Importance of catalyst–photoabsorber interface design configuration on the performance of Mo-doped BiVO₄ water splitting photoanodes

Olga A. Krysiak^{1,2} · João R.C. Junqueira¹ · Felipe Conzuelo¹ · Tim Bobrowski¹ · Justus Masa³ · Andrzej Wyszomolek⁴ · Wolfgang Schuhmann¹

Received: 8 February 2020 / Revised: 7 April 2020 / Accepted: 5 May 2020 / Published online: 18 May 2020
© The Author(s) 2020

Abstract

Photoelectrochemical water splitting is mostly impeded by the slow kinetics of the oxygen evolution reaction. The construction of photoanodes that appreciably enhance the efficiency of this process is of vital technological importance towards solar fuel synthesis. In this work, Mo-modified BiVO₄ (Mo:BiVO₄), a promising water splitting photoanode, was modified with various oxygen evolution catalysts in two distinct configurations, with the catalysts either deposited on the surface of Mo:BiVO₄ or embedded inside a Mo:BiVO₄ film. The investigated catalysts included monometallic, bimetallic, and trimetallic oxides with spinel and layered structures, and nickel boride (Ni_xB). In order to follow the influence of the incorporated catalysts and their respective properties, as well as the photoanode architecture on photoelectrochemical water oxidation, the fabricated photoanodes were characterised for their optical, morphological, and structural properties, photoelectrocatalytic activity with respect to evolved oxygen, and recombination rates of the photogenerated charge carriers. The architecture of the catalyst-modified Mo:BiVO₄ photoanode was found to play a more decisive role than the nature of the catalyst on the performance of the photoanode in photoelectrocatalytic water oxidation. Differences in the photoelectrocatalytic activity of the various catalyst-modified Mo:BiVO₄ photoanodes are attributed to the electronic structure of the materials revealed through differences in the Fermi energy levels. This work thus expands on the current knowledge towards the design of future practical photoanodes for photoelectrocatalytic water oxidation.

Keywords Photoelectrocatalysis · Water splitting · Catalysts · Oxygen evolution reaction · Bismuth vanadate · Thin film

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10008-020-04636-9>) contains supplementary material, which is available to authorized users.

✉ Wolfgang Schuhmann
wolfgang.schuhmann@rub.de

Olga A. Krysiak
olga.krysiak@rub.de

João R.C. Junqueira
joao.junqueira@rub.de

Felipe Conzuelo
felipe.conzuelo@rub.de

Tim Bobrowski
tim.bobrowski@rub.de

Justus Masa
justus.masa@cec.mpg.de

Andrzej Wyszomolek
andrzej.wyszomolek@fuw.edu.pl

- ¹ Analytical Chemistry – Center for Electrochemical Sciences (CES), Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Universitätsst. 150, 44780 Bochum, Germany
- ² College of Inter-Faculty Individual Studies in Mathematics and Natural Sciences, University of Warsaw, Banacha 2c, 02-097 Warsaw, Poland
- ³ Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany
- ⁴ Institute of Experimental Physics, Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland

Introduction

The heightened need and urgency to develop CO₂-emission-free and environmentally friendly energy systems has stimulated substantial research interest in potential alternatives to fossil energy sources [1]. Solar energy conversion into H₂ via photoelectrochemical (PEC) water splitting is one of the most studied approaches, mostly due to the tremendous energy potential of the sun (almost 10,000 times larger than the global energy consumption in 2017) and its ubiquitous prevalence [2]. As a consequence, considerable effort for solar energy conversion is put into the development of efficient photoelectrodes [3–5]. During solar-driven water oxidation, the photogenerated charges participate in the anodic and cathodic half reactions, so the interfacial reactions over the photoelectrodes are akin to the electrochemical processes occurring during water electrolysis in the absence of photo illumination [6]. This means that efficient light absorption by itself is not sufficient to realise efficient photoelectrodes for water splitting. In addition to efficient light absorption leading to generation of charge carriers, the transfer of these carriers to the surface and through the interface, limited lifetimes, and the possibility for recombination have to be addressed [7–10]. One practical approach for enhancing the efficiency of electrochemical water splitting in the dark is the use of electrocatalysts [11]. Electrocatalysts improve the kinetics of the involved reactions by lowering the reaction overpotentials and/or promoting interfacial charge transfer. It is therefore reasonable to envision that the efficiency of solar water splitting should be more favourable when electrocatalysts are used in combination with photoelectrodes. However, studies on photoelectrochemical water splitting where the photoanode is modified with various oxygen evolution reaction (OER) catalysts tend to yield results that are not easy to interpret [12–17]. Nonetheless, a notable requisite towards efficient photoanode/co-catalyst systems seems to be the existence of a certain compatibility between the photoanode material and the incorporated co-catalyst. That means that a co-catalyst exhibiting superior activity in combination with one semiconductor will not necessarily lead to a similar effect when in combination with another semiconductor [8]. Unfortunately, this compatibility is difficult to predict, hence necessitating extensive experimental studies to determine promising combinations. In this work, Mo-modified BiVO₄ was used as the semiconductor material, which was modified with various co-catalysts and tested for photoelectrochemical water oxidation. Since the discovery of its photocatalytic activity towards water oxidation by Kudo et al. in 1998 [18], BiVO₄ has emerged as one of the most promising semiconductor materials for photoanode production [19, 20]. BiVO₄ is comprised of inexpensive and non-toxic elements and has a moderate bandgap of 2.4 eV [21], which allows the absorption of electromagnetic radiation in the visible light range. The valence band edge is

located at a potential providing sufficient overpotential for the photo-generated holes to oxidise water [21]. Moreover, the effective masses of holes were reported to be lower than those of other semiconductors such as TiO₂, which should be favourable for charge carrier mobility [22]. Inherently, the photocatalytic activity of BiVO₄ for water splitting is limited by a substantial electron-hole recombination, weak charge transport properties, and low activity for water oxidation [23, 24]. The possibilities for overcoming these limitations include nanostructuring [25], doping with foreign elements [26] or combination with a suitable co-catalyst [17]. In this regard, doping with Mo was proven to reduce the majority carrier transport limitations, resulting in increased photocurrent densities [27, 28].

In a recent communication [13], significantly distinct behaviour of photoanodes modified with the same co-catalyst in two different configurations, with the co-catalyst either deposited on the surface of Mo:BiVO₄ or embedded inside a Mo:BiVO₄ film, was observed. However, in these studies, no general correlation between co-catalyst-modified photoanode architecture and performance could be definitively established owing to a small number of Mo:BiVO₄ and Ni, Fe, and Cr multicomposite co-catalysts studied. To extend knowledge of the influence of photoanode architecture and properties of the co-catalyst on photoelectrochemical water oxidation, and to test the generality of the observations, it is imperative for the study to be extended to a broader range of catalysts. Unfortunately, conventional highly active OER electrocatalysts do not always necessarily behave as active co-catalysts for photoelectrochemical water splitting. Therefore, the possibility to predict the activity of a particular co-catalyst in solar-driven water oxidation is not straightforward, which underscores the importance of a systematic empirical case-by-case study when evaluating the influence of co-catalysts on photoelectrochemical water oxidation [8, 29, 30].

