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Improving BiVO₄ photoanodes for solar water splitting through surface passivation[†]

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BiVO $_4$ has shown great potential as a semiconductor photoanode for solar water splitting. Significant improvements made during recent years allowed researchers to obtain a photocurrent density of up to 4.0 mA cm $^{-2}$ (AM1.5 sunlight illumination, 1.23 V $_{\rm RHE}$ bias). For further improvements of the BiVO $_4$ photoelectrodes, a deep understanding of the processes occurring at the BiVO $_4$ -H $_2$ O interface is crucial. Employing an electrochemical loading and removal process of NiO $_x$, we show here that carrier recombination at this interface strongly affects the photocurrents. The removal of NiO $_x$ species by electrochemical treatment in a phosphate electrolyte leads to significantly increased photocurrents for BiVO $_4$ photoelectrodes. At a bias of 1.23 V $_{\rm RHE}$, the Incident Photon-to-Current Efficiency (IPCE) at 450 nm reaches 43% for the passivated BiVO $_4$ electrode under back side illumination. A model incorporating heterogeneity of NiO $_x$ centers on the BiVO $_4$ surface (OER catalytic centers, recombination centers, and passivation centers) is proposed to explain this improved performance.

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Introduction

With a photocurrent onset potential of <0.2 V_{RHE} , and a photocurrent of 7.0 mA cm⁻² under AM1.5 solar light irradiation, BiVO₄ is predicted to be an efficient photoelectrode material for solar water splitting.¹⁻³ Very recently, it was shown that a photocurrent as high as 4.0 mA cm⁻² can be achieved using BiVO₄ thin film electrodes.¹ However, low photocurrent densities (<1.0 mA cm⁻² at 1.23 V_{RHE}) and high onset potentials for photocurrent (>0.6 V_{RHE})³ are frequently reported. Further improvements are needed before the full potential of BiVO₄ can be reached for artificial leaf devices.^{1,4}

To improve light-driven water splitting at BiVO₄ surfaces, various material properties such as bulk recombination, ^{1,5} electron transport ^{6,7} and the electron transfer across the interfaces ^{6,8} need to be optimized. Attempts have been made for BiVO₄ photoelectrodes to address these factors separately. ^{3,9} To improve the electron transfer across the oxide–water interface loading of the oxygen-evolution-reaction (OER) catalyst NiO_x/CoO_x onto the photoelectrodes has been under intensive research. ^{10–12} Though the performance improvements after CoO_x loading are verified in various oxide photoelectrodes, discussions arose recently ¹³

Departement of Chemistry, Kemiskt Biologiskt Centrum (KBC), Umeå Universitet, Linnaeus väg 6, S-901 87 Umeå, Sweden. E-mail: yongqi.liang@chem.umu.se † Electronic supplementary information (ESI) available: The reflection spectrum of the mirror for the illumination setup, the CVs for the characterization of BiVO₄ films in NaPi and NaBi, the light transmission spectrum of the BiVO₄ film, the CVs for NiO_x loading and removal onto the FTO substrate, the XPS spectra of BiVO₄ films, and comparison of the photoresponse of BiVO₄ with/without the sulfite hole scavenger. See DOI: 10.1039/c4cp00674g

whether the improvements are due to the catalytic effects of CoO_x^{14} or rather due to facilitating charge separation across the newly formed junction between the CoO_x layer and the photoelectrodes. Here we demonstrate the influence of surface recombination on the performance of BiVO_4 photoelectrodes and show that a heterogeneity exists within the amorphous NiO_x layer loaded onto the BiVO_4 surface. We elucidate this heterogeneity by selectively removing the catalytic NiO_x species from the BiVO_4 surface for OER without affecting the NiO_x species that minimizes the surface recombination.

Experimental section

 ${
m BiVO_4}$ films on FTO glass substrates (TEC15, Hartford) were prepared by following a reported procedure. Their Raman spectra show identical features to that reported previously. The ${
m SnO_2}$ interfacial layer was deposited in between ${
m BiVO_4}$ and FTO to improve the electron collection at the back contact.

