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# Oxygen vacancy regulation in Nb-doped Bi<sub>2</sub>WO<sub>6</sub> for enhanced visible light photocatalytic activity

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Novel Nb-doped Bi<sub>2</sub>WO<sub>6</sub> nanosheets have been successfully synthesized by a simple hydrothermal method. XRD, Raman spectra, XPS and SEM were adopted to analyze the structure and morphology of the samples, then the structure-dependent optical properties, photoelectric behavior and photocatalytic activities were investigated, and the structure–property relationship was also discussed. The results show that doping Nb<sup>5+</sup> can increase the oxygen vacancies in the Bi<sub>2</sub>WO<sub>6</sub> lattice and reduce the optical band gap of Bi<sub>2</sub>WO<sub>6</sub>. The oxygen vacancies also act as electron traps, which promote the separation of photogenerated carriers. Hence, compared with the pure Bi<sub>2</sub>WO<sub>6</sub>, the as-prepared Nb-doped Bi<sub>2</sub>WO<sub>6</sub> nanosheets exhibit enhanced visible-light photocatalytic activity for removing contaminants in water such as rhodamine B and tetracycline.

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## 1. Introductions

Heterogeneous photocatalysis offers tremendous potential for use in the field of environmental remediation and the conversion of photons into chemical energy.<sup>1–3</sup> In recent decades, TiO<sub>2</sub> semiconductors have become a typical photocatalyst for decomposition of organic contaminants and water splitting due to their good physical and chemical properties.<sup>4,5</sup> However, as a UV-driven photocatalyst, TiO<sub>2</sub> can only respond to UV light, which is less than 4% of sunlight reaching the Earth's surface.<sup>6,7</sup> In order to make better use of solar energy, more and more researchers have turned their attention to visible-light-driven photocatalysts.

As a simple Aurivillius-type compound, bismuth tungstate featuring its layered configuration consisting of alternating (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup> layers and (WO<sub>4</sub>)<sup>2–</sup> octahedral layers displayed excellent visible light photocatalytic activity.<sup>8–10</sup> However, for intrinsic semiconductors, the fast recombination of photo-generated electrons and holes seriously limited their quantum efficiency, which was also a key issue of pure Bi<sub>2</sub>WO<sub>6</sub> that needs to be solved. Many strategies have been proposed to promote the separation of photo-generated carriers, such as loading noble metals, constructing heterojunctions, doping ion elements and so on.<sup>11–14</sup> In these strategies, ion doping can introduce the doping level into the band gap, therefore not only reducing the recombination of photo-generated electron–hole pairs, but also further expanding light absorption to the visible wavelength range. It has been reported that F, Br, and N can

partially substitute the O-site, therefore raising the valence band,<sup>15–17</sup> whereas metallic ions such as Cd, Y, Gd can partially substitute the Bi-site.<sup>18–20</sup> Furthermore, co-doping such as F–Ce and lanthanide elements can efficiently expand the absorption range to visible light.<sup>21–23</sup> W-site substitution in Bi<sub>2</sub>WO<sub>6</sub> systems was another effective modification route, the different d orbital structure of heterogeneous ions substituting W<sup>6+</sup> would cause a change in the crystal structure and symmetry. Moreover, the electron mobility can be promoted due to the difference in the orbital energies of the heterogeneous ions, thereby improving photoelectron–hole separation efficiency.<sup>24</sup>

In this paper, Nb<sup>5+</sup> was applied to partially substitute W<sup>6+</sup> to modify the crystal structure of Bi<sub>2</sub>WO<sub>6</sub>, as well as to construct oxygen vacancies serving as an electron trap and widening the valence band, which would promote the separation of photo-generated carriers and improve the absorption efficiency of sunlight.<sup>25,26</sup> To the best of our knowledge, this is the first time Nb-doped Bi<sub>2</sub>WO<sub>6</sub> photocatalysts have been reported. The mechanism of the effects of Nb substitution on the Bi<sub>2</sub>WO<sub>6</sub> photocatalysts was studied on the basis of the crystal structure, electronic structure, and morphology of Bi<sub>2</sub>WO<sub>6</sub> photocatalysts.

## 2. Experimental

### 2.1 Materials

Chemicals (AR grade) involved in this work including bismuth nitrate (BiN<sub>3</sub>O<sub>9</sub>·5H<sub>2</sub>O), tungstic acid (H<sub>2</sub>WO<sub>4</sub>), oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O), ammonia (NH<sub>3</sub>·H<sub>2</sub>O), niobium oxide (Nb<sub>2</sub>O<sub>5</sub>), rhodamine B (RhB) and tetracycline (TC) were obtained commercially from Aladdin Reagent Co. Ltd. All chemicals were analytical grade reagents and were used without further purification.

