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# Fabrication of porous nanoflake BiMO<sub>x</sub> (M = W, V, and Mo) photoanodes *via* hydrothermal anion exchange†

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Most Bi-based photoelectrodes have suitable band gaps and can effectively promote the water oxidation reaction. However, simple preparation methods for Bi-based binary metal oxides as photoanodes are scarce. This paper describes a simple hydrothermal anion exchange method to synthesize Bi-based binary metal oxides with controlled morphologies. This synthesis process uses BiOI as the template and Bi source, which is eventually converted to Bi-based porous nanoflake photoanodes upon reaction with MO<sub>x</sub> (M = W, V, and Mo)-containing precursors. The photoanodes show well-shaped porous nanoflake morphologies and exhibit impressive photoelectrochemical properties compared to Bi-based photoanodes synthesized by conventional methods. These three samples possess long-term stability under solar irradiation and show considerable photocurrent for sulfite oxidation.

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## 1. Introduction

Photoelectrochemical (PEC) water splitting into hydrogen, driven by visible light, has attracted worldwide attention as a promising method to use solar energy.<sup>1–4</sup> In the aspect of photoelectrode preparation, there are many requirements, such as a simple process and better controllability. Specifically, obtaining a large specific area and good crystallinity is sometimes a major concern in choosing the preparation method. For example, TiO<sub>2</sub> photoelectrodes formed by various preparation methods exhibit different PEC performances. Zhang *et al.* synthesized TiO<sub>2</sub> thin film electrodes using a sol-gel method and the maximum photocurrent value was just 0.5 μA cm<sup>-2</sup>.<sup>5</sup> Another *in situ* growth method that formed branched TiO<sub>2</sub> nanorods on fluorine-doped tin oxide (FTO) led to a much higher photocurrent of 1.1 mA cm<sup>-2</sup> at 0.0 V *vs.* Ag/AgCl.<sup>6</sup> The improved photocurrent was ascribed to the fine crystallinity and increased surface area due to the better transportation of charge carriers and more reactive sites.

Compared with single metal oxides, very few simple and effective preparation methods of binary metal oxides have been developed. In the past decades, binary metal oxides containing Bi(III) have been identified as promising semiconductor electrodes in solar energy conversion.<sup>7–9</sup> BiMO<sub>x</sub> (M = V, C, P, W and

Mo) has been widely applied in photodegradation and photoelectrochemical reactions.<sup>10–14</sup> Among these popular Bi-based semiconductors, Bi<sub>2</sub>WO<sub>6</sub>, BiVO<sub>4</sub>, and Bi<sub>2</sub>MoO<sub>6</sub> can absorb visible light and have suitable band gaps to drive the water oxidation reaction to generate H<sub>2</sub> and reduce CO<sub>2</sub> to form other useful fuels.<sup>15</sup> Compared to the benchmark TiO<sub>2</sub> which only responds to UV light, most Bi-based binary metal oxides can drive the water oxidation reaction under visible light irradiation.<sup>8,16</sup> The common preparation methods for Bi-based binary metal oxides are dip-coating and spin-coating. However, the photoelectrodes synthesized by these conventional preparation methods show a planar structure and have a smaller specific area.<sup>17,18</sup> Developing new preparation methods for BiMO<sub>x</sub> photoanodes is an effective approach to enhance the photoactivity. For example, Bi<sub>2</sub>WO<sub>6</sub> (2.7–2.8 eV) is a photocatalyst for PEC water oxidation and photodegradation under visible light irradiation.<sup>19,20</sup> Generally, Bi<sub>2</sub>WO<sub>6</sub> thin films are synthesized by directly coating Bi<sub>2</sub>WO<sub>6</sub> nanoparticles on an electrode substrate using spin-coating,<sup>21</sup> dip-coating,<sup>22</sup> or electrostatic self-assembly deposition.<sup>23</sup> However, these existing coating techniques often result in compact films with relatively low activities due to the small specific area.<sup>24</sup> Only limited success has been reported for the direct synthesis of Bi<sub>2</sub>WO<sub>6</sub> films. Recently, Zhang *et al.* developed a hard-template-directed sol-gel method to prepare porous Bi<sub>2</sub>WO<sub>6</sub> thin films.<sup>25</sup> Subsequently, they synthesized a Bi<sub>2</sub>WO<sub>6</sub> photonic crystal film for visible-light-driven activity using a similar method.<sup>26</sup> They synthesized Bi<sub>2</sub>WO<sub>6</sub> photoelectrodes with a large specific area to enhance the light absorption. Most recently, Choi and co-workers prepared nanoporous BiVO<sub>4</sub> electrodes by first annealing BiOI and a vanadium precursor in air.<sup>27</sup> They created the BiVO<sub>4</sub> porous photoanodes by directly forming the sample on the

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† Electronic supplementary information (ESI) available: Experimental SEM images and the amount of hydrogen evolution of Bi<sub>2</sub>WO<sub>6</sub>, BiVO<sub>4</sub>, and Bi<sub>2</sub>MoO<sub>6</sub> photoelectrodes. See DOI: 10.1039/c6sc01803c



substrate to enhance the crystallinity. We believe that if Bi-based electrodes have both ordered morphology and good crystallinity, their PEC performances will be further improved.

