/CoPOM. High-resolution TEM images of Mo-BiVO_4 (d and e) and Mo-BiVO_4/CoPOM (f and g). (h) EDX elemental mappings of Mo-BiVO_4/CoPOM. The lattice spacing of 0.47 nm is characteristic of (110) planes of BiVO_4 (JCPDS card Number 14-0688).  

In order to further verify the presence of CoPOM in the Mo-BiVO_4/CoPOM and to investigate the surface chemical composition of the photoelectrode material, XPS analysis was carried out at BiVO_4, Mo-BiVO_4 and Mo-BiVO_4/CoPOM electrodes. As shown in Fig. S3a†, all expected signals of Mo, Bi, V, O, Na, Co and W elements are observed in the XP survey spectrum of Mo-BiVO_4/CoPOM, which indicates the successful preparation of the composite material. Two typical spin-orbit coupling peaks of Bi (at 164.3 eV and 159.1 eV for Bi 4f_{5/2} and Bi 4f_{7/2}, respectively) are assigned to Bi^{3+} in BiVO_4 (Fig. 2a and S3b†).  

The O 1s XP spectrum (Fig. 2b) can be fitted to two peaks located at 529.8 eV and 530.7 eV, which are assigned to lattice oxygen in BiVO_4 and surface hydroxyl oxygen, respectively.  

The vanadium signals (Fig. 2b and S3c†) can be fitted into two spin-orbit coupling peaks located at 524.0 eV (V 2p_{1/2}) and 516.6 eV (V 2p_{3/2}), which are characteristic of V^{5+} species in BiVO_4.
As shown in Fig. S3d†, the binding energies of the Mo 3d$_{3/2}$ (235.1 eV) and Mo 3d$_{5/2}$ (232.0 eV) peaks indicate that the molybdenum dopant is in the oxidation state of +VI.$^{58,62,67}$ The high-resolution XP spectrum of Co 2p (Fig. 2c) shows two core-level spin-orbit coupling peaks located at 797.1 (Co 2p$_{1/2}$) and 781.2 eV (Co 2p$_{3/2}$) with typical satellite peaks at 805.4 and 785.7 eV, indicating the presence of Co$^{2+}$.67–69 In Fig. 2d, the two spin-orbit splitting peaks at 37.6 eV and 35.4 eV attributed to W 4f$_{5/2}$ and W 4f$_{7/2}$ confirm the presence of W$^{6+}$.70 Importantly, the Co 2p and W 4f XPS signals of authentic CoPOM powder (Fig. S4†) are nearly identical to the corresponding XPS signals of the CoPOM in the electrode, which further corroborates the successful loading of CoPOM clusters into the porous structure of the Mo-BiVO$_4$/CoPOM photoelectrode.

Fig. 2. XP spectra of Mo-BiVO$_4$/CoPOM photoanode: (a) Bi 4f, (b) O 1s and V 2p, (c) Co 2p and (d) W 4f.

The UV-Vis electronic absorption spectra of BiVO$_4$, Mo-BiVO$_4$ and Mo-BiVO$_4$/CoPOM samples displayed in the ESI†, Fig. S5a and S5b† show that all samples exhibit comparable light absorption onsets at ~515 nm. In this context, we note that in the literature there are conflicting reports about whether BiVO$_4$ is a direct$^{71}$
or indirect\textsuperscript{72} bandgap semiconductor. The bandgap energies of all photoelectrodes were estimated to be \(\sim 2.56\) eV and \(\sim 2.50\) eV for direct and indirect optical transition, respectively, using the Tauc formalism (Fig. S5c and S5d\textsuperscript{†}). Importantly, these results reveal that the effects of Mo-doping and CoPOM deposition on the electronic absorption properties of BiVO\textsubscript{4} photoanodes are negligible, without any changes of the fundamental absorption edge, nor any significant parasitic light absorption by the CoPOM catalyst.