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## 2.2 Preparation

The Nb-doped  $\text{Bi}_2\text{WO}_6$  nanosheets were synthesized *via* a simple one-step hydrothermal method. Firstly, 2 mmol of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was dissolved in 40 mL of oxalic acid solution with concentration of  $1.25 \text{ mol L}^{-1}$ , and 1 mmol of  $\text{H}_2\text{WO}_4$  was added dropwisely to  $\text{Bi}(\text{NO}_3)_3$  solution. And then, a desired amount of  $\text{Nb}_2\text{O}_5$  was then added into the above solution. Then, the pH value of the mixture was adjusted to 7 with  $1 \text{ mol L}^{-1}$  of  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . Finally, the mixture was added into a 100 mL of Teflon-lined autoclave and filled with deionized water to 80% of the total volume. Then the autoclave was heated in an oven at  $180^\circ\text{C}$  for 24 h. After cooling the autoclave to room temperature naturally, the obtained yellow precipitate was washed with deionized water and absolute ethanol and then dried at  $60^\circ\text{C}$  in an oven. The resultant samples with expected molar ratio of Nb : W = 0.02, 0.05, and 0.07 were denoted as BWO-Nb2, BWO-Nb5 and BWO-Nb7, respectively. For comparison, the pure  $\text{Bi}_2\text{WO}_6$  was prepared through the similar method and denoted as BWO.

## 2.3 Characterization

Crystal structure of the as-prepared samples were characterized by powder X-ray diffraction on a PANalytical diffractometer (APEXII, Bruker, Germany) with Cu K $\alpha$  radiation ( $k = 0.1542$ ). UV-vis diffuse reflectance spectra were recorded on a UV-vis spectrophotometer (UV-4100, Hitachi, Japan) in the range 200–700 nm using  $\text{BaSO}_4$  as the reference sample. The morphology and particle sizes of samples were determined by scanning electron microscope (SU-8010, Hitachi, Japan). Raman spectra measurement was carried out by a Raman spectrometer (DXR SmartRaman, Thermo Fisher Scientific, USA). X-ray photoelectron spectrometer (VGMPK II, Thermo Fisher Scientific, USA) was employed to perform the X-ray photoelectron spectroscopy test. The photoluminescence emission spectra of as-prepared samples were detected on a steady-state spectrometer (FLS920, Edinburgh, UK), and the PL emission spectra were obtained at an excitation wavelength of 325 nm with a Xe lamp. Photoelectrochemical tests were carried out in a three-electrode system with Pt foil as the counter electrode and Ag/AgCl electrode as the reference electrode. The working electrodes were pure  $\text{Bi}_2\text{WO}_6$  or Nb- $\text{Bi}_2\text{WO}_6$  film coated on indium-tin oxide glass (ITO) and with  $0.5 \text{ mol L}^{-1}$  of  $\text{Na}_2\text{SO}_4$  solution as

electrolyte solution were measured at 0.1 V under visible light ( $\lambda > 420 \text{ nm}$ ). The electrochemical system (CHI 660E, Chenhua, China) was employed to record the photoelectrochemical experiment results. The electrochemical impedance spectra (EIS) were all measured at 0 V.

## 2.4 Evaluation of photocatalytic activity

Photocatalytic activities of pure  $\text{Bi}_2\text{WO}_6$  and Nb-doped  $\text{Bi}_2\text{WO}_6$  were investigated by degradation of RhB and TC under visible light irradiation ( $\lambda > 420 \text{ nm}$ , 300 W Xe lamp), the average light intensity was  $23 \text{ mW cm}^{-2}$ . First, the 50 mg of photocatalysts were ultrasound-dispersed in an aqueous solution of RhB ( $100 \text{ mL}$ ,  $10 \text{ mg L}^{-1}$ ) or 30 mg of photocatalysts were ultrasound-dispersed in an aqueous solution of TC ( $100 \text{ mL}$ ,  $20 \text{ mg L}^{-1}$ ). Then, the mixture was magnetically stirred in dark for 30 min to reach an adsorption-desorption equilibrium. Afterward, the photocatalysis reaction was started. During the photocatalysis reaction, 4 mL of mixture was taken at 20 min intervals and was centrifuged to remove the photocatalysts. The concentration of RhB and TC in supernatant fluid was determined by measuring the absorbance at 553 nm and 356 nm respectively by using UV-vis spectrophotometer (U-3010, Hitachi, Japan).

The experimental conditions of the free radical trapping experiment and cycling runs experiment are consistent with the conditions of the photocatalytic degradation experiment, except that an appropriate amount of a radical scavenger is added thereto. The recycled samples are recovered by centrifugation and dried as samples for the next cycle.

## 3. Results and discussions

### 3.1 Structure and morphology analysis

XRD patterns of as-prepared samples are shown in Fig. 1a. It can be observed that  $\text{Bi}_2\text{WO}_6$  with single Aurivillius phase can be synthesized *via* a hydrothermal method. The diffraction peaks of  $\text{Bi}_2\text{WO}_6$  can be exactly indexed to JCPDS 79-2381. Moreover, the diffraction intensity ratio of  $I(113)/I(200)$  of  $\text{Bi}_2\text{WO}_6$  is less than 2, indicating that the as-prepared samples occur a special anisotropic growth.<sup>27</sup> It can be observed that the (113) and (200) diffraction peaks of Nb-doped  $\text{Bi}_2\text{WO}_6$  regularly shift to a lower

