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## 3D nanostructured WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction derived from *Papilio paris* for efficient water splitting†

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We report on a novel butterfly wing-like WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction for photocatalytic water splitting, in which BiVO<sub>4</sub> is the primary visible light-absorber and WO<sub>3</sub> acts as an electron conductor. The heterojunction, which is prepared by a one-step sol-gel method, achieves high light absorption and charge separation efficiencies, even without a sacrificial agent, and produces a photocatalytic O<sub>2</sub> evolution of 20 μmol h<sup>-1</sup> mg<sup>-1</sup> under visible light irradiation (λ > 420 nm) and an incident photon-to-current conversion efficiency of ~10% at 380–450 nm, both at a potential of 1.23 V *versus* RHE. Compared to planar WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction, the 3D nanostructured WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction shows significantly improved photocatalytic performance due to the quasi-honeycomb structure inherited from the *Papilio paris* and the efficient separation of the photogenerated charge at the WO<sub>3</sub>/BiVO<sub>4</sub> interface. Synthesis details are discussed, with heterojunction morphologies and structures characterized by field emission scanning electron microscopy and X-ray diffraction.

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### Introduction

Photocatalytic water splitting into H<sub>2</sub> and O<sub>2</sub> using semiconductors is a very attractive and desirable way to meet the global energy challenge and solve environmental issues.<sup>1,2</sup> Although several semiconductor materials show photocatalytic activity, most of them have limited utility due to the high charge carrier recombination<sup>3</sup> and wide band gaps, which make them only active under UV light irradiation, and UV light represents merely 4–5% of the solar spectrum energy lies.<sup>4</sup> A range of attempts have been made to improve light absorption and charge separation efficiencies, including impurity doping,<sup>5–7</sup> loading co-catalysts,<sup>8,9</sup> and the introduction of nanoscale porosity.<sup>10,11</sup> Moreover, photocatalytic performance has also been improved by the formation of heterojunctions, which couple a large band gap semiconductor with a small band gap semiconductor. Heterojunctions have a more negative conduction band (CB) level, and the CB electrons can be injected from the small band gap semiconductor into the large band gap semiconductor, promising that the heterojunction can be more efficient than a single semiconductor system.<sup>12</sup>

Monoclinic BiVO<sub>4</sub> (mBiVO<sub>4</sub>) has become the top performer among all metal oxide photocatalysts under visible light owing to its relatively small band-gap energy (2.4 eV).<sup>13</sup> BiVO<sub>4</sub> based

heterostructures with other desirable semiconductors including ZnO,<sup>14</sup> WO<sub>3</sub>,<sup>12,15–19</sup> nanowires of Fe<sub>2</sub>O<sub>3</sub> (ref. 20) and others<sup>21–24</sup> have been shown to promote the separation of electron-hole pairs and anti-photocorrosion. Among the latest state-of-the-art BiVO<sub>4</sub>-based heterojunctions, the highest efficiency was achieved by a W doped WO<sub>3</sub>/BiVO<sub>4</sub> core/shell nanowire photoanode, synthesized on an FTO without an added catalyst, which produced a photocurrent of 3.1 mA cm<sup>-2</sup> under simulated sunlight and an incident photon-to-current conversion efficiency of ~60% at 300–450 nm, both at a potential of 1.23 V *versus* RHE.<sup>12</sup> However, the cumbersome process and difficulty in controlling the nanomorphology of the photoanode create obstacles in its practical use.

As a matter of fact, nature offers an astonishing variety of materials with exquisite 3D hierarchical structures, which cannot be easily synthesized using available nanotechnology to date. 3D hierarchical structures from nature often display an efficient light-harvesting capacity, particularly in the region of visible light, and the abundant biogenic elements endowed from biological systems can be preserved and incorporated into the final biotemplated materials to reduce the bandgap of photocatalysts,<sup>25</sup> leading to a new way to obtain efficient photocatalysts. Recently, we reported that a C-doped BiVO<sub>4</sub> photocatalyst with fine 3D hierarchical structures templated from *Papilio paris* butterfly wings fabricated by a novel one-step sol-gel and templating method enables simultaneous control of crystal phase, nanomorphology, and element carbon doping in a single process.<sup>26</sup> The improved photocatalytic performance was attributed to the synergetic effect of the unique morphology and doping control. We have also reported that the sequence of

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ceramic  $\text{WO}_3$  butterfly wings was also inherited from *Papilio paris*.<sup>27</sup> We verified that the quasi-honeycomb structure adapted from *Papilio paris* can help  $\text{WO}_3$  harvest visible light more efficiently and boost charge transport. Nevertheless, the efficiency of these photocatalysts is not sufficient due to the still limited charge separation efficiencies. Hence heterojunction nanoarchitectures coupled with the unique structures are expected to result in the highest photocatalytic activity.

In this study, we fabricate a novel 3D nanostructured  $\text{WO}_3/\text{BiVO}_4$  heterojunction derived from *Papilio paris* for photocatalytic water splitting, in which  $\text{BiVO}_4$  is the primary visible light-absorber and  $\text{WO}_3$  acts as an electron conductor. The heterojunction, which is prepared by a one-step sol-gel method, achieves the highest light absorption and charge separation efficiencies among  $\text{BiVO}_4$ -based powder composites, even without a sacrificial agent. In the following, we will describe the synthesis and characterization of the present  $\text{WO}_3/\text{BiVO}_4$  heterojunction in detail and explain the origin of the improved photocatalytic performance.

