Improving BiVO₄ photoanodes for solar water splitting through surface passivation†

Yongqi Liang* and Johannes Messinger

BiVO₄ 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 RHE bias). For further improvements of the BiVO₄ photoelectrodes, a deep understanding of the processes occurring at the BiVO₄–H₂O interface is crucial. Employing an electrochemical loading and removal process of NiOₓ, we show here that carrier recombination at this interface strongly affects the photocurrents. The removal of NiOₓ species by electrochemical treatment in a phosphate electrolyte leads to significantly increased photocurrents for BiVO₄ photoelectrodes. At a bias of 1.23 V RHE, the Incident Photon-to-Current Efficiency (IPCE) at 450 nm reaches 43% for the passivated BiVO₄ electrode under back side illumination. A model incorporating heterogeneity of NiOₓ centers on the BiVO₄ surface (OER catalytic centers, recombination centers, and passivation centers) is proposed to explain this improved performance.

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.⁴ 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.¹⁴

To improve light-driven water splitting at BiVO₄ surfaces, various material properties such as bulk recombination,⁵,⁶ electron transport⁵,⁷ and the electron transfer across the interfaces⁸,⁹ need to be optimized. Attempts have been made for BiVO₄ photoelectrodes to address these factors separately.³,¹⁰ To improve the electron transfer across the oxide–water interface loading of the oxygen-evolution-reaction (OER) catalyst NiOₓ/CoOₓ onto the photoelectrodes has been under intensive research.¹⁰⁻¹² Though the performance improvements after CoOₓ loading are verified in various oxide photoelectrodes, discussions arose recently¹³ whether the improvements are due to the catalytic effects of CoOₓ¹⁴ or rather due to facilitating charge separation across the newly formed junction between the CoOₓ layer and the photoelectrodes.¹⁵ Here we demonstrate the influence of surface recombination on the performance of BiVO₄ photoelectrodes and show that a heterogeneity exists within the amorphous NiOₓ layer loaded onto the BiVO₄ surface. We elucidate this heterogeneity by selectively removing the catalytic NiOₓ species from the BiVO₄ surface for OER without affecting the NiOₓ species that minimizes the surface recombination.

Experimental section

BiVO₄ 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 SnO₂ interfacial layer was deposited in between BiVO₄ and FTO to improve the electron collection at the back contact.⁶ NiOₓ loading onto BiVO₄ was carried out electrochemically according to a well-established method,¹⁶ and the formula of MOₓ (NiOₓ and CoOₓ) is used here to indicate the non-stoichiometric nature of the metal oxide–hydroxide layer deposited by this method. 1 mM Ni(NO₃)₂ 6H₂O (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 ~20 min. The removal of NiOₓ from the BiVO₄ surface was performed in a 0.2 M phosphate buffered aqueous electrolyte (NaPi) at pH = 7.0.
The photoelectrochemical characterization was carried out in 0.2 M NaBr at pH = 10.0. The potential of the BiVO$_4$ working electrode (0.283 cm$^2$) 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 (~85% between 300 nm to 600 nm, ~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 BiVO$_4$ film first for back side illumination, while the photons need to penetrate the electrolyte before they reach the BiVO$_4$ 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 second- or higher-order harmonics of light passing through the monochromator were removed using suitable long-pass filters (Schott).

The light intensity of the photons at wavelengths from 300 nm or higher-order harmonics of light passing through the monochromator were removed using suitable long-pass filters (Schott). The resulting spectra were processed using the Kratos software and 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), respectively. All peak positions of 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 $\times$ 0.7 mm$^2$ and pertained to an analysis depth of about 6 nm.

**Results**

Fig. 1 shows the performance of an as-prepared BiVO$_4$ photoelectrode. Both the CVs for the BiVO$_4$ 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 BiVO$_4$ electrodes.

The dark current for the as-prepared BiVO$_4$ 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 BiVO$_4$ cannot oxidize water efficiently (for a current density of 20 $\mu$A cm$^{-2}$) below an overpotential of 0.57 V. From the photocurrent curve of the as-prepared BiVO$_4$ electrode (Fig. 1), a current density of 0.54 mA cm$^{-2}$ (0.27 mA cm$^{-2}$) at 1.23 V$_{RHE}$ is obtained for the forward (reverse) scan. The onset potential is determined to be 0.40 V$_{RHE}$ (0.65 V$_{RHE}$).

