Tuning Light-Driven Water Splitting Efficiency of Mo-Doped BiVO₄: Optimised Preparation and Impact of Oxygen Evolution Electrocatalysts

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We present airbrush spray-coating as a reproducible method for the preparation of Mo-doped BiVO₄ (Mo:BiVO₄) as photo-absorber with different layer thicknesses and Mo content. Optimisation of layer thickness is aiming on diminishing limitations by the electronic conductivity within the photo-absorber, thus increasing the incident photon to current efficiency (IPCE) of the samples. Furthermore, the Mo to V ratio leading to the highest photocurrent density was determined, and the optimised Mo:BiVO₄ samples were decorated with a variety of oxygen evolution reaction (OER) electrocatalysts such as cobalt phosphate and layered double hydroxides. A mass loading gradient of Ni–Fe LDH was sprayed on top of the Mo:BiVO₄ photoanode for optimisation of the OER catalyst loading. The photocurrent density was enhanced by up to 5.8 times at 0.8 V vs. RHE in comparison with the pristine Mo:BiVO₄ sample in absence of any OER electrocatalyst.

1. Introduction

Photoelectrochemical (PEC) cells for water splitting are capable of producing clean and cost-efficient oxygen and hydrogen.[1] In order to absorb the highest energetic part of the atmospherically filtered solar spectrum, semiconductors with a low band gap are required.[2,3] Bismuth vanadate (BiVO₄) has a band gap of around 2.4 eV[4] and its valence band provides sufficient overpotential for the oxygen evolution reaction (OER). Hence, BiVO₄ is a promising material for photoanodes in PEC water splitting devices.[2,3–18]

However, despite its promising characteristics as photo-absorber material, BiVO₄ has limitations which yet have to be overcome for an efficient PEC device. Several studies demonstrated that utilising W or Mo as dopants significantly enhance the PEC performance of n-type BiVO₄ photoanodes.[5,11–16,18–21] This effect is due to improvement of the electronic conductivity of the base material upon addition of transition metals as dopants resulting in an enhancement of charge carriers separation which decreases the probability of its recombination in bulk.[8,12,16,18,21] Modification of the BiVO₄-electrolyte junction by means of oxygen evolution catalysts (OEC) diminishes efficiency losses associated with surface recombination and improves the activity towards the OER under illumination. The presence of OEC provides specialised active sites for water oxidation and consequently increases the kinetics for the OER.[5,15]

BiVO₄ has been previously prepared using various techniques such as electrodeposition,[5,7,23–27], sputter deposition,[8,28] and dip,[10,11,20] spin-[15,18,20] or spray-coating of suitable precursor materials.[30] Spray-coating is not dependent on the electrical conductivity of a given material and hence homogeneous films can be prepared on large sample areas.[31,32]

In the last years, a wide range of incident photon-to-current efficiency (IPCE) values were published for Mo:BiVO₄ photoanodes prepared using a variety of different techniques.[6,16,23–26,28–30,33–35] Moreover, in order to improve the efficiency, strategies such as a specific film architecture,[26] doping[8] and modification with OECs[15,21] were applied. Taking into consideration that for the calculation of the IPCE it is necessary to determine the current density, the film architecture is an important factor. Antony et al. showed that porous Mo:BiVO₄ films can achieve efficiencies almost twice as big as a similar planar layer.[14] Seabold et al. used FeOOH/Mo:BiVO₄ in a double stack to allow the rear electrode to absorb the light transmitted through the front one. Together these two electrodes reached IPCE values of up to ~60% at 1.23 V.[10] In accordance with the thermodynamic potential of the OER, IPCE values are in general reported at 1.23 V vs. reversible hydrogen electrode (RHE). However, at these conditions the semiconductor...
tor material only needs to provide enough photovoltage to overcome the inherent overpotentials associated with the OER. Only a handful of publications report IPCE values at a lower bias potential than 1.23 V. Zhong et al. reported an IPCE of ~6% at 0.8 V and 420 nm for W:BiVO₄[15] and Pilli et al. reached ~11% of efficiency for Mo:BiVO₄ at 0.92 V and 420 nm.[16] Following these approaches, we determined IPCE values at comparatively low bias potential of 0.8 V vs RHE. These conditions were selected to highlight the intrinsic properties of the material which are less dependent on the bias potential.