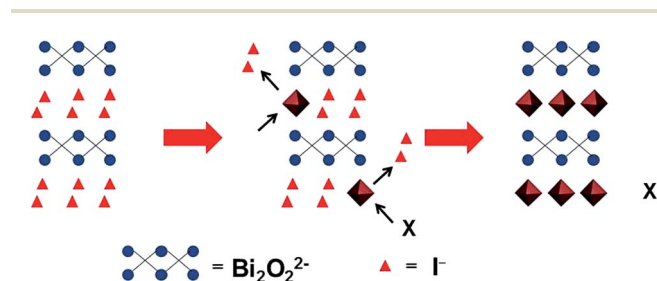
This paper describes an effective hydrothermal anion exchange route based on BiOI substrates to fabricate porous nanoflake electrodes of  $\text{Bi}_2\text{WO}_6$  (details in ESI†). This preparation method is unique in the sense that it can directly form the electrodes on the substrate, *e.g.*, *via* an *in situ* growth process, and results in  $\text{Bi}_2\text{WO}_6$  electrodes with ordered morphology. To verify the universality in dendritic Bi-based electrodes, we also prepared  $\text{BiVO}_4$  ( $\sim 2.4$  eV) and  $\gamma$ -type  $\text{Bi}_2\text{MoO}_6$  ( $\sim 2.5$  eV) porous nanoflakes with this hydrothermal anion exchange route.

## 2. Results and discussion

### 2.1 Crystal structure, morphology, and optical characterization of $\text{Bi}_2\text{WO}_6$ , $\text{BiVO}_4$ , and $\text{Bi}_2\text{MoO}_6$

Anion exchange was originally used for forming photocatalyst nanoparticles with a core-shell structure. Alivisatos *et al.* used an anion exchange process to form single-crystalline hollow ZnS nanoparticles.<sup>28</sup> Unlike cation exchange, the anion exchange in this work is accompanied by the nanoscale Kirkendall effect, yielding hollow nanoparticles. Meanwhile, it was thought that the anion exchange method could be extended to other binary or tertiary nanoparticles to produce hollow nanostructures. Then, Huang *et al.* synthesized  $\text{Bi}_2\text{WO}_6$  hollow microspheres with a similar process, and used the  $\text{Bi}_2\text{WO}_6$  microspheres to adsorb and reduce  $\text{CO}_2$  to methanol under visible light irradiation.<sup>29</sup> In this paper, we extend this method to synthesize Bi-based photoanodes. First, the BiOI nanoflake arrays are electrodeposited on a FTO substrate. Then, the  $\text{I}^-$  ions are replaced by  $\text{WO}_4^{2-}$  during a hydrothermal process. Finally, the  $\text{Bi}_2\text{WO}_6$  electrodes are synthesized after annealing. Additionally,  $\text{WO}_4^{2-}$  can be replaced by  $\text{VO}_3^-$  or  $\text{MoO}_4^{2-}$  to synthesize  $\text{BiVO}_4$  and  $\text{Bi}_2\text{MoO}_6$  *via* this hydrothermal anion exchange reaction, which is a general and effective process for preparing Bi-based photoanodes with nanoflake morphology. The reaction mechanism of the anion exchange is shown in Scheme 1.

Field-emission scanning electron microscopy (FESEM) images reveal that the three Bi-based binary metal oxides have a flake-like nanostructure (Fig. 1). As the starting templates, the BiOI films show a nanoflake morphology (Fig. 1a) with a 2  $\mu\text{m}$  height (Fig. 1a and S1a†). After the following hydrothermal



**Scheme 1** Schematic illustration of the hydrothermal anion exchange: from BiOI to Bi-based binary metal oxide.  $X = \text{WO}_4^{2-}$ ,  $\text{VO}_3^-$  or  $\text{MoO}_4^{2-}$ .



**Fig. 1** FESEM images of (a) BiOI, (b)  $\text{Bi}_2\text{WO}_6$ , (c)  $\text{BiVO}_4$ , and (d)  $\text{Bi}_2\text{MoO}_6$ .

anion exchange, the Bi-based binary metal oxides show irregular porous nanostructures (Fig. 1b–d), while the height is retained and is the same as the BiOI template (Fig. S1b–d†). The specific surface areas of the three Bi-based photoelectrodes ( $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$  and  $\text{Bi}_2\text{MoO}_6$ ) are about  $13.4 \text{ m}^2 \text{ g}^{-1}$ ,  $27.3 \text{ m}^2 \text{ g}^{-1}$  and  $30.0 \text{ m}^2 \text{ g}^{-1}$  respectively. The specific surface areas were calculated from the isotherms using the Brunauer–Emmett–Teller (BET) method and P-25 nanoparticles were used as the internal standard (details in ESI†).