## Experimental

### Materials

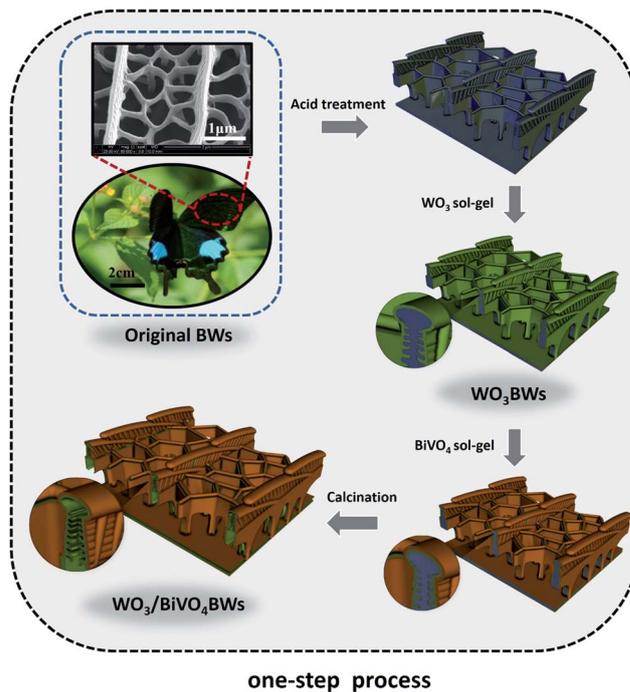
Butterfly wing biotemplates were purchased from Shanghai Natural Wild-Insect Kingdom Co., Ltd. Analytical grade reagents such as phosphotungstic acid 44-hydrate ( $\text{H}_3\text{PO}_{40}\text{W}_{12}$ ), bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ), ethanol, acetic acid, nitric acid, and tetramethylammonium hydroxide (TMAH) were purchased from Sino-pharm Reagent Chemical Co., Ltd.

### Synthesis

In a typical synthesis, first, *Papilio paris* butterfly wings, as biological templates, were air dried before use. The biological samples were pretreated by a mixture solution of acetic acid and ethanol for 6 h at room temperature and then washed with deionized water and air-dried for 24 h. The pretreated samples were carefully dipped into 20 wt% of phosphotungstic acid 44-hydrate ( $\text{H}_3\text{PO}_{40}\text{W}_{12}$ ) in ethanol solution and kept at 36 °C for 6 h, denoted as  $\text{WO}_3\text{BWs}$ .<sup>27</sup> Then,  $\text{WO}_3/\text{BiVO}_4$  heterojunction was achieved by a one-step sol-gel method and a two-step sol-gel method. In the one-step sol-gel process,  $\text{WO}_3\text{BWs}$  were washed with ethanol and dried overnight under vacuum at 60 °C and dipped into the  $\text{BiVO}_4$  sol-gel solution<sup>26</sup> and kept at 36 °C for 12 h. Finally, the samples were calcined in air at 500 °C with a constant heating rate of 1 °C  $\text{min}^{-1}$  to format the crystal and remove the organic templates ( $\text{WO}_3/\text{BiVO}_4\text{BWs}$ ). The synthesis process is illustrated in Scheme 1. For comparison,  $\text{WO}_3/\text{BiVO}_4\text{BWs}$  (two-step) were prepared by  $\text{WO}_3\text{BWs}$ , which were first calcined in  $\text{N}_2$  atmosphere at 800 °C to crystallize the  $\text{WO}_3$  and dipped into the  $\text{BiVO}_4$  sol-gel solution at last.

### Photocatalytic activity test

The photocatalytic activities of the samples were evaluated by the amount of oxygen split from water (Labsolar- $\text{H}_2$ , Perfect Light, China) under visible light. Portions of the solid samples



Scheme 1 The synthesis process of replication of butterfly wing in  $\text{WO}_3/\text{BiVO}_4\text{BWs}$ .

(10 mg) were introduced into a spectroscopic quartz probe cell, and the measurements were taken at room temperature under visible light irradiation from a 300 W Xe lamp (PLS-SXE300/300UV, Perfect Light, China) equipped with a cutoff filter L42. The visible light intensity is about 10 mW. The evolved gases were analyzed by gas chromatography with a thermal conductivity detector (GC7890II, Tianmei, Shanghai;  $\text{N}_2$  carrier gas).