The performance of photoanodes can be further improved by modifying the semiconductor surface with state-of-the-art OER electrocatalysts. Cobalt phosphate (Co–P) is straightforward to synthesise and it was shown to be advantageously used in combination with photoanodes such as i.e. Fe₃O₄[16] and BiVO₄[15,16,27,37] More recent investigations demonstrated high activity of layered double hydroxides (LDH) for the OER.[23,39–41] Some studies showed the decoration of BiVO₄ electrodes with LDHs to enhance the photocurrents. Typically, LDHs are directly generated on the surface of the photoanode via hydrothermal methods or electrochemical deposition.[15,26,31] Here, a simpler approach of modification with LDHs is proposed, based on initially preparing a LDH which is subsequently spray-coated on the surface of the Mo:BiVO₄ sample, hence allowing optimisation of the catalyst loading.

In this work, we present a comparatively simple and reliable preparation method for the reproducible and optimised preparation of Mo:BiVO₄ photoanodes. By means of a specifically designed spray-coating set-up combined with a dedicated software, homogeneous and reproducible Mo:BiVO₄ films with controllable layer thicknesses, Mo/V ratio and the possibility to assess the influence of OEC|M:BiVO₄ PEC systems were fabricated and investigated.

2. Results and Discussion

2.1. Mo:BiVO₄ as Photoanode

Prior to the modification of Mo:BiVO₄ samples with OECs, the photoabsorber preparation procedure was optimised, aiming on a highly reproducible Mo:BiVO₄ sample fabrication procedure which simultaneously reveals superior IPCE values and low difference in efficiency between back- and front-side illumination. The small difference between IPCE values obtained during front-side and back-side illumination is a compromise between electron conductivity within the Mo:BiVO₄ front-side and back-side illumination is a compromise between low electron and hole transfer to the Mo:BiVO₄-electrolyte interface. This is experimentally important for the later performed automatic measurements by means of the optical scanning droplet cell (OSDC; see below). Similar IPCE values were recorded for samples prepared at different days when the same preparation parameters were used, indicating the satisfactory reproducibility of the developed spray-coating procedure. A set of samples were prepared using six different spray parameters and their IPCE values under back- and front-side illumination at a bias potential of 0.8 V vs RHE were compared (Figure 1a,b). The results reveal, as expected, that the sample preparation plays an important role with respect to the PEC efficiency. Samples prepared with a spray increment of 4000 μm, a spray volume of 5 μL and 2 repetitions show increased IPCE values for both back- and front-side illumination. In Figure 1c, the ratio between the IPCE values for back- and front-side illumination is shown. As pointed out above, if this ratio is close to 1, one can assume that both electrons and holes have similar mobility.[5,15,20] For the samples with the highest IPCE values, the ratio is not higher than 1.5 until 500 nm. The sample with the highest IPCE values at a bias potential of 0.8 V vs RHE and at 420 nm showed an efficiency of 19%, while the other samples do not exceed 13%. Despite the IPCE values were obtained at about 400 mV lower bias potential, they were comparable with those obtained with other non-structured Mo-doped BiVO₄ samples reported in the literature under front-side illumination (Table 1).[20,23–26,30–33–35]
In other words, the spray-coated Mo:BiVO₄ photoanodes have a similar efficiency at a significant lower externally applied driving force. The layer thickness of the photoabsorber is known to have a significant impact on the PEC efficiency. This is a direct consequence of the charge carrier mobility of the material. [30]

Although increasing the layer thickness favours light absorption, it can concomitantly lead to lower efficiencies due to a larger bulk recombination probability. Seabold et al. reported the electron diffusion length for Mo:BiVO₄ to be ~300 nm. [10] Hence, photoanodes with thicker layers may be limited by electron mobility, leading to higher efficiencies under back-side irradiation assuming that the hole transport is faster. [15,16] Applying different spray parameters modulates the Mo:BiVO₄ film thickness, [31,32] leading to different IPCE values as shown in Figure 1a,b. The film thicknesses in dependence on the used spray parameters were determined by cross-section SEM micrographs (Figure S1).