Herein, the influence of modifying Mo-modified BiVO₄ (Mo:BiVO₄) photoanodes with various types of OER electrocatalysts on photoelectrochemical water oxidation was investigated. A set of OER catalysts with different structural and compositional properties were investigated to gain insight into the role of co-catalyst properties on performance. Additionally, the influence of the modified photoelectrode architecture on photoelectrochemical water oxidation, wherein the co-catalysts were deposited on the surface of Mo:BiVO₄ or embedded within Mo:BiVO₄, was also investigated.

Experimental

Materials and methods

Bismuth(III) nitrate pentahydrate (ACS Reagent, ≥ 98%), vanadyl acetylacetonate (98%), bis(acetylacetonato)dioxomolybdenum(VI), fluorine-doped tin oxide-coated glass

slides (surface resistivity $\approx 7 \Omega \text{ sq.}^{-1}$), sodium tetraborate decahydrate (ACR Reagent, $\geq 99.5\%$), chromium(III) nitrate nonahydrate (99%), iron(III) nitrate nonahydrate ($\geq 99.95\%$ trace metal basis), cobalt(II,III) oxide ($\geq 99.99\%$ trace metal basis), triethanolamine (ACS Reagent), ammonium hydroxide (ACS Reagent), nickel(II) chloride (98%), and cobalt nitrate hexahydrate (ACS Reagent) were purchased from Sigma-Aldrich. Acetic acid, glacial (ACS Reagent), ethanol absolute (ACS Reagent), and acetone (ACS Reagent) were purchased from VWR Chemicals. Nickel(II) nitrate hexahydrate (ACS Reagent) was purchased from Merck. Ultrapure water was used for preparation of all aqueous solutions.

All electrochemical measurements were performed in a three-electrode system containing an Ag|AgCl (3 mol dm⁻³ KCl) and a platinum wire as reference and counter electrodes, respectively, with 0.1 mol dm⁻³ sodium tetraborate, pH 9.3 as supporting electrolyte. The samples were analysed using a high-throughput optical scanning droplet cell (OSDC) [31, 32]. The dimensions of the working electrode were defined by the cell tip bearing an opening with an area of $(0.74 \pm 0.04) \text{ mm}^2$, and this value was used to calculate the current density. The lamp intensity (150 W Xe, LC8, Hamamatsu) was previously calibrated to 100 mW cm^{-2} . All measurements were conducted under chopped light front-side irradiation (5 s light/5 s dark) with a scan rate of 1 mV s^{-1} . The photocurrent depicted in the plots is the result of subtracting the current measured in the dark from the current measured under illumination at each chopping period (see Fig. S1, Supporting Information). All potentials are reported versus the reversible hydrogen electrode (RHE) recalculated from the Ag|AgCl|3 mol dm⁻³ KCl scale according to the following the equation:

$$U_{\text{RHE}} (\text{V}) = U_{\text{Ag|AgCl|3 mol L}^{-1} \text{ KCl}} + 0.210 + (0.059 \times \text{pH}) \quad (1)$$

The incident photon-to-current conversion efficiency (IPCE) measurements were conducted using a controlled monochromator incorporating a shutter (Instytut Fotonowy). A 150-W Xe lamp (Ushio) was used as light source. The individual non-illuminated open circuit potential (OCP) for each sample was determined beforehand and then used as the bias potential for the corresponding IPCE measurement. Subsequently, IPCE analysis at 1.23 V (vs. RHE) was performed. The presented IPCE values were determined according to Eq. (2):

$$\text{IPCE}(\%) = \frac{|j_{\text{Photo}} (\text{mA cm}^{-2})| \times 1239.8}{P_{\text{lamp}} (\text{mW cm}^{-2}) \times \lambda (\text{nm})} \quad (2)$$

where j_{Photo} is the photocurrent density, defined as the difference between current measured under illumination and in the dark divided by the geometric area of the working electrode;

1239.8 V nm is the result from the multiplication of Planck's constant (h) and the speed of light (c); and P_{lamp} is the calibrated power intensity for each wavelength (λ).

The absorbed photon-to-current efficiency (APCE) values for all described samples were calculated according to Eq. (3) [33]:

$$\text{APCE}(\lambda) = \frac{\text{IPCE}(\lambda)}{\eta_{e^-/h^+}} \quad (3)$$

where η_{e^-/h^+} is the absorbance ($\eta_{e^-/h^+} = 1 - 10^{-A}$), for 450 nm light.

A custom-designed cell with a working electrode opening of 1 cm^2 and a quartz window was utilised. The intensity of the light source for each wavelength was calibrated with a power thermal sensor coupled to a power meter (NOVA II, Ophir). The measured currents and applied potentials were controlled by means of an Autolab PGSTAT12 (Metrohm).

Detection of evolved oxygen was conducted by means of scanning photoelectrochemical microscopy (SPECM) [27, 34]. During an area scan the sample was polarised at 400 mV vs. Ag|AgCl|3 mol dm⁻³ KCl (1110 mV vs. RHE). A Pt tip polarised at -600 mV vs. Ag|AgCl|3 mol dm⁻³ KCl was used for O₂ reduction.

Raman spectra were obtained using a Renishaw inVia™ spectrometer connected with a 532-nm laser source and $\times 100$ optical objective (Olympus). The parameters used for recording spectra were as follows: wavelength between 50 and 1300 cm^{-1} , exposure time of 10 s, accumulation number = 6, and laser power of $2.65 \text{ mW } \mu\text{m}^{-2}$.

Morphological characterisation by SEM was conducted with a Quanta 3D FEG in high vacuum at 20 kV.

Absorbance spectra were obtained with a Cary 5000 UV-Vis-NIR spectrophotometer (Varian Inc., 1-nm spectral resolution).

Diffraction patterns were taken with a Bruker D8 Discover diffractometer with Debye–Scherrer geometry. The measurements were conducted using Cu K α radiation source ($\lambda = 1.540598 \text{ \AA}$), using a scan rate of 1° min^{-1} in 0.012° steps, covering a range of 2θ from 8 to 130° . Measurements were performed at room temperature.

Mo-modified bismuth vanadate electrode preparation

Fluorine-doped tin oxide (FTO)-coated glass substrates ($1.5 \text{ cm} \times 2.5 \text{ cm}$) were cleaned with a 10-g dm^{-3} Alconox® solution, rinsed with deionised water, and then with ethanol. Subsequently, the substrates were dried under argon flow. The procedure used for Mo:BiVO₄ sample spraying was described elsewhere [12]. First, solutions containing 10 mmol dm^{-3} VO(acac)₂ in pure ethanol and 10 mmol dm^{-3} of Bi(NO₃)₃·5H₂O in glacial acetic acid were prepared. Then, 20 mL from

each stock solution was placed in a 50-mL volumetric flask containing $\text{MoO}_2(\text{acac})_2$ in an amount equivalent to 1 mmol dm^{-3} and the flask was filled with ethanol. The so-prepared precursor solution was spread over the substrate surface by means of a spray-coating set-up containing a pressurised air nozzle connected to an automated position control unit, according to a procedure reported in ref [12]. To form the Mo:BiVO_4 layer, the spray-coated samples were annealed at 775 K for 1 h (heating ramp: 2 K min^{-1}) in a simulated air atmosphere (80% Ar and 20% O_2). After the annealing procedure, yellow-green films with a typical layer thickness of ca. 280 nm were obtained.