To investigate the combined effects of Mo-doping and modification by CoPOM on PEC performance of BiVO\textsubscript{4} photoanodes, the photocurrent density-potential (\(J\)-\(V\)) curves of BiVO\textsubscript{4}, Mo-BiVO\textsubscript{4} and Mo-BiVO\textsubscript{4}/CoPOM photoanodes were measured under intermittent AM 1.5G irradiation (1 sun) using a three-electrode setup in a 0.5 M sodium borate buffer electrolyte at pH 9.0 (Fig. 3a). The PEC performance of the photoanodes was optimized for (i) Mo doping concentration of BiVO\textsubscript{4}, (ii) calcination temperature of Mo-BiVO\textsubscript{4}, (iii) loading of the CoPOM in Mo-BiVO\textsubscript{4} and (iv) various pH values of borate electrolyte (the results of optimization protocols are summarized in ESI, Fig. S6\textsuperscript{†}). The content of Mo, Co and W elements in the Mo-BiVO\textsubscript{4}/CoPOM photoanode optimized for the highest PEC efficiency was 0.79 at\%, 0.95 at\% and 1.92 at\%, respectively, as estimated by the SEM-EDX analysis (Tab. S1\textsuperscript{†}), which is also in line with the elemental analysis based on XPS results (Tab. S2\textsuperscript{†}). The optimum
calcination temperature was 450 °C and the optimal PEC performance was achieved in a borate buffer at pH 9.0.

Fig. 3 (a) Linear-sweep voltammetry (LSV) curves recorded under intermittent AM 1.5G illumination in borate buffer (0.5 M, pH 9.0) at cathodic sweep of 10 mV s\(^{-1}\), (b) Open-circuit potential (OCP) transients recorded under interrupted AM 1.5G (1 sun) illumination in 0.5 M borate buffer under argon atmosphere, (c) photocurrent transients under AM 1.5G illumination, (d) stability chronoamperometric tests measured in borate buffer (0.5 M, pH 9.0) under AM 1.5G illumination (1 sun) at 0.74 V vs. RHE for all three photoanodes. All photocurrent measurements were carried out at least in triplicate, and representative average data are shown.

Fig. 3a shows the J-V curves of various optimized photoanode architectures under back-side illumination (from the FTO-glass side). The BiVO\(_4\) and Mo-doped BiVO\(_4\) photoanodes reach the photocurrent density of 0.65 mA cm\(^{-2}\) and 2.53 mA cm\(^{-2}\) at 1.23 V vs. RHE, respectively. After the modification by CoPOM, the highest photocurrent density of Mo-BiVO\(_4\)/CoPOM increases up to 4.32 mA cm\(^{-2}\) at 1.23 V vs. RHE, which is an enhancement by the factor of 6.6, and 1.7 with respect to BiVO\(_4\), and Mo-BiVO\(_4\), respectively. Importantly, both Mo-BiVO\(_4\) and Mo-BiVO\(_4\)/CoPOM photoanodes exhibit a remarkable cathodic shift of the photocurrent onset potential by
~0.5 V as compared to the pristine BiVO$_4$ photoanode, whereby the modification with CoPOM significantly increases photocurrents even at very low bias potentials, improving thus the fill-factor of the $J$-$V$ curve. In other words, the combination of Mo-doping and CoPOM modifications results in a substantial increase of the photovoltage available for driving the water splitting reaction. In order to further disentangle the effects of Mo-doping and Co-POM modification, we also directly compared the $J$-$V$ curves of Mo-free (undoped) BiVO$_4$/CoPOM with Mo-BiVO$_4$/CoPOM (Fig. S7†). Interestingly, the Mo-BiVO$_4$/CoPOM shows much higher photocurrents at relatively higher applied potentials (> 0.9 V vs. RHE), but at very low bias potentials (< 0.7 V vs. RHE) the situation is reversed and the Mo-free BiVO$_4$/CoPOM electrode yields even slightly higher photocurrents than the Mo-BiVO$_4$/CoPOM photoanode. These observations imply that (i) the combination of Mo-doping and Co-POM deposition significantly improves the photocurrent response in the whole potential range with respect to pristine BiVO$_4$, (ii) the enhancement due to the deposition of CoPOM is particularly pronounced at low bias potentials, *i.e.*, the beneficial negative shift of the photocurrent onset potential and improved fill-factor is mainly due to the CoPOM deposition, and (iii) at very low bias potentials the Mo-doping might even partially counteract the positive effects induced by the CoPOM deposition. The observation that the Mo-doping might be detrimental at relatively low bias potentials prompted us to measure the open-circuit photopotential (OCP) of all photoanodes (Fig. 3b). Under illumination, the observed OCP should correspond to the *quasi*-Fermi level of electrons $E_{Fn}$ (*i.e.*, the electrochemical potential of electrons) in the illuminated semiconductor, which in turn is directly related to the photocurrent onset potential (and the fill-factor at low bias potentials), and thus to the maximum achievable photovoltage of the water-splitting system. Indeed, the OCP results clearly show that for both Mo-BiVO$_4$ and Mo-BiVO$_4$/CoPOM the Mo-doping leads to a positive shift (by ~90 mV) of the maximum achievable *quasi*-Fermi level of electrons as compared to pristine BiVO$_4$. It should be noted that this observation is in stark contrast to the data for Mo-doped BiVO$_4$ (with similar doping concentration) reported by Ye *et al.*$^{32}$ who observed a slight negative shift of the OCP after Mo-doping. However, our observation of a positive shift of the OCP after the Mo-doping is completely in line with the observed decrease of photocurrent at low bias potentials induced by the Mo-doping (Fig. S7†), and suggests that the Mo-doping does not have only beneficial effects, such as the enhancement of
photocurrents at relatively high bias potentials, but also induces effects that are detrimental to the PEC performance.

