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Hydrogen Treatment and FeOOH overlayer: Effective approaches for enhancing the photoelectrochemical water oxidation performance of bismuth vanadate thin films

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Graphical Abstract

Highlights

- Dual modification, hydrogen treatment and FeOOH loading in rf-sputtered bismuth vanadate (BiVO₄) thin films.
- Iron oxyhydroxide, an oxygen evolution catalyst, improvement of the charge transport at the semiconductor/electrolyte interface.
- The resulting FeOOH/H:BiVO₄ photoanode achieve a considerably higher photocurrent density ($J_p \sim 2.16 \text{ mA cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$).
- The enhanced photocurrent of FeOOH/H:BiVO₄ photoanode is ascribed to an improved bulk charge transport.
- The dual modification strategy used here offers a simple but effective approach of improving the water oxidation performance of BiVO₄.

Abstract

The water oxidation capability of the promising photoanode bismuth vanadate (BiVO₄) is hampered by poor bulk electron transport and by high rates of charge recombination at the semiconductor/electrolyte interface. Here, we demonstrate that a dual modification of BiVO₄ by: (i) annealing in a hydrogen-containing environment and (ii) coating with FeOOH overlayer substantially enhances the water oxidation ability of BiVO₄ photoanodes. Hydrogen treated, FeOOH coated BiVO₄ photoanodes exhibit a water oxidation photocurrent density of 2.16 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$, which is 5 times higher than for untreated BiVO₄ films. Moreover, they showed an impressive low photocurrent onset potential of $-0.11 \text{ V}_{\text{RHE}}$. A stable photocurrent was observed for 1 h of water oxidation measurement at $1.23 \text{ V}_{\text{RHE}}$ under 1 Sun illumination. The enhanced photocurrent of FeOOH/H:BiVO₄ photoanode is ascribed to an improved bulk charge transport, as confirmed by impedance spectroscopy measurements and Mott-Schottky analysis. The cathodic shift of the onset potential originates from a lowering of the flat band potential and from an improvement of the charge transport at the semiconductor/electrolyte

interface. The dual modification strategy used here offers a simple but effective approach of improving the water oxidation performance of BiVO₄.

Key Words: Bismuth vanadate, FeOOH, hydrogen treatment, photoelectrochemical, solar hydrogen

1. Introduction

Artificial photosynthesis emerged as an alternative means to store solar energy in form of chemical bonds. Hydrogen production by photoelectrochemical (PEC) water splitting offers a particularly promising way of storing solar energy. The efficiency of hydrogen production in PEC water splitting is mainly dependent on the properties of photoactive materials used in PEC cell, i.e. the photoanode and/or photocathode [1]. In particular, the water oxidation half-cell reaction (hereinafter called oxygen evolution reaction, OER) is the one associated with most of the losses in PEC cells [2] and is therefore object of intense research.

Here, we examine BiVO₄ as photoanode material for the OER since it has the following favorable properties: it can be synthesized by inexpensive methods [3-4]; it possesses an optical band gap (2.4–2.6 eV) that allows for harvesting of visible light [5]; and it has a valence band edge that is sufficiently positive to drive the OER [6]. The theoretical efficiency of solar to hydrogen conversion (η_{STH}) is over 9%, corresponding to a photocurrent density up to 7.5 mA cm⁻² under simulated AM 1.5 light irradiation [7-8]. However, the achieved applied bias photon-to-current efficiency (ABPE) is much lower (1.75% at 0.6 V vs. RHE in case of nanoporous BiVO₄ modified by FeOOH/NiOOH dual-layer oxygen evolution catalysts) [9-10], due to the following factors: poor electron conduction (in spite of a lower effective electron mass than in e.g. TiO₂ [11]); high rates of bulk and surface recombination [12]; and slow OER kinetics [13].