Catalyst preparation

Synthesis of $\text{NiFe}(\text{NO}_3)$ layered double hydroxide (NiFe LDH)

NiFe LDH was synthesised according to the procedure described by Andronescu et al. [35]; $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.362 g, 15 mmol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.02 g, 5 mmol) were dissolved in decarbonated ultrapure water (100 mL) in the presence of triethanolamine (1.86 g, 12.5 mmol). An ammonium hydroxide solution (25 wt%) was added to the mixture under N_2 atmosphere until the pH value reached 8.5 (ca. 4 mL NH_4OH). The mixture was stirred for 2 h at room temperature and then kept in an oven at 60 °C for 14 h. The resulting mixture was filtered and washed with decarbonated ultrapure water (500 cm^{-3}). The precipitate was dried at 70 °C for 24 h.

Synthesis of $\text{CoFe}(\text{NO}_3)$ layered double hydroxide (CoFe LDH)

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (8.731 g, 30 mmol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (4.04 g, 10 mmol) were dissolved in decarbonated ultrapure water (200 mL) in the presence of triethanolamine (3.72 g, 25 mmol). An ammonium hydroxide solution (25 wt%) was added to the salt mixture under N_2 atmosphere until the pH value reached 8.5 (ca. 4 mL NH_4OH). The mixture was stirred for 2 h at room temperature and then kept in an oven at 60 °C for 14 h. The resulting mixture was filtered and washed with decarbonated ultrapure water (500 cm^{-3}). The precipitate was dried at 70 °C for 24 h.

Cobalt(II,III) oxide (Co_3O_4) an appropriate amount of a cobalt(II,III) oxide powder was dispersed in pure ethanol using tip sonication for 30 min and then diluted to attain the desired concentration of 0.02 mg cm^{-3} .

Synthesis of nickel boride (Ni_xB) Ni_xB was synthesised using a protocol adapted from ref. [36]. About 10.11 g (0.078 mol) of nickel(II) chloride was dissolved in 156 mL of water and continuously stirred. The solution was then deaerated, flushed with argon, and cooled down to 0 °C. About 5.9 g (0.156 mol) of sodium borohydride was dissolved in 156 cm^{-3} of 0.1 mol dm^{-3} NaOH solution, deaerated, and slowly added to the nickel(II) chloride solution. After stirring for 10 min, the

obtained black precipitate was collected and washed with 500 cm^{-3} of water, 400 cm^{-3} of ethanol, and 50 cm^{-3} of acetone. The precipitate was pyrolysed for 2 h at 300 °C under argon flow. The resulting powder was ground in a pestle and motor and dispersed in ethanol.

Nickel-iron spinel and NiFeCrO_4 inverse spinel NiFeCrO_4 and NiFeO_x were obtained by thermal decomposition of a mixture of nitrates of the respective metals mixed in a 1:1:1 (1:1) ratio at 800 °C for 6 h.

Catalyst deposition

Suspensions of previously synthesised catalysts (as mentioned in the “Catalyst preparation”) or a commercial Co_3O_4 powder were prepared in pure ethanol and sprayed on pre-annealed Mo:BiVO_4 samples (configuration on top) or mixed with the Mo:BiVO_4 precursor solution prior to the spraying procedure (configuration inside). The samples incorporating the catalyst into the semiconductor film were later annealed at 500 °C for 30 min in a simulated air atmosphere (argon 80% and oxygen 20%) for formation of the photoactive layer. Samples with the catalyst on top configuration were placed in an oven at 250 °C for 15 min to evaporate the solvent after catalyst deposition. No increase in photocurrent was observed using front-side illumination by increasing the Mo:BiVO_4 layer thickness in agreement with previous reports [12].

Results and discussion

Characterisation of obtained materials

Mo:BiVO_4 and catalyst-modified Mo:BiVO_4 photoanodes were prepared by spray coating followed by a heat treatment step as described in detail in the “Experimental section”. An automated spray-coating setup was used, which has been shown to lead to a controlled and reproducible fabrication of Mo:BiVO_4 -based photoelectrodes [12]. All the selected catalysts are proven oxygen evolution catalysts in electrochemical water splitting, and some of them, with the exception of Ni_xB , have also been evaluated in combination with BiVO_4 for photoelectrochemical water oxidation, including Co_3O_4 [37], NiFeO_x [38], and LDH structures [35, 39]. Irrespective of the catalyst structure and composition, materials containing Ni and Fe are known to be efficient OER catalysts [40, 41]. Therefore, we evaluated the activity of members of the spinel family: NiFeO_x (spinel) [38], NiFeCrO_4 (inverse spinel) [42], and Co_3O_4 [37], Ni_xB [36] and two-layered double hydroxides (LDH): NiFe LDH [35] and CoFe LDH [39] that were selected due to their reported high OER activity comparable to benchmark noble metal catalysts such as IrO_2 and RuO_2 .

Fig. 1 SEM images of pristine and catalyst-modified Mo:BiVO₄ films

Scanning electron microscopy (SEM) images (Fig. 1) reveal changes in the morphology of the Mo:BiVO₄ film after modification with the different catalysts. Whereas for the Mo:BiVO₄ samples a typical brain-like structure with features ranging in size from 100 to 500 nm was observed, the addition of catalysts caused a substantial change in morphology. For example, modification with NiFeCrO₄ induced the formation of particle-like structures, while modification with the other catalysts led to the formation of larger structures (Co₃O₄) or even rods (CoFe LDH). It is evident due to the formation of the porous films, that no matter the photoanode configuration, the catalyst is always in contact with the electrolyte. Moreover, the prepared photoanodes were characterised before and after photoelectrochemical measurements to probe for changes in the morphology or structure during reaction (see X-ray diffraction patterns, optical absorption, and Raman spectra in Figs. S2–S5, Supporting Information).

Photoelectrochemical performance

In order to evaluate the photoelectrocatalytic activity of the materials and define the optimal loading of the catalysts, large area samples (9 cm × 2 cm) with an increasing loading of catalyst along the *x*-axis were prepared. The fabricated samples were then examined using an optical scanning drop-cell (OSDC), which enabled a localised characterisation of the studied samples [43]. In this way, it was possible to follow the changes of current under illumination and in the dark (see Fig. S6, Supporting Information), with the resulting photocurrent calculated as the difference between the light and dark responses. Figure 2 presents a comparison of photocurrents recorded for a Mo:BiVO₄ sample (black lines) and for samples modified with the optimal loading for each specific catalyst evaluated in the two studied configurations (i.e., with the catalyst deposited on top of the photoabsorber: blue lines, or with the catalyst embedded into