Our experimental proof that the maximum achievable quasi-Fermi level of electrons is less negative after Mo-doping is significant and deserves a more detailed discussion. In this context, we point out that it is well-established that the maximum achievable photovoltage in metal oxide photoanodes is typically limited by the presence of intragap electron polaronic states formed upon self-trapping of excess electrons at reduced ionic sites (e.g., Fe$^{2+}$ in hematite Fe$_2$O$_3$, or V$^{4+}$ in BiVO$_4$) in the lattice, accompanied by the displacement of surrounding atoms via electron–phonon interactions, forming thus a quasi-particle called polaron.$^{73,74}$ As the electron polaron level is typically significantly below the conduction band edge, it effectively traps electrons, limits their mobility, acts as a recombination center, and therefore establishes an inherent limitation of the maximum achievable quasi-Fermi level of electrons and photovoltage. For both pristine and doped BiVO$_4$, it is reported that the excess electrons are localized in hybridized vanadium $3d_z^2$ orbitals,$^{75,76}$ which is accompanied by elongation of the V–O bond by ~0.1 Å and formation of small polarons located ca. 0.88 eV below the conduction band edge.$^{77}$ Doping by molybdenum substitutes V$^{5+}$ with ionized Mo$^{6+}$ dopants, whereby the excess electron is readily localized at V$^{4+}$ polaronic states.$^{75}$ The detrimental polaronic effects can be then (at least partially) avoided by applying a sufficient external electric bias, which, however, compromises the overall photoconversion efficiency. To summarize, the conductivity enhancement upon Mo-doping, which is apparent from enhanced photocurrents at higher bias potentials, is mainly due to the increased electron concentration, whereby the electron mobility is apparently not improved.$^{78}$ However, at low bias potentials the beneficial effect of the Mo-doping is counterbalanced by enhanced recombination due to the presence of deep electron polaron states,$^{75}$ which makes itself apparent by decreased photocurrents at low bias potentials and by a less negative OCP (i.e., less negative quasi-Fermi level of electrons) under irradiation.

In order to assess the dynamics of photogenerated charge carriers, transient photocurrent measurements of pristine BiVO$_4$, Mo-BiVO$_4$ and Mo-BiVO$_4$/CoPOM photoanodes were carried out at a moderate bias potential of +0.74 V vs. RHE under chopped AM 1.5G (1 sun) illumination (Fig. 3c). On the timescale of this experiment (~minutes), the photocurrent response indicates an excellent short-term stability.
Evidently, for both CoPOM-free photoanodes (red and blue line), the photocurrent spikes after switching on the light and negative current overshoots after switching off the light (see insert in Fig. 3c) are significantly more pronounced, demonstrating that in the absence of water oxidation catalyst the charge carriers are prone to intense surface recombination. In other words, in the absence of the CoPOM co-catalyst, the photogenerated holes do not react fast enough with water but accumulate in the surface layer of BiVO$_4$ or Mo-BiVO$_4$, enhancing thus the probability of recombination with electrons. The intense recombination of surface-accumulated holes and electrons leads to a rapid decrease of the photocurrent immediately after switching on the light, and continues even after the light is switched off, as apparent from the negative current overshoot after switching off the light. In contrast, the current spikes are less pronounced and the overshoots are nearly absent at the Mo-BiVO$_4$/CoPOM photoanode, which clearly demonstrates that the CoPOM co-catalyst efficiently extracts the holes photogenerated in the Mo-BiVO$_4$ layer and channels them to water molecules in the electrolyte solution. This explains the significant photocurrent enhancement upon the deposition of CoPOM shown in Fig. 3a and 3c. In this context, we also note that the addition of polyethylenimine (PEI) as a cationic linker has no effect on the performance of the photoanodes (Fig. S8†), which highlights the intrinsically good electronic communication between the CoPOM and BiVO$_4$.