NiO $_x$ loading onto BiVO $_4$ was carried out electrochemically according to a well-established method, ¹⁶ and the formula of MO $_x$ (NiO $_x$ and CoO $_x$) is used here to indicate the non-stoichiometric nature of the metal oxide–hydroxide layer deposited by this method. 1 mM Ni(NO $_3$) $_2$ ·6H $_2$ O (98%, Alfa-Aesar) was mixed with 0.1 M borate buffered aqueous electrolyte (NaBi) at pH = 10.0, and the precipitate was removed from the solution using a syringe filter (0.2 µm pore size membranes) after aging the solution in air for \sim 20 min. The removal of NiO $_x$ from the BiVO $_4$ surface was performed in a 0.2 M phosphate buffered aqueous electrolyte (NaPi) at pH = 7.0.

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The photoelectrochemical characterization was carried out in 0.2 M NaBi at pH = 10.0. The potential of the $BiVO_4$ working electrode (0.283 cm²) was controlled via a potentiostat (Autolab PG302N). A Ag/AgCl (3 M NaCl) electrode and a coiled Pt wire were used as the reference electrode (RE) and the counter electrode (CE) for the 3-electrode measurement, respectively. All the potentials in this paper were translated to the Reversible Hydrogen Electrode (RHE) scale by assuming the Nernstian behaviour for the oxide surfaces in aqueous solution. Unless mentioned otherwise, a scan rate of 50 mV s⁻¹ was used. The anodic scan is referred to as forward scan, and the cathodic scan is referred as reverse scan. An AM1.5 solar simulator (Sol3A, model 94043A, Newport) was used as the light source during PEC characterization. A UV-enhanced mirror (PAUV-PM-5010M-C, Melles Griot) with close-to-flat response across the whole spectrum ($\sim 85\%$ between 300 nm to 600 nm, $\sim 96\%$ for >1000 nm, Fig. S1, ESI†) was employed to flip the simulated sunlight from the vertical to the horizontal direction. The photons go through the FTO substrate before they reach the BiVO₄ film first for back side illumination, while the photons need to penetrate the electrolyte before they reach the BiVO₄ film for front side illumination. ¹⁷ The light intensity (100 mW cm⁻²) reaching the sample was calibrated using a thermopile detector (S302C, Thorlabs). For illumination at individual wavelengths, the white light from a tungsten-halogen lamp was dispersed through a monochromator (SpectraPro 2150, Acton). The secondor higher-order harmonics of light passing through the monochromator were removed using suitable long-pass filters (Schott).

The high resolution XPS spectra of the BiVO₄ samples were recorded via a Kratos Axis Ultra electron spectrometer equipped with a delay line detector. A monochromatic Al Ka radiation source operated at 150 W, a hybrid lens system with a magnetic lens, and a charge neutralizer were used for all measurements. The resulting spectra were processed using the Kratos software and background-corrected using a Shirley background. All peak positions for the spectra recorded at room temperature were shifted against the C 1s peak at 285.0 eV. The spectra were determined from averaged values obtained over an analysis area of 0.3 mm × 0.7 mm² and pertained to an analysis depth of about 6 nm.

The light intensity of the photons at wavelengths from 300 nm

to 600 nm was measured using a calibrated Si photodiode

Results

(PD300-UV, Ophir).

Fig. 1 shows the performance of an as-prepared BiVO₄ photoelectrode. Both the CVs for the BiVO4 electrode in the dark and under AM1.5 sunlight (front side illumination) were collected. The CV for the photoelectrode under AM1.5 sunlight illumination serves as the action curve. Since no characteristic parameter set (such as V_{oc} , I_{sc} , and fill factor for a photovoltaic device) is defined for photoelectrodes as yet, we take in this article the photocurrent under 1.23 V_{RHE} and the potential where the photocurrent curve crosses the potential-axis (the onset potential) as the criteria to compare the performances of BiVO₄ electrodes.