Fig. 2 Linear sweep voltammetry under illumination for Mo:BiVO₄ in the absence (black lines) and presence of different catalysts either on top (blue lines) or embedded inside (red lines) the semiconductor film. Scan rate: 1 mV s^{−1}. Electrolyte: 0.1 mol dm^{−3} sodium tetraborate, pH 9.3; front-side illumination with unfiltered white light

the photoabsorber film: red lines). For a proper comparison of the effect of catalyst incorporation, a pristine sample was prepared and characterised for each batch modified with catalyst. All examined catalysts, combined with the photoabsorber, showed an increase in photoelectrocatalytic activity, in at least one of the studied configurations. Moreover, in some particular cases (CoFe LDH, NiFeO_x, and NiFeCrO₄), both configurations afforded an increase in activity. The experimental results indicated that catalysts belonging to the same family cause a similar effect in the relative activity of the material. However, this observation was not true for the LDH-modified samples. CoFe LDH embedded in the semiconductor film provided a small increase in activity (Fig. 2b), while no noticeable increase in activity was observed for the case of NiFe LDH in the same configuration (Fig. 2c), in comparison with the pristine semiconductor. On the other hand, photoanodes prepared from the mixed transition metal oxides NiFeCrO₄ and NiFeO_x, both belonging to the spinel family, caused OER activity increase in both tested configurations, with a larger increase in activity observed when the catalysts were deposited on top of the semiconductor film. The largest increase in photoelectrocatalytic activity was observed for the inverse spinel (NiFeCrO₄) sample, which could be explained by the inherently higher activity of the catalyst itself. Moreover, it has been reported that trimetallic oxides containing Ni and Fe and the third element are highly active catalysts [41, 44]. On the other hand, the monometallic oxide Co₃O₄ only exhibited enhanced photoelectrocatalytic activity when the catalyst was embedded into the Mo:BiVO₄ semiconductor film, while a decrease in the measured photocurrents was observed when Co₃O₄ was deposited on the surface of Mo:BiVO₄. This observation is in agreement with recently reported results where the evaluated catalyst was constituted of a mixture of three different single transition metal oxides [13]. As previously explained,

this behaviour was the result of a blocking of the redox active centres for oxygen evolution or/and shielding photoabsorber from light when the catalyst was deposited on top of the semiconductor material, while increased activity was obtained after embedding the catalyst in the semiconductor film due to a downward band bending of the catalyst-modified Mo:BiVO₄. In addition, LDH catalysts have been shown to provide enhanced OER activity of BiVO₄ and Mo:BiVO₄ photoanodes when deposited on top of the semiconductor [12, 45, 46], whereas only marginal OER activity enhancement of the photoanode was observed when CoFe LDH was embedded into the Mo:BiVO₄ film. Moreover, the inclusion of NiFe LDH did not give rise to any noticeable increase in activity of the photoanode, but rather hampered the formation of Mo:BiVO₄ during sintering (see Fig. S7, Supporting Information, for more details), thereby adversely affecting the photoabsorber properties. As reported before for LDHs, the configuration on top has proven to be advantageous because it allows the creation of a surface state passivation layer and enables fast hole transfer from the photoabsorber into the catalyst layer [45, 46]. We also examined the use of a nickel boride (Ni_xB), which is known to be an active OER catalyst in the dark [36], as catalyst for the Mo:BiVO₄ photoanode. The deposition of amorphous Ni_xB on the surface of Mo:BiVO₄ enhanced its activity for photoelectrochemical water splitting [47]. Here, a crystalline form of Ni_xB deposited on the surface of Mo:BiVO₄ also led to enhancement of its photoelectrochemical water splitting activity.

In order to assess the efficiency of the different catalyst-modified Mo:BiVO₄ photoanodes in converting incident light at a suitable wavelength into electrical energy, the incident photon-to-current conversion efficiency (IPCE) was calculated. The obtained results (Fig. 3) were in good agreement with the recorded LSV measurements. For all the catalyst-modified

Fig. 3 Wavelength-dependent IPCE values of Mo:BiVO₄ film (black lines) modified with different catalysts on top (blue lines) and inside (red lines) the semiconductor film. Front-side illumination, measured in 0.1 mol dm⁻³ borate buffer (pH = 9.3) at 1.23 V vs. RHE

Mo:BiVO₄ photoanodes that exhibited enhanced photocurrent in the LSV measurements, a higher IPCE was also observed. Furthermore, efficiency of higher than 50% was attained in the visible light range for all the evaluated catalyst-modified Mo:BiVO₄ samples under their optimal configuration. Moreover, for samples modified with Co₃O₄ (Fig. 3a) and NiFeO_x (Fig. 3f) embedded into the Mo:BiVO₄ film, and the samples where NiFe LDH, Ni_xB, and NiFeCrO₄ were deposited on the surface, a certain activity at higher wavelengths where pristine Mo:BiVO₄ was not active was also observed. These results were also in agreement with optical absorption measurements (see Fig. S5, Supporting Information).

To confirm that the observed increase in measured photocurrents and calculated IPCE values are a result of an increased oxygen evolution from solar-driven water splitting, detection of evolved O₂ by means of scanning photoelectrochemical microscopy (SPECM) was conducted [27, 34]. For this, a microelectrode tip was used as a probe for the detection of O₂ evolved during water photo-oxidation at the semiconductor sample, while simultaneously enabling localised irradiation of the interrogated photoanode. The tip was positioned in close proximity to the analysed sample, and the current attained at the microelectrode and the sample during an area scan were recorded, using samples prepared with a homogeneous photoactive film incorporating the optimised amount of catalyst. The obtained maps of photocurrents and associated tip currents for all evaluated samples are compared in Fig. 4a and b. Higher recorded photocurrents were associated with larger oxygen reduction currents at the positioned tip electrode measured by SPECM, confirming that the observed increase in recorded photocurrent and IPCE values was a consequence of an increased efficiency for light-induced water oxidation leading to an enhanced O₂ evolution. Moreover, as summarised in Fig. 4c, for most of the samples the ratio between normalised currents was close to one, as reflected by a linear correlation between photocurrent and O₂ collection. An exception from this trend was the sample incorporating Co₃O₄ inside the Mo:BiVO₄ film, with a tip-to-sample current ratio below one. A possible explanation for the observed lower Faradaic efficiency might be the presence of photocorrosion processes for this sample.

Mechanistic explanation of the results

In order to develop models that explain the altered activity observed upon incorporation of the catalyst for the different samples, mainly four aspects must be considered: (i) change in the electronic structure, (ii) improvement of water oxidation kinetics, (iii) passivation of surface states hampering the Fermi level pinning, and (iv) influence on the charge carrier separation efficiency. Figure 5 presents that the Tauc plots for direct and indirect allowed transitions obtained for pristine and modified Mo:BiVO₄ electrodes (for comparison, see also

Tauc plots for BiVO₄ and Mo:BiVO₄; Fig. S8, Supporting Information). As can be observed, the addition of catalyst did not lead to a noticeable change of the band gap energy for allowed direct transitions (Fig. 5a), suggesting the absence of a major change in the electronic state density distribution, which is commonly observed in this kind of modified photoanodes [48]. Moreover, indirect transitions at around 3.0 eV and 3.5 eV, corresponding to transitions from different states in the valance band [22], were visible for all samples (Fig. 5b), which also support the assumption of the absence of significant alteration of the electronic structure.

In order to get information about the balance between maximal length of the path for photon absorption and minimal effective e⁻/h⁺ pair transport distance within the material, we calculated the absorbed photon-to-current efficiency (APCE). The calculated APCE and IPCE values are presented in Table 1.