The long-term stability of the photoanode and its PEC performance is an important issue not only with respect to possible applications, but in our case also with respect to fundamental questions regarding the stability and/or compositional changes of the used CoPOM polyoxometalate catalyst under PEC operational conditions. As illustrated in Fig. 3d, the photocurrent generated by the investigated photoanodes was measured at a constant potential of +0.74 V vs. RHE for four hours under simulated AM 1.5G (1 sun) illumination, and only a very slight (by ~15%), yet continuous, decline of photocurrent density was observed for the optimized Mo-BiVO$_4$/CoPOM electrode. The small perturbations of the photocurrent are likely related to the release of oxygen bubbles from the electrode surface, which can be observed by naked eye (see Video in the ESI†). The XRD patterns of all samples recorded after the PEC experiment show the typical diffraction peaks of monoclinic scheelite BiVO$_4$, indicating that the BiVO$_4$-based light absorber did not undergo any structural changes under the operating conditions (Fig. S9†, compared with Fig. S1a†). However, a question arises regarding the stability of the CoPOM co-catalyst under PEC operation since it has been reported...
that this polyoxometalate can – depending on experimental conditions – undergo conversion to cobalt oxide (CoO$_x$) which then often plays a chief role in water oxidation catalysis.$^{54,55}$ In order to shed light on the fate of CoPOM in our photoanodes during operation, we analyzed in detail both the composition of the Mo-BiVO$_4$/CoPOM photoanode after the PEC operation and the elemental composition of the electrolyte before and after the PEC experiments. First of all, we note that the small nanospheres attributed to CoPOM that could be seen before the PEC operation (Fig. 1f and 1g), were not observed anymore by HRTEM after the PEC operation (Fig. S10†), which indicates that the CoPOM cocatalyst has undergone (at least partially) morphological changes. Notably, the XPS analysis revealed that the signals related to the presence of W and Co are significantly weaker after the PEC operation (Fig. S11a†), whereby the XPS signature of Co is still well-detectable in the high-resolution XP spectrum and is very similar to the situation before the PEC operation (Fig. S11b†, compare with Fig. 2c). Notably, the surface content of both Co and W derived from the XPS analysis is significantly decreased and the W/Co atomic ratio increased after the PEC operation (Tab. S3†). However, EDX analyses performed both from the top-view (Tab. S4†) and from the cross-sectional view (Tab. S5†) clearly show that both W and Co are still present in the photoelectrode in significant amounts, albeit with a significantly higher W/Co ratio than before the PEC operation. In this context, it should be noted that quantitative EDX analysis is rather challenging in this case due to the overlap between the Si-K (from the underlying glass) and W-M lines and since the content of Co and W is very low. Yet, the above differences in the composition before and after the PEC operation, in particular the changing ratio of W/Co, indicate that at least a partial dissolution of CoPOM and/or conversion of CoPOM to cobalt and tungsten oxides can occur during the PEC operation. Interestingly, an analysis of the composition of the electrolyte solution before and after the PEC operation using inductively coupled plasma atomic emission spectrometry (ICP-AES) did not detect any Co, and the concentration of W also did not increase (Tab. S6†). While we cannot completely rule out the dissolution of CoPOM as the dissolved amount of Co and W might be below the detection limit of ICP-OES, our results indicate that a complete dissolution of CoPOM is not an issue. All the above observations suggest that, though the CoPOM catalyst does not dissolve in the electrolyte solution, it does undergo, at least partially, conversion to cobalt oxide, as previously reported for borate electrolytes by Finke et al.$^{54}$ In other words, under our PEC operating conditions, the CoPOM co-catalyst
should be rather conceived as a *pre-catalyst*, whereby a substantial part of water oxidation catalysis might be performed by cobalt oxide-based catalyst derived from CoPOM under operating conditions, as suggested by Finke *et al.* for CoPOM behavior in electrocatalysis.\textsuperscript{54} However, in this context, it should be also noted that the activity and stability of various cobalt oxide-based water oxidation catalysts can strongly depend on their precursor and operating conditions, as minute changes in composition can often exert strong effects on catalysis. For comparison, we have therefore also tested the performance of our Mo-BiVO\textsubscript{4} photoanode after modification with a CoPi co-catalyst (i.e., cobalt oxy-hydroxide formed upon photodeposition in Co\textsuperscript{2+} containing phosphate buffer) and with a CoO(OH)\textsubscript{x} co-catalyst (i.e., cobalt oxy-hydroxide deposited via a two-step impregnation process).\textsuperscript{11} These two photoanodes reached photocurrents slightly lower (by 9\% and 33\%, respectively) than the Mo-BiVO\textsubscript{4}/CoPOM photoanode (Fig. S12†), which confirms that the “pre-history” of the catalyst can make a difference to its activity in photoanodes, and that the CoPOM-derived water oxidation catalyst exhibits optimal performance.