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 NiO$_x$ onto BiVO$_4$. During the loading process (Fig. 2A), the peak of NiO$_x$ oxidation–reduction 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 NiO$_x$ loading, the potential bias needed for water oxidation decreased from 1.8 V$_{RHE}$ to <1.6 V$_{RHE}$. The increased dark current after NiO$_x$-loading onto BiVO$_4$ agrees well with previous reports\(^{16}\) which show that NiO$_x$ can effectively catalyze water oxidation. After treating the NiO$_x$ loaded BiVO$_4$ in 0.2 M NaP$^+$ 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 NiO$_x$ using phosphate before the electrochemical removal of NiO$_x$ could occur. The oxidation–reduction peak at 0.79 V$_{RHE}$/0.72 V$_{RHE}$ becomes obvious after the electrochemical removal of NiO$_x$ (Fig. 2B). This redox peak is tentatively assigned to the oxidation–reduction of tetrahedral coordinated VO$^2+$/VO$^{2+}$ species on the surface of BiVO$_4$, which is ~0.20 V less anodic than the octahedrally coordinated VO$_2^-$/VO$^{2+}$ redox couple in aqueous solution.\(^{18}\) The NiO$_x$ species loaded onto BiVO$_4$ are therefore suggested to cover some VO sites on the BiVO$_4$ surface.
and the removal of NiOx OER centers using phosphate exposes these VO sites again. These VOx species are proposed to be the OER centers for both the as-prepared BiVO4 electrodes and the BiVO4 electrodes that undergo the NiOx loading and phosphate treatment processes.

The XPS spectra were recorded to verify the loading of the NiOx centers onto the surface of the BiVO4 photoelectrode and their subsequent removal in phosphate buffer. As shown in the literature, 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 BiVO4 surface after NiOx 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 coordinated NiOx-OER centers on the surface of BiVO4, 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 BiVO4 samples after phosphate treatment, the XPS data do clearly demonstrate the partial removal of NiOx from the surface of BiVO4.

![Fig. 2](A) CVs for NiOx loading onto BiVO4 electrodes. A current density of ~0.1 mA cm⁻² for the NiOx oxidation peak (1.61 V_RHE) is typically obtained after 10 cyclic scans. (B) CVs for removal of NiOx in phosphate buffer (pH = 7.0). The cyclic scan (from 0.5 V_RHE to 1.8 V_RHE) starts in the anodic direction. The current at > 1.4 V_RHE drops close to zero during scanning, which indicates the removal of NiOx OER catalytic centers. Typically 4 cycles were used to ensure a complete removal of NiOx, OER catalytic centers. (C) CVs of a BiVO4 film electrode after electrochemical loading of NiOx, and (D) CVs for the BiVO4 film after removal of NiOx 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 NiOx OER centers on BiVO4.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The chemical composition on the surface of a series of BiVO4 photoelectrodes at different stages for treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-prepared BiVO4</td>
</tr>
<tr>
<td>Ni : Bi ratio</td>
<td>0.00 : 1</td>
</tr>
<tr>
<td>V : Bi ratio</td>
<td>0.94 : 1</td>
</tr>
</tbody>
</table>
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$_2$-loaded BiVO$_4$, 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_RHE (Fig. 2D). This suggests that any remaining Ni species is much less active for OER than the NiO$_2$ 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 BiVO$_4$ 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 BiVO$_4$ films and the NiO$_2$-removed BiVO$_4$ films, the hysteresis in the dark CVs is mostly caused by charging and discharging of the double-layer capacitance. For the NiO$_2$-loaded BiVO$_4$ films, the hysteresis in the dark CVs is mainly due to the oxidation–reduction of NiO$_2$ species. Since the O$_2$ molecules produced cannot desorb from the BiVO$_4$ surface fast enough, they will block the active OER sites on the BiVO$_4$ surface and cause further hysteresis for the BiVO$_4$ electrodes under high potential bias or sunlight illumination.

The effects of the NiO$_2$ loading-and-removal process on the surface of BiVO$_4$ are also observed during the steady state characterization. The stabilized photocurrent at 1.23 V_RHE increased slightly from 0.34 mA cm$^{-2}$ to 0.49 mA cm$^{-2}$ after NiO$_2$ loading, and then increased to 1.08 mA cm$^{-2}$ after the removal of NiO$_2$ (Fig. 3A). These values agree well with the photocurrent obtained 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$_2$ loading-and-removal procedure persists at least for a time period of ~1 h. The photocurrent for the passivated BiVO$_4$ photoelectrode slowly decreased from 1.08 mA cm$^{-2}$ to 0.91 mA cm$^{-2}$ during the first 2200 seconds. The incubation of the BiVO$_4$ 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 BiVO$_4$ electrode and the electrolyte. This proves that the effects of NiO$_2$ loading/removal on the photocurrent are stable.

