Promoting charge carrier utilization by integrating layered double hydroxide nanosheet arrays with porous BiVO₄ photoanode for efficient photoelectrochemical water splitting

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ABSTRACT The increasing exploration of renewable and clean power sources have driven the development of highly active materials for photoelectrochemical (PEC) water splitting. However, it is still a great challenge to enhance the charge utilization. Herein, we report a facile method to fabricate composite photoanode with porous BiVO₄ film as the photon absorber and layered double hydroxide (LDH) nanosheet arrays as the oxygen-evolution cocatalysts (OECs). The as-prepared BiVO₄/NiFe-LDH photoanode shows an excellent performance for PEC water splitting benefitting from the synergistic effect of the superior charge separation efficiency facilitated by porous BiVO₄ film and the excellent water oxidation activity resulting from LDH nanosheet arrays. A photocurrent density is 4.02 mA cm⁻² at 1.23 V vs. the reversible hydrogen electrode (RHE). Furthermore, the O₂ evolution rate at the surface of BiVO₄/NiFe-LDH photoanode is as high as 29.6 μmol h⁻¹ cm⁻² and the high activity for water oxidation is maintained for over 30 h. Impressively, the performance of the as-fabricated composite photoanode for PEC water splitting can be further enhanced through incorporating a certain amount of Co²⁺ cation into NiFe-LDH as OEC. The photocurrent density is achieved up to 4.45 mA cm⁻² at 1.23 V vs. RHE. This value is the highest yet reported for un-doped BiVO₄-based photoanodes so far.

Keywords: photoelectrocatalysis, water splitting, synergistic effect, layered double hydroxides, porous photoanode

INTRODUCTION

Photoelectrochemical (PEC) water splitting represents a promising and effective approach to ease the increasingly prominent energy crisis due to its utilization of abundant solar energy to obtain renewable energy [1–4].

Metal oxides acting as photoanodes for PEC light conversion, such as TiO₂ [5,6], α-Fe₂O₃ [7–10], WO₃ [11, 12], have attracted wide attention because of their low cost, environment-friendliness and stability under oxidizing conditions. Among them, BiVO₄ is the top performer due to its relatively small band gap, adequate conduction band edge position and moderate charge transport properties [13–18]. However, the low charge separation efficiency and slow oxygen evolution kinetics of the unmodified BiVO₄ need to be improved. Recently, a porous BiVO₄ photoanode was prepared by a novel thermal treatment of bismuthoxyiodide (BiOI) with the presence of vanadium salts [13]. Although the porous morphology of BiVO₄ can effectively suppress bulk carrier recombination and enhance light absorption, the low photocurrent and bad stability are disadvantageous to meet the practical application. Therefore, the development of a promising strategy to fabricate advanced photoanodes based on porous BiVO₄ with high photocurrent and durability is still highly desirable.

The efficiency of PEC water splitting depends on not only the bulk charge separation but also the surface reaction kinetics. Loading oxygen-evolution cocatalysts (OECs) has been considered as an effective approach to accelerate the surface reaction kinetics and reduce oxygen evolution reaction (OER) barrier of semiconductor materials [7,13,19,20]. Although traditional noble metal oxides, such as IrO₂ and RuO₂, are considered as the most active OER electrocatalysts for OECs in PEC cells [5,14], the high cost and low stability limit their extensive applications [7].

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To date, great efforts have been made to develop efficient photoanodes composed of promising semiconductors and highly active non-noble-metal OER electrocatalysts [8,13,15]. However, the instability and/or competing light absorbance in the visible light region of non-noble-metal OER electrocatalysts limit their applications in photoelectrocatalysis [7]. Currently, it has been found that layered double hydroxide (LDH) materials show surprisingly high OER performance [21–25]. They may serve as promising OEC candidates for PEC water splitting. Nowadays, they have been applied to some potential photoanodes, including TiO_2 [5], Fe_2O_3 [9], Ta_2N_3 [26], which have shown enhanced performances in both onset potentials and photocurrent densities. In addition, the LDHs are synthesized simply and grow on substrate easily in the form of nanostructure [22]. They also offer wide tunability of diverse metal species or ratios and a large interface spacing which may accelerate the ion diffusion [23]. These features guarantee that LDHs could be of wide potential as OECs for fabricating photoanodes with highly efficient PEC performance. Unfortunately, up to now, the reported composite photoanodes in which LDHs were used as OECs showed low photocurrent densities (less than 2.5 mA cm^{-2} at 1.23 V vs. the reversible hydrogen electrode (RHE)). Therefore, exploring the appropriate semiconductors as photon absorbers and the highly efficient LDHs as OECs to fabricate photoanodes for efficient and stable PEC water splitting becomes highly desirable. Very recently, a triadic quantum dot/LDH/ BiVO_4 photoanode with enhanced PEC water oxidation (2.23 mA cm^{-2} at 1.23 V vs. RHE)

has been reported by Xiang's group [17]. Nevertheless, the LDH/ BiVO_4 composite photoanode without sensitization of the quantum dots shows less improvement in photocurrent density compared with the pristine BiVO_4 . Therefore, integrating BiVO_4 with LDH as composite photoanode for highly efficient PEC water splitting is still a great challenge. Moreover, many reports have shown that ingenious photoanodes with improved separation of photogenerated charge carriers can be obtained through fabricating various nanostructures (such as ordered nanorod arrays [5], porous films [13], and heterogeneous nanoarrays [27–32]). Notably, the nanostructured electrocatalysts which can be used as OECs demonstrate many special features, such as more active sites, superhydrophilic and superaerophobicity [33–35]. Hence, the development of a facile method to fabricate the nanostructured OECs anchoring on porous photoanodes for highly efficient and steady PEC water splitting is highly desirable and still in its infancy. The study on the synergistic effect of porous photoanodes and nanostructured OECs remains a great challenge.