Furthermore, it is well established that the activity and stability of Co-based electrocatalysts can depend strongly on the electrolyte composition,\textsuperscript{80} and our group previously observed strong electrolyte effects on the stability of CoO(OH)\textsubscript{x} water oxidation co-catalysts in hybrid photoanodes.\textsuperscript{11} Therefore, we carried out a comparative analysis of the PEC operational stability of our photoanodes in borate and phosphate electrolytes. Specifically, we measured the linear sweep voltammetry under chopped illumination in the borate and the phosphate electrolyte at pH 9.0, and then repeated the measurement six times. In the borate buffer electrolyte at pH 9.0 (Fig. S13a-S13c†), the photocurrents for BiVO\textsubscript{4}, Mo-BiVO\textsubscript{4} and Mo-BiVO\textsubscript{4}/CoPOM photoanodes remained completely stable over all six cycles. In contrast, in the phosphate electrolyte at pH 9.0 (Fig. S13d-S13f†), the Mo-BiVO\textsubscript{4}/CoPOM exhibits a gradual decrease of photocurrents. The much higher operational stability of Mo-BiVO\textsubscript{4}/CoPOM photoanodes in a borate electrolyte is also clearly apparent from the long-term (4 hours) chronoamperometric measurement at +0.74 V vs. RHE under 1 sun irradiation (Fig. S14†). In this context, two points are noteworthy. First, the clearly detrimental effect of phosphate anions on the PEC performance stability of Mo-BiVO\textsubscript{4}/CoPOM is *not* simply related to the fact that the phosphate electrolyte is operated at pH 9.0 (i.e., beyond its ideal buffering pH range around pH ~7), whereas the borate electrolyte operates at its optimal buffering capacity (pH ~9), since
comparative experiments performed at pH 7.0 also revealed that the photocurrents at Mo-BiVO$_4$/CoPOM were more stable in the borate electrolyte than in the phosphate electrolyte (Fig. S15†). Second, similar to the case of the borate electrolyte, no cobalt could be detected in the phosphate electrolyte after PEC operation (Tab. S6†), suggesting that the dissolution of the co-catalyst is not the major reason for lower photoanode stability in phosphate electrolytes. We, therefore, conclude that the PEC operational stability of our photoanodes is related to the presence of specific electrolyte anions, whereby borate electrolytes are more beneficial as compared to phosphate electrolytes. Drawing on our previous discussion,$^{11}$ we assume that the Co (III/IV) ions, which are formed in situ during the water oxidation catalytic cycle and which represent, in terms of the HSAB theory, hard acid species, can interact more strongly with phosphate ions which are much harder bases than the relatively large borate anions (present mainly as tetraborates). We speculate that the relatively stronger interaction of cobalt ions with phosphate anions can induce, during the PEC operation, changes in the interaction between the BiVO$_4$ light absorber and the co-catalyst, which eventually results in lower observed stability of PEC performance in phosphate-containing electrolytes.