The electrodes were prepared according to the method from Kudo. Photoelectrochemical properties were evaluated with a three-electrode cell consisting of the prepared electrodes, a Pt electrode, and a saturated  $\text{Ag}/\text{AgCl}$  electrode as the working, counter, and reference electrodes, respectively. The working electrode was irradiated from the FTO side with visible-light through a cutoff filter (L42). The incident photon-to-photocurrent efficiency (IPCE) was calculated as follows:

$$[\text{IPCE}/\%] = 1240 \times [\text{photocurrent density}/\mu\text{A cm}^{-2}] / ([\text{wavelength}/\text{nm}] \times [\text{photo flux}/\text{Wm}^{-2}])$$

### Characterizations

The synthesized samples were examined by X-ray diffraction (XRD) on a D-max/2550 (Rigaku) X-ray diffractometer system operating at 1600 W power (40 kV, 40 mA) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ), at a scan rate of 4°  $\text{min}^{-1}$  and a step size of 0.050° in  $2\theta$ . The morphologies and microstructures of the samples were characterized using a FEI QUANTA TEG 250 scanning electron microscope (SEM) and a JEOL2011 transmission electron microscope (TEM). TEM specimens were



prepared by dispersing the synthesized samples in pure ethanol, and the powder was picked up by copper grids. UV-Visible (UV-Vis) diffuse reflectance spectra of all the samples were recorded using a PerkinElmer UV-Vis-NIR spectrophotometer (750S) in the spectral range of 200–800 nm, and Raman scattering measurements were obtained in back scattering geometry on a Via<sup>+</sup> Reflex from 150–1000  $\text{cm}^{-1}$ .

## Results and discussion

$\text{BiVO}_4$  has a narrow band gap (2.4 eV), and its conduction band is more negative than that of  $\text{WO}_3$ . Therefore coupling with photocorrosion resistant  $\text{WO}_3$ ,  $\text{WO}_3/\text{BiVO}_4$  heterojunctions<sup>15–19</sup> could be suitable for efficient photocatalytic water splitting under visible irradiation; see Fig. 1e. The quasi-honeycomb structure of *Papilio paris* butterfly wings is shown in Fig. S1,<sup>†</sup> which can absorb visible light to an utmost degree with over 95% absorption rate.<sup>28</sup> The morphologies of  $\text{WO}_3$ BWs,  $\text{WO}_3/\text{BiVO}_4$ BWs (two-step) and  $\text{WO}_3/\text{BiVO}_4$ BWs are shown in Fig. 1a–

c. The quasi-honeycomb and three-layer structures of the scales can clearly be seen in the three samples. Compared with the original butterfly wing, the replicas show a 20% shrinkage for both  $\text{WO}_3/\text{BiVO}_4$ BWs (two-step) and  $\text{WO}_3/\text{BiVO}_4$ BWs after calcination (Fig. 1b and c). The scales, neatly arranged on the surface of the structure of the *Papilio paris* butterfly wings, were completely retained by  $\text{WO}_3$  (Fig. 1a). The parallel ridges of the scales and nanoscale ribs were retained in the  $\text{WO}_3/\text{BiVO}_4$ BWs, indicating an extremely fine duplication of the original scale structures using the one-step sol-gel method (Fig. 1c), and the high-resolution TEM (HRTEM) images provide the 150 nm average pore diameter (Fig. 1d). However, the further finer and elaborate architectures in the ribs of the  $\text{WO}_3/\text{BiVO}_4$ BWs (two-step) disappear (Fig. 1b) because of the significant grain growth of  $\text{WO}_3$  particles when the calcination temperature reaches 800 °C, suggesting a poor photocatalytic performance.

Fig. 2a shows X-ray diffraction patterns of  $\text{WO}_3$ BWs,  $\text{BiVO}_4$ BWs, and  $\text{WO}_3/\text{BiVO}_4$ BWs. In the  $\text{WO}_3$ BWs, the peaks of 23.3, 23.8, and 24.6° are observed corresponding to (002), (020), and (200) planes for the monoclinic phase of  $\text{WO}_3$  (JCPDS 43-1035), which is known to show the highest photocatalytic effect compared to other crystal phases.<sup>29,30</sup> Compared with monoclinic  $\text{WO}_3$ , several new peaks appeared on the XRD spectra, and they could be indexed as other  $\text{W}_x\text{O}_y$  phases, such as  $\text{WO}_{2.9}$  and  $\text{W}_{18}\text{O}_{49}$ . This means that the bio-template resulted in multiple