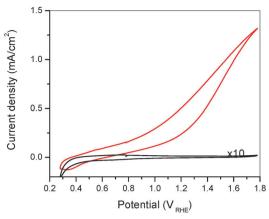


Fig. 1 Cyclic voltammograms (CVs) of the as-prepared BiVO₄ film electrode. Both the dark current (black) and the photocurrent under AM1.5 sunlight (red) are shown (front side illumination). The dark current data are amplified to show the absence of electrochemical water oxidation on BiVO4 in the potential region.

The dark current for the as-prepared BiVO₄ film (Fig. 1) is close to zero until 1.80 V_{RHE} . The near-zero current in the dark indicates that the native surface of BiVO4 cannot oxidize water efficiently (for a current density of 20 μ A cm⁻²) below an overpotential of 0.57 V. From the photocurrent curve of the as-prepared BiVO₄ electrode (Fig. 1), a current density of $0.54~\text{mA}~\text{cm}^{-2}~(0.27~\text{mA}~\text{cm}^{-2})$ at $1.23~\text{V}_{\text{RHE}}$ is obtained for the forward (reverse) scan. The onset potential is determined to be $0.40 \text{ V}_{\text{RHE}} (0.65 \text{ V}_{\text{RHE}})$.

The electrochemical processes for loading and removal of NiO_x onto $BiVO_4$ are shown in Fig. 2A and B, respectively. The appearance of the oxidation-reduction peaks at 1.57 $V_{RHE}/1.37$ V_{RHE}, which are assigned to the oxidation-reduction of NiO_x, directly confirms a successful loading of NiOx onto BiVO4. During the loading process (Fig. 2A), the peak of NiO_x oxidationreduction became more and more prominent as the electrode was electrochemically cycled between 0.50 V_{RHE} and 1.80 V_{RHE}. As a result of NiOx loading, the potential bias needed for water oxidation decreased from 1.8 V_{RHE} to <1.6 V_{RHE}. The increased dark current after NiOx-loading onto BiVO4 agrees well with previous reports¹⁶ which show that NiO_r can effectively catalyze water oxidation. After treating the NiOx loaded BiVO4 in 0.2 M NaPi electrolyte, the redox peak feature for NiOOH/Ni(OH)₂ disappears and the onset potential for water oxidation in the dark changes back to >1.8 V_{RHE} (Fig. 2B). The much decreased current density in the region of NiO_x oxidation-reduction in Fig. 2B compared to Fig. 2A is caused by a chemical removal of NiOx using phosphate before the electrochemical removal of NiOx could occur. The oxidation-reduction peak at 0.79 V_{RHE}/0.72 V_{RHE} becomes obvious after the electrochemical removal of NiOx (Fig. 2B). This redox peak is tentatively assigned to the oxidation-reduction of tetrahedral coordinated VO2+/VO2+ species on the surface of BiVO₄, which is ~ 0.20 V less anodic than the octahedrally coordinated VO2+-VO2+ redox couple in aqueous solution.18 The NiOx species loaded onto BiVO4 are therefore suggested to cover some VO sites on the BiVO4 surface

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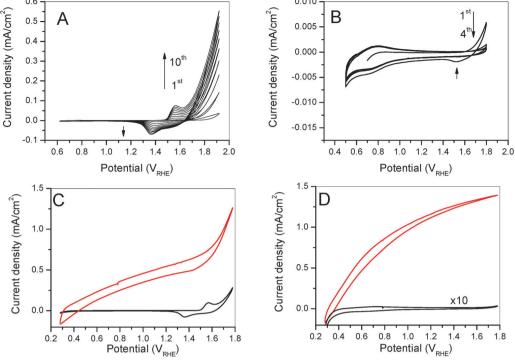