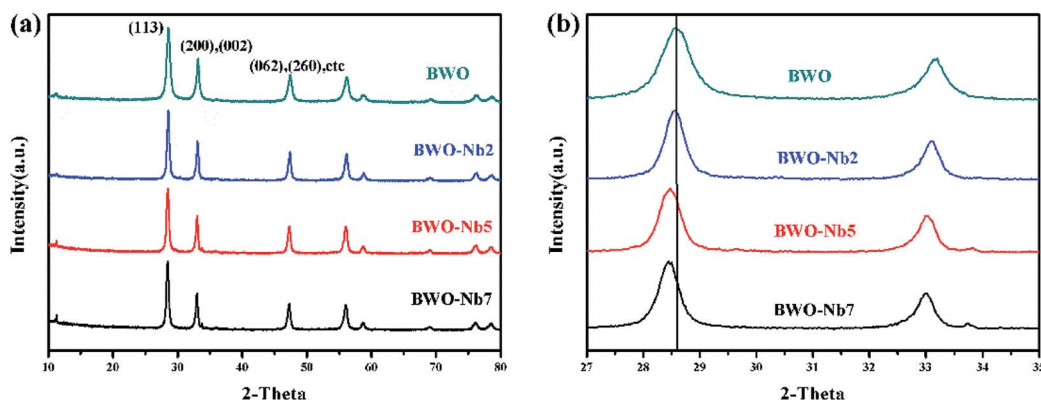


Fig. 1 (a) XRD patterns of BWO, BWO-Nb2, BWO-Nb5, BWO-Nb7, (b) the enlarged XRD patterns located from  $27^\circ$  to  $35^\circ$ .



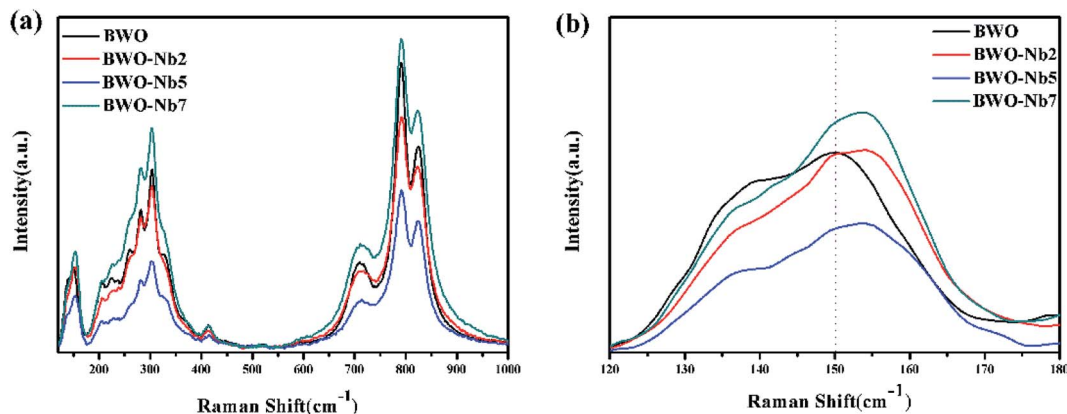


Fig. 2 (a) Raman spectra of BWO, BWO-Nb2, BWO-Nb5, BWO-Nb7; (b) magnified peaks located from 120  $\text{cm}^{-1}$  to 180  $\text{cm}^{-1}$ .

diffraction angle with the increase of doping amount of Nb element (Fig. 1b). This is mainly because that the replacement of  $\text{W}^{6+}$  by  $\text{Nb}^{5+}$  generates oxygen vacancies in  $\text{Bi}_2\text{WO}_6$ , leading to the enlargement of crystal face distance and slight change in crystal structure.<sup>28,29</sup>

Raman spectra of Nb-doped  $\text{Bi}_2\text{WO}_6$  and pure  $\text{Bi}_2\text{WO}_6$  are shown in Fig. 2a. The peaks located at 790 and 817  $\text{cm}^{-1}$  are related to the symmetric and asymmetric  $\text{Ag}$  modes of terminal O–W–O, and the band located at 707  $\text{cm}^{-1}$  is related to the antisymmetric bridging mode of the tungstate chain.<sup>30</sup> Meanwhile, the bands located at 256, 274 and 296  $\text{cm}^{-1}$  are assigned to the bending of apical O–W–O, and the band located at 406  $\text{cm}^{-1}$  corresponds to the bending of equatorial O–W–O. The peaks below 170  $\text{cm}^{-1}$  can be assigned to translations of the W

and B ions. Compared with pure  $\text{Bi}_2\text{WO}_6$ , the peaks of Nb-doped  $\text{Bi}_2\text{WO}_6$  located in the range of 400–1000  $\text{cm}^{-1}$  cannot be observed obvious shift with the increase of Nb doping content, suggesting the vibrational energy of the W–O stretching band and apical O–W–O band are not changed. Whereas, the peaks of Nb-doped  $\text{Bi}_2\text{WO}_6$  located at 150  $\text{cm}^{-1}$  regularly shift to high frequency with increasing Nb doping content. It indicates that the small amount of Nb doping changes the chemical environment of the element, resulting in the change of ion migration energy.<sup>31</sup>

Fig. 3 shows the high-resolution XPS spectra of BWO and BWO-Nb5 samples, respectively. It can be clearly seen from Fig. 3a that the orbital binding energy of Bi, Nb, W and O in the XPS spectrum of BWO-Nb5. In Fig. 3b, the 4d orbital binding