From a practical point of view, the applied bias photoconversion efficiency (ABPE) is the most important and informative performance metric for water splitting photoanodes. As presented in Fig. 4a, the maximum ABPE of 0.73% was determined for Mo-BiVO$_4$/CoPOM photoanode at a potential of +0.86 V vs. RHE, which is an enhancement by the factor of 24 and 2.5 compared to pristine BiVO$_4$ (~0.03% at +1.07 V vs. RHE) and Mo-BiVO$_4$ (~0.29% at +0.98 V vs. RHE), respectively. Apart from the significant increase of the photoconversion efficiency upon the combined effect of doping with Mo and modification with CoPOM, the fact that the maximum power point is shifted to more negative bias potentials is particularly important in view of more feasible integration with photocathodes for hydrogen evolution in tandem solar-driven water splitting systems.
In order to obtain further insight into the PEC operation of our photoanodes, the wavelength-resolved *incident photon-to-current conversion efficiency* (IPCE) was measured at +0.74 V vs. RHE under illumination from the backside (BS, *i.e.* from the substrate side) and frontside (FS, *i.e.* from the electrolyte side) (Fig. 4b). The photoaction spectra show an onset at ca. 510 nm, which is in line with the electronic absorption properties of the photoanodes (compare with Fig. S5†). The IPCE values are, independently of the illumination side, the highest for the Mo-BiVO₄/CoPOM photoanode, followed by Mo-BiVO₄ and pure BiVO₄ over the whole wavelength range, which is in line with the photocurrent performance under polychromatic light at the same bias, as shown in Fig. S16† in ESI (see also Fig. 3c). From the mechanistic point of view, it is often worth looking at the difference in IPCE values under the FS and BS.
illumination for a given photoelectrode. The most notable difference is in the behavior of the Mo-free pristine BiVO₄ photoanode as compared to Mo-BiVO₄ and Mo-BiVO₄/CoPOM photoanodes. While the latter two photoanodes show a very small difference in IPCE values recorded under the FS and BS illumination, the Mo-free pristine BiVO₄ photoanode exhibits much larger (by the factor of ~10) IPCE values under the BS illumination than under the FS illumination (for a detailed view see ESI, Fig. S17†). This is exactly what one expects for a porous photoanode in which the photocurrent is mainly limited by the transport of electrons through the porous network, i.e. by the electronic conductivity of BiVO₄. Under the FS illumination, most of the photogenerated electron-hole pairs are generated close to the film/electrolyte interface, and while the holes can readily react with water within the pores of the electrode, the electrons have to travel through the porous electrode to the underlying FTO back contact. Since under the BS illumination the electron-hole pairs are generated much closer to the FTO/film interface, the photogenerated electrons have a much shorter pathway to reach the FTO, resulting in significantly higher IPCE values under the BS illumination. Interestingly, the pristine BiVO₄ photoanode even exhibits a wavelength-dependent switching (at ~460 nm) of the sign of the photocurrent from anodic to cathodic under the BS illumination and from cathodic to anodic under the FS illumination. This behavior can be again rationalized by the dominant effect of the poor electron transport properties of pristine BiVO₄ on the photocurrent response, which, in combination with the different penetration depth of short (below 460 nm) and long (above 460 nm) wavelengths of light and with the generally higher intensity of the visible light as compared to UV light in our setup, can even result in the reversal of the photocurrent sign. In this context, we note that while the potential-dependent photocurrent switching has been reported for BiVO₄ photoelectrodes, the fact that at a specific bias potential (in our case a rather moderate bias potential of +0.74 V vs. RHE) the photocurrent switching at BiVO₄ can be controlled even by the light wavelength and by the illumination side has not been reported before, and would deserve further investigation given the importance of such phenomena for the development of photoelectrochemical optoelectronic switches. In contrast to the behavior of the pristine BiVO₄ photoanode that is dominated by its low electronic conductivity, the very small difference in IPCE values under the FS and BS illumination observed for both Mo-doped samples Mo-BiVO₄ and Mo-BiVO₄/CoPOM (Fig. 4b) nicely illustrate that the beneficial effect of Mo-doping consists mainly in improving the
electronic conductivity of Mo-BiVO₄ by increasing the electron concentration, as discussed in detail above.