Herein, we report a facile approach through anchoring LDH nanosheet arrays on the porous BiVO_4 to fabricate BiVO_4 /LDH photoanode for efficient PEC water splitting. Binary NiFe-LDH nanosheet arrays are selected as the model OECs to fabricate BiVO_4 /NiFe-LDH photoanode because of their facile preparation conditions and highly efficient OER activity [22,36]. As shown in Fig. 1, we synthesize the BiVO_4 photoanode with porous film to shorten the travel distance of photogenerated holes and reduce the recombination probability of charge carriers. Then, the

Figure 1 Schematic illustration for the fabrication of BiVO_4 /NiFe-LDH photoanode, its charge separation process and PEC water splitting mechanism.

NiFe-LDH nanosheet arrays are deposited on the porous BiVO₄ photoanode through a solution chemical growth. The as-prepared BiVO₄/NiFe-LDH photoanode shows excellent performance for PEC water splitting with greatly enhanced photocurrent density (4.02 mA cm⁻² at 1.23 V vs. RHE, 2.8 times higher than that of pristine BiVO₄) under AM 1.5G simulated sunlight (100 mW cm⁻²). The high activity for PEC water splitting can last for over 30 h. The enhanced PEC performance is attributed to the synergistic effect of the superior charge separation efficiency facilitated by porous film and the excellent water oxidation activity resulting from NiFe-LDH nanosheet arrays OEC layer. Moreover, considering that the element Fe plays a critical role in enhancing OER active (oxy)hydroxides [37,38], the effect of Fe/Ni ratio on PEC performance of BiVO₄/NiFe-LDH photoanode is discussed in detail. Furthermore, it is found that the performance of ternary NiFeCo-LDH fabricated by incorporating a certain amount of Co²⁺ cation into NiFe-LDH as OEC can be further enhanced, with the photocurrent density of 4.45 mA cm⁻² at 1.23 V vs. RHE, which is the highest among reported un-doped BiVO₄-based photoanodes known to date.

EXPERIMENTAL SECTION

Chemicals

All chemicals are analytical grade and used as received without further purification.

Synthesis of BiVO₄/NiFe-LDH photoanode

The fabrication process of BiVO₄/NiFe-LDH photoanode is illustrated in Fig. 1. First, the BiVO₄ photoanode with porous morphology was prepared on a fluorine-doped tin oxide (FTO) substrate via a previous reported thermal treatment of BiOI with the presence of vanadium salts (see the Supplementary information (SI)). Then, a solution chemical synthesis method was used to grow NiFe-LDH nanosheet arrays on the porous BiVO₄ photoanode. The BiVO₄/NiFe-LDH photoanodes with different molar ratios of Ni/Fe (pure Ni, 3:1, 1:1, 1:3, pure Fe) were fabricated. First, 3 mL aqueous solution containing 0.5 mmol urea and 0.2 mmol NH₄F was prepared. Ni(NO₃)₃·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in deionized water (DIW) to form Ni²⁺ and Fe³⁺ solution of 0.1 mmol mL⁻¹, respectively. Then Ni²⁺ and Fe³⁺ solution were added in the former solution at different mole ratios (pure Ni, 3:1, 1:1, 1:3, pure Fe) and the total volume of cation solution is 1 mL. Finally, the mixture solution was transferred into a 20-mL Teflon-lined autoclave in which the porous BiVO₄ photoanode was placed with the BiVO₄ side facing the wall

of the autoclave. After 6 h of reaction at 120°C, NiFe-LDH nanosheet arrays were grown on the porous BiVO₄ photoanode. The as-fabricated composites were thoroughly rinsed with DIW and dried at 60°C for 1 h before use. The molar ratios of Ni/Fe were quantified by energy dispersive spectroscopy (EDS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). In addition, the amounts of NiFe-LDH nanosheet arrays with different ratios of Ni/Fe decorated on porous BiVO₄ photoanode were also calculated. The detailed data mentioned above are summarized in Table S1.

Synthesis of BiVO₄/NiFeCo-LDH photoanode

The method was the same to that of the fabrication of the BiVO₄/NiFe-LDH photoanode with Ni/Fe ratio of 3/1 except that 0.02 mmol Co(NO₃)₃·6H₂O was added.

Characterization

Scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 scanning electron microscope (SEM, 3 kV). Transmission electron microscopy (TEM), scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) and high-resolution TEM (HRTEM) were obtained with FEI Tecnai G2 F20 system equipped with EDAX Genesis XM2 and HAADF. Specimens for TEM and HRTEM measurements were prepared via drop-casting a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air. The X-ray diffraction (XRD) patterns of the products were recorded with Bruker D8 Focus Diffraction System using a Cu K α source ($\lambda = 0.154178$ nm). UV-vis absorbance spectra were recorded on a Lambda 750S UV-vis-NIR spectrometer (Perkin-Elmer) equipped with an integrating sphere. The UV-vis absorption spectra of solid samples were collected in the range of 200–800 nm against BaSO₄ reflectance standard. The ratios of Ni/Fe in NiFe-LDH were analyzed by means of an ICP spectrometer (USA, Agilent 7700x). X-ray photoelectron spectra (XPS) analyses were performed on a PHI5000VersaProbe with Al K α (1486.6 eV) radiation. The base pressure was about 3×10^{-9} mbar. The binding energy was referenced to the C 1s line at 284.8 eV from adventitious carbon.