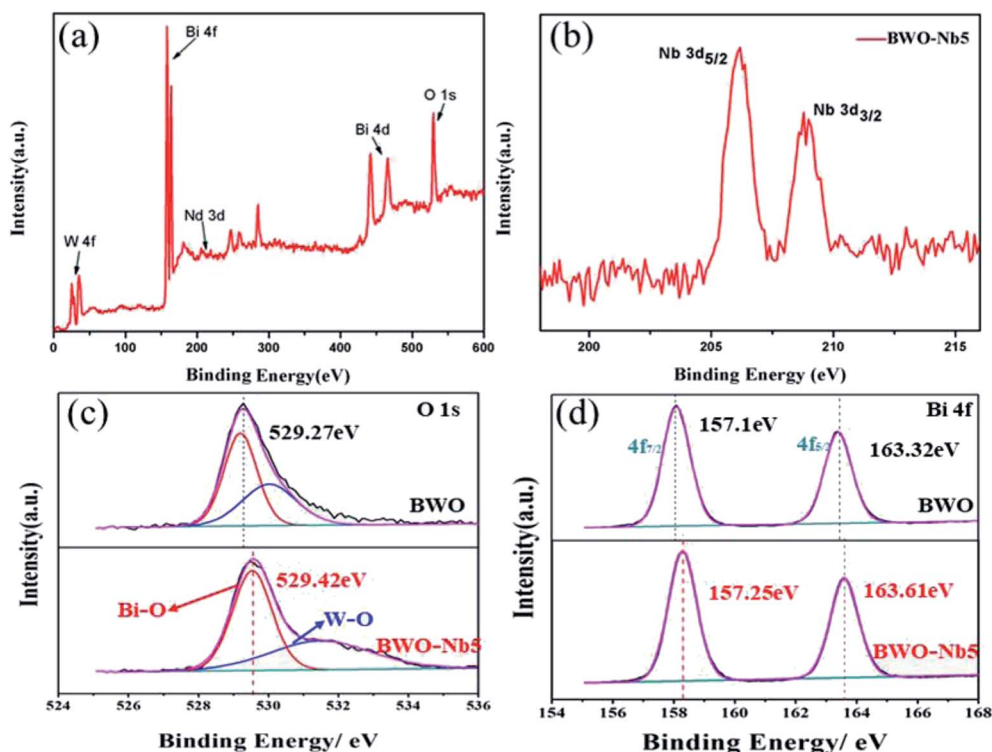


Fig. 3 (a) High-resolution XPS spectra of for BWO-Nb5; (b) Nb 3d spectrum for BWO-Nb5; (c) O 1s spectrum for BWO and BWO-Nb5 samples; (d) Bi 4f spectrum for BWO and BWO-Nb5 samples.



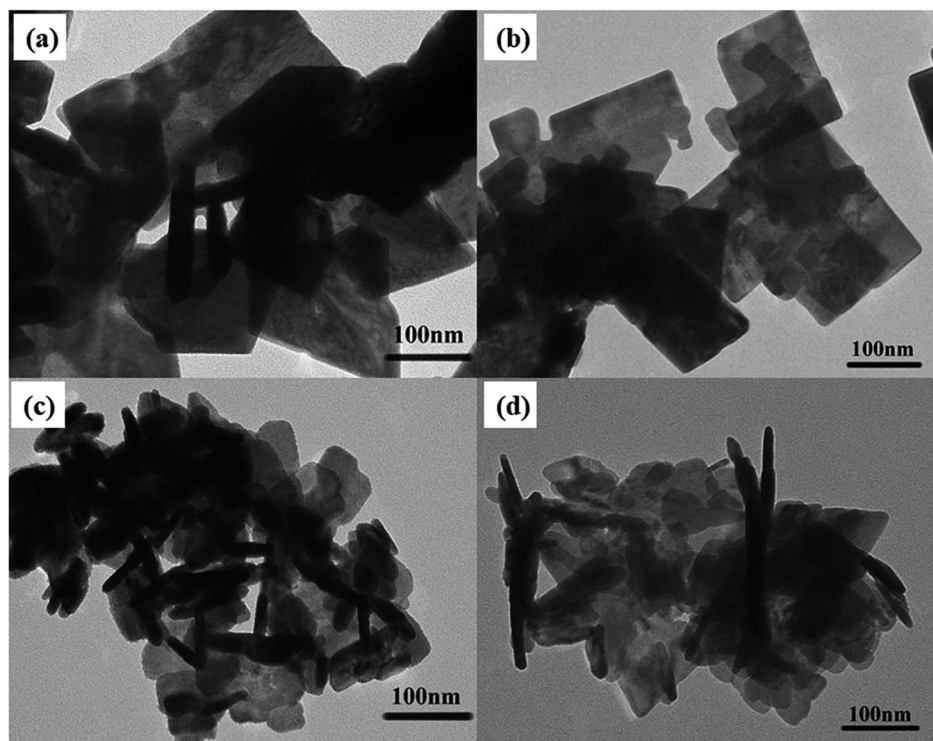


Fig. 4 (a) TEM images of BWO; (b) TEM images of BWO-Nb2; (c) TEM images of BWO-Nb5; (d) TEM images of BWO-Nb7.

