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To alleviate these limitations, numerous approaches have been developed to improve photocurrent densities. Water oxidation kinetics, mostly resulting in disappointing transport properties (hole diffusion length of ~ 70 nm), and sluggish photoelectrode still suffers from excessive electron–hole recombination, which can allow absorption of 11% visible light spectrum.

Bismuth vanadate (BiVO₄) is one of the most fascinating building blocks for the design and assembly of highly efficient artificial photosynthesis devices for solar water splitting. Our recent report has shown that a borate treated BiVO₄ (B-BiVO₄) results in an improved water oxidation performance. In this study, further improvement of both photoelectrochemical (PEC) activity and stability of B-BiVO₄ were successfully achieved by introducing NiFeV LDHs as an oxygen evolution catalyst and interfacial hole transporter. Benefiting from the synergistic effect of co-catalyst and borate pretreatment, the as-prepared NiFeV/B-BiVO₄ exhibited a high photocurrent density of 4.6 mA cm⁻² at 1.23 V_RHE and an outstanding onset potential of ~ 0.2 V_RHE with good long-term stability. More importantly, NiFeV was found to play a pivotal role in the critically efficient suppression of charge combination on BiVO₄ surface and acceleration of charge transfer rather than a mere electrocatalyst for water oxidation.

1. Introduction

Photoelectrochemical (PEC) water splitting is a promising way to produce hydrogen as a clean and renewable energy carrier using light-absorbing semiconductors. Since the photocatalytic water oxidation activity of monoclinic bismuth vanadate (BiVO₄) was discovered by Kudo et al. in 1998, BiVO₄ has drawn a tremendous level of attention in the domain of PEC water splitting by virtue of favorable band positions and a suitable bandgap of 2.4–2.5 eV, which can allow absorption of 11% visible light spectrum. Theoretically, the maximum photocurrent density and the solar-to-hydrogen conversion efficiency can reach as high as 7.5 mA cm⁻² and 9% under AM 1.5G illumination, respectively.

Unfortunately, a pure BiVO₄ photoelectrode still suffers from excessive electron–hole recombination (carrier mobility of ~ 4x10⁻³ cm² V⁻¹ s⁻¹), poor charge transport properties (hole diffusion length of ~ 70 nm), and sluggish water oxidation kinetics, mostly resulting in disappointing photocurrent densities.

To alleviate these limitations, numerous approaches have been proposed that usually combine effective synthesis methods with multiple modification strategies, including crystal facet engineering, construction of heterojunctions, substitutional doping, oxygen evolution catalyst (OEC) loading, post-synthetic treatments, etc. For example, a landmark work reported by Choi and co-workers displayed a nanoporous BiVO₄ film photoanode (mean particle size ~ 76 nm) via a two-step method of electrodeposition of BiOI and ensuing thermal conversion of BiOI to BiVO₄ by introducing a proper vanadium source. The resulting BiVO₄ exhibited a high charge separation efficiency in the bulk (η bulk) up to 90% without routine doping or heterojunction; and after assembling a NiOOH/FeOOH OEC, a remarkable photocurrent density of 4.5 mA cm⁻² at 1.23 V versus the reversible hydrogen electrode (RHE) was obtained under AM 1.5G illumination. Inspired by the natural photosystem II (PSII), Li and co-workers designed and fabricated a composite photoanode (mean particle size ~ 76 nm) via a two-step method of electrodeposition of BiOI and ensuing thermal conversion of BiOI to BiVO₄ by introducing a proper vanadium source. The resulting BiVO₄ exhibited a high charge separation efficiency in the bulk (η bulk) up to 90% without routine doping or heterojunction; and after assembling a NiOOH/FeOOH OEC, a remarkable photocurrent density of 4.5 mA cm⁻² at 1.23 V versus the reversible hydrogen electrode (RHE) was obtained under AM 1.5G illumination. Inspired by the natural photosystem II (PSII), Li and co-workers successfully demonstrated a CoPO₄/pGO/LDH/BiVO₄ composite photoanode, where BiVO₄, NiFeO₂ layered double hydroxide (LDH), partially oxidized graphene (pGO) and cobalt cubane molecular catalyst served as a light harvester, a hole storage layer, a charge transfer layer and an OEC, respectively. The composite photoanode possessed a remarkable photocurrent density of 4.45 mA cm⁻² with an ultralow onset potential of 0.17 V and superior stability. By combining p-n heterojunction engineering, work function adjustment and co-catalyst loading, Yang and co-workers successfully demonstrated a NiFeO₂/B-Cu₃N₅/Mo-BiVO₄ photoanode, culminating in achieving a 5.93 mA cm⁻² at 1.23 V_RHE (92% IPCE) with an astonishing applied bias photon-to-current efficiency (ABPE) of 2.67% at 0.54 V_RHE. In a very recent review, Lee and co-workers clearly elucidated the efficacies of established modification techniques on a BiVO₄ photoanode by applying a post-synthetic N₂ treatment, Mo doping, an electron transfer layer of SnO₂, and deposition of NiFeO₂ electrocatalyst. The bespoke NiFeO₂/Ni, 1% Mo:BiVO₄/SnO₂ photoanode also exhibited an enhanced efficiency.
outstanding PEC performance with 5.8 mA cm\(^{-2}\) and a maximum ABPE of 2.7%. It should be pointed out that loading OECs contributed most to the dramatic enhancement compared to other modifications,\(^3\) aiming at promoting the surface charge transfer at the semiconductor/electrolyte interface (\(\eta_{\text{surface}}\)) as well as long-term photostability.