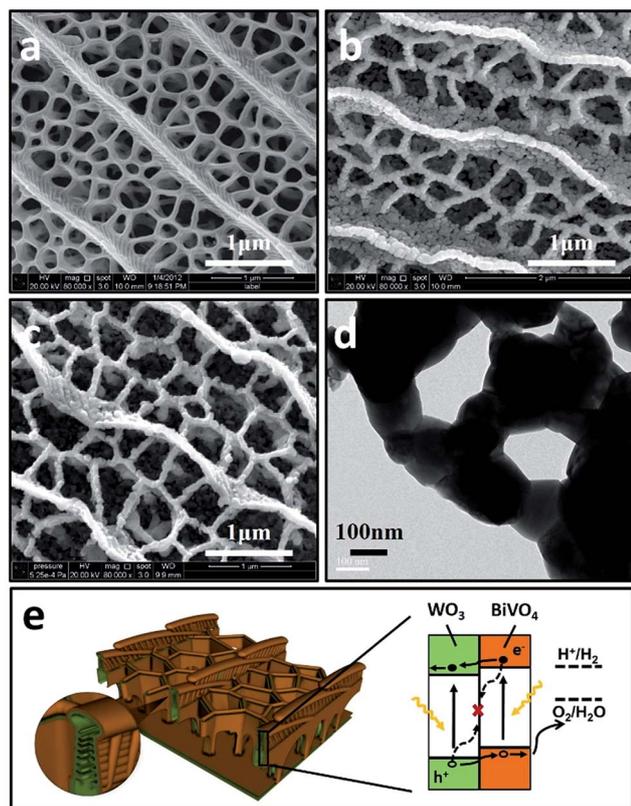


Fig. 1 The 3D nanostructured  $\text{WO}_3/\text{BiVO}_4$ BWs. (a–c) Scanning electron microscope (SEM) of  $\text{WO}_3$ BWs,  $\text{WO}_3/\text{BiVO}_4$ BWs (two-step) and  $\text{WO}_3/\text{BiVO}_4$ BWs. (d) Transmission electron microscope (TEM) images of the  $\text{WO}_3/\text{BiVO}_4$ BWs (150 nm average pore diameter). The  $\text{BiVO}_4$  consists of a single layer of densely packed nanoparticles. (e) Structural schematic and energy band diagram of the butterfly wing  $\text{WO}_3/\text{BiVO}_4$ BWs and type-II staggered heterojunction, in which charges generated in both the  $\text{BiVO}_4$  outside and  $\text{WO}_3$  inside can contribute to water oxidation. The band edges and water oxidation and reduction potentials are plotted on the reversible hydrogen electrode (RHE) scale.

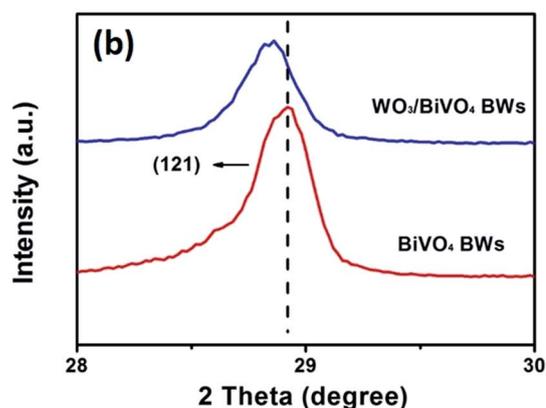
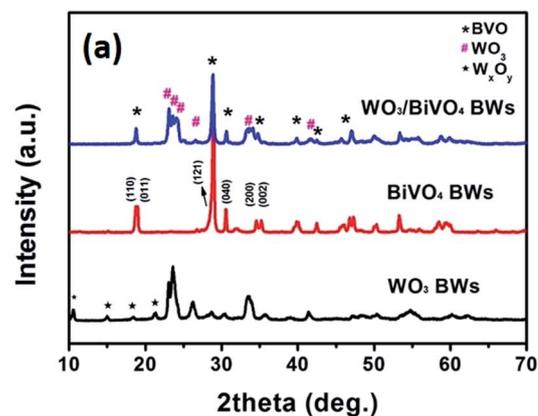


Fig. 2 XRD patterns of (a)  $\text{WO}_3$ BWs,  $\text{BiVO}_4$ BWs, and  $\text{WO}_3/\text{BiVO}_4$ BWs. (b) Magnified peaks of (120) planes in the range of  $2\theta$  from 28° to 30°.



tungsten oxide phases in the replicas. For bare  $\text{BiVO}_4$ BWs, the main peaks can be indexed as (110), (011), (121), (040), (200) and (002) planes, which can represent the monoclinic  $\text{BiVO}_4$  (JCPDS 14-0688) without any impurity phase, illustrating that the bio-template has been removed completely by calcination at 500 °C. In the case of  $\text{WO}_3/\text{BiVO}_4$ BWs, monoclinic  $\text{WO}_3$  and  $\text{BiVO}_4$  are the only phases detected in XRD measurements (Fig. 2a), demonstrating that a novel 3D nanostructured  $\text{WO}_3/\text{BiVO}_4$  heterojunction derived from *Papilio paris* with pure and high crystallinity can be achieved by the one-step sol-gel method mentioned before. As a result, the average grain size of the samples, calculated *via* the Scherrer formula, are 15.3, 27.2 and 30.5 nm, corresponding to  $\text{WO}_3$ BWs,  $\text{BiVO}_4$ BWs, and  $\text{WO}_3/\text{BiVO}_4$ BWs, respectively, while  $\text{WO}_3/\text{BiVO}_4$ BWs (two-step) shows 48.5 nm.

Fig. 2b exhibits a magnified view of (121) peaks, which show  $0.318^\circ$  shifts to lower angles in the  $\text{WO}_3/\text{BiVO}_4$ BWs, compared with the  $\text{BiVO}_4$ BWs. Pratap M. Rao *et al.* in 2014 have reported that  $\text{W}^{6+}$  dopes into  $\text{BiVO}_4$  by substituting for  $\text{V}^{5+}$  and acts as an electron donor in the  $\text{WO}_3/\text{BiVO}_4$  core/shell nanowire photoanode.<sup>12</sup> This shifting may be ascribed to lattice expansion due to the slight portion of W atoms incorporating from  $\text{WO}_3$ . These XRD results indicate that little W atoms have been well inserted into V sites of the host  $\text{BiVO}_4$  lattice, induces lattice expansion without forming any segregated impurity phase.<sup>12</sup> It has been known that impurity doping may form new bonds to promote the electron-hole separation efficiency.<sup>6</sup> Therefore, the  $\text{WO}_3/\text{BiVO}_4$ BWs are expected to show enhanced photocatalytic performance.