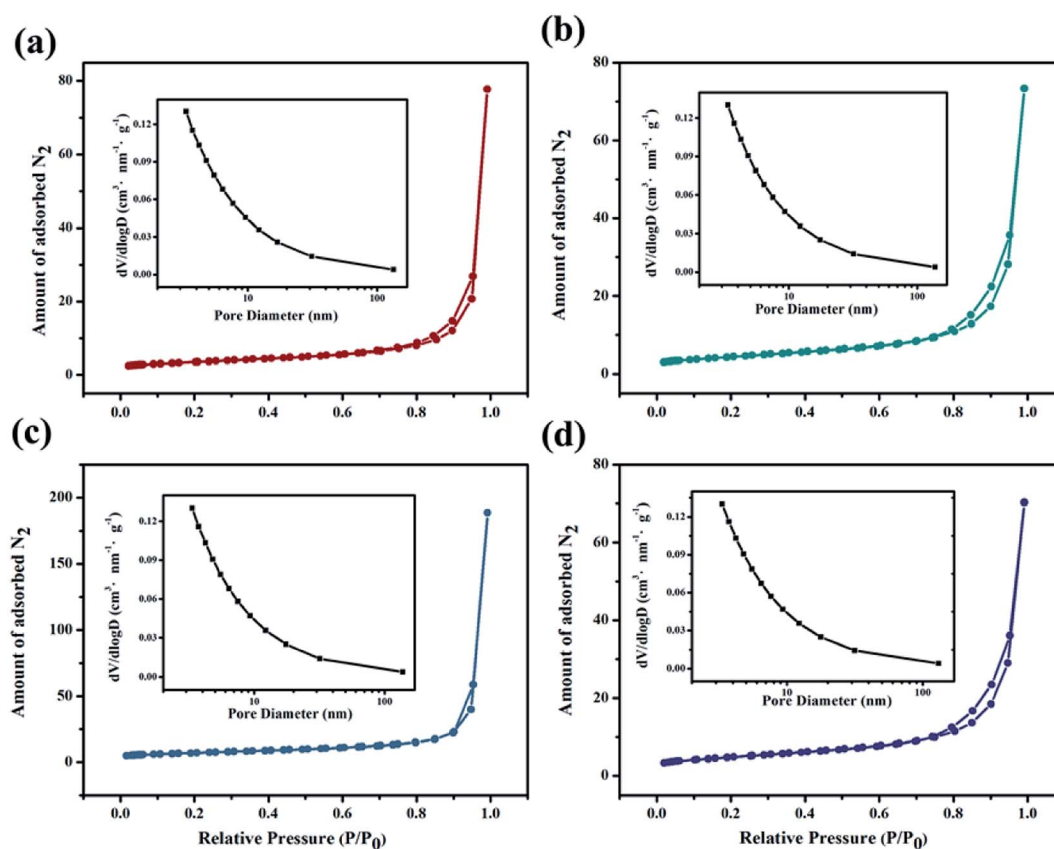


Fig. 5 Nitrogen adsorption–desorption isotherms and pore size distribution curves for prepared samples (a) BWO; (b) BWO-Nb2; (c) BWO-Nb5; (d) BWO-Nb7.





energy of Nb in the BWO-Nb5 sample is 206.2 eV and 208.9 eV corresponds to the Bi-Nb bond and Nb-O band, respectively. In Fig. 3c and d, the XPS spectra correspond to the O 1s and Bi 4f orbital binding energy in the BWO and BWO-Nb5 samples, respectively. Moreover, the binding energy of O 1s and Bi 4f XPS spectra of BWO-Nb5 shift to higher binding energy from 529.27 eV, 157.1 eV to 529.42 eV and 157.25 eV, which is mainly attributed to the high electronic effect of neighboring oxygen vacancies.<sup>9,32</sup> Introducing Nb into the lattice matrix of  $\text{Bi}_2\text{WO}_6$  formed oxygen vacancy as  $\text{Nb}^{5+}$  replaces  $\text{W}^{6+}$ , and the oxygen vacancy can decrease the electron density in the crystal, thereby strengthening the binding energy.<sup>33</sup>

Fig. 4a-d shows the TEM of the prepared BWO and BWO-Nb nanosheets. It can be clearly observed from the figure that the size of the Nb-doped  $\text{Bi}_2\text{WO}_6$  samples are significantly smaller than that of the pure  $\text{Bi}_2\text{WO}_6$ . At the same time, the thickness of the nanosheets is also greatly reduced. The reduction in size and thickness of the  $\text{Bi}_2\text{WO}_6$  nanosheets means greater surface area and surface active sites, resulting in greater photocatalytic activity.

The Fig. 5 shows the nitrogen adsorption-desorption isotherm for BWO and BWO-Nb samples. A pore-size-distribution curve was calculated from the desorption branch of nitrogen isotherm by the BJH method. The pore size distribution of the experimentally prepared BWO and BWO-Nb is within 10 nm, which indicates that the doping of Nb atoms does not affect the pore size of  $\text{Bi}_2\text{WO}_6$ . From the adsorption-desorption curve, the surfaces of BWO, BWO-Nb2, BWO-Nb5, and BWO-Nb7 were  $12.513 \text{ m}^2 \text{ g}^{-1}$ ,  $15.617 \text{ m}^2 \text{ g}^{-1}$ ,  $24.716 \text{ m}^2 \text{ g}^{-1}$ , and  $17.129 \text{ m}^2 \text{ g}^{-1}$ , respectively. The BET experimental results further demonstrate that the doping of Nb atoms reduces the particle size of  $\text{Bi}_2\text{WO}_6$  and thus has a larger surface area.