On the one hand, these recently flourished modification strategies have elevated BiVO\(_4\) to an unprecedented position as the most up-and-coming photoanode material. On the other hand, each of them developed thus far is often found to have limited efficacies in targeting all-round improvement toward all aspects of charge carrier kinetics, catalytic kinetics of water oxidation, and even light absorption, in terms of PEC performance and fundamental understanding of the material and working principles.\(^3\)\(^,\)\(^3\)\(^1\)\(^,\)\(^3\)\(^4\) The elaborately modified BiVO\(_4\)-based PEC devices are therefore in growing appeals toward practical applications.\(^2\)

In our previous work, a facile borate modification of BiVO\(_4\) photoanode (B-BiVO\(_4\)) was reported, delivering an impressive enhancement in PEC performance with a photocurrent density of \(\sim 3.5\) mA cm\(^{-2}\) at 1.23 V \(\text{RHE}\) without any doping or OEC decoration.\(^3\)\(^5\) Analogous phenomenon engendered by borate species was also presented in several reports.\(^3\)\(^6\)\^-\(^3\)\(^9\)\(^,\)\(^3\)\(^1\)\(^0\)\(^,\)\(^3\)\(^1\)\(^1\) However, the B-BiVO\(_4\) photoanode gradually lost its superior PEC performance within 1 h due to the photocorrosion of adsorbed borate groups leading by surface charge accumulation. In this study, we solved this problem via integration of a NiFe-based LDH, an excellent electrocatalyst for oxygen evolution accumulation. In this study, we solved this problem via integration of NiFeV co-modifications, the resulting NiFeV/B-BiVO\(_4\) for photoelectrodes.

2. Experimental section

2.1 Materials

Fluorine-doped tin oxide (FTO) coated glass substrates were purchased from Pilkington (\(\sim 8\) \(\Omega\) \(\text{cm}^{-2}\)) and were successively cleaned using Mill-Q water, ethanol and aceton. Bismuth nitrate pentahydrate (\(\text{Bi(NO}_3\)_3·5\(\text{H}_2\text{O}\), 98\%\)), vanadyl acetylacetonate (\(\text{VO(acac)}_2\), 98\%), nitric acid solution (\(\text{HNO}_3\), 70\%), boric acid (\(\text{H}_3\text{BO}_3\), 99.5\%), sodium hydroxide (\(\text{NaOH}\), 98\%), potassium iodide (\(\text{KI}\), 99\%), vanadium chloride(V\(\text{Cl}_3\)), 98\%), sodium carbonate (\(\text{Na}_2\text{CO}_3\), 99\%), sodium sulfate (\(\text{Na}_2\text{SO}_4\), 98\%), sodium hydroxide (\(\text{NaOH}\), 98\%), potassium hexahydrate (\(\text{K}_2\text{BO}_2\cdot6\text{H}_2\text{O}\), 85\%), Nafion\(^\text{TM}\) 117 containing solution (5\%), borax anhydrous (\(\text{Na}_2\text{B}_2\text{O}_4\), 98\%), and deuterium oxide (\(\text{D}_2\text{O}\), 99.9\%) were purchased from Sigma-Aldrich and used as received. All organic solvents including 2-propanol ethanol, absolute ethanol, and dimethyl sulfoxide (DMSO) were analytical reagent grade and used without further purification. Ultra-pure water (18.2 \(\text{M} \Omega \cdot \text{cm}^{-1}\)) supplied by a Milli-Q system (Merck Millipore) was used in all experiments.

2.2 Fabrication of BiVO\(_4\) and B-BiVO\(_4\)

The detailed fabrication processes of BiVO\(_4\) and B-BiVO\(_4\) photoanodes were essentially repeated according to our previous report and an established procedure from Choi’s group.\(^6\)\(^,\)\(^3\)\(^5\) In brief, 0.04 M \(\text{Bi(NO}_3\)_3\) and 0.4 M \(\text{KI}\) were successively added into 50 mL \(\text{HNO}_3\) aqueous solution (pH 1.7) with mild stirring for 15 min. Afterwards, a 20 mL of \(\text{EtOH}\) containing 0.23 M p-benzoquinone was mixed to the above solution with constant stirring. The electrodeposition of BiOI precursor was carried out using a standard three-electrode cell where an FTO, a saturated \(\text{Ag/AgCl}\) electrode, and a platinum wire electrode (1 x 1 cm\(^2\)) were used as the working electrode (WE), the reference electrode (RE), and the counter electrode (CE), respectively. The electrodeposition of BiOI precursor was carried out potentiostatically at -0.1 V \(\text{V}_{\text{BiO}}\) for 3 min at room temperature. The BiOI film was converted to B-BiVO\(_4\) by a thermal treatment in air at 450 °C for 2 h (ramping rate 2 °C min\(^{-1}\)) after covering the BiOI film with 80 \(\mu\)L of a DMSO solution containing 0.2 M \(\text{VO(acac)}_2\). After annealing, the electrodes were soaked in a 1 M \(\text{NaOH}\) solution for 30 min on a lab shaker to remove excess \(\text{V}_2\text{O}_5\) from the surface of B-BiVO\(_4\). The final bare BiVO\(_4\) electrodes were washed thoroughly with Milli-Q water and gently dried with air stream. A 1.0 M potassium borate (K\(\text{Bi}\)) buffer solution (pH = 9.3 ± 0.1, 1.0 M \(\text{H}_2\text{BO}_3\) adjusted by KOH) was used for both preparation of B-BiVO\(_4\) and the ensuing photoelectrochemical measurements.