PEC Measurements

PEC measurements were all achieved with back-side illumination and evaluated using a standard three-compartment cell, with porous photoanode (BiVO₄ or BiVO₄/NiFe-LDH electrodes) as the working electrode, the Pt foil as the counter electrode (1 cm $\times$ 2 cm, Tianjin Incole

Union Technology Co., Ltd.), and the saturated calomel reference electrode (SCE) as the reference electrode. The simulated solar illumination was obtained by passing light from a 300 W xelon lamp (Beijing China Education Au-light Co., Ltd) equipped with an AM 1.5 filter, and the power intensity of the incident light was calibrated to 100 mW cm^{-2} at the surface of the working electrode. All illuminated areas were 1 cm^2 . An electrochemical workstation (CHI 660D, Chenhua, Shanghai) was used. A $0.1 \text{ mol L}^{-1} \text{ KHCO}_3$ ($\text{pH} = 8.6$) was used as the electrolyte. Prior to measurements, the electrolyte was thoroughly deaerated by purging it with N_2 or CO_2 for 30 min. Chopped-light I - t characterizations were evaluated at an applied potential of $1.0 \text{ V vs. the reversible hydrogen electrode (RHE)}$ under chopped light irradiation (light on or off cycles: 30 s). Electrochemical impedance spectroscopy (EIS) was conducted by applying an alternating current (AC) cottage amplitude of 50 mV within the frequency range from 0.1 to $100,000 \text{ Hz}$ in $0.1 \text{ mol L}^{-1} \text{ KHCO}_3$ under the open-circuit potential and AM 1.5G illumination (100 mW cm^{-2}). The applied bias photo-to-current efficiency (ABPE) was calculated from the linear sweep voltammograms (LSV) curve assuming 100% Faradic efficiency using the following Equation (1):

$$\text{ABPE}(\%) = J \times (1.23 - E_{\text{RHE}}) / P_{\text{in}}, \quad (1)$$

where J is the photocurrent density, E_{RHE} is the applied bias between working electrode (WE) and RHE, and P_{in} is the incident illumination power density (AM 1.5G, 100 mW cm^{-2}). The measured potential vs. SCE was converted to the RHE scale according to the Nernst equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.241 + 0.0591 \text{pH}$. The monochromatic incident photo-to-electron conversion efficiency (IPCE) was measured at 1.0 V vs. RHE for BiVO_4 and $\text{BiVO}_4/\text{NiFe-LDH}$ photoanodes under monochromatic light irradiation by using an optical filter on the Xe lamp in the electrolyte of $0.1 \text{ mol L}^{-1} \text{ KHCO}_3$. The IPCE was calculated using Equation (2):

$$\text{IPCE} = (1240 J_{\text{mono}}) / (P_{\text{mono}} \lambda), \quad (2)$$

where J_{mono} and P_{mono} are the measured photocurrent density and irradiance at a specific wavelength, respectively, and λ is the wavelength of incident light.

RESULTS AND DISCUSSION

Morphology and structure characterization

Porous BiVO_4 photoanode was synthesized by electrodeposition and subsequent annealing according to the previous report [13] (see the details in SI). Fig. 2a, c shows that the

as-prepared porous BiVO_4 photoanode possesses sub-micron scale voids between the particles, which is attributed to the two-dimensional plate morphologies of BiOI crystals (Fig. S1) with ample space between them appearing to effectively limit the grain growth and the final grain size of BiVO_4 particles. Subsequently, the NiFe-LDH nanosheet arrays were anchored on the porous BiVO_4 photoanode through a solution chemical synthesis. From the top and cross-section view SEM images of $\text{BiVO}_4/\text{NiFe-LDH}$ in Fig. 2b, d, it is found that the surface of porous BiVO_4 photoanode is covered with a uniform nanosheet arrays film with a thickness of approximately $1.5 \mu\text{m}$. The uniform film of NiFe-LDH is composed of nanosheets with a thickness of about 50 nm interconnected with each other to form an open porous network structure, which allows for easy access of the electrolyte to all the nanosheets and the porous

Figure 2 Morphology and structure characterization. (a, b) Top view and (c, d) cross-section view SEM images of the porous BiVO_4 (a and c) and $\text{BiVO}_4/\text{NiFe-LDH}$ (b and d). The inset of (b) is the high magnification top view SEM image of $\text{BiVO}_4/\text{NiFe-LDH}$. The white arrows in (d) indicate the positions where the NiFe-LDH nanosheets are grown on the internal part of porous BiVO_4 film. (e, f) TEM images of $\text{BiVO}_4/\text{NiFe-LDH}$. The insets of (f) are the HRTEM images of BiVO_4 (bottom) and NiFe-LDH (upper right), respectively. The white square in (e) implies the position where the HAADF-STEM image is obtained. (g) HAADF-STEM image and the associated STEM-EDS elemental mapping images of $\text{BiVO}_4/\text{NiFe-LDH}$.

BiVO_4 film. In addition, the nanosheets are layer-like with a layer thickness of sub-10 nm (Fig. S2) and the interface spacing between the layers may accelerate the ion diffusion [23]. A cross-section view SEM image in Fig. 2d (the enlarged image shown in Fig. S3) further shows that the NiFe-LDH nanosheets not only grow on the surface of porous BiVO_4 film but also exist on the internal part of the porous BiVO_4 film (indicated by the white arrows), which indicates the NiFe-LDH nanosheets combine well with the porous BiVO_4 photoanode. A Ni/Fe molar ratio of 4.3:1 is obtained from energy dispersive X-ray (EDX) spectroscopy, which is close to the result of ICP spectrometry (Table S1). The XRD patterns display that BiVO_4 exhibits a monoclinic phase and the (003) reflection of typical LDH can be observed (Fig. S4). The XPS characterizations verify the decorating of NiFe-LDH on the porous BiVO_4 . The O 1s spectrum of the pristine BiVO_4 can be fitted into three peaks (Fig. S5a). The peak at 529.3 eV is characteristic of the O^{2-} species, while the other two peaks are attributed to surface labile oxygen, including OH^- (530.8 eV) and adsorbed molecular water (532.3 eV) [9,39]. The O^{2-} peak becomes weak, resulting from the coating of NiFe-LDH on BiVO_4 . At the same time, the OH^- peak becomes strong, which can be attributed to the OH^- group in NiFe-LDH [9,17]. The decorating of NiFe-LDH film on porous BiVO_4 was further characterized by TEM and STEM-EDS elemental mapping. As shown in Fig. 2e, f and Figs S6, S7, an obvious layer can be seen on the surface of BiVO_4 . The HRTEM image of the $\text{BiVO}_4/\text{NiFe-LDH}$ shows that the fringe spacings of 0.26 and 0.31 nm accord well with the spacing of the (101) lattice plane for NiFe-LDH and (-121) lattice plane for BiVO_4 , respectively. STEM-EDS elemental mapping images imply uniform signals for Bi, V, Ni, Fe, O elements, which demonstrates the homogeneous distribution of NiFe-LDH on BiVO_4 . These results suggest that BiVO_4 can be well

decorated with the NiFe-LDH, which is favorable for the charge transfer between the BiVO_4 and NiFe-LDH.