The crystallinity of the resulting  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$ , and  $\text{Bi}_2\text{MoO}_6$  electrodes is shown in the X-ray diffraction (XRD) patterns (Fig. 2). All of the three samples are well crystallized, and are consistent with orthorhombic  $\text{Bi}_2\text{WO}_6$  (JCPDF 39-0256), monoclinic  $\text{BiVO}_4$  (JCPDF 83-1699), and orthorhombic  $\text{Bi}_2\text{MoO}_6$  (JCPDF 77-1246). The atomic Bi : W, Bi : V, and Bi : Mo ratios in the  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$ , and  $\text{Bi}_2\text{MoO}_6$  electrodes were confirmed to be the expected atomic metal ratios (ESI, Table S1†) by energy-dispersive X-ray spectroscopy (EDS). Fig. S2† shows



**Fig. 2** XRD patterns of BiOI,  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$  and  $\text{Bi}_2\text{MoO}_6$ . Peaks marked with an asterisk originate from the FTO substrate.



transmission electron microscopy images of the three samples. The high-resolution transmission electron microscopy (HRTEM) images indicate that the fringe spacing values are 0.2735 nm, 0.3089 nm and 0.3125 nm, which are consistent with the (200) plane of  $\text{Bi}_2\text{WO}_6$ , the (112) plane of  $\text{BiVO}_4$ , and the (131) plane of  $\text{Bi}_2\text{MoO}_6$ , respectively. This result is in accordance with the XRD patterns (Fig. 2).

The UV-Vis absorption spectra of the  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$ , and  $\text{Bi}_2\text{MoO}_6$  electrodes (Fig. 3a) show that the absorption edges of the three Bi-based photoelectrodes were 430 nm, 505 nm, and 480 nm. According to the Tauc plots (Fig. S3†), the band gaps ( $E_g$ ) for the  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$ , and  $\text{Bi}_2\text{MoO}_6$  porous nanoflakes were estimated to be 2.87, 2.46, and 2.52 eV, respectively, in accordance with a previous study about Bi-based binary metal oxides.<sup>28</sup>

Furthermore, the conduction band (CB) and valence band (VB) positions of the three Bi-based semiconductors at the point of zero charge can be calculated. The absolute electronegativity ( $X$ ) of  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$ , and  $\text{Bi}_2\text{MoO}_6$  can be estimated to be 6.36, 6.04 and 6.31 from the literature.<sup>30–32</sup> The band gap energy ( $E_g$ ) can be estimated from the Tauc plots shown in Fig. S3† and Table S4.† The conduction band edge of a semiconductor can be estimated using an equation as follows:<sup>30</sup>

$$E_{\text{VB}}^0 = X - 4.5 + E_g/2$$

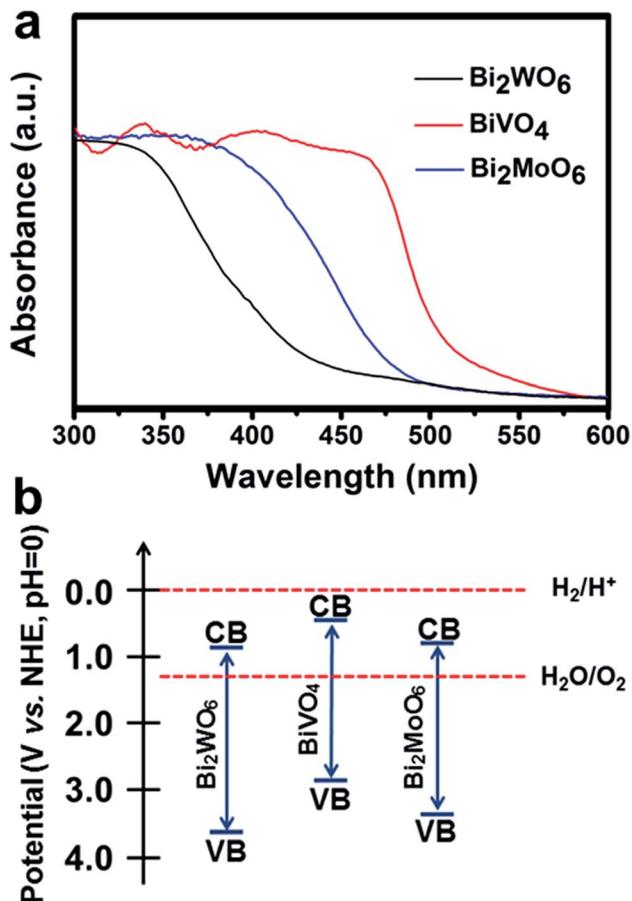


Fig. 3 UV-Vis absorption spectra (a) and schematic band diagrams (b) of  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$  and  $\text{Bi}_2\text{MoO}_6$ .