For B-BiVO\(_4\) preparation, a bare BiVO\(_4\) photoanode was immersed into above borate buffer in a capped brown vial and was then heated at 100 °C for 30 min in an oil bath to shorten the treatment time. After cooling, the resulting B-BiVO\(_4\) was taken out from the solution, rinsed with Milli-Q water and dried with a gentle air stream.

2.3 Synthesis of layered double hydroxides (LDHs) (NiFeV, NiV and NiFe)

The LDHs nanoparticles were synthesized according to a report from our group via a one-step hydrothermal method.\(^4\) The molar ratio of each elements in NiFeV (3:0:2:1), NiV (3:1), and NiFe (3:1) were tuned by mixing the corresponding NiCl\(_2\), FeCl\(_3\) and VCl\(_3\) in 80 mL \(\text{H}_2\text{O}\), while keeping the total amount of metal ions to 3.2 mmol. The suspension of Ni LDH in a mixed solvent of \(\text{H}_2\text{O}\), 2-propanol and naphion (4:1:0.04) with a concentration of 0.5 mg mL\(^{-1}\) was prepared for further co-catalyst loading onto B-BiVO\(_4\).

2.4 Fabrication of LDH/BiVO\(_4\) and LDH/B-BiVO\(_4\)

Prior to co-catalyst loading, the above LDHs nanoparticles suspension (0.5 mg mL\(^{-1}\)) was ultrasonicated for 2 h. A 5 \(\mu\)L of the resulting uniform suspension was then directly drop-casted onto BiVO\(_4\) or B-BiVO\(_4\) electrodes with an active area of 0.5 x 0.5 cm\(^2\) and was allowed to dry by evaporation at ambient conditions. In addition
2.5 Material characterization

The surface morphology and composition of LDH nanoparticles and the ensuing BiVO₄-based photoelectrodes were by field emission scanning electron microscope (FE-SEM, Hitachi, Regulus 8230) equipped with energy-dispersive X-ray electron spectroscope (EDX) detector (Oxford Ultim EXTREME). Transmission electron microscopy (TEM, JEOL JEM2100F) and high-resolution TEM (HRTEM) images were obtained with an acceleration voltage of 200 kV. The crystal structures of samples were characterized by powder X-ray diffraction (PXRD, D8 Advance Bruker with Cu Ka (λ=1.5406 Å) radiation. The surface chemical states and composition of the films were characterized by X-ray photoelectron spectroscope (XPS) (ESCALAB Xi+, Thermo Fisher, UK) with a monochromatized Al Kα radiation source (1486.6 eV). All binding energies were calibrated for specimen charging by referencing C 1s peak to 284.8 eV. Optical absorption of BiVO₄ photoanodes were tested by UV–vis diffuse reflectance spectrophotometer (UV3600, Shimadzu, Japan) spectrophotometer in the range of 300-800 nm.

2.6 Photoelectrochemical measurement

All photoelectrochemical tests were performed using a CHI 660E potentiostat at room temperature in the same three-electrode configuration except using the BiVO₄ photoanode as the WE. The illumination source was a NEWPORT LCS-100 solar simulator (type 94011A-ES, a 100 W Xenon arc lamp with an AM 1.5G filter). A 1.0 M potassium borate buffer solution (pH 9.3) worked as the electrolyte for ensuing water oxidation. For sulfite oxidation, 0.2 M Na₂SO₃ was added into the electrolyte for ensuing water oxidation. The recorded potential versus Ag/AgCl (E₁/₂) was converted against reversible hydrogen electrode (RHE) according to the Nernst equation:

\[ E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times \text{pH} \]  

The applied bias photon-current efficiency (ABPE) was calculated from LSV curves of BiVO₄ photoanodes:

\[ ABPE (\%) = \frac{(J_{sulfite} - J_{water}) \times (1.23 - V_{sulfite})}{J_{sulfite}} \times 100\% \]  

The light harvesting efficiency (LHE) of the BiVO₄ photoanode was calculated from UV-Vis diffuse reflectance spectra:

\[ LHE (\%) = (1 - 10^{-4}) \times 100\% \]  

where A is the light absorbance measured by UV-vis spectroscopy.