The UV-vis absorption spectra were used to investigate the optical properties of BiVO_4 photoanodes decorated with or without NiFe-LDH nanosheet arrays. To explore the influence of NiFe-LDH nanosheet arrays on the absorption of BiVO_4 , we illuminated the samples from the front and back side through UV-vis spectrometer, respectively. As shown in Fig. 3a, the results of UV-vis absorption spectra obtained from the front side show that the porous BiVO_4 photoanode exhibits a strong absorption in the visible light region with the absorption edge at approximately 518 nm, and its band gap is calculated to be 2.43 eV, in line with the previous reports [13,15]. After being decorated with NiFe-LDH nanosheet arrays, the absorbance of $\text{BiVO}_4/\text{NiFe-LDH}$ in the visible light region increases due to the visible light absorption of NiFe-LDH (red curve in Fig. 3a), while the absorption intensity of $\text{BiVO}_4/\text{NiFe-LDH}$ sharply decreases compared to the pristine BiVO_4 . However, when the UV-vis absorption spectra are obtained from the back side, the absorption intensity of $\text{BiVO}_4/\text{NiFe-LDH}$ electrode is approximate to the pristine BiVO_4 in addition to the increased visible light region which originates from the visible light absorption of NiFe-LDH (red curve in Fig. 3b). It is also found that the FTO shows no visible light absorption (cyan curve in Fig. 3b). These results suggest that the back-side illumination is an efficient way to suppress the absorption of NiFe-LDH which can compete with the BiVO_4 , as discussed in previous reports [13,40–42].

Enhanced PEC water splitting of $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode

To study the PEC performance of NiFe-LDH nanosheet arrays loaded on the porous BiVO_4 photoanode for water

Figure 3 UV-vis absorption spectra measured at different sides of samples: (a) front-side, (b) back-side. The insets in (a) and (b) are the corresponding schematic illustration of illumination, respectively. The blue arrows represent incident solar irradiation.

splitting, the samples were fabricated as photoanodes with a well-defined area of 1 cm^2 . All PEC properties were measured under AM 1.5G simulated sunlight (100 mW cm^{-2}) in a standard three-electrode electrochemical cell with a Pt foil as the counter electrode, an SCE as the reference electrode, and $0.1\text{ mol L}^{-1}\text{ KHCO}_3$ solution (pH 8.6) as the electrolyte. The optimal amount of NiFe-LDH decorated on porous BiVO_4 photoanode is discussed (Figs S8, S9). The front-side and back-side illumination LSV of BiVO_4 and $\text{BiVO}_4/\text{NiFe-LDH}$ photoanodes are shown

in Fig. 4a. The porous BiVO_4 photoanode can obtain a better photocurrent through back-side illumination than the front-side illumination, which is attributed to the photogenerated electrons having to travel longer distance being collected by FTO back contact under front-side illumination, in line with the previous reports [41,42]. After the decoration of NiFe-LDH nanosheet arrays as OEC layer, the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode exhibits significant improvement of back-side illumination photocurrent, reaching an AM 1.5G photocurrent of 4.02 mA cm^{-2} at

Figure 4 Effect of NiFe-LDH on PEC performance of the porous BiVO_4 photoanode. (a) The LSV curves, (b) ABPE curves of BiVO_4 and $\text{BiVO}_4/\text{NiFe-LDH}$ photoanodes under the front-side and back-side illumination. (c) LSV behavior chopped light illumination, (d) $I-t$ curves at a potential of 1.0 V vs. RHE under chopped light illumination, (e) EIS spectra measured at the open-circuit potential under illumination and (f) IPCE curves measured at a potential of 1.0 V vs. RHE for the pristine BiVO_4 and $\text{BiVO}_4/\text{NiFe-LDH}$ photoanodes.

1.23 V *vs.* RHE, which is 2.8 times higher than that of the pristine BiVO₄. This value is higher than other OECs decorated on un-doped BiVO₄ (Table S2) and some photoanodes decorated with NiFe-LDH as OECs, e.g., NiFe-LDH/Ta₃N₅ (1.7 mA cm⁻² at 1.23 V *vs.* RHE) [26], TiO₂/rGO/NiFe-LDH (1.74 mA cm⁻² at 1.245 V *vs.* RHE) [5], Mn-doping Fe₂O₃/NiFe-LDH (ca. 2.1 mA cm⁻² at 1.23 V *vs.* RHE) [9], quantum dot/LDH/BiVO₄ (2.23 mA cm⁻² at 1.23 V *vs.* RHE) [17]. It is even comparable to the porous BiVO₄ photoanode decorated with FeOOH/NiOOH dual OECs (4.2 mA cm⁻² at 1.23 V *vs.* RHE) [13]. The onset potential of BiVO₄ shifts negatively from 0.75 to 0.40 V after the NiFe-LDH nanosheet arrays decoration. Notably, the photocurrent of BiVO₄/NiFe-LDH photoanode under back-side illumination is higher than that under front-side illumination, which is attributed to not only the less photocurrent of BiVO₄ photoanode under the front-side illumination but also the competitive absorption of NiFe-LDH for the visible light. These results suggest that the as-fabricated BiVO₄/NiFe-LDH photoanode exhibits greatly enhanced photocurrent and the competitive absorption of OEC can be efficiently suppressed through the back-side illumination.