where 4.5 eV is the energy of free electrons on the hydrogen scale. The points of zero charge of the three samples ( $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$ , and  $\text{Bi}_2\text{MoO}_6$ ) are 8.7, 3.0 and 6.1, respectively.<sup>31,33,34</sup> Therefore, the calculated valence band edge at the point of zero charge can be corrected to pH 0 by the following method:

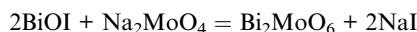
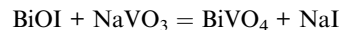
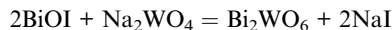
$$E_{\text{VB}} = E_{\text{VB}}^0 + \text{pH}_{\text{zpc}} \times 0.059$$

Then, the valence band edge can be calculated using an equation as follows:

$$E_{\text{CB}} = E_{\text{VB}} - E_g$$

## 2.2 Reaction mechanism of the hydrothermal anion exchange

Upon the introduction of  $\text{Na}_2\text{WO}_4$ ,  $\text{NaVO}_3$ , and  $\text{Na}_2\text{MoO}_4$  followed by hydrothermal treatments, the  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$ , and  $\text{Bi}_2\text{MoO}_6$  thin films were formed using the  $\text{BiOI}$  nanoflakes as templates, during which  $\text{I}^-$  ions were replaced by  $\text{WO}_4^{2-}$ ,  $\text{VO}_3^-$ , and  $\text{MoO}_4^{2-}$ . The chemical equations of the anion exchange process can be shown as follows:



As the diffusion rates of the  $\text{I}^-$  ions and the  $\text{WO}_4^{2-}$ ,  $\text{VO}_3^-$ , and  $\text{MoO}_4^{2-}$  ions are unequal, a continuous ion exchange will lead to a porous morphology. To verify the binary hypothesis, an inductively coupled plasma optical emission spectroscopy (ICP-OES) study was employed. Taking  $\text{Bi}_2\text{WO}_6$  as an example, a time-dependent ICP-OES study (Table S2†) shows the concentration of  $\text{I}^-$  ions in the residue after 0.5 h, 1 h, 2 h, and 3 h of hydrothermal anion exchange. As the anion exchange proceeds, the concentration of  $\text{I}^-$  ions increases at first and then reaches its maximum value after 2 h at 120 °C. In order to rule out the influence of  $\text{I}^-$  during the ICP-OES measurement, we put  $\text{BiOI}$  on FTO in the deionized water during the anion exchange and monitored the concentration of  $\text{I}^-$  ions in the residue after 0.5 h, 1 h, 2 h, and 3 h (Table S3†). The results indicate that the dissolution of  $\text{BiOI}$  can be ignored during the anion exchange process. Based on the morphology change from  $\text{BiOI}$  nanoflakes to  $\text{Bi}_2\text{WO}_6$  porous nanoflakes, two effects of the  $\text{BiOI}$  template could be identified in the ion exchange process: (i) the Bi source for  $\text{Bi}_2\text{WO}_6$  and (ii) the template for the nanoflake morphology.

To further explore the origin of the morphological change during the hydrothermal anion exchange process, FESEM images and XRD patterns of the  $\text{Bi}_2\text{WO}_6$  porous nanoflakes were obtained. Fig. S4† shows the XRD patterns of the  $\text{Bi}_2\text{WO}_6$  porous nanoflakes grown on FTO at 120 °C for 0.5, 1, and 2 h. From the XRD patterns, the peaks associated with the  $\text{BiOI}$  nanoflakes



faded away with increasing exchange time, such as the peaks at  $28.11^\circ$  and  $45.28^\circ$ . On the contrary, the peaks associated with the  $\text{Bi}_2\text{WO}_6$  porous nanoflakes gradually appeared with increasing growth time, such as the peaks at  $31.61^\circ$ ,  $46.88^\circ$  and  $55.68^\circ$ . The morphology change during the reaction is shown in Fig. S5 (details in the ESI†). Continuous anion exchange is the reason for the morphological change.

### 2.3 PEC water oxidation performances of $\text{Bi}_2\text{WO}_6$ , $\text{BiVO}_4$ , and $\text{Bi}_2\text{MoO}_6$

The PEC performance of the Bi-based electrodes under AM 1.5G ( $100 \text{ mW cm}^{-2}$ ) irradiation is examined (details in the ESI†). Fig. 4a shows the photocurrent density vs. potential ( $I$ - $V$ ) curves for the  $\text{Bi}_2\text{WO}_6$  porous nanoflakes in a  $0.1 \text{ M Na}_2\text{SO}_4$  aqueous electrolyte ( $\text{pH} = 6.8$ ). The photocurrent of the  $\text{Bi}_2\text{WO}_6$  porous nanoflakes is  $41 \mu\text{A cm}^{-2}$  at a potential of  $1.00 \text{ V vs. RHE}$ , which is about four times larger than the values reported.<sup>35,36</sup> When  $1 \text{ M Na}_2\text{SO}_3$  was added to the electrolyte as a hole scavenger, a remarkable increase in the photocurrent of  $130 \mu\text{A cm}^{-2}$  at  $1.0 \text{ V vs. RHE}$  was observed, with an onset of  $0.30 \text{ V vs. RHE}$  (Fig. 4a). It is observed that surface kinetics is an important factor for  $\text{Bi}_2\text{WO}_6$  electrodes.