Several efforts have recently been made to improve the energy conversion efficiency of BiVO₄, with the goals of: (i) increasing light-absorption efficiency, (ii) reducing hole transport

distance to match the diffusion length of holes, and (iii) achieving lower surface recombination rate than the OER rate. Strategies like n-type doping with W or Mo have shown beneficial effects on the charge transport properties [14-18]. On the other hand, unwanted change in VO₄ tetrahedron chains can have a damaging effect on the OER of BiVO₄ [19-20]. In recent years, annealing in hydrogen containing atmosphere offered a way of tailoring the optoelectronic properties of BiVO₄ [4, 21-22].

Additionally, coating BiVO₄ with overlayers have been used to shift the OER onset potential cathodically, thus requiring a lower applied potential to initiate the OER. Many compounds have proven effective in this respect, such as IrO₂, RuO₂, Co-Pi, Ni-Bi, FeOOH, and NiOOH [23-26]. The observed improvements can arise from one or more of the following effects: a higher turnover frequency for the OER, i.e. a co-catalytic effect, a reduction in surface recombination rate, an increased photovoltage and a lowered flat band potential. Among the various OECs, ferric oxyhydroxide (FeOOH) has been studied by several groups due to its abundance on earth and stability of water oxidation properties in neutral and alkaline conditions. FeOOH has three main phases (α , β and γ). It has been demonstrated that the FeOOH is a promising oxidation catalyst for PEC applications [24, 27-29]. Choi et al. [3, 9, 29] reported that γ -FeOOH is an efficient water oxidation catalyst for BiVO₄ electrode. Most of these works utilised the either amorphous or α -polymorph of FeOOH, whereas very few reports are available on β -FeOOH (*akaganéite*), which is confirmed to be a semiconductor with a direct band gap of 2.12 eV and can be used as a potential photocatalysts with a visible-light response [30].

In this work, we present a two-step modification approach to improve the PEC performance of BiVO₄ thin films towards the OER by combining bulk and surface modification. Interestingly, both treatments (annealing in hydrogen containing atmosphere and FeOOH overlayer) result in an increase of photocurrent density *and* in a shift of OER onset potential.

These two modifications bring about a synergistic effect, since we show that the two-step modification enhances the performance more than the individual modifications alone. In particular, the two-step modification leads to enhanced photocurrent density at 1.23 V_{RHE} by a factor of 5 (from 0.42 to 2.16 mA cm⁻²), and to an OER onset potential shift by almost 1 V (from 0.95 to -0.15 V_{RHE}). We employ physical and PEC characterization of the photoanodes to shed light on the mechanisms leading to the observed improvement in PEC performance.

2. Experimental Section

2.1 Synthesis of BiVO₄ thin films

Pristine BiVO₄ were deposited on indium-doped tin oxide (SnO₂:In, ITO) substrates by RF-magnetron sputtering using a bismuth vanadate target (Goodwill Metal Tech Co. Ltd., China; purity 99.99%). Before deposition, ITO substrates of size $\approx 1.5\text{ cm} \times 1.0\text{ cm}$ were cleaned by sonication in acetone, ethanol and water, and finally dried in N₂ gas flow. The sputtering chamber was initially pumped down to approximately 2.0×10^{-6} Torr and then research grade Argon (flow rate = 20 sccm) was introduced into the chamber while maintaining the deposition pressure at 2.5×10^{-2} Torr. Sputtering was carried out at a RF-power of 100 W at room temperature for 2 h. After deposition, samples were annealed at 450 °C for 2 h in air to obtain the monoclinic phase of BiVO₄.