Precise determination of the Mo:BiVO₄ layer thickness was performed for the sample with the highest measured IPCE values. A cross-section SEM image including an EDX map was obtained (Figure 2). From the EDX mapping three distinctive regions can be distinguished, thus allowing the individual assessment of the layer thickness for the underlying FTO and the sprayed Mo:BiVO₄ film. The lower layer is silicon rich and derives from the glass substrate. The middle one with ca. 630 nm is Sn rich and represents the FTO film. Finally, the upper one with ca. 280 nm is Bi rich and represents the sprayed Mo:BiVO₄ film. The Mo:BiVO₄ sample with the highest IPCE values reveals a layer thickness of ca. 280 nm, a value, which favourably coincides with the optimum film thickness of around 300 nm as found by Seabold et al. for dip-coated samples. [10]

After achieving the optimal sample preparation parameters for the Mo:BiVO₄ with fixed Mo-content, the same spray parameters were used for the fabrication of samples with varying Mo-amount while keeping the photoabsorber film thickness comparable. For varying the amount of Mo inside the photoabsorber film, an FTO stripe (9 cm in length) was initially coated with a homogeneous film of Bi and V precursors, followed by a linear mass loading gradient of the Mo precursor. Solutions containing 10 mM Bi and V precursors were sprayed with a constant volume of 5 μL with 2 repetitions. On top of this first Bi and V layer a 1 mM Mo precursor solution was sprayed varying the volume from 1 to 22 μL (1 repetition). Afterwards, the sprayed sample was annealed using the same conditions as for the previously optimised samples. This Mo-gradient sample was called \( \nabla \text{Mo@BiVO}_4 \). The calculation of the Mo/V ratio was performed with a series of EDX spectra along the Mo gradient (Figure S10), indicating that the spray-coating set-up allows the preparation of linear mass loading gradients.

In the presence of Mo, substitution of V atoms in the lattice occurs during annealing. [11,12] The difference in radii between the two transition metals can introduce small crystal structures distortions, [14] which potentially increases the electric fields at the semiconductor-electrolyte interface and enhances the separation of photogenerated charge carriers, [6,12,13] leading to higher photocurrents. To investigate V substitution by Mo inside the lattice, a series of Raman spectra was recorded along the Mo gradient (Figure 3a). Upon addition of Mo, the Raman spectra several characteristic features. First, the stretching mode at 826 cm\(^{-1}\) \( [\nu(V-O)] \) shifts to lower wavenumbers due to the replacement of the V atoms in the \( \text{VO}_4 \) tetrahedra, increasing the \( V-O \) mean bond length. [21,14] Furthermore, the presence of Mo influences the \( \text{VO}_4 \) asymmetric and symmetric deformation modes \( \delta_1(\text{VO}_4^3) \) and \( \delta_1(\text{VO}_4^3) \), which are normally located at 326 and 365 cm\(^{-1}\) in pure \( \text{BiVO}_4 \). These peaks fuse together into a broader one in the presence of Mo. Finally, a shoulder at 877 cm\(^{-1}\) appears assigned to the stretching mode of \( \text{Mo-O-Mo} \) [\( \nu_{3}(\text{Mo-O-Mo}) \) bonds]. [21]

The changes in the Raman spectra suggest that spraying the Mo gradient continuously modulates the material composition in a controlled way. In order to assess the dependence of the photocurrents on the Mo/V ratio, linear sweep voltammo-