### 3.2 Photocatalysis mechanism

DRS spectra of BWO-Nb5 and BWO samples are exhibited in Fig. 6. It can be seen that the absorption edge of BWO-Nb5 and BWO are observed to be 458 nm and 453 nm, respectively. Nb doping leads to the red shift of absorption edge of  $\text{Bi}_2\text{WO}_6$ . The

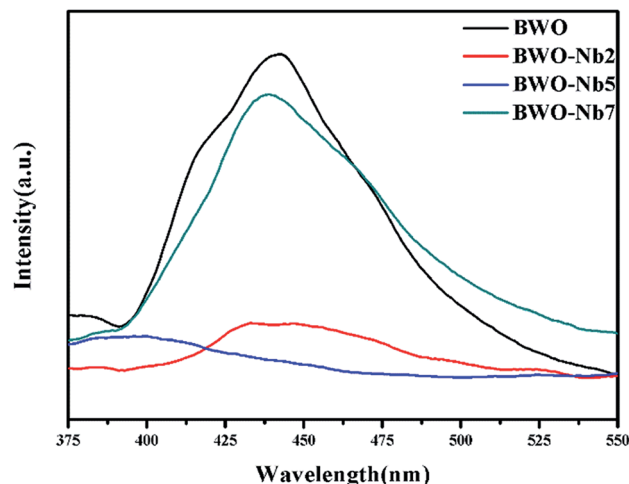


Fig. 7 PL spectra curves of BWO, BWO-Nb2, BWO-Nb5 and BWO-Nb7 samples.

band gap values of BWO-Nb5 and BWO estimated from the  $(\alpha h\nu)^{1/2}$  versus photon energy plots are about 2.68 eV and 2.73 eV, respectively.<sup>34</sup> The reduction of optical band gap for  $\text{Bi}_2\text{WO}_6$  may be resulted from the two factors: (1) the 4d orbital of  $\text{Nb}^{5+}$  and the 5d orbital of  $\text{W}^{6+}$  form a new conduction band. (2) The surface oxygen vacancies increase the valence bandwidth of  $\text{Bi}_2\text{WO}_6$ , which makes the valence band of  $\text{Bi}_2\text{WO}_6$  move up, which enhances the utilization of sunlight.

In order to investigate the separation efficiency of photo-generated carriers in photocatalysis reaction, PL emission spectrum testing was carried out. It can be seen from the Fig. 7 that the emission peaks of the four prepared samples near 430 nm, furthermore, the PL peak intensity of the Nb-doped  $\text{Bi}_2\text{WO}_6$  sample is lower than that of the pure  $\text{Bi}_2\text{WO}_6$ . The high electron effect of the oxygen vacancies can attract photo-generated electrons, thereby promoting the separation of photo-generated carriers. However, the excessive concentration of oxygen vacancies will become the recombination center of

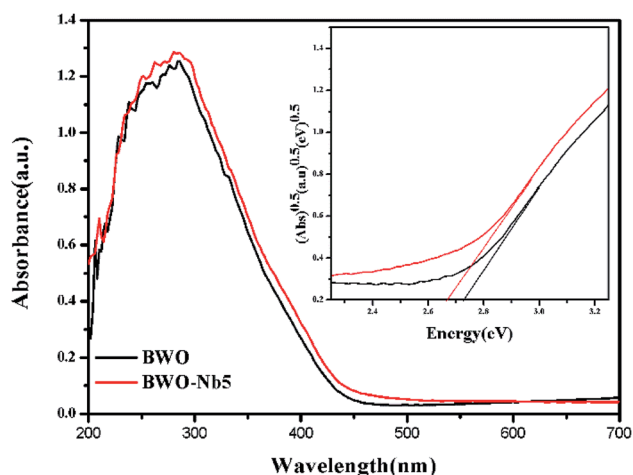


Fig. 6 UV-vis DRS spectra and plots of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  (the inset) of BWO and BWO-Nb5 samples.

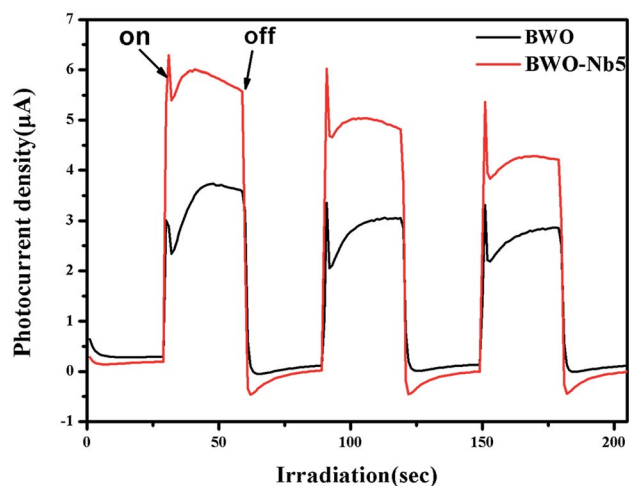


Fig. 8 Photocurrent response of BWO and BWO-Nb5 samples.



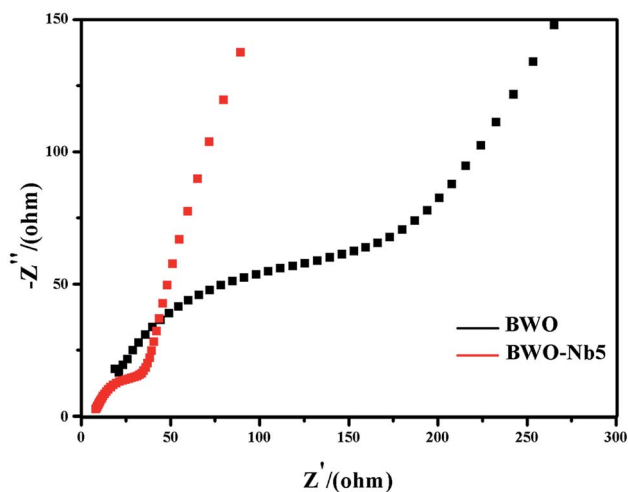


Fig. 9 EIS spectra of BWO and BWO-Nb5 samples.

photo-generated carriers.<sup>35</sup> Therefore, it is observed that with further increasing the Nb doping amount, the PL intensity of BWO-Nb7 increases instead.