2.2 Hydrogen treatment and FeOOH deposition

To improve the bulk properties of pristine BiVO₄ thin films for enhanced photoelectrochemical activity properties of pristine BiVO₄ thin films, the hydrogen treatment under partial pressure was carried out. For the hydrogen treatment under partial pressure, the annealing chamber was pumped down to 2.0×10^{-6} Torr and 20 sccm 5% H₂ balanced Ar was introduced into the chamber while maintaining the chamber pressure at 2×10^{-2} Torr. The annealing temperature was set at 400 °C for 10 h followed by cooling down for 1 h [31]. Further, to modify the surface properties of BiVO₄ and H:BiVO₄ thin films, a thin layer of β -FeOOH layer was deposited by electrodeposition

technique based on our pervious report procedures with slightly changed deposition parameters for optimization of maximum photocurrent [32]. The electrodeposition of β -FeOOH was carried out in a three electrode assembly where BiVO_4 coated indium doped tin oxide ($\text{SnO}_2\text{:In}$, ITO) glass as used as working electrode, Pt wire as counter electrode and Ag/AgCl saturated with KCl as reference electrode. The electrodeposition solution consisted of 5mM FeCl_3 + 5 mM KF + 0.1 M KCl + 1 M H_2O_2 in Milli-Q water and cyclic voltammetry were performed in the potential range 0 V to -0.3 V vs. Ag/AgCl (sat. KCl) with a sweep rate of 20 mV s^{-1} for 10 cycles at room temperature (Figure S1). The obtained samples were rinsed with mill-Q water and dried at room temperature to obtain the yellowish colored β -FeOOH layer over the BiVO_4 and H:BiVO_4 samples as shown in inset of Figure 2a.

2.3 Material Characterization

X-ray diffraction patterns were obtained using a Phillips X'Pert Pro setup with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) operated at 45 kV and 40 mA. Raman spectroscopic signatures were obtained by employing a LabRAM HR evolution Raman microscope. Scanning electron microscope (SEM) images were acquired using a Supra 60 VP microscope (Zeiss) operated at an acceleration voltage of 10 kV. UV-visible spectroscopic measurements were performed with a LAMBDA 1050 UV/vis/NIR spectrophotometer. To check the chemical state of the elements on the surface of pristine BiVO_4 , H:BiVO_4 and FeOOH/BiVO_4 samples, X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a PerkinElmer PHI 5000C ESCA system (base pressure $\sim 10^{-10}$ mbar) using monochromatic $\text{Al K}\alpha$ radiation. All spectra were calibrated using the C1s photoelectron component peak of amorphous carbon (284.8 eV) present in the sample.

2.4 PEC Characterization

The PEC measurements were performed in a three-electrode configuration on BiVO_4 films employed as working electrode, Pt as counter electrode and Ag/AgCl as reference electrode.

The 0.1M Na₂SO₄ (pH=7) was used as an electrolyte and prepared by adding the desired amount of Na₂SO₄ in milli-Q water followed by stirring for 1 hr at room temperature. The PEC cell was controlled using an Autolab Electrochemical Workstation (X-Pot Potentiostat). A 150 W Xe arc lamp with total power density of 100 mW cm⁻² equipped with a AM1.5 filter was used as light source. Linear sweep voltammetry scans under dark and illumination were measured in the potential range -1.0 to +1.0 V vs. Ag/AgCl with a scan rate of 20 mV s⁻¹. The working electrode potential with respect to saturated Ag/AgCl was converted to reversible hydrogen electrode (RHE) using the following formula [33]: $E_{RHE} = E_{Ag/AgCl} + 0.059 pH + E_{Ag/AgCl_0}$, where $E_{Ag/AgCl} = 0.199$ V. Electrochemical impedance spectroscopy (EIS) measurements were carried out under 1 Sun simulated illumination in the frequency range from 10⁵ to 0.1 Hz with AC signal amplitude of 10 mV. The capacitance-voltage profiles were determined at an applied AC voltage with a frequency of 1 kHz in the dark, and Mott-Schottky plots (C^{-2} vs. V_{app}) were generated by employing a common procedure in the literature [34].

