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# Synthesis of BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> Heterojunction with Enhanced Photocatalytic Activity under Visible-Light Irradiation

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**Abstract**

BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> photocatalysts were successfully synthesized by a simple two-step hydrothermal process, which involved the initial formation of BiPO<sub>4</sub> rod and then the attachment of Bi<sub>2</sub>S<sub>3</sub> through ion exchange. The as-synthesized products were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and UV-vis diffuse reflectance spectra (UV-vis DRS). It was found that BiPO<sub>4</sub> was regular rods with smooth surfaces. However, BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction had a rough surface, which could be attributed to the attachment of Bi<sub>2</sub>S<sub>3</sub> on the surface of BiPO<sub>4</sub> rods. The BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> composite exhibited better photocatalytic performance than that of pure BiPO<sub>4</sub> and Bi<sub>2</sub>S<sub>3</sub> for the degradation of methylene blue (MB) and Rhodamine B (RhB) under visible light. The enhanced photocatalytic performance could be ascribed to synergistic effect of BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction, in which the attached Bi<sub>2</sub>S<sub>3</sub> nanoparticles could improve visible-light absorption and the BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction suppressed the recombination of photogenerated electron-hole pairs. Our work suggested that BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction could be a potential photocatalyst under visible light.

**Keywords:** BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub>; Photocatalytic activity; Hydrothermal method; Heterojunction photocatalyst

**Background**

Currently, semiconductor photocatalysts have attracted a lot of interests due to their widely applications for the degradation of organic contaminants [1–4] and generation of hydrogen from water [5]. Generally speaking, a highly efficient photocatalyst must have a wide photoabsorption range, as well as the low recombination rate of photogenerated electron-hole pairs. Therefore, it is also a challenge to develop a new compound with high photocatalytic efficiency under visible light [6–9].

As a potential photocatalyst, BiPO<sub>4</sub> has recently been extensively studied [10–12]. It has been reported that the photocatalytic activity of BiPO<sub>4</sub> is strongly dependent on its crystal structure [13] and the monoclinic phase BiPO<sub>4</sub> showed a better photocatalytic performance than that of P25 for the photodegradation of organic contaminants under UV irradiation [14]. However, BiPO<sub>4</sub> had a wide band gap of about 3.8 eV and thus can only be excited

by UV light to generate electron-hole pairs [11]. In order to improve the visible-light utilization of BiPO<sub>4</sub>, many efforts have been taken. Lin et al. fabricated Ag<sub>3</sub>PO<sub>4</sub>/BiPO<sub>4</sub> heterojunction with enhanced photocatalytic ability under visible-light irradiation [15]. Duo et al. reported that BiPO<sub>4</sub>/BiOCl heterojunction also had enhanced photocatalytic activity [16]. Li et al. found that BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction could efficiently respond to visible-light irradiation [17]. Besides, Zhang et al. reported that BiPO<sub>4</sub>/reduced graphene oxide composites with specific surface areas had better photocatalytic activity for the degradation of MB [18]. Whereas, coupling of BiPO<sub>4</sub> with other semiconductors is still meaningful for improving light absorption in the visible spectrum and suppressing the recombination of the photogenerated electron-hole pairs more effectively.

Bi<sub>2</sub>S<sub>3</sub>, a small band gap semiconductor (1.3 eV), has a high photoabsorption coefficient [19–21]. Hence, it can usually be used as a potential visible-light photocatalyst through combination from other semiconductors to improve light absorption and separation efficiency of

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photogenerated electron-hole pairs, such as CdS/Bi<sub>2</sub>S<sub>3</sub> [22], BiVO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> [23], Bi<sub>2</sub>S<sub>3</sub>/BiOBr [24], and so on.

In this study, we reported the preparation of a novel BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterostructure and their photocatalytic properties were evaluated by the degradation of MB and RhB under visible light. As expected, the as-prepared BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction exhibited enhanced visible-light photocatalytic activity and a possible mechanism was presented.

## Methods

### Materials and Preparation

All reagents were of analytical purity (Sinopharm Chemical reagent Co., Ltd., China) and used without further purification.