The PEC performances of  $\text{BiVO}_4$  and  $\text{Bi}_2\text{MoO}_6$  were also measured under the same conditions as  $\text{Bi}_2\text{WO}_6$ . The photocurrent of the  $\text{BiVO}_4$  porous nanoflakes is  $200 \mu\text{A cm}^{-2}$  at a potential of  $1.00 \text{ V vs. RHE}$  (Fig. 4b), while the samples synthesized by  $\text{BiVO}_4$  nanoparticles on FTO reached only  $75 \mu\text{A cm}^{-2}$  at the same potential.<sup>37,38</sup> For the sulfite oxidation reaction, the  $\text{BiVO}_4$  photoelectrodes show a considerably high value of  $1280 \mu\text{A cm}^{-2}$  at  $1.0 \text{ V vs. RHE}$ , with an onset potential of  $0.19 \text{ V vs. RHE}$ . The porous nanoflake morphology of our  $\text{BiVO}_4$  photoelectrodes was completely different compared to other  $\text{BiVO}_4$  nanostructures. For photoelectrodes, an ordered morphology can increase the specific area and then provide more exposed reaction active sites. Compared with

conventional preparation methods, our  $\text{BiVO}_4$  material has an ordered nanoflake morphology resulting from the anion exchange process.

Fig. 4c shows the photocurrent-potential plots of the  $\text{Bi}_2\text{MoO}_6$  electrode. Compared with other reported  $\text{Bi}_2\text{MoO}_6$  photoanodes, our  $\text{Bi}_2\text{MoO}_6$  porous nanoflakes have better PEC performances.<sup>18,34</sup> The maximum photocurrent of  $\text{Bi}_2\text{MoO}_6$  photoanodes formed by the existing preparation methods was just about  $13 \mu\text{A cm}^{-2}$  under visible light irradiation which limited the application of  $\text{Bi}_2\text{MoO}_6$  photoanodes in PEC water oxidation reactions. The  $\text{Bi}_2\text{MoO}_6$  porous nanoflakes exhibit outstanding photoactivities compared to other  $\text{Bi}_2\text{MoO}_6$  photoanodes formed by the conventional preparation methods. The photocurrent values are still low compared to Choi's work.<sup>27</sup> This may be because there was less photocatalyst per unit area and so the PEC performances were reduced. However, our preparation method was more convenient and easier to control. During the process of forming the  $\text{BiVO}_4$  electrode, we used  $\text{NaVO}_3$  solution as the precursor which was environmentally friendly instead of vanadyl acetylacetonate.

Additionally, we have acquired the photoconversion efficiencies of the three samples (details in the ESI†). The photoconversion efficiencies of  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$  and  $\text{Bi}_2\text{MoO}_6$  were  $0.0117\%$  at  $0.82 \text{ V vs. RHE}$ ,  $0.0529\%$  at  $0.86 \text{ V vs. RHE}$  and  $0.0472\%$  at  $0.78 \text{ V vs. RHE}$  (Fig. 4d) respectively. These values have a little increase compared with the references. Although such improvements haven't essentially changed the poor photoactivities of Bi-based electrodes, it can be seen that the answer is not out of reach.

In order to explore the steady-state performance of the three Bi-based electrodes, the photocurrent-time ( $I$ - $t$ ) plots in a  $0.1 \text{ M Na}_2\text{SO}_4$  aqueous electrolyte ( $\text{pH} = 6.8$ ) under AM 1.5G irradiation at a constant applied bias of  $1.0 \text{ V vs. RHE}$  are shown in Fig. 5a. The  $I$ - $t$  plots show that the photocurrents of  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$ , and  $\text{Bi}_2\text{MoO}_6$  photoanodes remain stable at  $40$ ,  $150$ , and  $120 \mu\text{A cm}^{-2}$ , respectively, over a  $4 \text{ h}$  period. The good stability of semiconductors is an important precondition to be applied on a large scale. The  $I$ - $t$  plots indicate that all of the three Bi-based electrodes have potential application in PEC water splitting reactions.