3. Result and Discussion

The formation and preservation of monoclinic phase of BiVO₄ (JCPDS 83-1698) crystal structure before and after hydrogen treatment and FeOOH deposition can be induced from the XRD patterns (Figure S2) and Raman spectra (Figure S3). Some additional XRD peaks with relatively high intensities are assigned to the underlying ITO substrate (JCPDS 06-0416), as indicated in Figure S2. The XRD patterns of the FeOOH/BiVO₄ and FeOOH/H:BiVO₄ samples indicate that β -FeOOH is also present, with peaks at 27.98°, 30.52°, 41.72° and 46.09° (the two peaks at 30.52° and 46.09° overlap with the relatively strong peak from the BiVO₄ layer). Further evidence of the presence of FeOOH is given by the Raman spectra. In addition to the Raman vibrational modes at around 129 cm⁻¹, 210 cm⁻¹, 324 cm⁻¹, 364 cm⁻¹, 640 cm⁻¹ and 829 cm⁻¹ (corresponding to BiVO₄) [35], an additional peak at 720 cm⁻¹ (Figure S3), characteristic of β -FeOOH [36], was observed.

The surface morphology of pristine BiVO_4 , H:BiVO_4 and FeOOH/BiVO_4 composite films is shown in Figure 1. All films show a homogeneous coverage of the ITO substrate. The pristine BiVO_4 film (Figure 1a) shows dense aggregates of irregularly shaped BiVO_4 grains (with characteristic dimension of 30–40 nm) forming a coarse surface, similar to previously reported BiVO_4 films [37]. Hydrogen treatment at 400°C results in larger grains with sharp grain boundaries (Figure 1b). A significant change in surface morphology with noticeable small valleys and hills is observed when $\beta\text{-FeOOH}$ was electrodeposited (Figure 1c) on BiVO_4 . The morphology of the electrodeposited FeOOH on BiVO_4 film (Figure 1c) appears to have a thin layer of $\beta\text{-FeOOH}$ crystallites with larger, sharp edge particles of BiVO_4 (ca. 30–40 nm diameter) in the background. The cross-sectional view of SEM image (Figure S4) displays a dense and homogeneous morphology and the estimated film thickness is approximately 250 nm.

Figure 1. Scanning electron microscopy (SEM) images of (a) pristine BiVO_4 , (b) H: BiVO_4 and (c) FeOOH/ BiVO_4 thin films deposited on ITO coated glass. Inset of (b) and (c) show higher magnification images of H: BiVO_4 and FeOOH/ BiVO_4 , respectively.

The optical absorbance spectra were measured using UV–vis spectroscopy and the spectra recorded in the wavelength range between 300 nm and 1100 nm is presented in Figure 2a. All samples show strong absorption in the near UV, and partially in the visible light region. This is supported by the fact that the samples appear yellow (inset (i) of Figure 2a). A slightly darker color (inset (ii) of Figure 2a) can be seen on H:BiVO_4 samples as a result of the hydrogen treatment. The absorption edge for pristine BiVO_4 is observed in the visible-light region at ~ 475 nm, which is characteristic of monoclinic BiVO_4 [38]. After hydrogen treatment and FeOOH

deposition, a red shift in absorption edge to 500 nm is observed. The band gap energy for all the samples was determined using the equation, $(\alpha h\nu) = A(h\nu - E_g)^n$, where α is absorption coefficient, A is a constant, h is Planck's constant, ν is the frequency of incident light, E_g is the band gap energy of the material and n is a constant related to the type of optical transition ($n = 2$ for indirect band gap and $n = 1/2$ for direct band gap). Since BiVO_4 is a direct band gap semiconductor [39], a graph of $(\alpha h\nu)^2$ vs. $h\nu$ was plotted for all the samples as shown in Figure 2b. Extrapolation of the linear portion of the graph yielded an intercept on the $h\nu$ axis that corresponds to an energy band gap of 2.66 and 2.60 eV for pristine and H: BiVO_4 samples, respectively. The FeOOH coated samples showed a slightly reduced band gap of 2.63 and 2.52 eV for FeOOH/ BiVO_4 and FeOOH/H: BiVO_4 samples (Figure 2b), respectively.