Moreover, Fig. 3 presents the Raman spectra of the  $\text{WO}_3$ BWs,  $\text{BiVO}_4$ BWs, and  $\text{WO}_3/\text{BiVO}_4$ BWs in the 150–1000  $\text{cm}^{-1}$  region. The bands at 827, 723, 367, 324, 210 and 128  $\text{cm}^{-1}$  in the  $\text{BiVO}_4$ BWs correspond to the typical vibrations of monoclinic  $\text{BiVO}_4$ . The band at 827 is assigned to the typical symmetric V–O stretching mode,<sup>31</sup> and the one with a weak shoulder at about 712  $\text{cm}^{-1}$  assigned to the antisymmetric V–O stretching mode, whereas those at 367 and 324  $\text{cm}^{-1}$  are attributed to the typical symmetric and antisymmetric bending modes of the vanadate anion.<sup>32,33</sup> Raman vibrations centered at 135, 214, 708 and 785  $\text{cm}^{-1}$ , characteristic of pure  $\text{WO}_3$ , are also detected in the

$\text{WO}_3$ BWs. The bands at 708 and 785  $\text{cm}^{-1}$  are identified as the O–W–O bending and stretching mode, respectively.<sup>32</sup>

As seen from Fig. 3, in the case of  $\text{WO}_3/\text{BiVO}_4$ BWs, it is clear that a shift of the Raman band to the lower wavenumber, from 827 to 810  $\text{cm}^{-1}$  assigned to symmetric V–O bond stretching mode, reveals that the average lone-range symmetry of the  $\text{VO}_4$  tetrahedral becomes less regular. The blue-shift is due to the W-doping effect where W has been inserted into the V sites of the  $\text{BiVO}_4$  lattice to form the W–O bond, which has the bond length shorter than that of the V–O bond. Furthermore, the band at 785  $\text{cm}^{-1}$  attributed to O–W–O bonds is broad and shifted to 810  $\text{cm}^{-1}$  in  $\text{WO}_3/\text{BiVO}_4$ BWs, probably due to the formation of the  $\text{WO}_3/\text{BiVO}_4$  heterojunction structures, which generate a new W–O–V bond,<sup>33</sup> consistent with XRD results. It has been reported that formation of new bonds can promote electron-hole separation efficiency of photocatalysts. It would be expected that  $\text{WO}_3/\text{BiVO}_4$ BWs should perform the best in the photocatalytic  $\text{O}_2$  production experiments.

To investigate the optical absorption properties of the samples, UV/Vis spectroscopy was conducted, and the results are shown in Fig. 4. Light absorption of the bare  $\text{WO}_3$ BWs starts at around 475 nm in correspondence with its band gap energy. For the bare  $\text{BiVO}_4$ BWs, the onset of light absorption is around 520 nm, again corresponding to its band gap energy. In the  $\text{WO}_3/\text{BiVO}_4$ BWs, the main absorption edge has a red-shift of more than 20 nm compared with pure  $\text{BiVO}_4$ BWs. It indicates that the band-gap energy of the samples is affected by the quasi-honeycomb structure of *Papilio paris* butterfly wing, and the quasi-honeycomb structure can enhance visible light absorption, which has been reported by us before.<sup>26</sup> Moreover, compared with  $\text{BiVO}_4$ BWs and  $\text{WO}_3$ BWs,  $\text{WO}_3/\text{BiVO}_4$ BWs exhibits an increased photoabsorption at wavelengths between 200 nm and 480 nm, which is probably due to the formation of the heterojunction structure. The optical band-gap energies of the three samples are estimated from the absorption spectra using the following relationship:

$$\alpha h\nu = A(h\nu - E_g)^n$$

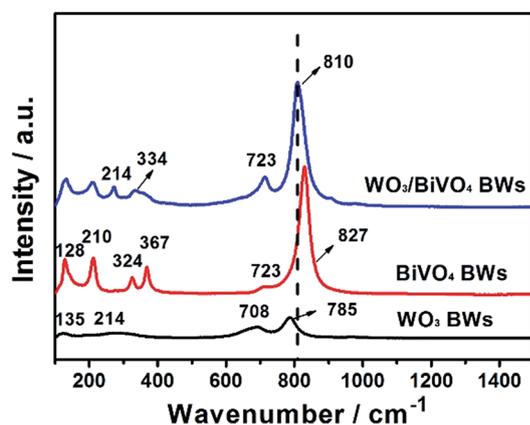


Fig. 3 Raman spectra of  $\text{WO}_3$ BWs,  $\text{BiVO}_4$ BWs, and  $\text{WO}_3/\text{BiVO}_4$ BWs.