The hydrogen evolution rate of the three samples were also measured in a  $0.1 \text{ M Na}_2\text{SO}_4$  aqueous electrolyte ( $\text{pH} = 6.8$ )

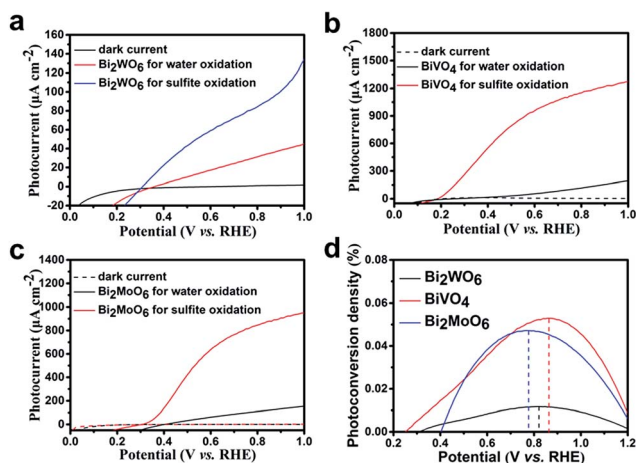


Fig. 4 Current-potential plots for (a)  $\text{Bi}_2\text{WO}_6$ , (b)  $\text{BiVO}_4$  and (c)  $\text{Bi}_2\text{MoO}_6$  under AM 1.5G ( $100 \text{ mW cm}^{-2}$ ) illumination in a  $0.1 \text{ M Na}_2\text{SO}_4$  aqueous electrolyte ( $\text{pH} = 6.8$ ) and  $1 \text{ M}$  sodium sulfite ( $\text{pH} = 6.3$ ); (d) photoconversion efficiency of the three samples for the water oxidation reaction.

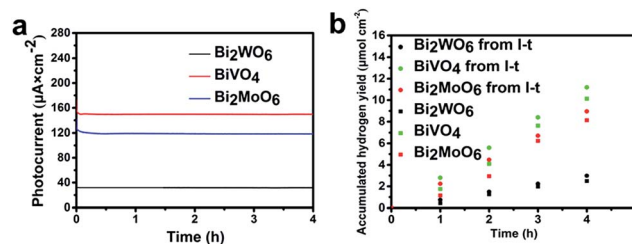


Fig. 5 (a) Photocurrent-time plots, and (b)  $\text{H}_2$  production from water splitting reaction in a PEC cell of  $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$  and  $\text{Bi}_2\text{MoO}_6$  under AM 1.5G ( $100 \text{ mW cm}^{-2}$ ) illumination in a  $0.1 \text{ M Na}_2\text{SO}_4$  aqueous electrolyte ( $\text{pH} = 6.8$ ). The constant potential of the photocurrent-time plots and  $\text{H}_2$  production in a PEC cell is  $1.0 \text{ V vs. RHE}$ .



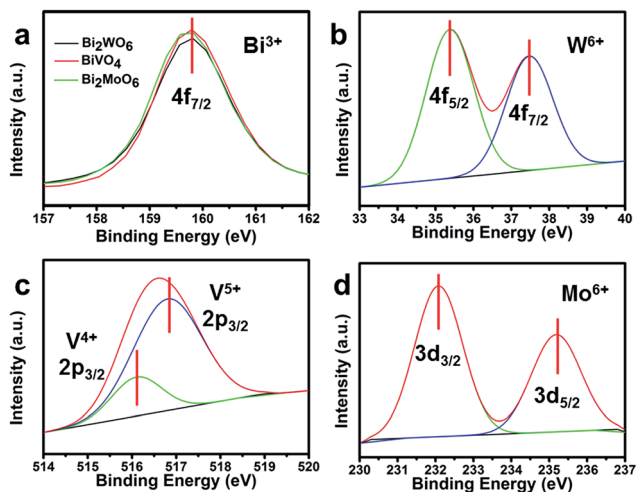


Fig. 6 (a) Bi4f XPS spectra of the three Bi-based photoelectrodes; (b) W4f XPS spectra of  $\text{Bi}_2\text{WO}_6$ ; (c) V2p XPS spectra of  $\text{BiVO}_4$ ; and (d) Mo3d XPS spectra of  $\text{Bi}_2\text{MoO}_6$ .

under AM 1.5G at a constant applied bias of 1.00 V vs. RHE (Fig. 5b and details in the ESI<sup>†</sup>). The  $\text{H}_2$  production rates of all three samples remain constant with average values of 0.625, 2.533, and 2.031  $\mu\text{mol h}^{-1} \text{cm}^{-2}$  during a 4 h reaction period. According to the photocurrent in Fig. 5a, the theoretical  $\text{H}_2$  production rates of all three samples ( $\text{Bi}_2\text{WO}_6$ ,  $\text{BiVO}_4$  and  $\text{Bi}_2\text{MoO}_6$ ) are 0.746, 2.798, and 2.238  $\mu\text{mol h}^{-1} \text{cm}^{-2}$  and the faradaic efficiencies are 83.8%, 90.6%, and 90.8%, respectively. The loss of faradaic efficiency may be because of the heat loss in the process of reaction and the system error of our devices.