Fig. 2 (A) CVs for NiO $_{\rm X}$ loading onto BiVO $_{\rm 4}$ electrodes. A current density of \sim 0.1 mA cm $^{-2}$ for the NiO $_{\rm X}$ oxidation peak (1.61 V $_{\rm RHE}$) is typically obtained after 10 cyclic scans. (B) CVs for removal of NiO $_{\rm X}$ in phosphate buffer (pH = 7.0). The cyclic scan (from 0.5 V $_{\rm RHE}$ to 1.8 V $_{\rm RHE}$) starts in the anodic direction. The current at > 1.4 V $_{\rm RHE}$ drops close to zero during scanning, which indicates the removal of NiO $_{\rm X}$ OER catalytic centers. Typically 4 cycles were used to ensure a complete removal of NiO $_{\rm X}$ OER catalytic centers. (C) CVs of a BiVO $_{\rm 4}$ film electrode after electrochemical loading of NiO $_{\rm X}$, and (D) CVs for the BiVO $_{\rm 4}$ film after removal of NiO $_{\rm X}$ OER centers. Both the dark current (black) and the photocurrent under the simulated AM1.5 sunlight for front side illumination (red) are shown. The dark current data in panel D are amplified to show the absence of NiO $_{\rm X}$ OER centers on BiVO $_{\rm 4}$.

and the removal of NiO_x OER centers using phosphate exposes these VO sites again. These VO_x species are proposed to be the OER centers for both the as-prepared BiVO_4 electrodes and the BiVO_4 electrodes that undergo the NiO_x loading and phosphate treatment processes.

The XPS spectra were recorded to verify the loading of the NiO_x centers onto the surface of the BiVO_4 photoelectrode and their subsequent removal in phosphate buffer. As shown in the literature, 19,20 V atoms at the surface are found to be partly leached out (V:Bi ratio <1). Therefore, the concentration of Ni on the surface is quantified through the ratio between Ni and Bi by using the amount of Bi as an internal reference. As summarized in Table 1, a high concentration of Ni (Ni:Bi = 5.96:1) was detected on the BiVO_4 surface after NiO_x loading in a borate electrolyte. After phosphate treatment, the ratio between Ni and Bi on the surface decreased to 0.59. The decrease of Ni content not only directly proves that the phosphate removes the loosely

Table 1 The chemical composition on the surface of a series of BiVO₄ photoelectrodes at different stages for treatment

	As-prepared BiVO ₄	NiO_x loaded BiVO ₄ , as deposited	NiO_x loaded BiVO ₄ , after phosphate treatment
Ni:Bi ratio	0.00:1	5.96:1	0.59:1
V:Bi ratio	0.94:1	0.48:1	0.40:1

coordinated NiO_x -OER centers on the surface of $BiVO_4$, but also shows that a small fraction of more tightly bound Ni remains attached to the surface. Although the exact Ni:Bi ratio varies from 0.3 to 0.6, for different $BiVO_4$ samples after phosphate treatment, the XPS data do clearly demonstrate the partial removal of NiO_x from the surface of $BiVO_4$.

Fig. 2C and D shows the effects of the NiO_r loading-andremoval process on the performance of the BiVO₄ photoelectrodes in a NaBi electrolyte (without Ni²⁺ in the solution). After electrochemical NiO_x loading onto the BiVO₄ electrode (shown in Fig. 2A), a dark-current is observed at $> 1.50 \, V_{RHE}$ for the $BiVO_4$ electrode (Fig. 2C). The current peak at 1.56 V_{RHE} is assigned to the oxidation of Ni(OH)₂ to NiOOH.²¹ When the scan direction is reversed, a bump between 1.2 V_{RHE} and 1.5 V_{RHE} appears in the CV. The bump in the CV curve is assigned to the reduction of NiOOH to Ni(OH)₂. The peak positions are in agreement with the data shown in Fig. 2A. The >100 mV separation between the oxidation peak and the reduction peak indicates that the redox process is not reversible. The large widths of the oxidation-reduction peaks are related to the fact that multiple forms of Ni(OH)₂ (α -Ni(OH)₂ and β -Ni(OH)₂) and NiOOH (β-NiOOH and γ-NiOOH) which might also include Ni⁴⁺ species are involved during the oxidation-reduction.²² The steep increase in the anodic current after NiO_x oxidation indicates that water oxidation occurs electrochemically in the dark. From the photocurrent curve for NiOx loaded BiVO4 (Fig. 2C), a current