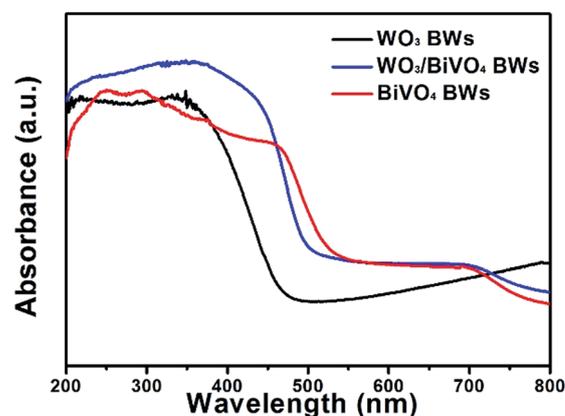


Fig. 4 UV-Vis absorbance spectra of  $\text{WO}_3$ BWs,  $\text{BiVO}_4$ BWs, and  $\text{WO}_3/\text{BiVO}_4$ BWs.



where  $E_g$  is the band-gap energy of allowed transitions (eV),  $h$  is Planck's constant ( $6.626 \times 10^{-34}$  J s),  $\alpha$  and  $\nu$  are the absorption coefficient and light frequency, respectively, and  $A$  is a constant. The band gap energy for BiVO<sub>4</sub>BWs is measured to be about 2.4 eV, which is smaller than that of WO<sub>3</sub>/BiVO<sub>4</sub>BWs (2.46 eV) and WO<sub>3</sub>BWs (2.69 eV). Thus, the absorption range of the WO<sub>3</sub>BWs is enhanced by coupling of BiVO<sub>4</sub> having a smaller band gap energy. Thus, the band-gap energy of the samples is affected by the quasi-honeycomb structure of *Papilio paris* butterfly wings and the heterojunction coupled by WO<sub>3</sub> and BiVO<sub>4</sub>. The small difference in band gap has a significant influence on the photocatalytic performance, which will be discussed later with the results of oxygen production from water splitting.

We further measure photocurrents of WO<sub>3</sub>BWs, BiVO<sub>4</sub>BWs, and WO<sub>3</sub>/BiVO<sub>4</sub>BWs by depositing each material on ITO electrodes. A fast and strong photocurrent response is observed for each switch-on/off event in both WO<sub>3</sub>/BiVO<sub>4</sub>BWs and BiVO<sub>4</sub>-BWs-deposited electrodes under visible light (Fig. 5a). Under

visible light irradiation ( $\lambda > 420$  nm), the photocurrent of WO<sub>3</sub>/BiVO<sub>4</sub>BWs electrode (2.5  $\mu$ A) is approximately 5 times higher than that of the BiVO<sub>4</sub>BWs electrode (0.5  $\mu$ A), which indicates that the separation efficiency of photo-induced electrons and holes is improved significantly through the electronic interaction between BiVO<sub>4</sub> and WO<sub>3</sub>, as expected from the results in Fig. 5a. In contrast, no photocurrent is recorded for WO<sub>3</sub>BWs under visible light irradiation, which implies no photocatalytic O<sub>2</sub> evolution from water splitting under visible light gap.

The incident photon-to-photocurrent efficiency (IPCE) spectra of WO<sub>3</sub>BWs, BiVO<sub>4</sub>BWs, and WO<sub>3</sub>/BiVO<sub>4</sub>BWs are shown in Fig. 5b, in which the electrodes are measured at 1.23 V (vs. Ag/AgCl) in 0.5 M Na<sub>2</sub>SO<sub>4</sub> using monochromatic light controlled with band pass filters. The IPCE is defined by the following equation:

$$[\text{IPCE}/\%] = 1240 \times [\text{photocurrent density}/\mu\text{A cm}^{-2}] / [(\text{wavelength}/\text{nm}) \times (\text{photo flux}/\text{Wm}^{-2})]$$

The WO<sub>3</sub>BWs shows rising IPCE from 480 nm and the BiVO<sub>4</sub>BWs from 540 nm, in agreement with their band gap energies. The WO<sub>3</sub>/BiVO<sub>4</sub>BWs also shows the onset of IPCE at 540 nm similar to BiVO<sub>4</sub>BWs. Moreover, the WO<sub>3</sub>/BiVO<sub>4</sub>BWs electrode performs at an excellent anodic photocurrent with 10.8% of an IPCE at 400 nm at 1.23 V vs. Ag/AgCl, whereas the trivial IPCE of WO<sub>3</sub>BWs at 0.3% (at 380 nm) and BiVO<sub>4</sub>BWs at 0.7% (at 400 nm) is observed. Despite the range of light absorption of BiVO<sub>4</sub>BWs being larger than WO<sub>3</sub>/BiVO<sub>4</sub>BWs, the photoactivity was much less because of poor charge transfer characteristics as evidenced by the photocurrents study discussed above. Because WO<sub>3</sub> cannot absorb light with wavelength between 500 and 540 nm, the IPCE in this range for WO<sub>3</sub>/BiVO<sub>4</sub>BWs originates from the absorption by the BiVO<sub>4</sub> layers. However, unlike bare BiVO<sub>4</sub>, the WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction can utilize light at 500–540 nm for water oxidation because the good charge transfer characteristic at the interface induces rapid transfer of photoelectrons formed in BiVO<sub>4</sub> to WO<sub>3</sub>. One order of magnitude enhancement in photoconversion efficiency indicates that WO<sub>3</sub>/BiVO<sub>4</sub>BWs may result in the best photocatalytic activity.