X-ray photoelectron spectroscopy (XPS) was employed to characterize the valence state of the elements in the three Bi-based semiconductors. The XPS peak at 159.8 eV for the three Bi-based samples corresponds to the  $\text{Bi}4f_{7/2}$  spectrum (Fig. 6a).<sup>39,40</sup> For  $\text{Bi}_2\text{WO}_6$ , the characteristic peaks of  $\text{W}4f_{7/2}$  at 35.4 eV and  $\text{W}4f_{5/2}$  at 37.5 eV, are attributed to the W atoms in the 6+ oxidation state (Fig. 6b).<sup>40</sup> Similar with  $\text{Bi}_2\text{WO}_6$ , the characteristic peaks of  $\text{Mo}3d_{3/2}$  and  $\text{Mo}3d_{5/2}$  can be observed in Fig. 6d.<sup>41</sup> However, the asymmetric  $\text{V}2p_{3/2}$  signals were decomposed into two peaks at 516.1 and 516.8 eV for  $\text{BiVO}_4$  (Fig. 6c), attributable to the surface  $\text{V}^{4+}$  and  $\text{V}^{5+}$  species with  $\text{V}^{5+} : \text{V}^{4+}$  at about 79.8% : 20.2%.<sup>42</sup> The surface  $\text{V}^{4+}$  defect sites may be a part of the slow surface kinetics because the unsaturated valence ions can be re-oxidized during the water oxidation process.<sup>43</sup>

### 3. Conclusions

In summary, we have demonstrated a simple and characteristic preparation method of hydrothermal anion exchange to synthesize Bi-based porous nanoflake electrodes. Starting from  $\text{BiOI}$  templates, a  $\text{Bi}_2\text{WO}_6$  electrode can be easily prepared, which exhibits an ordered porous nanoflake morphology. Furthermore, the synthesis is based on an *in situ* growth method that can improve the crystallinity and the Bi-based electrodes have an ordered nanoflake morphology to increase

the surface area. The  $\text{BiVO}_4$  porous nanoflakes on the FTO coated glass exhibit an improved photocurrent of 200  $\mu\text{A cm}^{-2}$  for water oxidation and 1280  $\mu\text{A cm}^{-2}$  for sulfite oxidation at a potential of 1.00 V vs. RHE under AM 1.5G irradiation. The  $\text{Bi}_2\text{WO}_6$  and  $\text{Bi}_2\text{MoO}_6$  electrodes also exhibit enhanced PEC performance compared with the electrodes formed by the conventional preparation methods. All three samples have excellent stability and display the potential to be promising photoelectrodes for hydrogen production. This general preparation method can successfully synthesize Bi-based photoanodes with nanoflake morphology. This method can simplify the synthesis process of Bi-based photoelectrodes and promote their applications in PEC water oxidation reactions.

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### Notes and references

- P. Zhang, J. Zhang and J. Gong, *Chem. Soc. Rev.*, 2014, **43**, 4395–4422.
- F. E. Osterloh, *Chem. Soc. Rev.*, 2013, **42**, 2294–2320.
- A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253–278.
- J. Graetz, *Chem. Soc. Rev.*, 2009, **38**, 73–82.
- S. Yuan, J. Mu, R. Mao, Y. Li, Q. Zhang and H. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5719–5725.
- F. Su, T. Wang, R. Lv, J. Zhang, P. Zhang, J. Lu and J. Gong, *Nanoscale*, 2013, **5**, 9001–9009.
- S. M. Sun and W. Z. Wang, *RSC Adv.*, 2014, **4**, 47136–47152.
- N. Zhang, R. Ciriminna, M. Pagliaro and Y. J. Xu, *Chem. Soc. Rev.*, 2014, **43**, 5276–5287.
- N. Zhang, M. Q. Yang, S. Liu, Y. Sun and Y. J. Xu, *Chem. Rev.*, 2015, **115**, 10307–10377.
- H. Fu, S. Zhang, T. Xu, Y. Zhu and J. Chen, *Environ. Sci. Technol.*, 2008, **42**, 2085–2091.
- W. Xiong, D. Sikdar, M. Walsh, K. J. Si, Y. Tang, Y. Chen, R. Mazid, M. Weyland, I. D. Rukhlenko, J. Etheridge, M. Premaratne, X. Li and W. Cheng, *Chem. Commun.*, 2013, **49**, 9630–9632.
- F. Dong, W.-K. Ho, S. C. Lee, Z. Wu, M. Fu, S. Zou and Y. Huang, *J. Mater. Chem.*, 2011, **21**, 12428.
- G. Li, Y. Ding, Y. Zhang, Z. Lu, H. Sun and R. Chen, *J. Colloid Interface Sci.*, 2011, **363**, 497–503.
- L. Zhou, W. Wang and L. Zhang, *J. Mol. Catal. A: Chem.*, 2007, **268**, 195–200.
- F. Duan, Q. Zhang, Q. F. Wei, D. J. Shi and M. Q. Chen, *Progr. Chem.*, 2014, **26**, 30–40.