The efficiency of the BiVO₄/NiFe-LDH photoanode was further assessed through the ABPE of the BiVO₄/NiFe-LDH photoanode. The ABPE of BiVO₄ and BiVO₄/NiFe-LDH photoanodes are calculated by their LSV curves, assuming 100% Faradic efficiency, as shown in Fig. 4b. At an applied potential of about 0.75 V *vs.* RHE, the maximum ABPE of 1.07% can be achieved for BiVO₄/NiFe-LDH photoanode. Moreover, the high efficiency achieved at a potential as low as 0.75 V *vs.* RHE provides a promising approach for assembling a tandem cell (water splitting [18,43–48] or oxygen evolution coupling CO₂ reduction to fuels [11,49,50]) or a PEC diode [1]. To further investigate the photoresponse of the BiVO₄ and BiVO₄/NiFe-LDH photoanodes, transient photocurrent measurements were carried out by LSV and chronoamperometry under chopped light illumination. As shown in Fig. 4c, the two samples all display a prompt and reproducible photocurrent response with respect to the on/off cycles of the irradiation signal. Amperometric *I*-*t* curves also depict the fast response toward irradiation stimulation. The current density of BiVO₄/NiFe-LDH shows a great enhancement compared with the pristine BiVO₄, which is in high accordance with the LSV results and further demonstrates the importance of NiFe-LDH as OEC for water oxidation. Moreover, the square profiles and steady photocurrent density of the transient photocurrent response in

the BiVO₄/NiFe-LDH photoanode indicate a fast surface oxidation kinetics, suppressed electron-hole recombination and excellent photochemical stability. Taking the visible light absorbance of NiFe-LDH into account shown in Fig. 2, the LSV curve of the pure NiFe-LDH nanosheet arrays is used to make sure whether it makes any contribution to the photocurrent density. The LSV curves in the dark and light show no photocurrent response (Fig. S10). That is, although the NiFe-LDH nanosheet arrays can absorb the visible light, the NiFe-LDH nanosheet arrays show no light response under AM 1.5G light, which can be neglected. The photogenerated holes for water oxidation in the BiVO₄/NiFe-LDH photoanode are mainly come from the porous BiVO₄ film while the NiFe-LDH nanosheet arrays are only functioned as OEC to increase the amount of holes involved in the water oxidation reaction.

The element Fe is proved to be effective for enhancing the OER activities of (oxy)hydroxides due to the enhanced structure disorder and conductivity of Fe-doping (oxy)hydroxides by previous experiment and theoretical calculation results [37,38]. This drives us to explore the influence of mole ratios of Ni/Fe in NiFe-LDH on the PEC activity of BiVO₄/NiFe-LDH photoanode. The BiVO₄/NiFe-LDH photoanodes with different molar ratios of Ni/Fe (pure Ni, 3:1, 1:1, 1:3, pure Fe) were synthesized by adding different molar ratios of corresponding metal nitrates (the photoanodes are labelled as BiVO₄/NiFe-LDH-(Ni, 3:1, 1:1, 1:3, Fe), respectively). SEM images (Fig. S11) show that the morphology of NiFe-LDH varies from nanosheet to nanorod with the decreased content of Ni²⁺. This suggests that the morphology of the NiFe-LDH could be tuned by varying the content of Ni²⁺. In addition, the actual Ni/Fe molar ratio in the LDHs measured by the EDX and ICP is different from the initial molar ratio of Ni²⁺ and Fe³⁺, which is attributed to that one of metal cations is preferentially incorporated into the LDH nanosheets during the formation of LDHs [51,52]. The PEC performances of the above composite photoanodes were evaluated by LSV curves (Fig. S12). The BiVO₄/NiFe-LDH-(3/1) exhibits the best PEC activity among the samples, giving the lowest onset potential and best photocurrent at 1.23 V *vs.* RHE. The results obtained from the LSV curves are summarized in Table S1. The NiFe-LDH-(3/1) nanosheet arrays grown on FTO glass also shows the best OER activity (Fig. S13). These results show that the BiVO₄/NiFe-LDH photoanode obtained from the addition of Ni²⁺ and Fe³⁺ with a 3:1 molar ratio shows the best performance in PEC water splitting, with the optimal molar of Ni and Fe enhancing the catalytic activity of NiFe-LDH as OEC.

It is proposed that the existence of OECs layer in photoanodes can decrease the reaction barriers for water oxidation and facilitate the holes transfer to the photoanode/electrolyte interface [5,15], conducing to greatly improved PEC performance. The EIS analysis provides information about the interfacial properties of the photoanodes (Fig. 4e). The diameter of the semicircle in EIS reflects the electron transfer resistance, which subjects the electron transfer kinetics of the redox probe at the photoanode interface. Fig. 4e shows the typical EIS curves for the pristine BiVO_4 and $\text{BiVO}_4/\text{NiFe-LDH}$ photoanodes in $0.1 \text{ mol L}^{-1} \text{ KHCO}_3$ under AM 1.5G light illumination. A smaller diameter is observed in the curve of $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode under illumination relative to the pristine BiVO_4 , which means that the resistance of NiFe-LDH/electrolyte interface is much smaller than the BiVO_4 /electrolyte interface. This indicates a conduction effect of the NiFe-LDH OEC layer on the charge transfer process could decrease the charge transfer barrier at the photoanode interface. As a result, the oxygen evolution reaction barrier is reduced by decreasing the charge transfer barrier as reported in previous reports [5,15]. Water oxidation is easier to realize due to the decreased reaction barrier, so a noticeable cathodic shift of the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode appears in the onset potential compared to the pristine BiVO_4 observed from the dark LSV curves (Fig. S14). Moreover, the hierarchical NiFe-LDH layer can provide sufficient surface active sites and the porous structures are in favor of ion diffusion and oxygen escape. The monochromatic incident photo-to-electron conversion efficiency (IPCE) measured at 1.0 V vs. RHE of $\text{BiVO}_4/\text{NiFe-LDH}$ is about 4.3 times that of the pristine BiVO_4 , reaching up to 56% at 450 nm and varying between 54%–56% at 400–450 nm. The profiles of all these IPCE

curves are consistent with the UV-vis absorption spectrum of BiVO_4 . These results further confirm that only BiVO_4 acts as a visible light responsive photocatalyst, and the visible light absorption by NiFe-LDH cannot drive the PEC water splitting.