Further valuable insights into the effects of Mo-doping and the role of CoPOM co-catalyst on the PEC performance can be gained by determining the charge separation efficiency ($\eta_{sep}$) and the hole transfer efficiency ($\eta_{tr}$) as a function of applied potential (Fig. 4c and 4d), employing the methodology developed by Dotan et al. and Hamann et al. (for details see ESI†). Firstly, by integrating the electronic absorption spectra (Fig. S5b†) over the reference AM1.5G photon flux spectra, the maximum theoretically achievable photocurrents $J_{max}$ were calculated to be 7.37 mA cm$^{-2}$, 7.36 mA cm$^{-2}$ and 7.34 mA cm$^{-2}$ for BiVO₄, Mo-BiVO₄ and Mo-BiVO₄/CoPOM, respectively. The photocurrent density of both Mo-BiVO₄ and Mo-BiVO₄/CoPOM photoanodes in the presence of Na₂SO₃ acting as a readily oxidizable reducing agent (i.e., sacrificial hole scavenger) is significantly higher than that of pristine BiVO₄ and reaches 6.5 mA cm$^{-2}$ as compared to 3.2 mA cm$^{-2}$ at 1.23 V vs. RHE, respectively (Fig. S18†). Based on the above results, the charge separation efficiency $\eta_{sep}$ was calculated and plotted in Fig. 4c. Notably, $\eta_{sep}$ for Mo-BiVO₄ and Mo-BiVO₄/CoPOM is significantly higher than for pristine BiVO₄ in a wide potential range, whereby the enhancement is increasingly pronounced at more positive bias potentials. This behavior is in line with our finding that the beneficial effects of the improvement of electronic conductivity upon Mo-doping are more pronounced at positive bias potentials, whereby at very low bias potentials the positive effects are traded off against the detrimental effects of Mo-doping associated with increased concentration of intragap electron polaronic states. Interestingly, at higher bias potentials (> 0.7 V vs. RHE), the Mo-doped Mo-BiVO₄ exhibits also an improved interfacial hole transfer efficiency $\eta_{tr}$ with respect to pristine BiVO₄ (Fig. 4d). This positive effect of Mo-doping on $\eta_{tr}$ can be interpreted as partial mitigation of excessive hole accumulation in the surface states, as reported recently by Selli et al.²⁶ After the deposition of Co-POM, the hole transfer efficiency $\eta_{tr}$ (Fig. 4d) is greatly enhanced over the entire potential range and shifted to more cathodic potentials. For example, at 1.23 V vs. RHE, the $\eta_{tr}$ increases from 13.1% for BiVO₄ to 37.8% after Mo-doping (Mo-BiVO₄) up to 63.0% for Mo-BiVO₄/CoPOM photoanode. Importantly, the charge separation efficiencies ($\eta_{sep}$) for Mo-BiVO₄/CoPOM and Mo-BiVO₄ are nearly identical in the whole potential range (Fig. 4c), which clearly indicates that the beneficial effect of CoPOM deposition
consists chiefly in enhancing the catalysis of water oxidation. This is a significant result since the effect of co-catalysts on photocurrent enhancement at BiVO₄ photoanodes is a much-debated issue and, apart from enhancing the catalysis of water oxidation, other effects of various co-catalyst (e.g., improved charge extraction or passivation of surface states) are often reported to be responsible for photocurrent enhancement in the literatures.⁴⁻⁷ Our results unambiguously demonstrate that in our photoanodes the beneficial effect of CoPOM deposition consists mainly in enhancing the rate of water oxidation by photogenerated holes.

![Fig. 5](image)

Fig. 5 (a) Dioxygen evolution and (b) corresponding photocurrent transients recorded under AM 1.5G one sun illumination at 0.74 V vs. RHE in a borate electrolyte (0.5 M, pH 9.0). All measurements were carried out at least in triplicate, and representative average data are shown.