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**Table 1. Front-side illumination IPCE values at 420 nm of Mo:BiVO₄ samples prepared with different techniques.**

| Prep.  | pH  | \( U \) [V vs. RHE] | IPCE\(_{420nm} \) | Ref. |
|--------|-----|----------------------|------------------|------|
| SprayC | 9.3 | 0.80                 | 19 %             | T. W.|
| CVD    | 7.0 | 1.23                 | ~ 45 %           | [33] |
| Dip-C⃣ | 7.0 | 1.23                 | ~ 42 %           | [29] |
| ED⃣    | 7.0 | 1.23                 | ~ 23 %           | [23] |
| ED     | 9.0 | 1.23                 | ~ 20 %           | [6]  |
| ED     | 7.0 | 1.23                 | ~ 54 %           | [24] |
| ED     | 7.0 | 1.12                 | ~ 4 %            | [22] |
| ED     | 7.0 | 1.23                 | ~ 57 %           | [26] |
| LbL    | 7.0 | 1.23                 | ~ 15 %           | [34] |
| Sputter| 7.0 | 1.40                 | ~ 46 %           | [28] |
| SingleC| 7.0 | 1.20                 | ~ 15 %           | [35] |
| SpinC  | 7.0 | 1.25                 | ~ 17 %           | [16] |
| SpinC  | 7.0 | 1.00                 | ~ 42 %           | [30] |

[a] 300 mWcm\(^{-2}\), [b] Back-side illumination.
In order to obtain information on the structural changes dependent on the Mo loading, the sample \( \text{V}\text{Mo:BiVO}_4 \) was cut along the gradient and XRD patterns were recorded. The pristine \( \text{BiVO}_4 \) sample shows diffraction patterns of the underlying FTO and pure \( \text{BiVO}_4 \) (pdf 01-074-4894), indicating the formation of the desired material in accordance with the obtained Raman spectra in Figure 3a. The XRD pattern reveals that with increasing Mo content, few peaks merge. The reflections of the 200 plane and the 002 plane at 34.5° and 35.2° combine, and additionally the 240 plane at 46.6° and 042 plane at 47.2° fuse. These modifications are caused by a transformation of the monoclinic scheelite like structure of \( \text{BiVO}_4 \) into a tetragonal one, as previously described in literature.\(^{[6,14,19,43]} \) The peak at 59.2° merges into the peak at 58.6° upon Mo doping as already observed by Park et al.\(^{[14]} \) The region with the highest measured photocurrents, has a larger degree of crystallinity with sharper peaks. Finally, the XRD pattern corresponding to the region with the highest Mo content do not show the formations of any additional MoO\(_x\) phases, indicating that Mo atoms are solvated into \( \text{BiVO}_4 \) over the whole studied range.

In Figure 3b, the photocurrent densities at an applied bias potential of 1.23 V vs. RHE and the Raman shift for the \( V-O \) stretching mode are plotted against the increased Mo-content. The first displayed point represents pure \( \text{BiVO}_4 \). In the absence of Mo, the photoanode produces the lowest photocurrent density and shows the typical Raman band at around 829 cm\(^{-1}\). As soon as a small amount of Mo was integrated into the \( \text{BiVO}_4 \) lattice, a sharp increase in the photocurrent density was recorded, accompanied by a gradual Raman peak shift to shorter wavenumbers (up to 816 cm\(^{-1}\)).

At 25 mm in the Mo gradient, the highest photocurrent density was observed. The prepared photoanodes are flat thin films without 3D architecture, and together with the small geometric area and the slow scan rate, the highest photocurrent density \( j_{\text{RHE}} = \frac{j_{\text{RHE}}}{j_{\text{dark}}} \) measured at 1.23 V vs. RHE was about 755 \( \mu \text{A cm}^{-2}\). For higher Mo loadings, a slow but constant decrease of photoactivity was measured, followed by a stabilisation of the Raman shift at ca. 818 cm\(^{-1}\). Nonetheless, the combined analysis of the Raman spectra changes and the PEC \( j_{\text{RHE}} \) indicates the existence of an optimum doping level with Mo.\(^{[29]} \)