Notably, the improved photocurrent and water oxidation kinetics of $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode originate from the increased charge separation efficiency on the surface of the photoanode [8]. It is well known that the oxidation of sulfite is thermodynamically and kinetically more facile than that of water [13,15]. The PEC performance is also examined in the presence of $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_3$ which is served as a hole scavenger. Fig. 5a shows the LSV curves of the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode in $0.1 \text{ mol L}^{-1} \text{ KHCO}_3$ with and without Na_2SO_3 as a hole scavenger. The efficiency of surface charge separation is determined by the gap between the two LSV curves of water and Na_2SO_3 oxidation. As the NiFe-LDH nanosheet arrays are introduced as OEC, the gap between $J_{\text{H}_2\text{O}}$ and $J_{\text{Na}_2\text{SO}_3}$ is greatly reduced. For a quantitative analysis, the surface charge separation efficiency (η_{surf}) is determined with the following equation: $\eta_{\text{surf}} = J_{\text{H}_2\text{O}}/J_{\text{sulfite}}$. The calculated efficiencies presented in Fig. 5b indicate that the η_{surf} for the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode is 2.2 times higher than that of the pristine BiVO_4 photoanode at 1.23 V vs. RHE . These results suggest that the improved photocurrent and lowering onset potential of the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode over pristine BiVO_4 photoanode is attributed to the improved surface charge separation efficiency [8].

Effect of the electrolyte on the PEC performance of $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode

It is well known that the alkaline condition is favorable for promoting O_2 evolution. Previous reports have shown that

Figure 5 Charge separation efficiency of $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode. (a) LSV curves of the pristine BiVO_4 and $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode measured in $0.1 \text{ mol L}^{-1} \text{ KHCO}_3$ with (solid lines) and without (dashed lines) $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_3$ as a hole scavenger under AM 1.5G irradiation. (b) The charge separation efficiency (η_{surf}) on the surface of pristine BiVO_4 and $\text{BiVO}_4/\text{NiFe-LDH}$ photoanodes.

the LDHs can exhibit high electrocatalytic activity in alkaline conditions with pH 13 and 14 [21,22,36]. However, the LSV curves in Fig. 6a show that the BiVO₄/NiFe-LDH photoanode exhibits the worst PEC performance in KOH electrolyte compared with the K₂SO₄ and KHCO₃ electrolyte. Noticeably, as displayed in Fig. 6b, after light irradiation for 3 h, about 94% of initial stable state photocurrent is maintained in KHCO₃, while this value is 51% in K₂SO₄

and less than 10% in KOH. The optical photographs of the BiVO₄/NiFe-LDH photoanodes after 3 h PEC test also show that the photoanode turns black from light yellow in KOH, while there is no obvious change in other electrolytes. After dark for a time interval of several minutes, the photoanodes were illuminated again. The LSV curves before and after *I-t* test in Fig. 6d–f show that the photocurrent is sharply decreased in KOH but slightly decreased in KHCO₃, which

Figure 6 Effect of the electrolyte on the PEC performance of the BiVO₄/NiFe-LDH photoanode. (a) The LSV curves, (b) *I-t* curves at a potential of 1.0 V vs. RHE under light illumination for the BiVO₄/NiFe-LDH photoanode in 0.1 mol L⁻¹ KHCO₃ (black), 0.1 mol L⁻¹ K₂SO₄ (red) and 0.1 mol L⁻¹ NaOH (blue). (c) The optical photographs of the BiVO₄/NiFe-LDH photoanode after PEC test for 3 h in different electrolytes: (I) reference sample without test; (II) 0.1 mol L⁻¹ KHCO₃; (III) 0.1 mol L⁻¹ K₂SO₄; (IV) 0.1 mol L⁻¹ KOH. (d–f) The LSV curves of the BiVO₄/NiFe-LDH photoanode before and after PEC test for 3 h in (d) 0.1 mol L⁻¹ KHCO₃, (e) 0.1 mol L⁻¹ K₂SO₄ and (f) 0.1 mol L⁻¹ KOH.

are in line with the results of I - t curves in Fig. 6b. These results clearly reveal the superiority of KHCO_3 weak alkaline solution as the supporting electrolyte for better PEC performance on the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode.