The photocurrent density arising from PEC performance (J_{PEC}) can be described as follows:

\[ J_{PEC} = J_{abs} \times \eta_{bulk} \times \eta_{surface} \]  

where \( J_{abs} \) is the photocurrent density at 100% internal quantum efficiency, which is obtained by integrating the distribution of solar power density \( f(\lambda) \) with light absorption LHE of the photoanode.\(^{48,49} \) \( e \) is the elementary charge (1.602 × 10⁻¹⁹ C).

The \( n_{bulk} \) is the yield of the photogenerated holes from the bulk that reach the electrode/electrolyte interface; and \( \eta_{surface} \) is the charge injection efficiency of those surface-reaching holes into the electrolyte for ensuing water oxidation.

\[ \eta_{bulk}(\%) = \frac{J_{water}}{J_{abs}} \times 100\% \]  

\[ \eta_{bulk}(\%) = \frac{J_{water}}{J_{water} + J_{imp}} \times 100\% \]  

where \( J_{water} \) and \( J_{imp} \) are the photocurrent density for PEC water oxidation and sulfite oxidation, respectively.

The H/D KIE values can be defined as:

\[ K^{1H/2D} = \frac{J_{2D}}{J_{1H}} \times 100\% \]  

where \( k_{H} \) and \( k_{D} \) are the rate constants, and \( J_{1H} \) and \( J_{2D} \) are the photocurrent density measured in a 0.1 M Na₂B₄O₇ H₂O and D₂O solutions, respectively. The pD value was calculated by adding 0.4 to the pH of the sample.

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the value of pH meter reading. The overpotentials ($\eta$) in $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ solutions were corrected according to the previous literature.$^{20}$

3. Results and discussion

The bare BiVO$_4$ film photoanode was fabricated according to a procedure previously employed,$^6$ while the NiFe LDH nanoparticles were synthesized by a typical one-pot hydrothermal method.$^{46}$ Then the preparation of NiFeV/BiVO$_4$ was a simple two-step process. The borate pretreatment was performed according to our previous report.$^{35}$ Subsequently, a diluted suspension of NiFeV LDH was drop-casted onto the surface of B-BiVO$_4$ electrode, instead of the in-situ hydrothermal/solvothermal growth$^{10,50-52}$ and electrodeposition,$^{53-55}$ the in-situ effect was not observed due to the very low loading amount on the surface of B-BiVO$_4$ particles. However, BiVO$_4$ is sensitive to the pH of electroplating solution and the applied potential during electrolysis,$^{56-58}$ and the relatively high temperature of the hydrothermal process might cause detrimental surface etching on BiVO$_4$. Considering the instability of borate treated BiVO$_4$,$^{35}$ it is clearly challenging to maintain the pre-enhanced PEC activity of B-BiVO$_4$ when loading OECs. In this case, drop-casting OEC co-catalysts was expected to keep the B-BiVO$_4$ electrode surface intact to the maximum extent. Prior to the physical characterization and PEC testing, the mass loading of NiFeV LDH was optimized to 10 $\mu$g cm$^{-2}$ for the subsequent experiments.

The UV/Vis absorption spectrum of B-BiVO$_4$ was almost unchanged after NiFeV LDH loading, indicating the band gap of B-BiVO$_4$ and NiFeV/B-BiVO$_4$ were the same (2.54 eV). The X-ray diffraction (XRD) patterns of the NiFeV LDH, B-BiVO$_4$ and NiFeV/B-BiVO$_4$ electrodes were shown in Fig. S3†. Apart from the FTO signals, all XRD peaks can be attributed to monoclinic BiVO$_4$. After drop-casting of NiFeV LDH on the B-BiVO$_4$ electrode, a discernable reflection peak at $\Theta = 11.4^\circ$ can be observed in the pattern of the NiFeV/B-BiVO$_4$ compared to that of bare BiVO$_4$, which could be attributed to the (003) lattice plane of NiFeV.$^{40-42}$ However, extra main diffraction peaks of NiFeV LDH were too weak to identify due to the very low loading amount on the surface of B-BiVO$_4$.$^{50,61}$

The morphology of the NiFeV LDHs were first studied by transmission electron microscopy (TEM). NiFeV LDHs display rippled nanosheets with the size of several hundred nanometers and the thickness of ~3–5 nm, which is in accordance with previous reports in spite of small differences in the ratio of each metal element.$^{50-52}$ The aggregates with laminations were observed by field emission scanning electron microscopy (FE-SEM), and the atomic ratios of Ni, Fe, and V were determined by EDX analysis (Fig. S4†), showing that the Ni:Fe:V molar ratio (2.83:0.22:1) was close to the ratio of the starting materials (3:0.2:1). The SEM images in Fig. 1b illustrated that NiFeV nanosheets distributed over the surface of BiVO$_4$ with aggregate phases (occurred during the drying stage of drop-casting), which was also confirmed by the corresponding elemental mappings. Drop-casting of NiFeV LDH on BiVO$_4$ did not alter the quintessential worm-like morphology of the latter, which was characterized by a dendritic diameter of 300–400 nm and an average thickness around ~650 nm (Fig. S5†).