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density of 0.55 mA cm $^{-2}$ (0.44 mA cm $^{-2}$) at 1.23 V_{RHE} is

obtained for the forward (reverse) scan. The onset potential for the photocurrent is determined to be 0.31 V_{RHE} (0.45 V_{RHE}) for the forward (reverse) scan.

After the phosphate treatment of the NiO_x-loaded BiVO₄, the redox peak feature for NiOOH to Ni(OH)2 disappears and the current in the dark is again close to zero up to 1.80 $V_{\rm RHE}$ (Fig. 2D). This suggests that any remaining Ni species is much less active for OER than the NiO_x species represented by the redox wave shown in Fig. 2C. On the other hand, the photocurrent at 1.23 V_{RHE} goes up to 1.18 mA cm⁻² (1.13 mA cm⁻²) for the forward (reverse) scan. The onset potential for the photocurrent becomes 0.31 V_{RHE} (0.37 V_{RHE}) for the forward (reverse) scan.

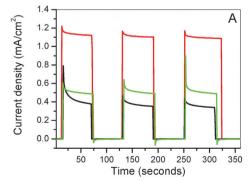
For BiVO₄ films lower anodic currents are generally observed during the reverse scan than for the forward scan, both in the dark and under illumination. For the as-prepared BiVO₄ films and the NiO_x-removed BiVO₄ films, the hysteresis in the dark CVs is mostly caused by charging and discharging of the double-layer capacitance. For the NiOx-loaded BiVO4 films, the hysteresis in the dark CVs is mainly due to the oxidationreduction of NiOx species. Since the O2 molecules produced cannot desorb from the BiVO4 surface fast enough, they will block the active OER sites on the BiVO4 surface and cause further hysteresis for the BiVO₄ electrodes under high potential bias or sunlight illumination.

The effects of the NiO_x loading-and-removal process on the surface of BiVO₄ are also observed during the steady state characterization. The stabilized photocurrent at 1.23 V_{RHE} increased slightly from $0.34~\text{mA}~\text{cm}^{-2}$ to $0.49~\text{mA}~\text{cm}^{-2}$ after NiO_x loading, and then increased to 1.08 mA cm⁻² after the removal of NiOx (Fig. 3A). These values agree well with the photocurrent determined from the CVs shown in Fig. 2. The measurements at a long time scale (Fig. 3B) further show that the improvement in the photocurrent through the NiO_x loading-and-removal procedure persists at least for a time period of ~ 1 h. The photocurrent for the passivated BiVO₄ photoelectrode slowly

decreased from 1.08 mA cm⁻² to 0.91 mA cm⁻² during the first 2200 seconds. The incubation of the BiVO₄ photoelectrode in the dark (from 2200 seconds to 2300 seconds) does not affect the photocurrent upon the next illumination. On the other hand, bubbling air through the electrolyte (during the dark period between 2700 seconds and 2900 seconds) changes the photocurrent back to 1.09 mA cm⁻². This suggests that the activity loss during the first 2200 seconds is caused by gas bubbles accumulated on the surface, which block the contact between the BiVO4 electrode and the electrolyte. This proves that the effects of NiOx loading/removal on the photocurrent are stable.

In contrast, the photocurrent does not increase over long-time characterization of the as-prepared BiVO₄ electrodes in 0.2 M NaPi (ESI,† Fig. S2). This demonstrates that the above described improvement is not simply caused by extra electrolysis in the presence of phosphate anions, but that rather a prior loading of NiO_x is required. It is also noted that the effects of the NiO_x loading-and-removal process on the surface of BiVO₄ are repeatable. A second loading of NiO_x onto the passivated BiVO₄ will change the CVs back into those shown in Fig. 2C and a following electrochemical removal of NiOr OER centers from BiVO4 in a NaPi electrolyte will recover the photocurrent as shown in Fig. 2D.