To understand the role of KHCO_3 electrolyte in improving the PEC performance of $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode, we explored the stability of pristine BiVO_4 and $\text{BiVO}_4/\text{NiFe-LDH}$ photoanodes in above three electrolytes, respectively. As shown in Fig. S15a, on one hand, after soaking in the above electrolytes for one day, the porous BiVO_4 photoanode is stable in KHCO_3 and K_2SO_4 solution, while it is gradually etched or metamorphic by KOH solution, as indicated by the brown color of photoanode after soaking in KOH solution. The LSV curves of the porous BiVO_4 (Fig. S15b) after soaking in the above three electrolytes show that the PEC activity of the porous BiVO_4 photoanode could keep unchanged in KHCO_3 solution, while it is decreased in K_2SO_4 and KOH solution, especially sharp decreased in KOH solution. These results suggest that the porous BiVO_4 photoanode is stable in KHCO_3 weak alkaline solution [11,53]. The instability of $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode in KOH may originate from the instability of pristine BiVO_4 photoanode. On the other hand, owing to the water oxidation reaction process involving the removal of protons, it is imaginable that slow oxidation reaction kinetics may be not only blocked by the inappropriate modification of OECs, but also closely interrelated with the poor proton-accepting capability of the supporting electrolyte [54,55]. In K_2SO_4 neutral electrolyte, the diffusion process of protons is slow so that the photogenerated holes accumulation and the slow water oxidation kinetics of photoanodes are unavoidable [10,56,57]. For the BiVO_4 photoanode, the photogenerated hole accumulation usually results in the recombination of photogenerated carriers, which is unfavourable for water

splitting [13]. Comparing with K_2SO_4 , the mechanism of KHCO_3 weak alkaline electrolyte in promoting the PEC performance of $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode can be explained by its better proton-accepting ability. The reasons of the bad PEC stability and activity of $\text{BiVO}_4/\text{NiFe-LDH}$ in K_2SO_4 may be attributed to the following two points [10,55–57]: (1) the poor chemical stability of NiFe-LDH due to the acidic neighbouring environment after O_2 evolution; (2) the kinetic bottleneck of water oxidation associated with low protons removing rate in K_2SO_4 electrolyte. The above results suggest that it is important to facilitate the kinetics of water oxidation, which is associated with both the OECs and electrolytes. Through the cooperative optimization of both OECs and electrolytes, we can achieve the efficient and stable O_2 evolution on photoanodes.

Water photoelectrolysis on $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode

To verify that the measured photocurrent of the photoanode originates from water splitting rather than any other undesired side reaction, the OER and hydrogen evolution reaction (HER) was examined. The photoanode is held at 1.0 V vs. RHE under AM 1.5G (100 mW cm^{-2}). The PEC water splitting test was carried out more than 30 h to make sure its long-term stability. The amount of H_2 evolved from counter electrode (Pt foil) and O_2 evolved from the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode were measured by the gas chromatography, respectively. As shown in Fig. 7a, the rate for O_2 evolution at the surface of $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode is $29.6 \mu\text{mol h}^{-1} \text{ cm}^{-2}$, and there is no obvious decay in this performance at the initial 3 h. This performance is comparable with Mn-doping $\text{Fe}_2\text{O}_3/\text{NiFe-LDH}$ ($9.18 \mu\text{mol h}^{-1} \text{ cm}^{-2}$, 2 h) [9], Co-Pi/GCN/ BiVO_4 ($25.5 \mu\text{mol h}^{-1} \text{ cm}^{-2}$, 2 h) [28] and $\text{Fe}_2\text{O}_3/\text{FeOOH}$ ($10.1 \mu\text{mol h}^{-1} \text{ cm}^{-2}$, 70 h) [7] photocells. In addition, the high PEC activity of $\text{BiVO}_4/$

Figure 7 Water photoelectrolysis on the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode. (a) Detection of O_2 and H_2 in initial 3 h, (b) I - t curve at a potential of 1.0 V vs. RHE under light illumination for the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode. Dashed line in (a) is the theoretical result based on the number of transferred electrons. The insert of (b) is the cross-section view SEM image of the $\text{BiVO}_4/\text{NiFe-LDH}$ photoanode after 30 h PEC test.

NiFe-LDH photoanode can be lasted over 30 h observed from the *I-t* curve for water splitting as shown in Fig. 7b. The SEM image of BiVO₄/NiFe-LDH photoanode after 30 h long-term test (inset of Fig. 7b) shows that the morphology of BiVO₄/NiFe-LDH photoanode almost does not change. This can be attributed to the high efficient porous BiVO₄ photoanode and the good contact between the NiFe-LDH nanosheet arrays and porous BiVO₄ photoanode [7,13]. The gas generation rates of H₂ and O₂ for the BiVO₄/NiFe-LDH-Pt PEC device is close to 2:1 (Fig. 7a). The Faradic efficiencies of the BiVO₄/NiFe-LDH photoanode are 93% and 90%, determined by the measurement of the evolved H₂ and O₂ gas, respectively. The numbers are lower than the expected (100%), which may be the result of the gas leak during measurement [30]. This indicates that nearly all the charge carriers in the circuit are used for water splitting. Thus, these results suggest that the synergistic effect of the porous BiVO₄ photoanode and nanostructure NiFe-LDH makes the integrated BiVO₄/NiFe-LDH photoanode not only shorten the transport distances for the charge carriers but also passivate some surface defects, efficiently suppressing the bulk recombination and surface recombination of the photogenerated charges.

More importantly, the efficient and stable PEC performance of BiVO₄/NiFe-LDH in KHCO₃ makes it a good candidate for fabricating photoanode-driven PEC system which is versatile in fuel products due to the availability of various cathode electrocatalysts. For example, considering that the electrocatalysts of CO₂ reduction are active in CO₂-saturated KHCO₃ (or NaHCO₃) solution, the electrocatalysts which can control the efficiency and selectivity of CO₂ reduction, such as Cu nanowire array electrodes which have shown efficient CO₂ reduction [58], can be selected as cathode to fabricate BiVO₄/NiFe-LDH (photoanode)-cathode PEC device, as displayed in Fig. S16. High yield and selectivity of hydrocarbons may be obtained from CO₂ and water through fabricating BiVO₄/NiFe-LDH with the low onset potential and high photocurrent as photoanode and appropriate electrocatalysts of CO₂ reduction as cathodes at lower applied potential. The efforts to explore the relationship between yield or selectivity of hydrocarbons and applied potential are underway in our group.