### 3. Decoration of Mo:BiVO\(_4\) with OECs

After optimisation of the photoanode by assessing a suitable layer thickness and optimising the Mo/V ratio, \( \text{Mo:BiVO}_4 \) photoanodes were modified with five different OECs and tested for enhanced PEC efficiency. We chose cobalt phosphate due to its known synergetic effects with BiVO\(_4\), Ni–Fe LDH, Co–Fe LDH and Mn–Co LDH were chosen due to the high OER activity of layered double hydroxides.\(^{[23,38–40]} \) For photoanode modification, highly diluted catalyst suspensions were sprayed onto \( \text{Mo:BiVO}_4 \) surfaces in order to prevent shading of the irradiated light by the OEC loading.

Taking into consideration that PEC systems are more limited by surface recombination at low bias potentials\(^{[37]} \) and that holes cannot efficiently be used towards OER at low bias potentials, the low consumption of holes causes charge carrier accumulation at the surface followed by recombination processes. In the presence of OEC higher IPCE values are expected due to suppression of surface recombination and the presence of specialised active sites for the OER which improve the reaction kinetics.\(^{[22]} \)

For PEC performance determination and assessment of the effects of the OEC, front-side illumination IPCE of the OEC-decorated \( \text{Mo:BiVO}_4 \) (OEC | \( \text{Mo:BiVO}_4 \)) samples were measured under different experimental conditions. Firstly, at a lower applied bias potential at which the system is limited by a low driving force, followed by the application of a mild bias potential to increase the driving force. These experimental conditions were selected to address the influence of the OECs on the PEC efficiency. Prior to the IPCE measurements, the non-illuminated potential difference between the OEC | \( \text{Mo:BiVO}_4 \) and the reference electrode was determined individually for...
each sample. At these experimental conditions, it was considered that the sum of the sample OCP and the photovoltage was the only driving force for the OER.

This specific dark OCP was applied as anodic potential for the IPCE assessment. The dark OCP for Mo:BiVO₄ samples was determined to be around 600 mV vs. RHE. The samples decorated with OECs in general revealed a slight cathodic shift (less positive values) of their OCP compared to the samples without OEC. This difference in the OCP was not higher than 50 mV for all cases (Table S1). Hence, it was considered to be insignificant for IPCE interpretation.

Figure 4 summarises the IPCE values at 420 nm from the OEC/Mo:BiVO₄ samples. The samples were measured at OCP and an applied bias potential of 0.8 V vs. RHE, as well as at pH 9.3 and at pH 9.3 in the presence of SO₄²⁻ (the complete IPCE measurements are shown in Figure S2).

In the case of Co–P, the efficiency was more than doubled when compared with Mo:BiVO₄, demonstrating that improved hole transfer to the OEC and/or decreased surface recombination processes were achieved in the presence of Co–P. In order to compare the intrinsic properties of the OECs, a mild bias potential of 0.8 V vs. RHE was applied. At this bias potential, Mo:BiVO₄ in absence of an OEC reached an IPCE value of 19% at 420 nm. However, in contrast to our initial assumption, no substantial improvement of the IPCE values was observed in the presence of OECs. Co–Fe LDH allowed a slightly higher efficiency of 1%. Hence, it has to be concluded that the system is either limited by slow hole transfer from the photoanode towards OEC or the presence of the opaque OEC layer decreases the incident illumination on the Mo:BiVO₄. To evaluate this hypothesis, IPCE studies were conducted in the presence of sodium sulphite, a redox couple that exhibits a lower anodic overpotential than water oxidation. In the presence of sodium sulphite, it can be supposed that the hole transfer is likely no longer limiting leading to higher IPCE values. As shown in Figure 4 for the experiments performed at 0.8 V, larger IPCE values were obtained in the presence of sodium sulphite. Moreover, similar IPCE values were calculated when the samples were measured at 0.8 V in pH 9.3 and at OCP in the presence of sodium sulphite. Since addition of sodium sulphite in the electrolyte led to a decrease of the IPCE values in the case of the application of 0.8 V bias potential, we conclude that covering the Mo:BiVO₄ surface with the selected OECs did not improve hole transfer towards oxygen evolution, but may decrease to a certain extent surface recombination processes.[22]