For employing BiVO₄ for solar fuel production in, for example, artificial leaf devices the high energy photons need to be absorbed by the water exposed BiVO₄ and the low energy photons need to be absorbed by a second material of lower band gap (such as Si). Considering this, front-side illumination was used above for the photocurrent collection from the BiVO₄ photoelectrodes. On the other hand, BiVO₄ photoelectrodes are known to perform better under back side illumination than under front side illumination due to the sluggish electron transport inside BiVO₄. 3,6 To allow direct comparisons with the performance of BiVO4 reported earlier, the IPCE spectrum under back-side illumination for the BiVO₄ electrode (under the bias of 1.23 V_{RHE}) was collected (Fig. 4A) after the NiO_x-OER centers were removed. The IPCE steadily increases from zero at 510 nm to a plateau at \sim 440 nm,



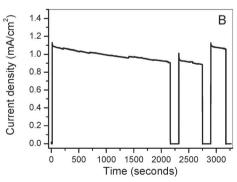
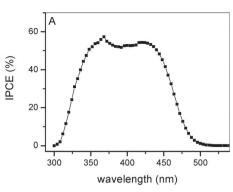


Fig. 3 Chronoamperometric characterization of the BiVO₄ electrodes biased at 1.23 V_{RHE}. (A) The as-prepared BiVO₄ film electrode (black), BiVO₄ film electrode after NiO_x loading (green), and $BiVO_4$ film electrode after electrochemical removal of NiO_x OER centers (red). The measurements started with the condition that the BiVO₄ electrode was kept in the dark, the white-light is chopped on and off approximately every 60 seconds. (B) Current-time trace for the passivated BiVO₄ electrode on a long-time scale. The measurement started in the dark. At 10 seconds, 2300 seconds and 2900 seconds, the shutter was opened. At 2200 seconds and 2700 seconds, the shutter was closed. Between 2700 seconds and 2900 seconds, air was passed through the electrolyte to remove the O_2 bubbles accumulated on the surface of the BiVO₄ electrode.

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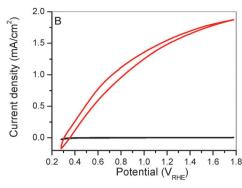


Fig. 4 (A) The IPCE spectrum of the $BiVO_4$ photoelectrode after NiO_x OER center removal (biased at 1.23 V_{RHE} in a 0.2 M NaBi electrolyte, under back side illumination). (B) The CVs of the same $BiVO_4$ photoelectrode in the dark (black), and under back side illumination (red).

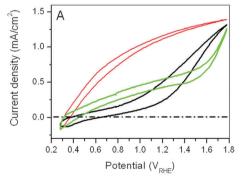
and remains almost constant until it starts to decrease at $\sim\!350$ nm. The decrease is due to the absorption of the photons by the FTO glass. While the trend in the IPCE spectrum is similar to that reported previously, the absolute values of IPCE increased significantly. The IPCE at 450 nm reaches 43% for the passivated BiVO₄ photoelectrode. By assuming that the IPCEs are independent of the light intensity, a photocurrent of 2.30 mA cm $^{-2}$ is predicted for the same BiVO₄ photoelectrode under simulated sunlight by integrating the IPCE spectrum (collected at a low light intensity of $\sim\!10~\mu\mathrm{W}~\mathrm{cm}^{-2}$) over the standard AM1.5 sunlight (light intensity of 100 mW cm $^{-2}$) spectrum.