### Synthesis of BiPO<sub>4</sub>

BiPO<sub>4</sub> was prepared by a facile hydrothermal method. Firstly, 0.5 g of PVP was dissolved in a beaker with deionized water (50 mL) under stirring. Secondly, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and NaH<sub>2</sub>PO<sub>4</sub>·12H<sub>2</sub>O (molar ratio of 1:1) were added into the solution. After the pH of the reaction system was adjusted to 3 by HNO<sub>3</sub>, the solution was transferred into a 100-mL Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. When the system cooled down to room temperature naturally, the resulting product was harvested and washed with deionized water and absolute alcohol for several times. Finally, the as-prepared products were dried at 60 °C for 12 h.

### Synthesis of BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> Photocatalyst

The BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> photocatalyst was prepared through an in situ ion exchange process. Typically, 0.1 g of PVP was dissolved in 50 mL of ethylene glycol, followed by the addition of 0.456 g of BiPO<sub>4</sub> under stirring to achieve suspension. Then, a certain amount of thiourea (the amount of thiourea was 0.086, 0.172, and 0.573 g, and they are named as BB-1, BB-2, and BB-3, respectively.) was added into above suspension and the solution was transferred into a 100-mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 140 °C for 3 h. After the autoclave was cooled to room temperature naturally, the precipitates were collected and washed with water and ethanol several times. The BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> products were dried at 60 °C for 12 h. For comparison, pure Bi<sub>2</sub>S<sub>3</sub> was prepared through hydrothermal method according to the literature [25].

### Characterization of the As-prepared Samples

The phase of the samples was measured by XRD (D/Max-IIIC, Shimadzu) using an X-ray diffractometer with Cu K $\alpha$  radiation. The morphology was analyzed by SEM on Hitachi S-4600 and TEM (FEI Tecnai G20). UV-vis DRS was tested on a Shimadzu UV240

UV-vis spectrophotometer with BaSO<sub>4</sub> as a reference material. The elemental composition of the samples was analyzed by X-ray photoelectron spectrometer (XPS, USA Thermo ESCALAB 250).

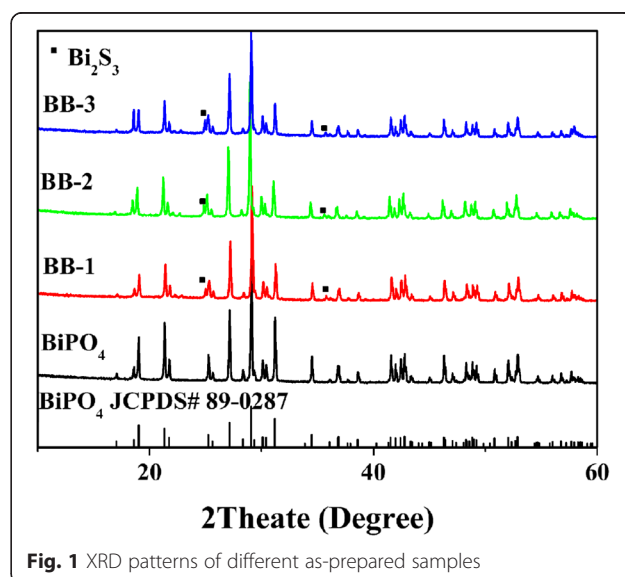
### Photocatalytic Activity

The photocatalytic performance of BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction photocatalyst was evaluated by the degradation of MB and RhB under visible light. In each experiment, 50 mg of different photocatalysts were added into 100 mL of MB or RhB solution (10 mg/L) in a reactor. Before irradiation, the mixture was magnetically stirred for 30 min in the dark to achieve the adsorption/desorption equilibrium between dye and photocatalysts. Then, the solution was irradiated by visible light under continuous stirring. At a defined time interval, about 3 mL of solution was extracted from the reactors and then centrifuged to remove catalysts before analysis. Finally, MB (RhB) solution was analyzed through a UV-vis spectrophotometer. The degradation rate could be obtained through the formula [26]:  $\eta = C_i/C_0 \times 100\%$ , where  $C_i$  was the absorbance of MB (RhB) which was measured every 30 min, and  $C_0$  was the absorbance of MB (RhB) before light up.