On the basis of the above results, the photocatalytic activities of the samples were tested for O<sub>2</sub> evolution from water splitting under visible light range. Fig. 6 shows the amount of evolved O<sub>2</sub> by solar light from boiled water. The amount of evolved O<sub>2</sub> from aqueous solution after 1 h from the WO<sub>3</sub>/BiVO<sub>4</sub>BWs is ca. 200  $\mu$ mol, which is 5 times as much as that of the BiVO<sub>4</sub>BWs (ca. 42  $\mu$ mol), the highest photocatalytic O<sub>2</sub> evolution among all the tested samples. The total evolved O<sub>2</sub> after 5 h from the WO<sub>3</sub>/BiVO<sub>4</sub>BWs is ca. 950  $\mu$ mol, which is more than 7.6 times that of the BiVO<sub>4</sub>BWs (ca. 125  $\mu$ mol). On the contrary, WO<sub>3</sub>/BiVO<sub>4</sub>BWs (two-step) shows ca. 35  $\mu$ mol (Fig. S2, ESI†) and WO<sub>3</sub>BWs produces no oxygen under visible light irradiation. The results suggest that the WO<sub>3</sub>/BiVO<sub>4</sub>BWs performs the best photocatalytic activities, compared with other hierarchical porous photocatalysts from bio-templates that we have reported

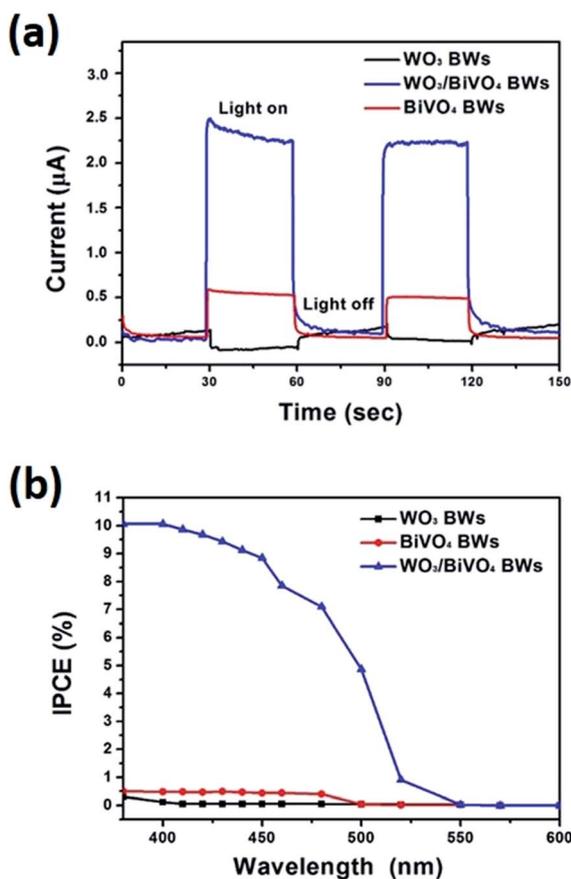


Fig. 5 (a) Photocurrent responses of WO<sub>3</sub>BWs, BiVO<sub>4</sub>BWs, and WO<sub>3</sub>/BiVO<sub>4</sub>BWs under visible light irradiation ( $\lambda > 420$  nm). (b) Incident photon to current conversion efficiency (IPCE) of the WO<sub>3</sub>BWs, BiVO<sub>4</sub>BWs, and WO<sub>3</sub>/BiVO<sub>4</sub>BWs. The IPCE was measured at 1.23 V (vs. Ag/AgCl) under 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution. The three-electrode cell consists of a prepared electrode, a Pt electrode, and a saturated Ag/AgCl electrode as the working, counter, and reference electrodes, respectively. The working electrode was irradiated from the FTO side with visible-light through a cutoff filter (L42).



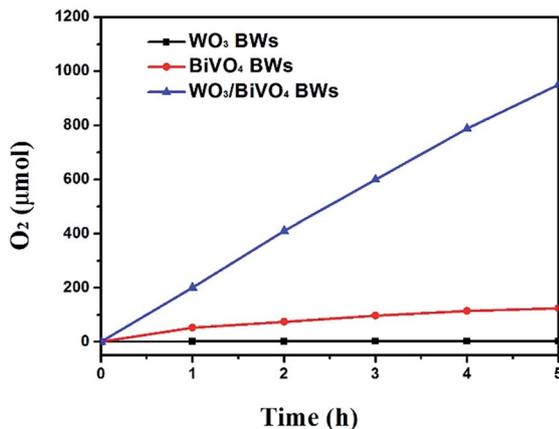


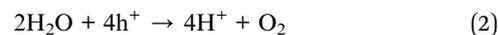
Fig. 6 Photocatalytic O<sub>2</sub> evolution of WO<sub>3</sub>BWs, BiVO<sub>4</sub>BWs, and WO<sub>3</sub>/BiVO<sub>4</sub>BWs under visible light irradiation ( $\lambda > 420$  nm). The amount is kept the same for all the samples.

before.<sup>26,27</sup> This result shows that the WO<sub>3</sub>/BiVO<sub>4</sub>BWs are stable and indeed oxidize water into O<sub>2</sub>.

From all the results presented above, a possible mechanism for photocatalytic O<sub>2</sub> evolution from water splitting by the WO<sub>3</sub>/BiVO<sub>4</sub>BWs has been proposed and illustrated in Fig. 7. We attribute the significantly enhanced photocatalytic performance of WO<sub>3</sub>/BiVO<sub>4</sub>BWs under visible light to more absorption of visible light as well as more efficient transfer of photogenerated electrons. The unique quasi-honeycomb structure allows more visible light waves to penetrate deep inside the photocatalyst, thus improving the light absorption capability and the formation of heterojunctions which enhances the separation of photogenerated electron-hole pairs and thus reduces charge

recombination rate as evidenced by the photocurrent responses analysis.