Figure 2: (a) UV-vis-NIR absorption spectra and (b) Tauc's plot for BiVO_4 , H: BiVO_4 , FeOOH/ BiVO_4 and FeOOH/H: BiVO_4 thin films samples. Inset of (a) shows the digital picture of (i) BiVO_4 , (ii) H: BiVO_4 and (iii) FeOOH/ BiVO_4 samples.

In order to study the chemical modification of BiVO_4 with hydrogen treatment and after FeOOH deposition, XPS measurements were carried out on pristine BiVO_4 , H: BiVO_4 , FeOOH/ BiVO_4 and FeOOH/H: BiVO_4 samples. Figure 3a and 3b show the core levels of Bi(4f) and V(2p) XPS spectra of the BiVO_4 and H: BiVO_4 samples, respectively. The Bi(4f_{5/2}) and Bi(4f_{7/2}) lines were found at the binding energy values of 164.2 and 158.9 eV in BiVO_4 and H: BiVO_4 samples, respectively (Figure 3a). Also, the V(2p_{1/2}) and V(2p_{3/2}) lines were found at

the binding energy values of 523.5 and 515.9 eV in BiVO₄ and H:BiVO₄ samples, respectively (Figure 3b). According to Silversmit et al., [40] the V(2p_{3/2}) position for the V⁵⁺ and V⁴⁺ states should be located at about 517.2 and 515.8 eV, respectively. In both, pristine and H:BiVO₄ samples, the V(2p_{3/2}) peak is found at 515.9 eV, which matches very well with V⁴⁺ state. Thus, it appears as the hydrogen treatment does not affect the oxidation state of V in BiVO₄ state (Figure 3b). However, in a few studies it has been reported that hydrogen treatment can create additional oxygen vacancies in metal oxide semiconductors, which results in partial reduction, i.e. Ti⁴⁺ to Ti³⁺ in case of TiO₂, Fe³⁺ to Fe²⁺ in case of hematite and V⁵⁺ to V⁴⁺ for BiVO₄, [41-44]. Figure 3c show the core-level O(1s) spectra of BiVO₄ and H:BiVO₄, FeOOH/BiVO₄ and FeOOH/H:BiVO₄. Pristine BiVO₄ sample exhibits two distinct peaks at binding energy of 529.5 and 530.9 eV. The value of 529.5 eV observed in all samples is consistent with the value reported for BiVO₄. The hydrogen treated BiVO₄ exhibits a relatively lower peak intensity at 529.5 eV (in comparison to the higher peak intensity at 530.9 eV in pristine BiVO₄) indicating that the concentration of hydroxyl groups on H:BiVO₄ surface was decreased by the annealing in hydrogen atmosphere. However, the relative high intensity of O(1s) peak in FeOOH/BiVO₄ in comparison to the pristine BiVO₄ shows that the concentration of hydroxyl groups is high, which is consistent with previous reports on FeOOH (for which the OH peak makes up about 45% of the total O(1s) peak area) [45-46]. Further, the Fe(2p) XPS spectra (Figure 3d) collected on the FeOOH/BiVO₄ and FeOOH/H:BiVO₄ samples show the presence of Fe³⁺ species on the surface of BiVO₄. Therefore, the XPS result confirms the presence of a thin layer of FeOOH over the BiVO₄.

Figure 3. (a) Fitted XPS core level spectra for (a) Bi(4f) (b) V(2p) for pristine BiVO₄ and H:BiVO₄, thin films. (c) Fitted O(1s) core level spectra for pristine BiVO₄, H:BiVO₄, FeOOH/BiVO₄ and FeOOH/H:BiVO₄ and (d) Fe(2p) spectra for FeOOH/BiVO₄ and FeOOH/H:BiVO₄ thin films.