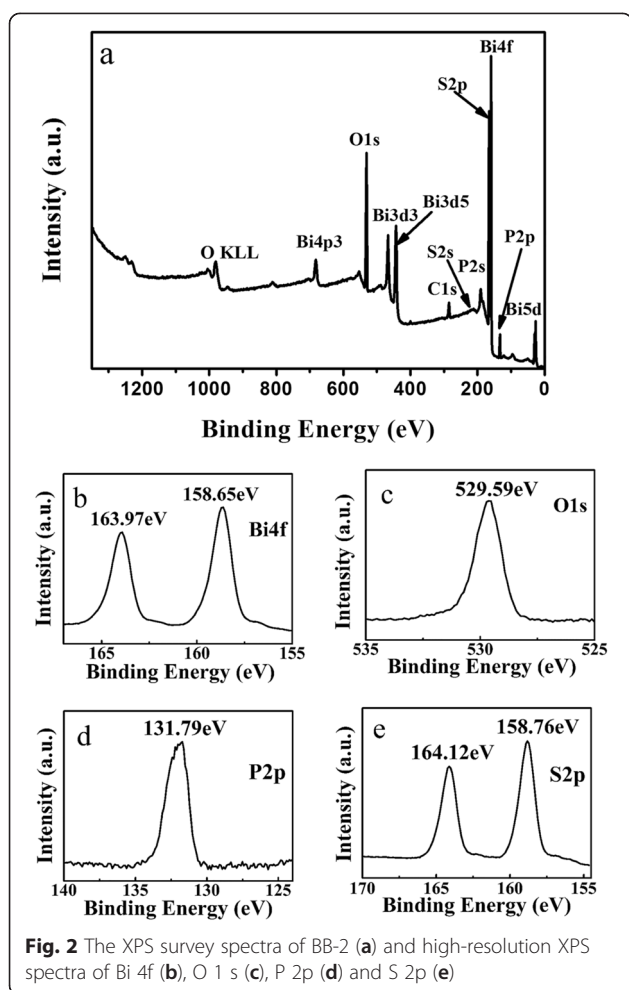
## Results and Discussion

### Phase and Crystal Structure Analysis

Figure 1 shows the XRD patterns of BiPO<sub>4</sub> and BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction with different Bi<sub>2</sub>S<sub>3</sub> contents. In the pure BiPO<sub>4</sub>, all the diffraction peaks are well matched with the monoclinic phase of BiPO<sub>4</sub> (JCPDS File No. 89-0287), indicating that the as-prepared BiPO<sub>4</sub> has the high purity. On the other hand, the BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> composites exhibit a mixture of two crystalline phases. One can be identified as BiPO<sub>4</sub>, and the others originate from rutile Bi<sub>2</sub>S<sub>3</sub> [25]. Furthermore, the intensities