In all cases the IPCE values were smaller than the calculated APCE. These results suggest that the decreased efficiency arises from poor transport or interfacial kinetics. To separate those factors additional calculations were made.

Lin and Boettcher [29, 30] suggested and examined the existence of so-called “adaptive” and “buried” semiconductor/electrocatalyst junctions. Adaptive junctions were described to be formed by electrocatalysts, which are permeable to the electrolyte. In this case, the interface energetic changes during operation as charge accumulates in the catalyst, which means that the effective barrier height for electron exchange depends on the applied potential. On the other hand, buried junctions are formed by dense, ion-impermeable electrocatalysts, where, in consequence, the interface charge remains unaffected during operation and behaves like a Schottky junction. This theory could only be applied in case of deposition of catalysts on the surface of the photoanode and, in addition, the authors suggested that the type of formed junction strongly depends on the deposition method. However, this theory is not sufficient to explain the results obtained in the present study, since a different behaviour has been observed for catalysts deposited by the same method. Moreover, the possible improvement of water oxidation kinetics has been previously claimed for BiVO₄ photoanodes modified with CoO_x and CoPi [49], where the authors suggested as a possible explanation the lowering of the activation energy of the charge transfer reaction. The same effect can be obtained by passivation of the surface states present in Mo:BiVO₄. Various materials including transition metal oxides (mostly Ni-containing oxides), Ti, and W have been used for passivation of surface states [8, 38, 50–53]. As a result, the Fermi level of the photoanode material is not pinned to the surface states and can be shifted to an energy level more suitable for water splitting. Another important factor, which needs to be considered, is the formation of a Schottky-type heterojunction after bringing Mo:BiVO₄ in contact with a material having a different work function [54]. This will influence

Fig. 4 Measurements performed using SPECM for pristine Mo:BiVO₄ and Mo:BiVO₄ samples modified with different catalysts in the two evaluated configurations. **a** Current recorded with the 25- μm diameter Pt-microelectrode probe polarised at -0.6 V (vs. Ag|AgCl|3 mol dm⁻³ KCl) for collection of evolved O₂. **b** Associated local irradiation photocurrent for the evaluated samples, electrode polarised at 1.23 V vs. RHE.

Experiments performed in 0.1 mol dm⁻³ borate buffer (pH=9.3). **c** Correlation between tip current and sample photocurrent measured for pristine and catalyst-modified Mo:BiVO₄ samples. Average and standard deviation are presented for the different points measured over each sample (black dots in panels (a) and (b), $N=126$). The values were normalised by the maximum current obtained at the tip and sample, respectively

the space charge region in Mo:BiVO₄, which will then alter the bulk charge carrier separation efficiency. With the assumption

that pinning of the Fermi level is not the case or is at least limited, after bringing the semiconductor photoanode in contact

Fig. 5 Tauc plots for **a** direct allowed and **b** indirect allowed transitions for pristine Mo:BiVO₄ and catalyst-modified Mo:BiVO₄ photoanodes calculated from IPCE values. The dashed lines represent catalysts deposited on top, and the solid lines represent catalysts incorporated into the film

with another material exhibiting a higher Fermi level, the upward band bending of the photoanode will be increased, causing a limitation of its photoelectrochemical water oxidation activity [14, 55].

Table 2 presents a comparison of surface and bulk charge carrier separation efficiencies for a pristine Mo:BiVO₄ sample and samples modified with the different evaluated catalysts. Apart from a couple of exceptions, the calculated values are in agreement with the measured photocurrents, i.e., for higher measured photocurrents higher charge carrier separation efficiencies were observed in comparison with pristine Mo:BiVO₄. The only samples out of this trend were the ones modified with LDHs and Ni_xB catalysts both embedded into the semiconductor film. In the case of the LDHs, a decreased stability of the photoelectrocatalytic film itself was responsible for the observed behaviour (see Fig. S7, Supporting Information). In the case of Ni_xB, despite an increase in photogenerated carriers in the bulk (η_{bulk}), the recorded photocurrent was significantly lower compared to the pristine semiconductor material, which was probably the result of a significant decrease in charge separation efficiency at the surface (η_{surf}).

Having in mind all the above-mentioned considerations and obtained experimental results, the following model is proposed (see a summary in Fig. 6 and impedance measurement results in Figs. S9–S11 and Table S1, Supporting Information). BiVO₄ is a semiconductor with valance and

conduction bands separated by a bandgap within which the corresponding Fermi level is located. After immersing the photoanode in the electrolyte solution, the Fermi level of the material is split into Fermi levels of electrons and holes. The latter one is in equilibrium with the potential of the redox couple present in the electrolyte solution, which also causes band bending. BiVO₄ is an n-type semiconductor, meaning that an upward band bending will take place under illumination. Furthermore, depending on the kinetics of the different processes involved (see Fig. 6a, green and red arrows) upon application of a large enough overpotential, oxygen evolution from water splitting will be eventually achieved. For efficient photoelectrocatalytic water oxidation, a fast electron excitation from the valance to the conduction band, subsequent transfer of the excited electrons to the back contact, and the transfer of the generated holes to the electrode interface (green arrows in Fig. 6a) need to occur faster than the band-to-band and surface recombination processes (red arrows in Fig. 6a). In the case of electrodes modified with catalysts, for all the samples with an observed increase of recorded photocurrents, the surface recombination rate was limited, with the exception of NiFeCrO₄, where a small decrease of η_{surf} was observed. This indicates that the addition of catalyst, independent of the configuration, seems to passivate the surface recombination centres. The behaviour of the Co₃O₄ catalyst (Fig. 6b) is similar to previously observed behaviour reported for a multicomposite catalyst

Table 1 APCE, IPCE, and IPCE/APCE ratio for a pristine Mo:BiVO₄ photoanode and Mo:BiVO₄ photoanodes modified with various oxygen evolution catalysts deposited on top or embedded into the semiconductor film, calculated for 450 nm light

	Mo:BiVO ₄	Mo:BiVO ₄ + Co ₃ O ₄		Mo:BiVO ₄ + Co/Fe LDH		Mo:BiVO ₄ + Ni/Fe LDH		Mo:BiVO ₄ + NiFeCrO ₄		Mo:BiVO ₄ + NiFeO _x		Mo:BiVO ₄ + Ni _x B	
		Inside	Top	Inside	Top	Inside	Top	Inside	Top	Inside	Top	Inside	Top
APCE(%)	18.9	33.1	14.9	28.7	42.5	28.5	41.3	19.1	28.4	27.2	31.5	15.4	25.5
IPCE(%)	15.8	26.3	6.3	27.4	34.3	22.6	35.4	16.8	24.7	22.5	22.4	10.9	21.9
IPCE/APCE	0.84	0.80	0.42	0.96	0.81	0.80	0.86	0.88	0.87	0.83	0.71	0.71	0.86

Table 2 Percentage of surface and bulk charge carrier separation efficiencies calculated from optical absorption measurements (for details see the Supporting Information) for a pristine Mo:BiVO₄ photoanode and Mo:BiVO₄ photoanodes modified with various oxygen