The effect of hydrogen treatment and surface modification by FeOOH on the PEC performance of the BiVO₄ photoanodes was determined by measuring the photocurrent density under steady state and chopped light illumination. The cyclic voltammetry curves measured under dark condition for bare ITO, pristine BiVO₄ and FeOOH on ITO substrate are shown in Figure S5. The photocurrent density versus applied potential ($J_{ph}-V_{app}$) curves obtained under steady state illumination condition are shown in Figure 4a and the photocurrent onset potential is obtained from the Butler plots shown in Figure S6. All the photoanodes shows anodic photocurrent as expected thanks to the n-type characteristic of BiVO₄. The pristine BiVO₄ photoanode exhibits quite poor PEC response with a photocurrent density of 0.42 mA cm⁻² at 1.23 V_{RHE} and an onset potential of 0.95V_{RHE}. The low photocurrent density and highly anodic

onset potential are likely due to high bulk charge recombination rate, and high surface recombination rate and/or low OER rate, respectively [47]. Hydrogen treatment leads to an increase of photocurrent density (from 0.42 to 1.06 mA cm⁻² at 1.23 V_{RHE}) and a cathodic shift of onset potential (from 0.95V_{RHE} to 0.61 V_{RHE}). Hydrogen treatment in BiVO₄ at 400 °C was found to yield the best PEC performance in our previous study [4]. These results are also in agreement with earlier work showing that the incorporation of hydrogen leads to a shift in Fermi level toward the conduction band edge while maintaining the n-type character of BiVO₄ [23].

Figure 4: (a) Linear sweep voltammograms and (b) Calculated applied bias photon-to-current conversion efficiency for the pristine BiVO₄, H:BiVO₄, FeOOH/BiVO₄ and FeOOH/H:BiVO₄ photoanodes as a function of applied potential vs RHE measures in 0.1M Na₂SO₄ under 1 Sun illumination.

The surface modification by FeOOH leads to a further cathodic shift of onset potential and to a significantly higher photocurrent (Figure 4a and Table S1). Deposition of FeOOH on pristine BiVO₄ lowered the photocurrent onset potential up to 0.32 V_{RHE} and generated water oxidation photocurrents of 1.66 mA cm⁻² at 1.23 V_{RHE}. The increase in photocurrent is most likely thanks to the improved bulk charge transport [16-17, 25], as will be confirmed by EIS analysis. After the deposition of FeOOH on the surface of H:BiVO₄, the FeOOH/H:BiVO₄ photoanode shows a further enhancement in photocurrent density to 2.16 mA cm⁻² at 1.23 V_{RHE}. Also, the FeOOH/H:BiVO₄ photoanode has a remarkably low onset potential of -0.15 V_{RHE}. The similar trend in photocurrent density is also obtained under the chopped light illumination. Figure S7 represents the transient photocurrent spectra measurements under chopped illumination at 1.23 V_{RHE} for all the four photoelectrodes. From the transient photocurrent spectra it is clear that no significant photocurrent can be observed as soon as the light turned off and the light on–off cycles are reproducible.

Additionally, we have calculated the applied bias photon-to-current conversion efficiency (ABPE) for all samples by using following equation [48]:

$$\text{ABPE} = J_p \left(\frac{1.23 - V_{\text{App}}}{I_o} \right) \times 100$$

where J_p is the photocurrent density at the applied bias, V_{app} is the applied bias (vs. RHE), and I_o is the power density of the incident light. The ABPE for all photoanodes calculated by using the $J_{\text{ph}}-V_{\text{app}}$ curves are plotted as function of V_{app} and shown in Figure 4b. The pristine BiVO₄ shows an ABPE of 0.07% at 1.1 V_{RHE}. The H:BiVO₄ exhibits a 3-fold improvement in maximum ABPE (0.21% at 0.9 V_{RHE}). The FeOOH loading on pristine BiVO₄ and H:BiVO₄ samples significantly enhances ABPE. Addition of FeOOH on pristine BiVO₄ achieves an ABPE of 0.7% at 0.65 V_{RHE}. The highest photoconversion efficiency of 1.73% at a significantly lower potential of 0.23 V_{RHE} is achieved with FeOOH on H:BiVO₄.