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X-ray photoelectron spectroscopy (XPS) measurement was carried out to examine the elemental composition of NiFeV/B-BiVO$_4$ surface by taking the C 1s peak at 284.8 eV as a standard reference (Fig. 2a). As expected, the noticeable Ni $2p$ and Fe $2p$, V $2p$, Bi $4f$, and O $1s$ signals can be identified in the V 2p spectrum of Fig. 2d. As can be seen from Fig. 2e, the binding energies of 158.9 eV and 164.2 eV can be ascribed to the Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively. The O $1s$ core-level spectra (Fig. 2f), two peaks can be clearly identified.$^{47,62}$ In particular, the peak at 529.8 eV belongs to lattice oxygen, clearly originating from BiVO$_4$. While the O $1s$ peak at 531.7 eV is associated with surface hydroxy species, in...
Fig. 3 (a) Linear sweeping voltammetry (LSV) curves of BiVO$_4$, B-BiVO$_4$, NiFeV/BiVO$_4$, and NiFeV/B-BiVO$_4$ photoanodes under AM 1.5G illumination in a 1.0 M potassium borate buffer at pH 9.3 (scan rate: 10 mV s$^{-1}$). (b) ABPE curves of photoanodes calculated from LSV curves. (c) IPCEs of photoanodes at 1.23 $V_{RHE}$. (d) Transient photocurrents curves under chopped illumination at a constant bias of 0.6 $V_{RHE}$. (e) Charge separation efficiencies ($\eta_{\text{separation}}$) in bulk of photoanodes estimated by comparing the photocurrent density of sulfite oxidation and the maximum theoretical photocurrent density from light absorption (according to AM 1.5G solar spectrum and the UV–vis absorbance). (f) Surface charge transfer efficiency ($\eta_{\text{surface}}$) of photoanodes obtained from LSV curves of water oxidation and sulfite oxidation. (g) EIS curves of BiVO$_4$, NiFeV/BiVO$_4$, and NiFeV/B-BiVO$_4$ photoanodes under AM 1.5G illumination in a 1.0 M potassium borate buffer at pH 9.3. (h) Open-circuit voltages ($V_{oc}$) of photoanodes in dark (solid) and under AM 1.5G simulated illumination (hollow).

In our case, it was closely related to both chemisorption of [B(OH)$_2$]$_n$ upon borate treatment$^{25, 61}$ and NiFeV modification (Fig. S6†). Although no obvious B 1s signals were detected,$^{26}$ overall, the XPS spectra indicated that NiFeV LDHs were successfully loaded onto the surface of B-BiVO$_4$ photoanode.

The PEC water oxidation activities of NiFeV/B-BiVO$_4$ and other relevant photoanodes were measured in a 1.0 M potassium borate buffer solution at pH 9.3 under AM 1.5 G simulated illumination. As shown in Fig. 3a, the photocurrent density of the bare BiVO$_4$ at 1.23 $V_{RHE}$ was about 1.6 mA cm$^{-2}$. NiFeV/BiVO$_4$ and NiFeV/B-BiVO$_4$ showed much earlier photocurrent onsets (defined at 0.1 mA cm$^{-2}$ photocurrent density) of 0.22 $V_{RHE}$ and 0.21 $V_{RHE}$, respectively) and generated higher photocurrent in the low bias region ($E < 0.6 V_{RHE}$), which is also corroborated by the dark current density results (Fig. S7†). In the high bias region ($E > 0.9 V_{RHE}$), the PEC performance of B-BiVO$_4$ was parallel to NiFeV/BiVO$_4$. After the borate and NiFeV LDH co-modification, the photocurrent density of the NiFeV/B-BiVO$_4$ reached 4.6 mA cm$^{-2}$, significantly outperforming either of the singly modified photoanodes (~3.5 mA cm$^{-2}$). Such a synergistic effect is also presented in the applied bias photon-to-current efficiency (ABPE) and incident photon-to-current conversion efficiency (IPCE) measurements (Fig. 3b and 3c). The maximum ABPE of NiFeV/B-BiVO$_4$ was 1.85% at 0.62 $V_{RHE}$, which is 8 times as high as that of unmodified BiVO$_4$ (0.23% at 0.91 $V_{RHE}$); and the IPCE of the NiFeV/B-BiVO$_4$ reached a maximum of ~80% at 1.23 $V_{RHE}$ at the wavelength ~380 nm. It is important to note here that photocurrent increase in low bias region for NiFeV/B-BiVO$_4$ goes beyond simple accumulation of effects from NiFeV LDH and borate species, displaying a truly synergistic behavior (Fig. 3a) and indicating the positive cooperation between two co-modifications. Compared with previously reported BiVO$_4$ photoanodes modified with LDH co-catalyst, the PEC performance of NiFeV/B-BiVO$_4$ is ranked among the best (Table S1†). For example, Wang and co-workers deposited a ternary NiFeY LDH on BiVO$_4$ and the resulting photoanode exhibits remarkable PEC performance (~5.2 mA cm$^{-2}$ at 1.23 $V_{RHE}$) with an outstanding stability at 0.8 $V_{RHE}$ over 25 h, while its onset potential (0.31 $V_{RHE}$) remained reasonably high. The CoPO$_4$/gGO/LDH/BiVO$_4$ composite photoanode, reported by Li and co-workers, had an unprecedentedly low onset potential (0.17 V) and a high photocurrent (4.45 mA cm$^{-2}$); however, it required laborious
multistep procedures to obtain an integrated photoanode using four components.