**Fig. 1** XRD patterns of different as-prepared samples

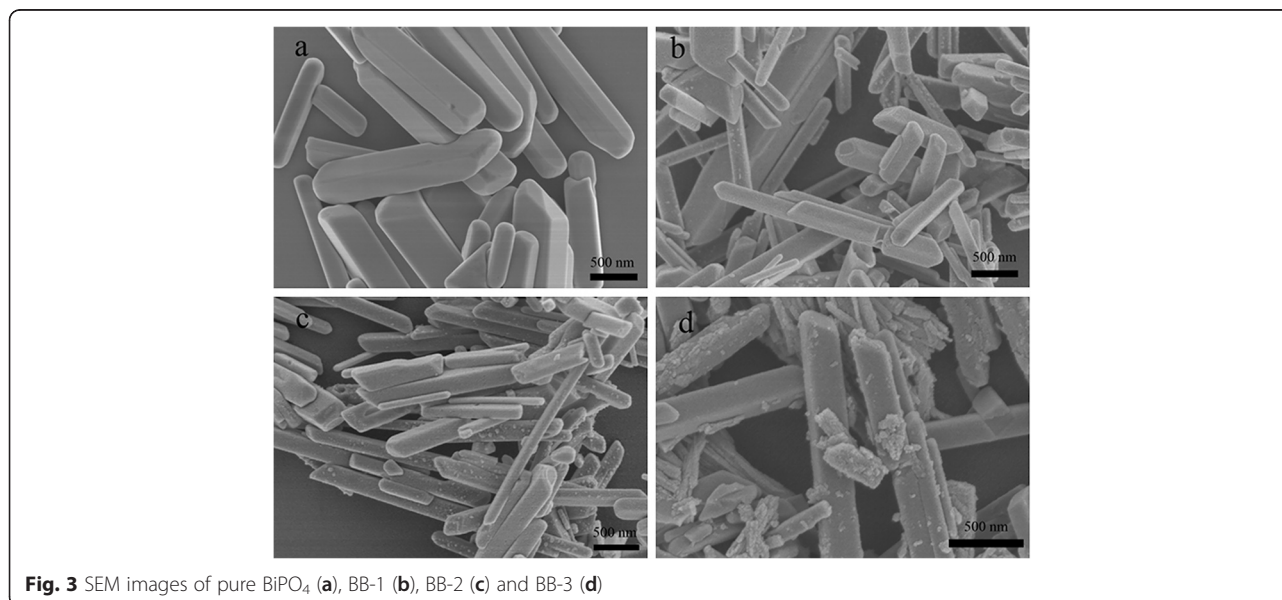


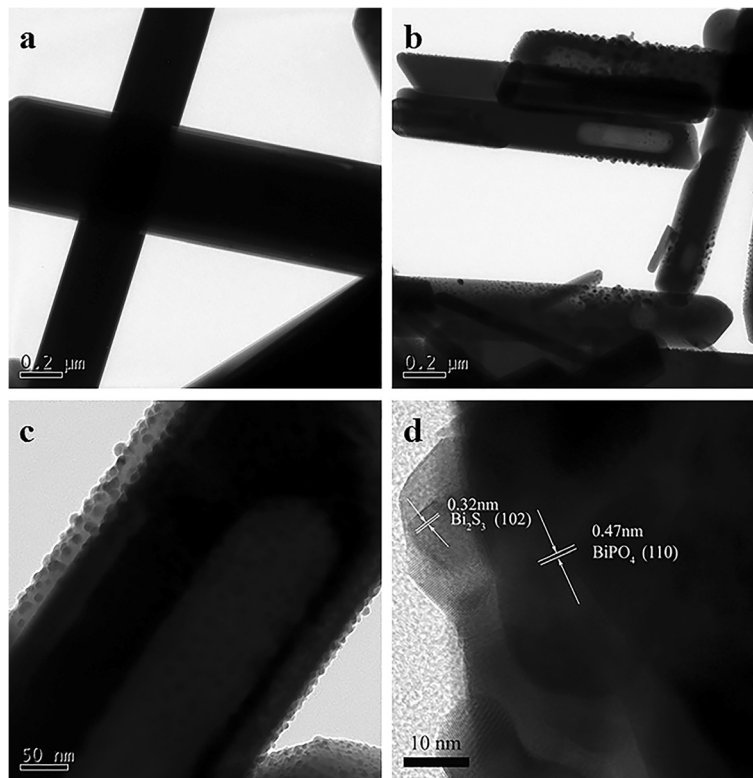
of corresponding to diffraction peaks of  $\text{Bi}_2\text{S}_3$  gradually strengthen along with the increase of the  $\text{Bi}_2\text{S}_3$  content, while those of  $\text{BiPO}_4$  simultaneously weaken. No other characteristic peaks of impurity are detected, suggesting that  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  composites are only composed of  $\text{BiPO}_4$  and  $\text{Bi}_2\text{S}_3$  phases.

The surface chemical composition of BB-2 is analyzed by XPS and the results are shown in Fig. 2. The XPS survey spectrum (Fig. 2a) shows that BB-2 contains Bi, P, S, and O elements, which is consistent to XRD results. Besides, C 1s peak is also seen in XPS survey spectrum, which can be attributed to adventitious hydrocarbon from instrument. Two peaks appear at 163.97 and 158.65 eV in Fig. 2b, which are corresponding to Bi  $4f_{5/2}$  and Bi  $4f_{7/2}$  peaks of  $\text{Bi}^{3+}$ , respectively [27]. In Fig. 2c, O 1s peak appeared at 529.59 eV, in which it can be attributed to lattice oxygen in crystalline  $\text{BiPO}_4$  [28]. In Fig. 2d, the P 2p XPS peak appeared at 131.79 eV, suggesting that P exists in the oxidation of  $\text{P}^{5+}$ . On the other hand, the binding energies of 164.12 and 158.76 eV are attributed to S 2p peaks (Fig. 2e), which prove the existence of  $\text{S}^{2-}$  [29].