- 16 L. S. Zhang, H. L. Wang, Z. G. Chen, P. K. Wong and J. S. Liu, *Appl. Catal., B*, 2011, **106**, 1–13.
- 17 L.-W. Zhang, Y.-J. Wang, H.-Y. Cheng, W.-Q. Yao and Y.-F. Zhu, *Adv. Mater.*, 2009, **21**, 1286–1290.
- 18 Y. Man, R. Zong and Y. Zhu, *Acta Phys.-Chim. Sin.*, 2007, **23**, 1671–1676.
- 19 L. Zhang and Y. Zhu, *Catal. Sci. Technol.*, 2012, **2**, 694.
- 20 Y. H. Zhang, N. Zhang, Z. R. Tang and Y. J. Xu, *Chem. Sci.*, 2013, **4**, 1820–1824.
- 21 X. Zhao, Y. Wu, W. Yao and Y. Zhu, *Thin Solid Films*, 2007, **515**, 4753–4757.
- 22 J. P. Li, X. Zhang, Z. H. Ai, F. L. Jia, L. Z. Zhang and J. Lin, *J. Phys. Chem. C*, 2007, **111**, 6832–6836.
- 23 C. Ng, A. Iwase, Y. H. Ng and R. Amal, *J. Phys. Chem. Lett.*, 2012, **3**, 913–918.
- 24 G. Zhang, Z. Hu, M. Sun, Y. Liu, L. Liu, H. Liu, C.-P. Huang, J. Qu and J. Li, *Adv. Funct. Mater.*, 2015, **25**, 3726–3734.
- 25 N. Tian, Y. Zhang, H. Huang, Y. He and Y. Guo, *J. Phys. Chem. C*, 2014, **118**, 15640–15648.
- 26 L. Zhang, C. Baumanis, L. Robben, T. Kandiel and D. Bahnemann, *Small*, 2011, **7**, 2714–2720.
- 27 T. W. Kim and K. S. Choi, *Science*, 2014, **343**, 990–994.
- 28 J. Park, H. Zheng, Y. W. Jun and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2009, **131**, 13943–13945.
- 29 H. Cheng, B. Huang, Y. Liu, Z. Wang, X. Qin, X. Zhang and Y. Dai, *Chem. Commun.*, 2012, **48**, 9729–9731.
- 30 Q. Xiao, J. Zhang, C. Xiao and X. Tan, *Catal. Commun.*, 2008, **9**, 1247–1253.
- 31 X. Chang, T. Wang, P. Zhang, J. Zhang, A. Li and J. Gong, *J. Am. Chem. Soc.*, 2015, **137**, 8356–8359.
- 32 H. Huang, L. Liu, Y. Zhang and N. Tian, *J. Alloys Compd.*, 2015, **619**, 807–811.
- 33 C. Wang, L. Zhu, M. Wei, P. Chen and G. Shan, *Water Res.*, 2012, **46**, 845–853.
- 34 M. Long, W. Cai and H. Kisch, *Chem. Phys. Lett.*, 2008, **461**, 102–105.
- 35 S. Y. Chae, E. S. Lee, H. Jung, Y. J. Hwang and O.-S. Joo, *RSC Adv.*, 2014, **4**, 24032.
- 36 S. Lin, L. Liu, J. Hu, Y. Liang and W. Cui, *Appl. Surf. Sci.*, 2015, **324**, 20–29.
- 37 S. Sun, W. Wang, D. Li, L. Zhang and D. Jiang, *ACS Catal.*, 2014, **4**, 3498–3503.
- 38 D. Eisenberg, H. S. Ahn and A. J. Bard, *J. Am. Chem. Soc.*, 2014, **136**, 14011–14014.
- 39 Y. Ma, Y. Jia, L. Wang, M. Yang, Y. Bi and Y. Qi, *Phys. Chem. Chem. Phys.*, 2016, **18**, 5091–5094.
- 40 J. Tian, Y. Sang, G. Yu, H. Jiang, X. Mu and H. Liu, *Adv. Mater.*, 2013, **25**, 5075–5080.
- 41 B. Yuan, C. Wang, Y. Qi, X. Song, K. Mu, P. Guo, L. Meng and H. Xi, *Colloids Surf., A*, 2013, **425**, 99–107.
- 42 M. Wang, Q. Liu, Y. Che, L. Zhang and D. Zhang, *J. Alloys Compd.*, 2013, **548**, 70–76.
- 43 Y. Yang, Y. Ling, G. Wang, T. Liu, F. Wang, T. Zhai, Y. Tong and Y. Li, *Nano Lett.*, 2015, **15**, 7051–7057.