Under chopped light illumination (Fig. 3d), the unmodified BiVO$_4$ showed large photocurrent transient spikes for each light on-off cycle. On the contrary, these transient spikes were eliminated to a large extent in the NiFeV/B-BiVO$_4$ photoanode, implying the severe surface recombination on BiVO$_4$ was significantly decreased after borate and NiFeV co-modification. Theoretically, the measured photocurrent density ($J_{\text{PEC}}$) is governed by the relation: $J_{\text{PEC}}=s_{\text{abs}} \times \eta_{\text{bulk}} \times \eta_{\text{surface}}$, where $s_{\text{abs}}$ is the photon absorption rate expressed as current density at 100% internal quantum efficiency; $\eta_{\text{bulk}}$ refers to the yield of the photogenerated holes that reach the electrode/electrolyte interface; and $\eta_{\text{surface}}$ describes the charge injection efficiency of surface-reaching holes into the electrolyte for water oxidation. To gain an in-depth understanding of synergistic effects on carrier kinetics, $\eta_{\text{bulk}}$ and $\eta_{\text{surface}}$ of BiVO$_4$ photoanodes were investigated carefully. As can be seen from Fig. 3e, the $\eta_{\text{bulk}}$ of all photoanodes were over 80% at 1.23 $V_{\text{RHE}}$, benefiting from the well-established synthesis method of BiVO$_4$ by Choi and co-workers. There was almost no difference in $\eta_{\text{bulk}}$ between BiVO$_4$ and B-BiVO$_4$, whereas the $\eta_{\text{bulk}}$ of NiFeV was somewhat improved after loading NiFeV LDHs. That small increment of $\eta_{\text{bulk}}$, however, was not expected to contribute much to the remarkable activity of the NiFeV/B-BiVO$_4$ photoanode. Additionally, the Mott-Schottky (MS) plots (Fig. S8†) showed that, at each frequency, the slopes of both B-BiVO$_4$ and NiFeV/BiVO$_4$ were marginally lower than that of bare BiVO$_4$, suggesting the donor density of BiVO$_4$ just slightly increased. Overall, these results fully indicated that both borate and NiFeV modifications had little effect on bulk properties within the BiVO$_4$ electrode. By comparing the photocurrent densities of photoanodes with and without Na$_2$SO$_3$ as a hole scavenger (Fig. 3f and Fig. S9†), a superior $\eta_{\text{surface}}$ of NiFeV/B-BiVO$_4$ was near 90% at 1.23 $V_{\text{RHE}}$, which was 3 times higher than bare BiVO$_4$ (31%). What is especially noteworthy is that the $\eta_{\text{surface}}$ of NiFeV/BiVO$_4$ was much better than that of B-BiVO$_4$ at a lower applied bias; when the bias was further increased to $\geq 1.0$ $V_{\text{RHE}}$, the $\eta_{\text{surface}}$ of B-BiVO$_4$ became comparable to that of NiFeV/BiVO$_4$. The trends of the $\eta_{\text{surface}}$ were consistent with their PEC performances (Fig. 3a) and evinced that both of borate and LDH modifications were efficient in accelerating the surface charge carrier kinetics for OER.

The interfacial carrier kinetics was further investigated by electrochemical impedance spectroscopy (EIS). As can be seen in Fig. 3g, semicircles of Nyquist plots for all photoanodes fitted well with an equivalent circuit model (inset in Fig. 3g) of a series resistance ($R_s$), an interfacial charge transfer resistance ($R_{\text{ct}}$) and a constant phase angle element (CPE) $\left(\eta_{\text{trans}}\right)$. All modified photoanodes featured noticeably smaller semicircles in EIS plots compared to bare BiVO$_4$. In particular, $R_{\text{ct}}$ of NiFeV/B-BiVO$_4$ was only 289.2 Ohm (Table S2$^\dagger$) at 0.6 $V_{\text{RHE}}$, implying the fastest charge transfer at the electrode/electrolyte interface by borate and NiFeV co-modification, which was demonstrated in the trends of $\eta_{\text{surface}}$ in Fig. 3f. The band bending was further investigated by open-circuit voltage ($V_{\text{oc}}$) measurements. The photovoltage of a photoanode arises from splitting of electron and hole quasi-Fermi level under steady-state light illumination, which acts as a driving force for injecting the photogenerated holes into the electrolyte for OER. According to several previous works, the simple integration of OECs on the surface of photoanodes could enlarge the difference in photovoltage between the dark and light conditions, resulting in greater band bending. Smith and co-workers also reported that the photocharged BiVO$_4$ photoanodes in a borate buffer solution obtained a favorable band bending, which is responsible for the strong suppression of surface recombination. In Fig. 3h, the photovoltage of BiVO$_4$, B-BiVO$_4$, NiFeV/BiVO$_4$, and NiFeV/B-BiVO$_4$ were 0.22 V, 0.27 V, 0.33 V and 0.37 V, respectively. After NiFeV and borate co-modification, a greater driving force for water oxidation with more efficient charge separation in the photoanode was obtained, which resulted in more negative onset potential for OER.