The Fig. 8 shows a comparison of the visible-light photocurrent responses contributed by BWO and BWO-Nb5. Both

BWO and BWO-Nb5 samples exhibited rapid visible light response photocurrent, whereas BWO-Nb5 samples showed higher photocurrent than BWO samples, indicating more efficient photoinduced charge separation and transfer in BWO-Nb5 samples. It can be seen that the photocurrent from BWO-Nb5 is about 1.85 times higher than the photocurrent from BWO, which indicates that the surface oxygen vacancies generated by the Nb doping greatly promote photogenerated charge transfer.

The electrochemical impedance spectroscopy (EIS) was also adopted to investigate BWO and BWO-Nb5 electrodes, which is another valid electrochemical strategy to measure the transfer and separation efficiency of photo-generated carriers. Generally, a smaller EIS arc radius suggests an effective separation of photo-generated carriers and fast interfacial charge transfer. As shown in Fig. 9, the EIS arc radius of BWO-Nb5 is smaller than that of BWO, indicating the higher mobility and separation efficiency of interfacial photo-generated carriers in BWO-Nb5.

### 3.3 Evaluation of photocatalytic activity

As shown in Fig. 10, Nb-doped  $\text{Bi}_2\text{WO}_6$  samples exhibit much better photocatalytic activity than pure  $\text{Bi}_2\text{WO}_6$ . The BWO-Nb5 displays the highest photocatalytic efficiency. The first-order linear relationship is revealed by the plots of  $\ln(C/C_0)$  vs.

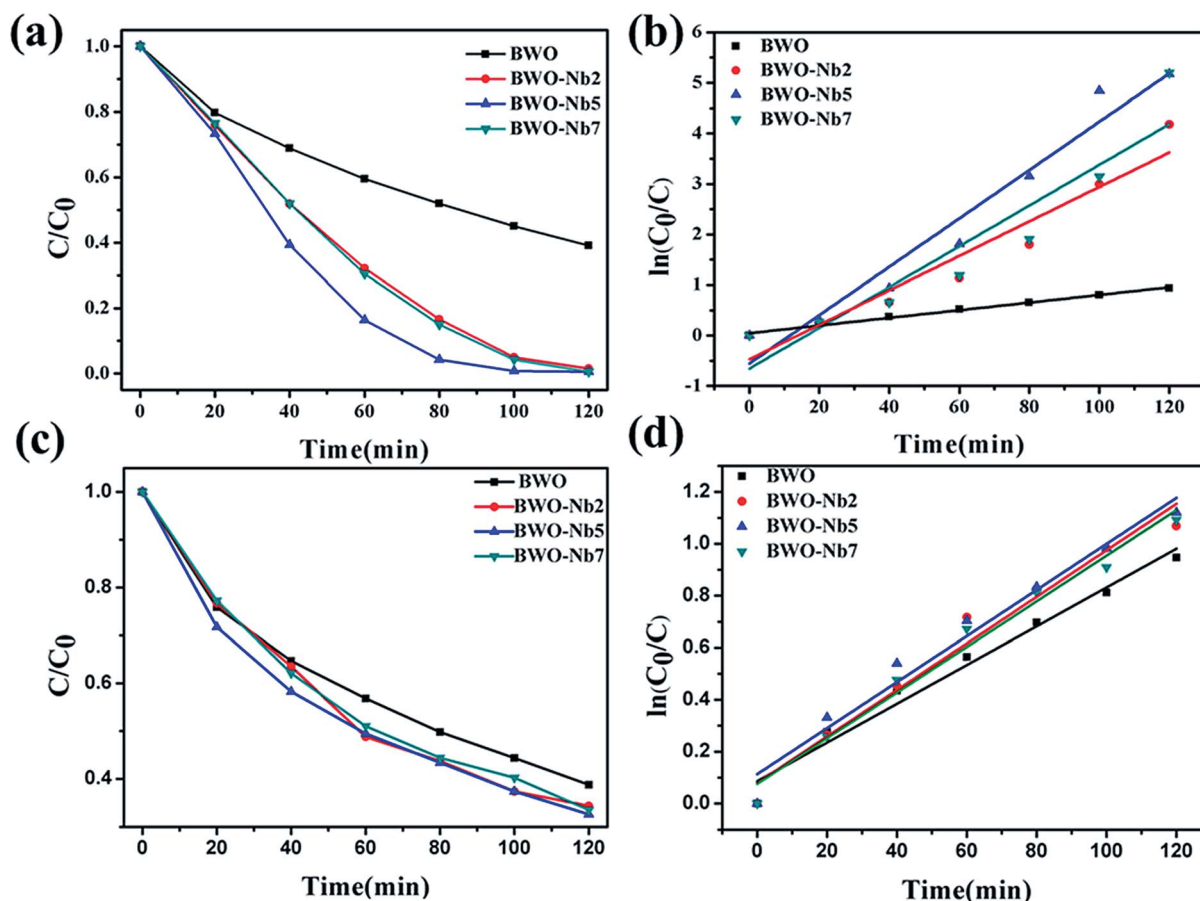


Fig. 10 (a) Dynamic curve of RhB over different samples; (b) photodegradation rates of RhB over different samples; (c) dynamic curve of TC over BWO-Nb and BWO; (d) photodegradation rates of TC over BWO-Nb and BWO.