In contrast, the photocurrent does not increase over long-time characterization of the as-prepared BiVO$_4$ 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$_2$ is required. It is also noted that the effects of the NiO$_2$ loading-and-removal process on the surface of BiVO$_4$ are repeatable. A second loading of NiO$_2$ onto the passivated BiVO$_4$ will change the CVs back into those shown in Fig. 2C and a following electrochemical removal of NiO$_2$ OER centers from BiVO$_4$ in a NaPi electrolyte will recover the photocurrent as shown in Fig. 2D.

For employing BiVO$_4$ for solar fuel production in, for example, artificial leaf devices the high energy photons need to be absorbed by the water exposed BiVO$_4$ 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 BiVO$_4$ photoelectrodes. On the other hand, BiVO$_4$ photoelectrodes are known to perform better under back side illumination than under front side illumination due to the sluggish electron transport inside BiVO$_4$. To allow direct comparisons with the performance of BiVO$_4$ reported earlier, the IPCE spectrum under back-side illumination for the BiVO$_4$ electrode (under the bias of 1.23 V_RHE) was collected (Fig. 4A) after the NiO$_2$-OER centers were removed. The IPCE steadily increases from zero at 510 nm to a plateau at ~440 nm,

![Fig. 3](image-url)
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 BiVO\(_4\) 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 BiVO\(_4\) photoelectrode under simulated sunlight by integrating the IPCE spectrum (collected at a low light intensity of \( \sim 10 \) \( \mu \)W cm\(^{-2}\)) over the standard AM1.5 sunlight (light intensity of 100 mW cm\(^{-2}\)) spectrum.

The CVs of the same BiVO\(_4\) 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\(_{\text{RHE}}\), 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 BiVO\(_4\) film only absorbs max. \( \sim 90\% \) of the photons of wavelengths from 300 nm to 600 nm (Fig. S3, ESI†). Secondly, \( \sim 10\% \) less photons for this spectral region than that for the corresponding AM1.5 spectrum are available to excite BiVO\(_4\) photoelectrodes, due to the loss caused by the mirror in our setup (Fig. S1, ESI†). After taking these two factors into consideration, the photocurrent obtained under the simulated sunlight accounts for \( \sim 90\% \) of the predicted value. The \( \sim 10\% \) loss of the photocurrent for the BiVO\(_4\) photoelectrode observed experimentally is attributed to the increased carrier recombination in the bulk 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.
To explain the results, the microscopic structure of the electrodeposited NiO is considered. The electrodeposited NiO is made of disorderly connected Ni–O cubes. At the edges of the NiO cluster, borate or phosphate is coordinated. The ability to remove NiO species, which are loaded in a NaB/CoO electrolyte, by treatment with NaPi is rooted in the higher binding strength of phosphate to NiO than of borate to NiO. This is consistent with a recent report that borate favors larger-size NiO/CoO domains due to its weaker binding force than phosphate.

The nanosized NiO 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 species, and the amorphous nature of electrodeposited NiO further allows the existence of various species with different coordination environments and/or valence states. As a result, heterogeneity in the NiO layer is almost unavoidable. The heterogeneity within the NiO 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 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 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 NiOx loading onto BiVO4 passivates the native recombination centers from BiVO4, it 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 species that constitute the OER catalytic centers and the newly introduced recombination centers. On the other hand, the NiO 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 passivation centers, the photocurrent for the photoelectrodes is greatly improved after treating NiOx coated 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 VO2 sites on the native BiVO4 surface is a slow process, which is evidenced from the close-to-zero dark current up to 1.8 VBE 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 (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 NiOx 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 NiOx centers, which are located at >1.9 VBE, do have the possibility to serve as the OER center in light, though they are not as active as the NiO center presented in Fig. 2C. However, the absence of dark-current (dark current in Fig. 1 and 2D) shows that the remaining NiOx centers would be very inefficient OER catalysts, not significantly better than VO2 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 NiO layer on BiVO4 allows phosphate anions to selectively remove the two NiO species which serve as the OER catalytic centers and the carrier recombination centers, while the NiO 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.

Acknowledgements

The authors were supported by the Artificial Leaf Project Umeå (K&A Wallenberg foundation), the Solar Fuels Strong Research Environment Umeå (Umeå University), Vetenskapsrådet and the Swedish Energy Agency (Energimyndigheten). We thank Andrey Shchukarev for the XPS characterization and Hans-Martin Berends for stimulating discussions and comments to the manuscript.

‡ Note: During the reviewing process, a paper from Choi et al. was published. Although both the BiVO4 film and the NiOx 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.
References