	Mo:BiVO ₄	Mo:BiVO ₄ + Co ₃ O ₄		Mo:BiVO ₄ + Co/Fe LDH		Mo:BiVO ₄ + Ni/Fe LDH		Mo:BiVO ₄ + NiFeCrO ₄		Mo:BiVO ₄ + NiFeO _x		Mo:BiVO ₄ + Ni _x B	
		Inside	Top	Inside	Top	Inside	Top	Inside	Top	Inside	Top	Inside	Top
η_{surf}	65	95	28	49	99	98	93	96	59	59	76	16	96
η_{bulk}	10.1	13.3	9.4	8.0	23.8	5.1	15.5	14.0	13.2	14.5	20.1	13.9	13.6

comprised of Ni, Fe, and Cr oxides [13], where the configuration on top resulted in decreased activity due to deprivation of the photoabsorber of light. In contrast, the configuration incorporating the catalyst embedded in the semiconductor film increased the activity towards water oxidation as a result of decreased surface recombination and lowering of the Fermi level, as manifested by additional downward bending of the band edge. For NiFe LDH and CoFe LDH

evolution catalysts deposited on top or embedded into the semiconductor film. Method based on ref. [56]. Calculations for an applied potential of 1.23 V vs. RHE and 450 nm light

Fig. 6 Band diagrams for **a** pristine and **b–e** catalyst-modified Mo:BiVO₄ before and after contact with the redox electrolyte. CB conduction band, VB valence band, E_F Fermi level

Fermi level within the Mo:BiVO₄ bandgap or most probably due to destabilisation of the photoabsorber structure by incorporation of the LDH catalysts. Considering the spinel-modified samples (NiFeCrO₄ and NiFeO_x; Fig. 6d), where both configurations showed an improved activity of the material in comparison with pristine Mo:BiVO₄, the configuration on top was characterised by the formation of a Ni-based passivation layer as previously described [38, 50, 51, 53]. The observed difference in the activity of the photoanodes modified with the different catalysts belonging to the spinel family was a consequence of the characteristic intrinsic activity of the different spinels [42, 44, 57]. Embedding the spinel catalyst into the semiconductor film resulted in an analogous effect to incorporation of the oxide catalysts, namely, lowering of the Fermi level and causing an additional downward bending of the band edge. The observed difference in activity can be explained by various degrees of modification of the Fermi level energy by different catalysts. Finally, for the last examined catalyst (Ni_xB; Fig. 6e), deposition of the catalyst on top of the semiconductor material seemed to passivate the surface states leading to an increased activity, while incorporation into the semiconductor film led to a decrease of OER activity implying an increased upward band bending.

Conclusions

We evaluated the photoelectrocatalytic activity of various OER catalysts including monometallic, bimetallic, and trimetallic oxides with layered and spinel structures, metal borides, and layered double hydroxides, in combination with a Mo:BiVO₄ photoanode in two distinct design configurations, deposited on top or incorporated into the semiconductor film. For the evaluated catalysts, at least one of the two tested catalyst-Mo:BiVO₄ photoanode configurations afforded increased photocurrents towards water photo-oxidation in comparison with the pristine semiconductor, meanwhile, modification of Mo:BiVO₄ with the spinel bimetallic and trimetallic oxides as catalyst boosted photoelectrocatalytic water oxidation independent of the used film configuration. Overall, the type of interface formed between the photoabsorber and the incorporated catalyst rather than the nature of the catalyst played a more important role in enhancing the photoanode activity. The observed differences in photoelectrocatalytic activity of the different catalyst-modified Mo:BiVO₄ photoanodes are attributed to the electronic structure of the materials as manifested by the observed differences in the Fermi energy levels. This work broadens the knowledge on the design of photoactive materials and is envisioned to contribute in shaping future research concerning the fabrication of more efficient photoanodes.

Acknowledgements We gratefully acknowledge Grzegorz Cichowicz and Prof. Michał Cyrański for performing XRD measurements.

Funding information Open Access funding provided by Projekt DEAL. The authors received financial support from the DFG within the framework of the SPP1613 (SCHU929/12-1 and 12-2). O.A. Krysiak received financial support from the Deutsche Bundesstiftung Umwelt.

Data availability Experimental details, composition, and structural characterisation by XRD, Raman, and UV-Vis spectra, electrode photograph, additional Tauc plots, and calculation of charge separation yields are available in the Supporting Information file.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Sharif A, Raza SA, Ozturk I, Afshan S (2019) The dynamic relationship of renewable and nonrenewable energy consumption with carbon emission: a global study with the application of heterogeneous panel estimations. *Renew Energy* 133:685–691. <https://doi.org/10.1016/j.renene.2018.10.052>
- Jacobson MZ, Delucchi MA, Bauer ZAF, Goodman SC, Chapman WE, Cameron MA, Bozonnat C, Chobadi L, Clonts HA, Enevoldsen P, Erwin JR, Fobi SN, Goldstrom OK, Hennessy EM, Liu J, Lo J, Meyer CB, Morris SB, Moy KR, O'Neill PL, Petkov I, Redfern S, Schucker R, Sontag MA, Wang J, Weiner E, Yachanin AS (2017) 100% clean and renewable wind, water, and sunlight all-sector energy roadmaps for 139 countries of the world. *Joule* 1(1): 108–121. <https://doi.org/10.1016/j.joule.2017.07.005>
- Valdés Á, Brillet J, Grätzel M, Gudmundsdóttir H, Hansen HA, Jónsson H, Klüpfel P, Kroes GJ, le Formal F, Man IC, Martins RS, Nørskov JK, Rossmeisl J, Sivula K, Vojvodica A, Zäch M (2012) Solar hydrogen production with semiconductor metal oxides: new directions in experiment and theory. *Phys Chem Chem Phys* 14(1):49–70. <https://doi.org/10.1039/c1cp23212f>
- Liang Y, Tsubota T, Mooij LPA, van de Krol R (2011) Highly improved quantum efficiencies for thin film BiVO₄ photoanodes. *J Phys Chem C* 115(35):17594–17598. <https://doi.org/10.1021/jp203004v>
- Jin T, Diao P, Wu Q, Xu D, Hu D, Xie Y, Zhang M (2014) WO₃ nanoneedles/ α -Fe₂O₃/cobalt phosphate composite photoanode for efficient photoelectrochemical water splitting. *Appl Catal B Environ* 148–149:304–310. <https://doi.org/10.1016/j.apcatb.2013.10.052>