4. Evaluation of a Gradient of Ni–Fe LDH on top of Mo:BiVO₄

As shown in the results above, the OECs were deposited on the surface of the optimised Mo:BiVO₄. However, the subtle influence of an OEC on surface recombination and on the hole transfer to the catalyst may not address the limiting step in the overall reactions. Evidently, a complex interplay of not linearly independent parameters does not allow a rational step-by-step optimisation. Hence, since the chosen OEC loading was arbitrary we used the accuracy of the developed spray-coating system to establish a loading gradient of Ni–Fe LDH along a Mo:BiVO₄ sample.

Increasing, OEC loading may diminish the incident light to the photoabsorber,[48] thus decreasing the PEC efficiency. First, photocurrents were measured along the length of the bare Mo:BiVO₄ sample. Afterwards, the sample was decorated with a linearly increasing loading of Ni–Fe LDH (sample called \( \nabla Ni–Fe LDH | Mo:BiVO₄ \)), and finally linear sweep voltammograms were recorded under chopped polychromatic light to derive the PEC activity of the \( \nabla Ni–Fe LDH | Mo:BiVO₄ \) in dependence on the Ni–Fe LDH loading using the OSDC (Figure 5).

First, the dark current at high bias potentials of 1.74 V vs. RHE was plotted vs. the sample position (Figure 5a). In the absence of Ni–Fe LDH (black squares), the \( j_{\text{dark}} \) does not change along the sample, however, in presence of increasing loading with Ni–Fe LDH, the dark current density gradually increases, evidencing the acquisition of the desired gradient loading of the electrocatalyst. Besides increasing the dark current density, the presence of Ni–Fe LDH substantially enhanced the PEC performance (Figure 5b). For all catalyst loadings, the activity towards oxygen evolution was at least two times higher at 0.8 V vs. RHE as compared to pristine Mo:BiVO₄.

Larger photocurrents were measured with increasing Ni–Fe LDH loading until a plateau was reached at ~45 mm. Further addition of Ni–Fe LDH does not lead to an additional increase in photocurrent density. A section of the chopped-light LSV is demonstrated in Figure 5c. A sharp increase in the current densities is noticed after opening the shutter. The ratio between the current density measured at 0.8 V vs. RHE under illumination of Mo:BiVO₄ and Ni–Fe LDH | Mo:BiVO₄ was calculated. A maximum ratio was reached at 45 mm with a 5.8 times rise in photocurrent density compared with the pristine Mo:BiVO₄. In the presence of larger amounts of Ni–Fe LDH, the PEC activity remains still higher than pristine Mo:BiVO₄. However, the

![Figure 4. IPCE values for different OEC/Mo:BiVO₄ systems at 420 nm. The samples were measured under front-side illumination in 0.1 M sodium tetraborate, pH 9.3 or 0.1 M sodium tetraborate and 0.1 M sodium sulphite, pH 9.3 at different bias potentials, data from Figure S2.](image-url)
57 56 55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 39 38 37 36 35 34 33 32 30 29 28 27 26 25 24 23 22 21 19 18 17 15 14 12 11 10 8 7 6 4 3 2 1

Average (n = 3) photocurrent density at 0.8 V vs. RHE in the in the absence (black) and presence of a linear gradient increase of Ni–Fe LDH loading (blue). (c) Linear sweep voltammetry under chopped light in absence presence of a linear gradient increase of Ni–Fe LDH. With an optimum Ni–Fe LDH mass loading up to 5.8 x larger photocurrent density at 0.8 V vs. RHE was obtained in comparison with the pristine Mo : BIVO₄. The results show the applicability of the spray-coater set-up for reliable and precise high-throughput optimisation of photoabsorber/OEC systems.