Furthermore, we have evaluated the photoactivity of the samples under a constant applied potential of 1.23 V_{RHE} using chopped light as shown in Figure S7. Initially, when switching on the light, an anodic spike of photocurrent was observed in all the samples followed by a stable photocurrent. The photocurrent values increased from 0.46 mA cm⁻² for pristine BiVO₄ to 1.06 mA cm⁻² for H:BiVO₄ and 1.92 mA cm⁻² after FeOOH deposition on BiVO₄. The stabilized photocurrent reached 2.34 mA cm⁻² for FeOOH/H:BiVO₄. These values agree well with those determined from the J_{ph} - V_{app} characteristics under continuous light illumination (Figure 4a). Longer measurements with dual modified, hydrogen treatment and FeOOH loading, BiVO₄ photoanodes show that the improvement in photocurrent persists at least for ~1 h (Figure S8).

After the PEC measurements, Mott-Schottky analysis was performed on all samples. From the Mott-Schottky plots (Figure 5), the charge carrier density and flat band potentials were calculated using the Mott-Schottky equation [49]:

$$\frac{1}{C^2} = \left(\frac{2}{q\epsilon_o\epsilon N_D A^2} \right) \left(V_{APP} - V_{FB} - \frac{kT}{q} \right)$$

where C is the space charge capacitance, q is the electron charge, ϵ is the dielectric permittivity of vacuum, $\epsilon = 68$ is the relative dielectric constant of BiVO₄ [50], N_D is the donor density (cm⁻³), V_{app} is the electrode potential applied, V_{FB} is the flat band potential, k is the Boltzmann's constant, and T is the absolute temperature. The donor density can be calculated from the slopes of Mott-Schottky curve using the equation $N_D = 2/(q\epsilon_o\epsilon)[d(1/C^2)/dV]^{-1}$. The calculated values of N_d increases from 2.37×10^{17} in the BiVO₄ sample to 5.15×10^{17} in the H:BiVO₄ sample, then further increases to 9.80×10^{18} and 1.24×10^{20} for FeOOH/BiVO₄ and FeOOH/H: BiVO₄, respectively. As a consequence of the changes in N_D , the width L_d of the space-charge layer at the photoelectrode/electrolyte interface changed according to the following relationship: $L_D = [(2\epsilon_o\epsilon)/(qN_D) (V-V_{FB})]^{1/2}$ (see Table S2 for calculated values). The flat band potentials can be determined from the extrapolation of linear fit of Mott-Schottky plots with the x-axis. The flat-

band potential (V_{FB}) of the FeOOH/H:BiVO₄ photoanode was calculated to be -0.15 V_{RHE} as shown in Figure 5, which is about 500 mV more negative than pristine BiVO₄. A more negative V_{FB} is beneficial for anodic reactions such as the OER. A decrease in V_{FB} leading to cathodic shift of OER onset potential has recently been observed for Fe₂O₃ photoanodes after prolonged oxidation treatments [51]. We highlight here that for our samples, the difference between onset potential and V_{FB} is actually increasing in the following order: BiVO₄ > H:BiVO₄ > FeOOH/BiVO₄ > FeOOH/H:BiVO₄. This is an indication that there are further mechanisms than just a lowering of V_{FB} (suppression of surface recombination, increase of OER rate, increase of photovoltage), leading to the cathodic shift of onset potential. Interestingly, the difference between onset potential and V_{FB} for the FeOOH/H:BiVO₄ sample is as small as 40 mV, which suggests that we are close to exploiting the full potential of BiVO₄ in terms of bias needed to initiate the OER.