6. Walter MG, Warren EL, McKone JR et al (2010) Solar water splitting cells. *Chem Rev* 110(11):6446–6473. <https://doi.org/10.1021/cr1002326>
7. Brus VV, Lang F, Fengler S et al (2018) Doping effects and charge-transfer dynamics at hybrid perovskite/graphene interfaces. *Adv Mater Interfaces* 499:1800826:1–1800826:7. <https://doi.org/10.1002/admi.201800826>
8. Zachäus C, Abdi FF, Peter LM, van de Krol R (2017) Photocurrent of BiVO₄ is limited by surface recombination, not surface catalysis. *Chem Sci* 5(5):3712–3719. <https://doi.org/10.1039/C7SC00363C>
9. Abdi FF, van de Krol R (2012) Nature and light dependence of bulk recombination in co-pi-catalyzed BiVO₄ photoanodes. *J Phys Chem C* 116(17):9398–9404. <https://doi.org/10.1021/jp3007552>
10. Stein H, Müller S, Schwarzburg K et al (2018) Charge carrier lifetimes in Cr-Fe-Al-O thin films. *ACS Appl Mater Interfaces* 10(42):35869–35875. <https://doi.org/10.1021/acsami.8b04900>
11. Fabbri E, Haberer A, Waltar K, Kötzt R, Schmidt TJ (2014) Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction. *Catal Sci Technol* 4(11):3800–3821. <https://doi.org/10.1039/c4cy00669k>
12. Junqueira JRC, Bobrowski T, Krysiak OA, Gutkowski R, Schuhmann W (2019) Tuning light-driven water splitting efficiency of Mo-doped BiVO₄: optimised preparation and impact of oxygen evolution electrocatalysts. *ChemCatChem* 11(24):6417–6424. <https://doi.org/10.1002/cctc.201901646>
13. Krysiak OA, Junqueira JRC, Conzuelo F, Bobrowski T, Wilde P, Wyszniak A, Schuhmann W (2020) Tuning light-driven water oxidation efficiency of molybdenum-doped BiVO₄ by means of multicomposite catalysts containing nickel, iron and chromium oxides. *ChemPlusChem* 85(2):327–333. <https://doi.org/10.1002/cplu.201900701>
14. Hermans Y, Murcia-López S, Klein A, van de Krol R, Andreu T, Morante JR, Toupance T, Jaegermann W (2019) Analysis of the interfacial characteristics of BiVO₄/metal oxide heterostructures and its implication on their junction properties. *Phys Chem Chem Phys* 21(9):5086–5096. <https://doi.org/10.1039/c8cp07483f>
15. Qiu J, Hajibabaei H, Nellist MR, Laskowski FAL, Oener SZ, Hamann TW, Boettcher SW (2018) Catalyst deposition on photoanodes: the roles of intrinsic catalytic activity, catalyst electrical conductivity, and semiconductor morphology. *ACS Energy Lett* 3(4):961–969. <https://doi.org/10.1021/acsenergylett.8b00336>
16. Xu Z, Wang H, Wen Y, Li W, Sun C, He Y, Shi Z, Pei L, Chen Y, Yan S, Zou Z (2018) Balancing catalytic activity and interface energetics of electrocatalyst-coated photoanodes for photoelectrochemical water splitting. *ACS Appl Mater Interfaces* 10(4):3624–3633. <https://doi.org/10.1021/acsami.7b17348>
17. Li D, Shi J, Li C (2018) Transition-metal-based electrocatalysts as cocatalysts for photoelectrochemical water splitting: a mini review. *Small* 14(23):1704179:1–1704179:22. <https://doi.org/10.1002/sml.201704179>
18. Kudo A, Ueda K, Kato H, Mikami I (1998) Photocatalytic O₂ evolution under visible light irradiation on BiVO₄ in aqueous AgNO₃ solution. *Catal Lett* 53(3/4):229–230. <https://doi.org/10.1023/A:1019034728816>
19. Park Y, McDonald KJ, Choi K-S (2013) Progress in bismuth vanadate photoanodes for use in solar water oxidation. *Chem Soc Rev* 42(6):2321–2337. <https://doi.org/10.1039/c2cs35260e>
20. Kim JH, Lee JS (2019) Elaborately modified BiVO₄ photoanodes for solar water splitting. *Adv Mater*:1806938:1–1806938:35. <https://doi.org/10.1002/adma.201806938>
21. Walsh A, Yan Y, Huda MN, al-Jassim MM, Wei SH (2009) Band edge electronic structure of BiVO₄: band edge electronic structure of BiVO₄: elucidating the role of the Bi s and V d orbitals. *Chem Mater* 21(3):547–551. <https://doi.org/10.1021/cm802894z>
22. Zhao Z, Li Z, Zou Z (2011) Electronic structure and optical properties of monoclinic clinobisvanite BiVO₄. *Phys Chem Chem Phys* 13(10):4746–4753. <https://doi.org/10.1039/c0cp01871f>
23. Vinke I, Diepgrond J, Boukamp B et al (1992) Bulk and electrochemical properties of BiVO₄. *Solid State Ionics* 57(1–2):83–89. [https://doi.org/10.1016/0167-2738\(92\)90067-Y](https://doi.org/10.1016/0167-2738(92)90067-Y)
24. Cooper JK, Gul S, Toma FM, Chen L, Liu YS, Guo J, Ager JW, Yano J, Sharp ID (2015) Indirect bandgap and optical properties of monoclinic bismuth vanadate. *J Phys Chem C* 119(6):2969–2974. <https://doi.org/10.1021/jp512169w>
25. Huang Z-F, Pan L, Zou J-J, Zhang X, Wang L (2014) Nanostructured bismuth vanadate-based materials for solar-energy-driven water oxidation: a review on recent progress. *Nanoscale* 6(23):14044–14063. <https://doi.org/10.1039/c4nr05245e>
26. Luo W, Wang J, Zhao X, Zhao Z, Li Z, Zou Z (2013) Formation energy and photoelectrochemical properties of BiVO₄ after doping at Bi³⁺ or V⁵⁺ sites with higher valence metal ions. *Phys Chem Chem Phys* 15(3):1006–1013. <https://doi.org/10.1039/c2cp43408c>
27. Gutkowski R, Khare C, Conzuelo F, Kayran YU, Ludwig A, Schuhmann W (2017) Unravelling compositional effects on the light-induced oxygen evolution in Bi(V–Mo–X)O₄ material libraries. *Energy Environ Sci* 10(5):1213–1221. <https://doi.org/10.1039/c7ee00287d>
28. Vannier RN, Mairesse G, Abraham F, Nowogrocki G (1993) Incommensurate superlattice in Mo-substituted Bi₄V₂O₁₁. *J Solid State Chem* 103(2):441–446. <https://doi.org/10.1006/jssc.1993.1120>
29. Lin F, Boettcher SW (2014) Adaptive semiconductor/electrocatalyst junctions in water-splitting photoanodes. *Nat Mater* 13(1):81–86. <https://doi.org/10.1038/nmat3811>
30. Nellist MR, Laskowski FAL, Lin F, Mills TJ, Boettcher SW (2016) Semiconductor-electrocatalyst interfaces: theory, experiment, and applications in photoelectrochemical water splitting. *Acc Chem Res* 49(4):733–740. <https://doi.org/10.1021/acs.accounts.6b00001>
31. Sliozberg K (2015) High-throughput photoelectrochemical characterization of semiconductor thin film materials libraries. Ph.D dissertation, Ruhr-Universität Bochum
32. Meyer R, Sliozberg K, Khare C, Schuhmann W, Ludwig A (2015) High-throughput screening of thin-film semiconductor material libraries II: characterization of Fe-W-O libraries. *ChemSusChem* 8(7):1279–1285. <https://doi.org/10.1002/cssc.201402918>
33. Chen Z, Dinh H, Miller E (2013) Photoelectrochemical water splitting: standards, experimental methods, and protocols. *Briefs in energy*. Springer
34. Conzuelo F, Sliozberg K, Gutkowski R, Grütze S, Nebel M, Schuhmann W (2017) High-resolution analysis of photoanodes for water splitting by means of scanning photoelectrochemical microscopy. *Anal Chem* 89(2):1222–1228. <https://doi.org/10.1021/acs.analchem.6b03706>
35. Andronescu C, Barwe S, Ventosa E, Masa J, Vasile E, Konkana B, Möller S, Schuhmann W (2017) Powder catalyst fixation for post-electrolysis structural characterization of NiFe layered double hydroxide based oxygen evolution reaction electrocatalysts. *Angew Chem Int Ed* 56(37):11258–11262. <https://doi.org/10.1002/anie.201705385>
36. Masa J, Sinev I, Mistry H et al (2017) Ultrathin high surface area nickel boride (Ni_xB) nanosheets as highly efficient electrocatalyst for oxygen evolution. *Adv Energy Mater* 7(17):1700381:1–1700381:8. <https://doi.org/10.1002/aenm.201700381>
37. Lichterman MF, Shaner MR, Handler SG, Brunschwig BS, Gray HB, Lewis NS, Spurgeon JM (2013) Enhanced stability and activity for water oxidation in alkaline media with bismuth vanadate photoelectrodes modified with a cobalt oxide catalytic layer produced by atomic layer deposition. *J Phys Chem Lett* 4(23):4188–4191. <https://doi.org/10.1021/jz4022415>