Experimental Section

All chemicals were from Sigma Aldrich and were used as received if not mentioned otherwise. Fluorine-doped tin oxide (FTO) glass substrates (1.5 × 2.5 cm) were cleaned with a 10 g/L Alconox® solution, rinsed with deionised water followed by ethanol and drying under argon flow. The spray pyrolysis procedure of Abdi et al. was adapted for modifying the FTO glass. Stock solutions containing 10 mM of Bi(NO₃)₃ · 5 H₂O (> 98 %) in glacial acetic acid (VWR) and 10 mM VO(acac)₂ (> 98 %) in pure ethanol (Fisher Chemical) were prepared. An aliquot of 20 mL from each stock solution was transferred to a 50 mL volumetric flask containing an equivalent of 1 mM of MoO₃(acac)₂ (> 98 %) and the volume was completed with pure ethanol.

The precursor solution was spray-deposited on the substrate by means of a spray-coating apparatus based on a pressurised air nozzle, mounted on an automated position control unit. A defined volume of the material was supplied via a syringe pump (Cavro XCS +, Tecan Systems) towards the air nozzle, creating an aerosol, which was sprayed on top of the FTO substrate. The nozzle was kept at a distance of 5.5 cm above the substrate during the spray-coating procedure. The FTO substrates were placed on a heating block at 200 °C for instantly evaporating the solvent, hence reducing agglomeration effects and forming a homogeneous thin film. The spray parameters were controlled using a specifically developed software written in Microsoft Visual Basic 6.0: spray increment including the distance between two consecutive dispensing locations, spray volume and number of repetitions (the number of times the procedure is repeated). To form the Mo : BIVO₄ layer, the spray-coated samples were annealed at 775 K for 1 h (heating ramp 2 K min⁻¹) in a simulated air atmosphere (argon 80 % and oxygen 20 %). After the annealing procedure, yellow-green films were obtained.

Cobalt phosphate (Co–P) was photoelectrochemically deposited following a procedure by Abdi et al. at 600 mV vs. Ag | AgCl (3 M KCl) for 300 s under 800 mW cm⁻² white light intensity in a solution containing 0.5 mM CoCl₂ and 0.1 M KH₂PO₄ pH 7.27 Ni–Fe LDH, Co–Fe LDH and Mn–Co LDH were synthesised by a co-precipitation method (see Experimental part in the Supporting Information). Suspensions containing 0.02 mg mL⁻¹ of the LDH were prepared in pure ethanol and sonicated for stabilisations. After OEC spray-deposition onto pre-annealed Mo : BIVO₄ samples, the samples were placed in an oven at 250 °C for 15 min for complete solvent evaporation. No optical or SEM topography differences were observed after the modification of the photoabsorber with the different OECs. The gradient samples were achieved by means of spray-coating using an in-house developed software which allows to control the sprayed volume with respect to the X and Y-axis nozzle position. An increasing spray volume from 0 to 44 μL (0.02 mg mL⁻¹ suspension, deposition coefficient

5. Conclusions

Molybdenum modified bismuth vanadate samples were fabricated using a reliable method producing homogeneous and reproducible films over large FTO substrates (above 20 cm²). Samples with different spray-coating parameters were prepared with controlled layer thicknesses in order to optimise the photoabsorber itself, aiming on increasing the IPCE values. Mo : BIVO₄ samples were obtained with similar efficiency measured under back- and front-side illumination, indicating that the prepared samples were less limited by bulk electron mobility.

The photoanode layer thickness was assessed with SEM and EDX to be approximately 280 nm. The activity of the BIVO₄ based photoabsorbers was optimised by tuning the Mo content showing highest PEC activity. As a final optimisation approach, a sprayed gradient of Ni–Fe LDH was applied to the samples creating a linear mass loading gradient of Ni–Fe LDH. With an optimum Ni–Fe LDH mass loading up to 5.8 x larger photocurrent density at 0.8 V vs. RHE was obtained in comparison with the pristine Mo : BIVO₄. The results show the applicability of the spray-coater set-up for reliable and precise high-throughput optimisation of photoabsorber/OEC systems.