According to the literature, for a WO<sub>3</sub> film in Na<sub>2</sub>SO<sub>4</sub>, a flat-band potential of  $V_{fb} = 0.15$  V (vs. SCE) was reported by Patil,<sup>34</sup> while the  $V_{fb}$  of BiVO<sub>4</sub> was reported as  $-0.62$  V (vs. SCE) by Sayama<sup>35</sup> and Li<sup>36</sup>. It is generally known that the bottoms of the conduction bands in several n-type semiconductors are more negative by 0.1 V than the flat band potential.<sup>37</sup> In the photocatalytic oxygen evolution process (Fig. 7), illumination photons create electron-hole pairs in the WO<sub>3</sub>/BiVO<sub>4</sub>BWs at the solid/solution interface. These electron-hole pairs separate and reach the photocatalyst surface by diffusion. Owing to the positive conduction band position ( $>0$  eV vs. NHE at pH = 7), only the reaction of holes with water to produce O<sub>2</sub> can occur spontaneously (eqn (2)).



With the bottom of the BiVO<sub>4</sub> conduction band more positive than that of WO<sub>3</sub>, it is favorable for the electrons to travel from the BiVO<sub>4</sub> conduction band to WO<sub>3</sub>. Hence, electrons generated in the BiVO<sub>4</sub> will first travel radially inward to the WO<sub>3</sub> in the WO<sub>3</sub>/BiVO<sub>4</sub>BWs, and then travel to the current collector through WO<sub>3</sub>, in turn suppressing electron-hole recombination. Although BiVO<sub>4</sub> absorbs a larger fraction of solar light than WO<sub>3</sub> due to its narrower band gap as shown in Fig. 4, electrons and holes formed in BiVO<sub>4</sub> are not fully utilized for water decomposition reaction because its poor transfer characteristics lead to recombination. However, the holes can migrate to the semiconductor/electrolyte interface either directly or after transfer from WO<sub>3</sub> to BiVO<sub>4</sub>. The reduced recombination naturally induces photoactivity enhancement.

## Conclusions

In summary, a novel 3D nanostructured WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction derived from *Papilio paris* for photocatalytic water splitting is fabricated by a one-step sol-gel method. The quasi-honeycomb structure of the original butterfly wings is kept perfectly in the heterojunction. The photocurrents of WO<sub>3</sub>/BiVO<sub>4</sub>BWs (2.5  $\mu\text{A}$ ) is approximately 5 times higher than that of a BiVO<sub>4</sub>BWs (0.5  $\mu\text{A}$ ), and an incident photon-to-current conversion efficiency of  $\sim 10\%$  at 380–450 nm (1.23 V versus RHE), indicating a higher product of light absorption and charge separation efficiencies. The WO<sub>3</sub>/BiVO<sub>4</sub>BWs, in which BiVO<sub>4</sub> is the primary visible light-absorber and WO<sub>3</sub> acts as an electron conductor, achieved an excellent photocatalytic O<sub>2</sub> evolution of 20  $\mu\text{mol h}^{-1} \text{mg}^{-1}$  under visible light irradiation, which is 5 times higher than BiVO<sub>4</sub>BWs, even without a sacrificial agent. The enhanced photocatalytic performance is attributed to not only the unique quasi-honeycomb structure with an efficient visible light-harvesting capacity, but also to improved separation efficiency of photo-induced electrons and holes through the electronic interaction in the WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction. These promising results open new possibilities in the

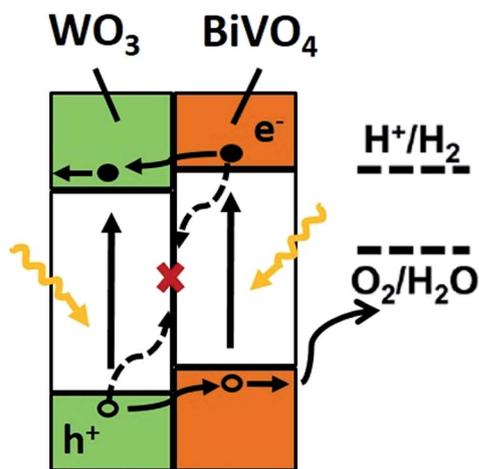


Fig. 7 Depiction of the energy diagram of the WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction (at pH 7) and electron transport process. Suggested mechanism for the photocatalytic O<sub>2</sub> evolution by WO<sub>3</sub>/BiVO<sub>4</sub>BWs under visible-light. The conduction band of WO<sub>3</sub> and BiVO<sub>4</sub> are  $-0.52$ , and  $0.05$  eV, respectively. Electrons from BiVO<sub>4</sub> flow to the conduction band of WO<sub>3</sub>. Valence electrons of BiVO<sub>4</sub> are excited to the conduction band state by absorbing visible light, which can convert oxygen molecules in the solution to singlet oxygen.



design of highly photoactive heterojunction photocatalysts inherited from bio-templates for water-splitting systems.

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