It has been reported that both reduced charge surface recombination and enhanced water oxidation kinetics could contribute to the improved surface charge transfer efficiency. In order to understand which one is the main reason for the synergistically enhanced PEC performance, intensity modulated photocurrent spectroscopy (IMPS) was performed in the low bias region (0.3-0.6 $V_{\text{RHE}}$). The dynamic kinetic rate constants can be described as charge transfer rate constant ($k_{\text{trans}}$) and surface recombination rate constant ($k_{\text{rec}}$), respectively. According to the generalized theory of IMPS, as the frequency increases, the relaxation in the concentration of photogenerated holes at the semiconductor surface is characterized by $f_{\text{max}}$ (at the apex of the upper semicircle), where $2n_{\text{f,max}} = k_{\text{trans}} + k_{\text{rec}}$.

$$f_{\text{max}} = \frac{k_{\text{trans}} + k_{\text{rec}}}{2n_{\text{f,max}}}$$

The charge transfer efficiency, in terms of $k_{\text{trans}}/(k_{\text{trans}} + k_{\text{rec}})$, can be derived from the intersections of the semicircle with the real axis at low and high frequency (i.e., $I_1$ and $I_2$, respectively), where $I_1/I_2 = k_{\text{trans}}/(k_{\text{trans}} + k_{\text{rec}})$. 

![Fig. 3](image_url)
analogously observed in CoPi/BiVO$_4$ most potentials (BiVO$_4$ 16, 20, 43) an increase in water oxidation rates. Generally, loading an OEC catalyst on a photoanode should result in enhancement (inter alia over the entire potential range. These results coincided with the indicating that the charge recombination was greatly suppressed over the entire potential range. In sharp contrast, significantly lower $k_{rec}$ of bare BiVO$_4$ did not change significantly over the entire potential range (Fig. 4c). In sharp contrast, significantly lower $k_{rec}$ values are observed for NiFeV/B-BiVO$_4$. Even at the lowest applied bias of 0.3 V$_{RHE}$, the $k_{rec}$ of bare BiVO$_4$ was up to 15.9 s$^{-1}$, which was larger than NiFeV/B-BiVO$_4$ (4.6 s$^{-1}$) by a factor of 3.5. Most notably, at the point of maximum ABPE value of NiFeV/B-BiVO$_4$ (i.e., 0.6 V$_{RHE}$), this ratio approached 90, indicating that the charge recombination was greatly suppressed over the entire potential range. These results coincided with the enhancement (inter alia E < 0.6 V$_{RHE}$) of photocurrent density of NiFeV/B-BiVO$_4$ (Fig. 3a) and further confirmed the dominating role of NiFeV co-catalysts within the synergy.

Generally, loading an OEC catalyst on a photoanode should result in an increase in water oxidation rates. However, $k_{trans}$ of bare BiVO$_4$ appeared higher than that of NiFeV/B-BiVO$_4$ to some degree at most potentials (Fig. 4d). This abnormal phenomenon has also been analogously observed in CoPi/BiVO$_4$. NiFeO$_3$/Fe$_2$O$_3$, Co-LaFeO$_3$/BiVO$_4$, and so on. It should be noted that the smaller $k_{trans}$ measured here on NiFeV/B-BiVO$_4$ does not certainly suggest a slower water oxidation. This is because the $k_{trans}$ derived from IMPS more likely reports on the rate-determining steps (RDS) of the complex charge transfer processes from the photoelectrode to water. Moreover, NiFeV LDH has been confirmed as an efficient water oxidation catalyst according to our electrochemical testing (Fig. S10†) and related literatures. Furthermore, the actual charge transfer efficiency $k_{trans}$($k_{trans}$+$k_{rec}$) of NiFeV/B-BiVO$_4$ was evidently higher than bare BiVO$_4$ (Fig. S11†), owing to minimized recombination, displaying the same trend as the $n_{surface}$ results in Fig. 3f. To further support this experimentally, H/D kinetic isotope effect (KIE) was assessed by comparing photocurrent densities at different overpotentials (after corrections) in 0.1 M anhydrous borax (Na$_2$B$_4$O$_7$) H$_2$O and D$_2$O solutions (Fig. S12†). Herein, H/D KIE studies serve to investigate the proton transfer kinetics and probe the RDS in water oxidation process on the surface of BiVO$_4$. The KIE of bare BiVO$_4$ photoanode approached to 1.5, in agreement with the previous report, indicating that the RDS of PEC water oxidation on BiVO$_4$ involved proton transfer process. B-BiVO$_4$ showed a moderate KIE value of ~ 1.2, which indicated a slight acceleration of proton transfer. After loading LDH co-catalysts, both NiFeV/BiVO$_4$ and NiFeV/B-BiVO$_4$ displayed negligible H/D kinetic isotope effects (KIE ≈ 1.0) at all applied potentials, suggesting that the proton transfer is no longer involved in the RDS. Moreover, it revealed that hole transfer into the LDH co-catalysts (instead of catalytic processes...
of water oxidation on BiVO₄ surface) is rate-limiting, indicative of very fast subsequent injection of photogenerated holes into electrolyte. It might be therefore concluded that the synergetic effects of borate and NiFeV co-modifications not only increased the overall rate of water oxidation, but also promoted charge transfer and reduced the charge recombination.