Figure 5. (a) Dark current density at 1.74 V vs. RHE in absence (black) and presence of a linear gradient increase of Ni–Fe LDH loading (blue). (b) Average (n = 3) photocurrent density at 0.8 V vs. RHE in the in the absence (black) and presence of a linear gradient increase of Ni–Fe LDH loading (blue). (c) Linear sweep voltammetry under chopped light in absence (dashed line) and presence of Ni–Fe LDH (full lines) with different loadings, scan rate 1 mV s⁻¹ in 0.1 M sodium tetraborate, pH 9.3. Arrows indicate shutter switching.
5·10⁻¹⁴ µL·µm⁻¹) was deposited onto the Mo:BiVO₄ photoanode (8.8 cm wide) for the fabrication of TiNi–Fe LDH/Mo:BiVO₄ sample, with an interval of 4000 µm between two consecutive deposition.[26]

All electrochemical measurements were performed in a three-electrode system containing a Ag/AgCl (3 M KCl) and a Pt wire as reference and counter electrode, respectively, with 0.1 M sodium tetaborate, pH 9.3, as supporting electrolyte. The samples were analysed using a high-throughput optical scanning droplet cell (OSDC).[19] The circular area of the working electrode was defined by the cell tip opening diameter of 0.735 ± 0.037 mm and this value was utilised to calculate the current density. Linear sweep voltammetry was performed in the potential range between -0.25 and 1.15 V vs. Ag/AgCl (3 M KCl) at 1 mVs⁻¹ with the shutter being closed and open for 5 s each. The lamp intensity (150 W Xe, LCB, Hamamatsu) was calibrated to 100 mW·cm⁻². The photocurrent densities (jphoto) were calculated by subtracting the dark current density (jdark) from the current density measured under illumination. All potentials are reported versus the reversible hydrogen electrode (RHE) following the Equation (1).

\[ U_{RHE} = U_{Ag/AgCl} + 0.210 + (0.059 \times \text{pH}) \]

The IPCE measurements were performed using a controlled monochromator integrated with a shutter (Instytut Fotonowy). A 150 W Xe lamp (Ushio) was used as light source. For the back and front-side illumination experiments, a cell with a quartz window and a working electrode opening of 1 cm² was used. The light intensity for each wavelength was calibrated (Pmonoch) with a power thermal sensor connected to a power meter (NOVA II, Ophir). The bias potential and the measured currents were controlled using an Autolab PGSTAT12 (Metrohm-Autolab). Before conducting the IPCE measurements, the non-illuminated open circuit potential (OCP) for each sample was determined, which was then used as the reference for the bias potential for the IPCE measurement. A following IPCE analysis at 0.8 V vs. RHE was performed. The IPCE values were calculated using Equation (2).

\[ \text{IPCE} = \frac{j_{\text{photo}} \times \text{mW/cm}^2}{P_{\text{monoch}} \times \text{mW/cm}^2} \times \lambda \langle \text{nm} \rangle \]

Raman spectra were obtained using a Jobin-Yvon iHR550 spectrometer coupled with a 532 nm Ventus LASER source and an optical lens with 60 times magnification (Olympus). Spectra were collected between 200 and 900 nm using: grating 1800, front entrance: 1000, exposure time: 3 s and accumulation number: 10. SEM micrographs and EDX analyses were recorded with a Quanta 3D FEG in high lens with 60 times magnification (Olympus). Spectra were collected using a high-throughput optical scanning droplet cell (OSDC).[19] SEM and EDX images. Dainea Medina, Patrick Wilde and Stefan Banse are acknowledged for the synthesis of some of the OECs used for this study.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Bismuth vanadate · Mo-doped bismuth vanadate · photoelectrocatalysis · oxygen evolution catalyst · oxygen evolution

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