Effect of ternary NiFeCo-LDH on porous BiVO₄ photoanode

Impressively, the adjustment of metal ions in LDHs may provide more active sites and enhance the surface reaction kinetics of LDH [24]. Incorporation of a third metal ion has been proposed as a strategy to improve the activity of NiFe-LDH by affecting the conductivity and the structure

of the binary catalyst [23,24,59]. Thus, we select Co²⁺ as a third metal ion to synthesize ternary NiFeCo-LDH anchoring on porous BiVO₄ photoanode (BiVO₄/NiFeCo-LDH). As shown in Fig. 8, the PEC activity of the as-fabricated BiVO₄/NiFeCo-LDH photoanode can be further enhanced compared to the BiVO₄/NiFe-LDH photoanode, with an AM 1.5G photocurrent of 4.45 mA cm⁻² at 1.23 V vs. RHE, which is the highest among un-doped BiVO₄-based photoanodes known to date. The dark LSV curve of the BiVO₄/NiFeCo-LDH for water oxidation shows better current compared with the BiVO₄/NiFe-LDH (Fig. S17a). In addition, a smaller diameter is observed in the EIS curve of BiVO₄/NiFeCo-LDH photoanode under illumination relative to BiVO₄/NiFe-LDH photoanode (Fig. S17b), which means that the resistance of NiFeCo-LDH/electrolyte interface is much smaller than the NiFe-LDH/electrolyte interface. These results suggest that the porous BiVO₄ photoanodes decorated with the ternary LDH can obtain better PEC performance. It is believed that the PEC performance of the porous BiVO₄ photoanode with ternary LDH as OEC can be further enhanced through searching more appropriate third metal ions and adjusting the optimal ratio of metal ions incorporating into NiFe-LDH.

CONCLUSIONS

In summary, we have presented that the BiVO₄/NiFe-LDH photoanode with NiFe-LDH nanosheet arrays as the OEC can effectively promote charge separation and the surface reaction kinetics of the porous BiVO₄ photoanode simultaneously, benefitting from the synergistic effect of porous BiVO₄ film as photon absorber and the nanostructured NiFe-LDH as OEC. The as-prepared BiVO₄/NiFe-LDH photoanode with the Ni/Fe ratio of 3:1 shows photocurrent density of 4.02 mA cm⁻² at 1.23 V vs. RHE, which is 2.8 times higher than that of the pristine BiVO₄. An improved ABPE of 1.07% at 0.75 V vs. RHE can be achieved. Moreover, the gas generation rate of H₂ and O₂ for the BiVO₄/NiFe-LDH photoanode-Pt PEC device is close to 2:1, and the O₂ evolution rate at the surface BiVO₄/NiFe-LDH photoanode is as high as 29.6 μmol h⁻¹ cm⁻² at the initial 3 h. The high activity for water oxidation can be lasted for over 30 h in KHCO₃ weak alkaline electrolyte. Undoubtedly, the composite photoanode is a good candidate for fabricating BiVO₄/NiFe-LDH (photoanode)-cathode PEC device which is versatile in fuel products due to the availability of various cathode electrocatalysts. The effect of electrolytes on PEC performance of BiVO₄/NiFe-LDH photoanode is also investigated. It demonstrates that the efficient and stable O₂ evolution on

Figure 8 Effect of ternary NiFeCo-LDH on porous BiVO₄ photoanode. (a) The LSV curves, (b) ABPE curves, (c) LSV behavior under chopped light illumination, (d) *I-t* curves at a potential of 1.0 V vs. RHE under chopped light illumination for the pristine BiVO₄, BiVO₄/NiFe-LDH and BiVO₄/NiFeCo-LDH photoanodes.

photoanodes can be achieved through the cooperative optimization of both OECs and the electrolytes. Interestingly, the performance of the as-fabricated composite photoanode for PEC water splitting can be further enhanced, with a photocurrent density of 4.45 mA cm⁻² at 1.23 V vs. RHE, through incorporating a certain amount of Co²⁺ cation into NiFe-LDH as OEC. This value is the highest among un-doped BiVO₄-based photoanodes known to date. The adjustable species and ratios of metal ions in LDHs make the LDHs the promising candidates as OECs in PEC devices. Considering that the outstanding performance can be achieved through using un-doped porous BiVO₄ film as only photon absorber and nanostructured LDHs as OECs, further improvement of the PEC cell efficiency is expected when various strategies of tuning the compositions [16] or forming heterojunctions [29,40,60] and tandem cells [18,46] are used to enhance absorption and photogenerated carriers' separation of semiconductors. Therefore, our work could provide a new strategy to fabricate composite photoanodes effectively promoting charge utilization and the surface reaction kinetics for PEC water splitting and

other solar-to-fuel energy conversion applications.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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水滑石纳米片阵列/多孔BiVO₄复合光阳极用于高效光电催化分解水

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摘要 可再生清洁能源的不断探索推动了高活性的光电催化分解水材料的开发. 然而, 提高光电材料的载荷子利用率仍是材料与光电化学领域的一个重要挑战. 本文报道了一种简单的方法来构筑由多孔BiVO₄薄膜作为光吸收剂和水滑石(LDH)纳米片阵列作为产氧助催化剂(OECs)的复合光阳极. 由于多孔BiVO₄膜高效的电荷分离效率和LDH纳米片阵列优异的水氧化活性协同效应, 所制备的BiVO₄/NiFe-LDH光阳极展现出优异的光电催化分解水性能, 在1.23 V(相对于可逆氢电极(RHE))下光电流密度达4.02 mA cm⁻². 此外, BiVO₄/NiFe-LDH光阳极表面的O₂产生速率高达29.6 μmol h⁻¹ cm⁻², 并且活性可以维持30小时以上. 此外, 通过将一定量的Co²⁺离子掺杂到NiFe-LDH中作为OEC, 可以进一步增强复合光阳极的性能. 在1.23 V(相对于RHE)下, 光电流密度高达4.45 mA cm⁻², 该值是目前报道的基于未掺杂BiVO₄光阳极的最高值.