The CVs of the same BiVO₄ electrode in the dark and under simulated AM1.5 sunlight (back side illumination) were also collected and are shown in Fig. 4B. At 1.23 V_{RHE} , a photocurrent of 1.57 mA cm⁻² (1.51 mA cm⁻²) is obtained. Two factors need to be considered before addressing the difference between the experimental value and the predicted value. Firstly, the BiVO₄ film only absorbs max. ~90% of the photons of wavelengths from 300 nm to 600 nm (Fig. S3, ESI†). Secondly, ~10% less photons for this spectral region than that for the

corresponding AM1.5 spectrum are available to excite BiVO₄ photoelectrodes, due to the loss caused by the mirror in our setup (Fig. S1, ESI \dagger). After taking these two factors into consideration, the photocurrent obtained under the simulated sunlight accounts for ~90% of the predicted value. The ~10% loss of the photocurrent for the BiVO₄ photoelectrode observed experimentally is attributed to the increased carrier recombination in the bulk⁵ as the light intensity increases to 100 mW cm⁻² (for AM1.5 sunlight).

Discussion

Our results can be summarized as follows: (i) the NiO_x loading onto $BiVO_4$ photoelectrodes only slightly increases the photocurrents at low biases, despite the fact that it does improve the OER kinetics in the dark; (ii) a subsequent treatment of NiO_x loaded $BiVO_4$ photoelectrodes in a phosphate electrolyte removes the NiO_x OER catalytic centers and effectively improves the photocurrent for the $BiVO_4$ photoelectrodes (Fig. 5A); and (iii) a small fraction of NiO_x remains bound to the surface after the NiO_x loading/depletion procedure.



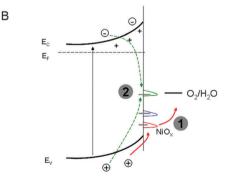


Fig. 5 (A) Comparison between the CVs for the $BiVO_4$ film electrode at various stages of treatment. For clarity, only the photocurrent curves from Fig. 1 and Fig. 2C and D are re-drawn. (Black) As-prepared $BiVO_4$ film, (green) $BiVO_4$ film after electrochemical loading of NiO_x , and (red) $BiVO_4$ film after removal of NiO_x OER centers. (B) The scheme shows the competing pathways for the photogenerated carriers at the $BiVO_4$ - H_2O interface. Pathway 1 (red) represents the water oxidation by the holes and pathway 2 (green) represents the carrier recombination through a recombination center at the surface. Three types of surface states located at different energy levels inside the band gap of $BiVO_4$ are shown, catalytic center for OER (red), passivation center (blue), the recombination center (green). They are proposed to be generated upon NiO_x loading and to represent structurally different coordination environments. For the as-prepared $BiVO_4$ photoelectrodes and the $BiVO_4$ photoelectrodes to undergo the NiO_x loading and NiO_x OER center removal process, VO_x centers on the surface are proposed to be the OER centers.

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To explain the results, the microscopic structure of the electrodeposited NiO_x is considered. The electrodeposited NiO_x is made of disorderly connected Ni-O cubes. At the edges of the NiO_x cluster, borate or phosphate is coordinated. The ability to remove NiOx species, which are loaded in a NaBi electrolyte, by treatment with NaPi is rooted in the higher binding strength of phosphate to NiOx than of borate to NiOx. This is consistent with a recent report that borate favors largersize NiO_x/CoO_x domains due to its weaker binding force than phosphate.24

The nanosized NiO_x domains are anchored to the surface of BiVO₄ via the dangling bonds from BiVO₄. Various coordination environments exist on the surface of BiVO₄ for the NiO_x species, and the amorphous nature of electrodeposited NiO_x²² further allows the existence of various species with different coordination environments and/or valence states. As a result, heterogeneity in the NiOx layer is almost unavoidable. The heterogeneity within the NiO_x layer is furthermore supported by the large widths of the oxidation-reduction peaks. Our present data suggest the presence of at least three different types of NiO_r species on the surface of BiVO₄: the OER catalytic centers, the recombination centers and the passivation centers (Fig. 5B).