38. Liang Y, Messinger J (2014) Improving BiVO₄ photoanodes for solar water splitting through surface passivation. *Phys Chem Chem Phys* 16(24):12014–12020. <https://doi.org/10.1039/c4cp00674g>
39. Medina D, Barwe S, Masa J, Seisel S, Schuhmann W, Andronescu C (2019) Optimizing the synthesis of Co/Co–Fe nanoparticles/N-doped carbon composite materials as bifunctional oxygen electrocatalysts. *Electrochim Acta* 318:281–289. <https://doi.org/10.1016/j.electacta.2019.06.048>
40. Gong J, Li C, Wasielewski MR (2019) Advances in solar energy conversion. *Chem Soc Rev* 48(7):1862–1864. <https://doi.org/10.1039/c9cs90020a>
41. Gerken JB, Shaner SE, Massé RC et al (2014) A survey of diverse earth abundant oxygen evolution electrocatalysts showing enhanced activity from Ni–Fe oxides containing a third metal. *Energy Environ Sci* 7(7):2376–2382. <https://doi.org/10.1039/c4ee0436a>
42. Singh RN, Singh JP, Lal B, Thomas MJK, Bera S (2006) New NiFe₂–xCr_xO₄ spinel films for O₂ evolution in alkaline solutions. *Electrochim Acta* 51(25):5515–5523. <https://doi.org/10.1016/j.electacta.2006.02.028>
43. Slizoberg K, Schäfer D, Erichsen T, Meyer R, Khare C, Ludwig A, Schuhmann W (2015) High-throughput screening of thin-film semiconductor material libraries I: system development and case study for Ti–W–O. *ChemSusChem* 8(7):1270–1278. <https://doi.org/10.1002/cssc.201402917>
44. Chen JYC, Miller JT, Gerken JB, Stahl SS (2014) Inverse spinel NiFeAlO₄ as a highly active oxygen evolution electrocatalyst: promotion of activity by a redox-inert metal ion. *Energy Environ Sci* 7(4):1382–1386. <https://doi.org/10.1039/c3ee43811b>
45. Sinclair TS, Gray HB, Müller AM (2018) Photoelectrochemical performance of BiVO₄ photoanodes integrated with [NiFe]-layered double hydroxide nanocatalysts. *Eur J Inorg Chem* 2018(9):1060–1067. <https://doi.org/10.1002/ejic.201701231>
46. Zhu Y, Ren J, Yang X, Chang G, Bu Y, Wei G, Han W, Yang D (2017) Interface engineering of 3D BiVO₄/Fe-based layered double hydroxide core/shell nanostructures for boosting photoelectrochemical water oxidation. *J Mater Chem A* 5(20):9952–9959. <https://doi.org/10.1039/c7ta02179h>
47. Dang K, Chang X, Wang T, Gong J (2017) Enhancement of photoelectrochemical oxidation by an amorphous nickel boride catalyst on porous BiVO₄. *Nanoscale* 9(42):16133–16137. <https://doi.org/10.1039/c7nr06636h>
48. Walsh A, Da Silva JLF, Wei S-H (2008) Origins of band-gap renormalization in degenerately doped semiconductors. *Phys Rev B* 78(7). <https://doi.org/10.1103/PhysRevB.78.075211>
49. Wang D, Li R, Zhu J, Shi J, Han J, Zong X, Li C (2012) Photocatalytic water oxidation on BiVO₄ with the electrocatalyst as an oxidation cocatalyst: essential relations between electrocatalyst and photocatalyst. *J Phys Chem C* 116(8):5082–5089. <https://doi.org/10.1021/jp210584b>
50. Kim J, Park H, Hannon JB, Bedell SW, Fogel K, Sadana DK, Dimitrakopoulos C (2013) Layer-resolved graphene transfer via engineered strain layers. *Science* 342(6160):833–836. <https://doi.org/10.1126/science.1242988>
51. Liu R, Zheng Z, Spurgeon J, Yang X (2014) Enhanced photoelectrochemical water-splitting performance of semiconductors by surface passivation layers. *Energy Environ Sci* 7(8):2504–2517. <https://doi.org/10.1039/c4ee00450g>
52. Shi Q, Murcia-López S, Tang P, Flox C, Morante JR, Bian Z, Wang H, Andreu T (2018) Role of tungsten doping on the surface states in BiVO₄ photoanodes for water oxidation: tuning the electron trapping process. *ACS Catal* 8(4):3331–3342. <https://doi.org/10.1021/acscatal.7b04277>
53. Steier L, Herraiz-Cardona I, Gimenez S, Fabregat-Santiago F, Bisquert J, Tilley SD, Grätzel M (2014) Understanding the role of underlayers and overlayers in thin film hematite photoanodes. *Adv Funct Mater* 24(48):7681–7688. <https://doi.org/10.1002/adfm.201402742>
54. Milnes AG (2012) Heterojunctions and metal semiconductor junctions. Elsevier, New York
55. Barroso M, Cowan AJ, Pendlebury SR, Grätzel M, Klug DR, Durrant JR (2011) The role of cobalt phosphate in enhancing the photocatalytic activity of α -Fe₂O₃ toward water oxidation. *J Am Chem Soc* 133(38):14868–14871. <https://doi.org/10.1021/ja205325v>
56. Dotan H, Sivula K, Grätzel M, Rothschild A, Warren SC (2011) Probing the photoelectrochemical properties of hematite (α -Fe₂O₃) electrodes using hydrogen peroxide as a hole scavenger. *Energy Environ Sci* 4(3):958–964. <https://doi.org/10.1039/c0ee00570c>
57. Yan X, Tian L, Li K et al (2016) FeNi₃/NiFeO_x nanohybrids as highly efficient bifunctional electrocatalysts for overall water splitting. *Adv Mater Interfaces* 3(22):1600368:1–1600368:8. <https://doi.org/10.1002/admi.201600368>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.