Figure 5: Mott-Schottky plots of BiVO₄, H:BiVO₄, FeOOH/BiVO₄ and FeOOH/H:BiVO₄ under dark in 0.1M Na₂SO₄ (pH 7) using a three-electrode system

Finally, the results from EIS are summarized in Figure 6a in the form of Nyquist plots (i.e. negative imaginary vs. real component of the total impedance Z). The total impedance

follows the trend: $\text{BiVO}_4 > \text{H:BiVO}_4 > \text{FeOOH/BiVO}_4 > \text{FeOOH/H:BiVO}_4$. Such trend is commensurate with the performance of the electrodes in terms of J_{ph} - V_{app} curves. The traces for the samples with and without FeOOH show two and one semicircle, respectively. For this reason, we chose different equivalent circuits to perform data fit. For the samples without FeOOH, we used a modification of the Randle's circuit (see the yellow dashed box in Figure 6b, characterized by a resistance R_s in series with the parallel of another resistance R_1 and a constant phase element CPE_1). For the samples including FeOOH, we used the circuit enclosed in the green dashed box of Fig. 6b. This circuit has an additional parallel of a resistance R_2 and a constant phase element CPE_2 . We chose CPE's instead of pure capacitances owing to the better data fit. The impedance of a CPE is a hybrid between a resistor and a capacitor and CPE's are used often to describe capacitors with non-uniform spatial properties. It is nonetheless possible to calculate an effective capacitance from the CPE parameters and from the respective parallel resistance. Results from the fitting are summarized in the table in Figure 6c. The hydrogen treatment results in decrease of R_1 of a factor 14 and 44 for samples with and without FeOOH, respectively. Since R_1 corresponds to the charge transport resistance in BiVO_4 , this is a confirmation of the beneficial role of the hydrogen treatment on the bulk charge transport, i.e. within BiVO_4 . Interestingly, the hydrogen treatment on samples containing FeOOH also reduced the resistance R_2 of a factor of 5. Since R_2 is the resistance associated with charge transfer at the electrode/electrolyte interface, this is an indication that hydrogen treated BiVO_4 forms a junction with FeOOH of higher quality with respect to charge transport. It is worth mentioning that these measurements are not conclusive in determining whether the observed shift in onset potential originates from a reduced surface recombination rate, or by an increase of the OER, or by both. The role of overlayers such as FeOOH is not completely understood yet, as they sometimes appear to behave as true catalysts (i.e. increase the OER rate), and sometimes as suppressors of surface recombination [52], depending on which photoabsorber

they are deposited, as well as fabrication conditions. Elucidating the mechanism(s) behind the beneficial effect of FeOOH on BiVO₄ will require further investigation.

Figure 6: (a) EIS spectra (shown in form of Nyquist plots) for pristine BiVO₄, H:BiVO₄, FeOOH/BiVO₄ and FeOOH/H:BiVO₄ photoanodes recorded at 1.23 V_{RHE} under 1 Sun simulated irradiation (AC frequency range: 10⁵–0.1 Hz, AC amplitude 10 mV). (b) The equivalent circuits used to fit EIS data for electrodes without FeOOH (enclosed in the orange dashed box) and for electrodes with FeOOH (enclosed in the green dashed box). (c) Values of relevant parameters extracted from fitting of EIS data. C₁ and C₂ indicate the effective capacitances extracted from the correspondent constant phase elements CPE₁ and CPE₂.

4. Conclusion

Hydrogen treated BiVO₄ thin films coupled with β -FeOOH overlayers exhibit superior PEC water splitting performance as compared to bare BiVO₄ samples. The best performing FeOOH/H:BiVO₄ electrode yields a remarkable photocurrent of 2.16 mA cm⁻² at 1.23 V_{RHE}. Moreover, the OER onset potential is as cathodic as -0.11 V_{RHE}, just 40 mV higher than the flat band potential. Additionally, the FeOOH/H:BiVO₄ electrode showed no appreciable deterioration over 1 h of chronoamperometry at 1.23 V_{RHE}. The enhanced photocurrent upon the dual modification is originated by reduced bulk recombination thanks to more efficient charge transport, as confirmed by impedance spectroscopy characterization. The cathodic shift of the OER onset potential is partly attributed to the lowering of the flat band potential, partly to reduced surface recombination or enhanced OER rate. Conclusively, it can be said that FeOOH/H:BiVO₄ allows higher efficiency for water splitting at low bias voltage than bare

BiVO₄ and such combination is promising for future research on heterojunction based on this semiconductor.

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Notes

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