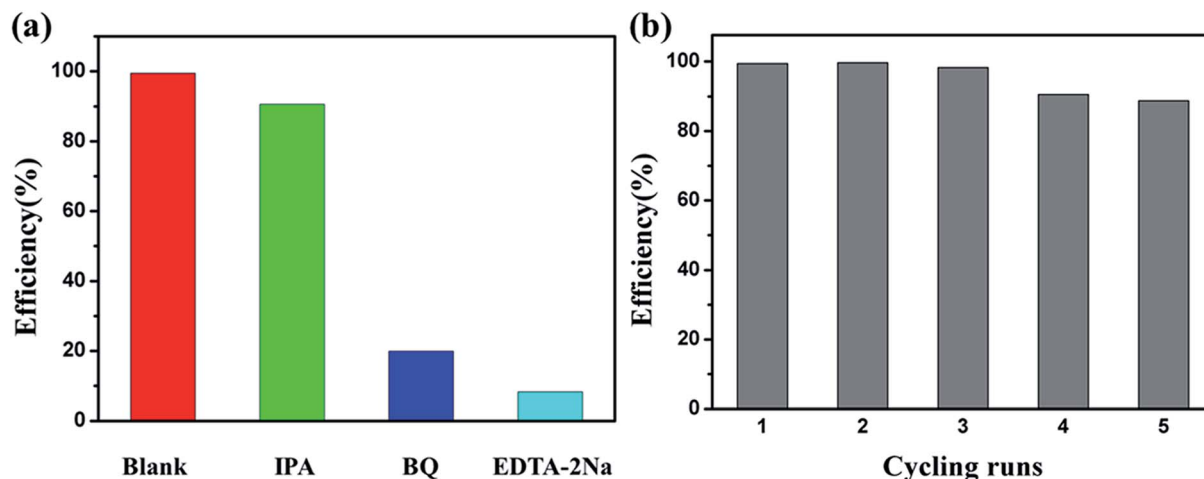


Fig. 11 (a) Photocatalytic degradation of RhB over BWO-Nb5 photocatalysts alone and with the addition of IPA, BQ, or EDTA-2Na; (b) photocatalytic degradation of RhB cycling test of BWO-Nb5.

irradiation time ( $t$ ). The photocatalytic activities of all Nb-doped  $\text{Bi}_2\text{WO}_6$  are better than pure  $\text{Bi}_2\text{WO}_6$ . In more detail, the degradation rate of BWO-Nb5 was 6.373 times that of BWO in the degradation of rhodamine B; the degradation rate of BWO-Nb5 was 1.4 times that of BWO in the degradation of TC.

In order to reveal the photocatalytic mechanism of BWO-Nb5 photocatalyst, we selected the main active substance capture agent for photocatalytic degradation experiments in Fig. 11a. With the addition of isopropanol (IPA, 2 mM, hydroxyl radical scavenger), the degradation efficiency of RhB was not significantly reduced, indicating that hydroxyl ( $\cdot\text{OH}$ ) is not the main active substance for RhB degradation. However, when the scavenger benzoquinone (BQ, 0.1 mM) was added to scavenge the superoxide radical  $\cdot\text{O}_2^-$ , the degradation profile of RhB was significantly reduced. The results show that superoxide radical  $\cdot\text{O}_2^-$  is one of the active substances degraded by RhB. When disodium edetate (EDTA-2Na, 10 mM) was used to remove photogenerated holes ( $\text{h}^+$ ) in the reaction system, BWO-Nb5 hardly degraded RhB. The results of photocatalytic mechanism experiments show that  $\cdot\text{OH}$  has little effect on the photodegradation process of RhB,  $\text{h}^+$  and  $\cdot\text{O}_2^-$  are the main active substances.

As shown in Fig. 11b, in order to test the stability of BWO-Nb5, five cycles of photodegradation of the RhB experiment were tested, and the BWO-Nb5 catalyst did not show any significant loss of activity. Cycling experiments showed good photocatalytic degradation stability of BWO-Nb5.

## 4. Conclusions

In summary, Nb-doped  $\text{Bi}_2\text{WO}_6$  nanosheets were successfully synthesized by a hydrothermal method. The oxygen vacancies in  $\text{Bi}_2\text{WO}_6$  crystals can be regulated by adjusting Nb doping. It is obvious that the effect of Nb doping has two aspects: on the one hand, Nb doping produces oxygen vacancies, which reduces the optical band gap of  $\text{Bi}_2\text{WO}_6$  and enhances the separation and transfer of photogenerated carriers; on the other hand, Nb doping reduced the crystal size of  $\text{Bi}_2\text{WO}_6$  with a larger surface

area. Hence, the Nb-doped  $\text{Bi}_2\text{WO}_6$  exhibits enhance photocatalytic activities in degradation of RhB and TC under visible light irradiation compared with pure  $\text{Bi}_2\text{WO}_6$ .

## Conflicts of interest

The authors confirm that they have no conflict of interest.

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