Finally, in order to provide a direct evidence for dioxygen evolution at our photoanodes, we performed photoelectrocatalytic OER measurements (Fig. 5a) in a borate solution (pH 9.0) at 0.74 V vs. RHE under AM 1.5G (1 sun) illumination. As expected, the Mo-BiVO₄/CoPOM photoanode exhibits an excellent oxygen evolution rate with an average faradaic efficiency of oxygen evolution of 102.1% ± 6.2% (calculated from three measurements; the error is taken as ±1σ, σ = standard deviation), which demonstrates that the conversion of H₂O to O₂ by photogenerated holes is practically quantitative and no side reactions (e.g., photocorrosion or H₂O₂ evolution) occur. Similar results were obtained for Mo-BiVO₄ (100.0% ± 12.0%), whereby at pristine BiVO₄ the faradaic efficiency was slightly lower (90.3% ± 8.3%), suggesting a minor role of side reactions, possibly related to the photocorrosion.⁸⁸ These results suggest that Mo-doping has also a beneficial effect on the stability of the photoanodes under the PEC operation, which again might be related to the
decreased charge accumulation in the surface states, since excessive hole accumulation in the surface states can be expected to render the dissolution of BiVO$_4$ more facile.

3. Conclusion

In this study, we showcase a remarkably powerful strategy for enhancing the performance of bismuth vanadate photoanodes for water oxidation by combining the bulk doping of BiVO$_4$ with molybdenum and its surface modification with a well-defined molecular cobalt polyoxometalate (CoPOM = Na$_{10}$[Co$_4$(H$_2$O)$_2$(PW$_9$O$_34$)$_2$]) via a simple binder-free impregnation protocol. The best-performing optimized Mo-BiVO$_4$/CoPOM photoanode exhibits a photocurrent density of 4.32 mA cm$^{-2}$ at 1.23 V vs. RHE under AM 1.5G (1 sun) illumination and an applied-bias photoconversion efficiency (ABPE) of ~0.73%, which is an improvement by the factor of 24 and 2.5 compared to pristine BiVO$_4$ and Mo-BiVO$_4$, respectively. Notably, our detailed mechanistic investigations disentangle and elucidate the respective contributions of the Mo-doping and modification with CoPOM to the performance enhancement for water oxidation. The positive effect of Mo-doping is shown to be related to enhanced electronic conductivity and passivation of surface states. However, these beneficial effects are operative only at relatively high applied bias potentials (> 0.9 V vs. RHE), whereas at lower bias potentials (< 0.7 V vs. RHE) they are counterbalanced by strongly detrimental effects related to increased concentration of electron polaronic states induced by the Mo-doping. In other words, there is an inherently negative impact of Mo-doping on the maximum achievable photovoltage in Mo-doped BiVO$_4$ photoanodes, an important aspect that has not been fully recognized and experimentally elucidated so far. The deposition of CoPOM enhances photocurrents in the whole potential range. Importantly, the beneficial effect of CoPOM deposition is unambiguously demonstrated to be related to the enhancement of water oxidation catalysis, whereby the borate electrolytes show a more beneficial effect on the stability of PEC performance as compared to phosphate-based electrolytes. Furthermore, the experimental evidence shows that under the PEC operating conditions the molecular CoPOM is, at least partially, disintegrated and converted to cobalt oxide, and is therefore best conceived as a pre-catalyst. Taken together, our work establishes CoPOM-derived catalysts as effective water oxidation catalysts at BiVO$_4$ photoanodes, provides new insights into the combined effects of Mo-doping and modification with
molecular cobalt polyoxometalates on the PEC performance of BiVO₄, and suggests that further progress in the development of BiVO₄ photoanodes depends critically on devising alternative doping strategies to overcome the negative polaronic effects associated with bulk doping of BiVO₄, since these detrimental effects set fundamental limits to the maximum achievable photovoltage and thus compromise the overall photoconversion efficiency.

Data availability
All datasets related to this work are available from zenodo.org under DOI:10.5281/zenodo.10401296.

Conflicts of interest
There are no conflicts to declare.

Author Contributions
C. S. and R. B. conceptualized and supervised the study, and acquired funding. F. F., D. M., R. G., D. G., M. M. E. and R. L. performed investigations, acquired and analyzed data. All co-authors wrote and reviewed the manuscript.

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