In our previous report, the adsorption of borate on the surface of BiVO₄ resulted in a molecular level modification, which reduced surface charge trapping, and thereby a significant increase in the photocurrent of B-BiVO₄. However, that improvement gradually degenerated within short-term photolysis (Fig. 5a and Fig. S13†). The degradation of efficiency was likely caused by the accumulation of photogenerated holes at the B-BiVO₄ surface, where they easily recombined with electrons and could not be consumed for water oxidation quickly. When using the electrolyte with Na₂SO₃ hole scavenger (Fig. 5b), the photocurrent of B-BiVO₄ was maintained after 1 h photolysis at 0.6 VₚHₑₚ in that electrolyte. After NiFeV LDH modification, as illustrated in Fig. 5c, the NiFeV/B-BiVO₄ photoanode exhibited a good stability and about 95% of the initial photocurrent density was retained after 8h photolysis. Longer stability test (24 h at 0.6 VₚHₑₚ) of NiFeV/B-BiVO₄ showed that over 80% of the initial photocurrent density was maintained (Fig. S14†). Besides, high faradaic efficiency of 95% was obtained for NiFeV/B-BiVO₄ (Fig. S15†); both the morphology of BiVO₄ and nanostructures of the catalysts did not show obvious changes after stability tests (Fig. S16†). The improvement of photostability could be attributed to the improved interfacial charge transfer efficiency by NiFeV catalyst, which can reduce surface recombination and kinetically suppress photocorrosion.29, 72, 81 Besides, it has been reported that the injection of surface-reaching holes into OECs was thermodynamically favorable compared to direct transfer to the solution and the catalysts were typically permeable for electrolyte and redox-active.44 Therefore, holes can accumulate throughout the LDHs, thereby diminishing surface recombination.30

**Scheme 1.** Schematic illustration of working principles in (a) bare BiVO₄ and (b) NiFeV/B-BiVO₄ photoanode.

These results clearly demonstrated that loading LDH co-catalysts onto B-BiVO₄ did not only further enhance photocurrent density and lower the onset potential but also significantly improved the stability of B-BiVO₄. Such a synergetic effect of borate treatment and LDH modification can also be realized on NiFe/B-BiVO₄ (Fig. S17†) and NiV/B-BiVO₄ photoanodes (Fig. S18†), which can achieve photocurrents of ~ 3.7 mA cm⁻² and ~ 4.3 mA cm⁻² at 1.23 VₚHₑₚ respectively with relatively low onset potentials (~ 0.25 VₚHₑₚ) and good stabilities.

From the above discussions, the overall effects of charge transfer and surface recombination are schematically summarized in Scheme 1. For the bare BiVO₄, the photogenerated holes can be directly consumed for water oxidation or trapped by surface state and recombined with electrons. The co-modification has little improvement on the intrinsically decent charge separation of bare BiVO₄. The self-anchored borate species serve as a passivator contributing to the decrease of surface charge recombination as well as a ligand in modifying the catalytic site for water oxidation.35, 36 And the main role of NiFeV LDH is to efficiently suppress surface recombination and promote interfacial charge transfer efficiency, thereby improving PEC performance and stability simultaneously. The high intrinsic catalytic activity of NiFeV LDH is also conducive to a greater driving force for water oxidation and a lower onset potential.

**4. Conclusions**

In conclusion, our work provided insights into the rational design of BiVO₄ based photoanode for highly efficient PEC water splitting combined with post-synthetic borate treatment and NiFeV co-catalyst loading. The optimized NiFeV/B-BiVO₄ photoanode achieved a remarkable photocurrent density of 4.6 mA cm⁻² with an ultra-low onset potential (0.2 VₚHₑₚ) with a high half-cell high solar-energy conversion efficiency of 1.85% at 0.6 VₚHₑₚ. It is worth noting that NiFeV/B-BiVO₄ exhibited a strong photocurrent increase at a low applied bias range (~ 0.6 VₚHₑₚ). More importantly, studies on NiFeV/B-BiVO₄ surface kinetics further evidenced the outstanding contribution of NiFeV co-modification on the suppression of charge recombination and the promotion of charge transfer efficiency. Moreover, loading NiFeV co-catalyst significantly improves the stability of borate-treated BiVO₄. This work has revealed and emphasized the significance of the synergy of co-modifications in photoelectrochemical devices.

**Conflicts of interest**

There are no conflicts to declare.

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