Within the picture that three types of NiO_x centers exist on the surface of BiVO₄, the results we observed are explained as follows: the relatively poor performance of the as-prepared BiVO₄ photoelectrodes is mainly due to the native recombination centers (resulting from the dangling bonds) at the surface. The NiO_x loading onto BiVO₄ passivates the native recombination centers from BiVO₄, provides effective catalytic centers for OER and, unfortunately, also introduces new recombination centers. As a net result, the performance of the BiVO₄ electrodes improves only to a small extent and under some conditions can even decrease (data not shown) after NiOx loading. Coordinating with phosphate anions under electrochemical conditions removes the NiO_x species that constitute the OER catalytic centers and the newly introduced recombination centers. On the other hand, the NiOx passivation centers, which are proposed to coordinate to the surface more strongly than the other two species, remain at the BiVO₄ surface. The remaining fraction was confirmed by XPS (Table 1). As a result of the presence of NiO_x passivation centers, the photocurrent for the photoelectrodes is greatly improved after treating NiO_x loaded BiVO₄ film with phosphate anions.

On the surface of BiVO₄ electrodes, there is a kinetic competition between the transfer of holes to OER catalysts (then to H₂O molecules, pathway 1 in Fig. 5B) and the transfer of holes to surface states, which eventually recombine with trapped electrons (pathway 2 in Fig. 5B). The OER at the VO_x sites on the native BiVO₄ surface is a slow process, which is evidenced from the close-to-zero dark current up to 1.8 V_{RHE} presented in Fig. 1. An improved performance of BiVO₄ photoelectrodes can therefore be either due to an increase in the rate of hole transfer to NiO_x (and further to H₂O) or due to a decrease in the rate of hole transfer to the surface states. In a recent paper,8 the suppression of surface recombination for

BiVO₄ photoelectrodes was reported by accelerating the hole transfer to H₂O through loading of the OER catalyst. Our data, which were obtained after removing the NiOx OER catalyst, demonstrate that the blocking of carrier transfer to the surface states leads to significant improvements in the performance of BiVO₄ photoelectrodes.‡

One referee proposes that a small remaining fraction of NiO_x after phosphate treatment may still become catalytically active for water oxidation under illumination. Due to the high driving force of the photoexcited holes at the valence band edge for BiVO₄, the remaining NiO_x centers, which are located at $> 1.9 \, V_{RHE}$, do have the possibility to serve as the OER center in light, though they are not as active as the NiOx center presented in Fig. 2C. However, the absence of dark-current (dark current in Fig. 1 and 2D) shows that the remaining NiO_x centers would be very inefficient OER catalysts, not significantly better than VO_x itself. As the photocurrents for the phosphate treated NiOx/BiVO4 electrode are much higher than those for the as-prepared BiVO₄ photoelectrode (Fig. 5A), it clearly demonstrates that the improvement is not due to the presence of the OER catalysts.

Conclusions

The passivation of the surface states between BiVO₄ and H₂O is achieved by electrochemical treatment of the NiOx coated BiVO₄ electrodes in a phosphate electrolyte. This causes a passivation of surface states on BiVO₄ which in turn effectively improves the performance of photoelectrodes in the low-bias region. The heterogeneity of the NiOx layer on BiVO4 allows phosphate anions to selectively remove the two NiOx species which serve as the OER catalytic centers and the carrier recombination centers, while the NiO_r centers that passivate the surface stays on the surface of BiVO₄. Identifying suitable OER catalysts or introducing a suitable interfacial layer that do not sacrifice the passivating effects reported here promises further improvement of BiVO4 photoelectrodes.

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[‡] Note: During the reviewing process, a paper from Choi et al. was published.²⁵ Although both the BiVO₄ film and the NiO_x loading are different from ours, they also report that minimizing the carrier recombination at the interface is important for improving the performance of BiVO4 photoelectrodes. An inert layer of FeOOH was found by them to passivate the interface thus effectively increasing the photocurrent. The two different methods to treat the BiVO4 surface are now being researched in our lab for the elucidation of microscopic origins of the passivation.

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