### Morphology Analysis

Figure 3 shows the SEM images of  $\text{BiPO}_4$  and  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  composites. It can be seen from Fig. 3a that pure  $\text{BiPO}_4$  shows regular rod shape with diameter of 200–400 nm and the length of 500–2000 nm. It should be noted that these rods have smooth surfaces. Figure 3b–d shows the SEM images of different  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  composites. Compared with pure  $\text{BiPO}_4$ , the surfaces of  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  composites become rough. Furthermore, with the increasing amount of additive thiourea, more  $\text{Bi}_2\text{S}_3$  nanoparticles can be observed on the surface of  $\text{BiPO}_4$  rods gradually, which is also consistent to XRD results.





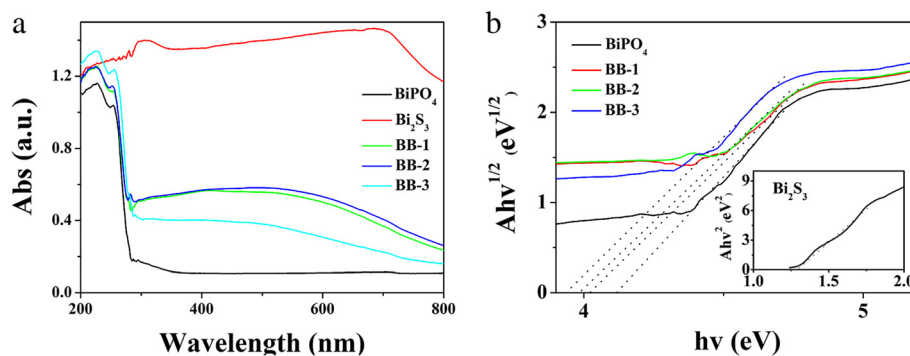
**Fig. 4** TEM images of  $\text{BiPO}_4$  (a), BB-2 (b, c), and HRTEM image of BB-2 (d)

TEM and HRTEM images are shown in Fig. 4, which display identified results as those of SEM analysis. From Fig. 4a, one can see that pure  $\text{BiPO}_4$  are regular rods with a smooth surface. While  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  heterojunction shows a rough surface, suggesting the successful attachment of  $\text{Bi}_2\text{S}_3$  on the surface of  $\text{BiPO}_4$  rods. Furthermore, the lattice spacings can be clearly seen in the corresponding HRTEM image (Fig. 4d). The fringe spacing of 0.47 nm is indexed to the (1 1 0) lattice plane of monoclinic  $\text{BiPO}_4$ , while 0.32 nm is agreed with the (1 0 2) lattice plane of  $\text{Bi}_2\text{S}_3$ . Therefore, it can be summarized that

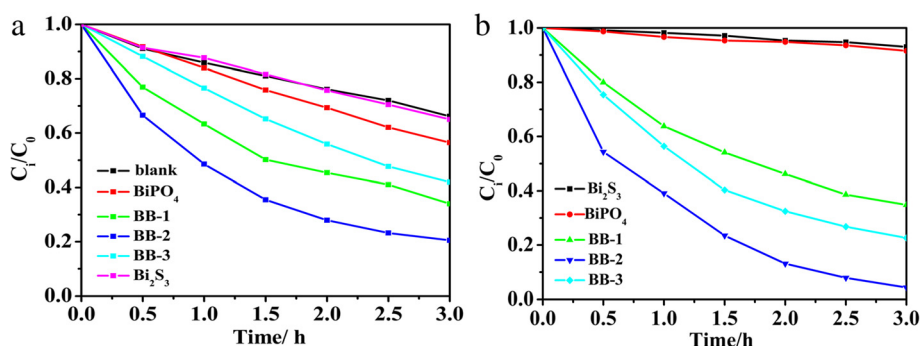
$\text{BiPO}_4/\text{Bi}_2\text{S}_3$  heterojunction is achieved through a facile ion-exchange method.

#### UV-vis Analysis

Figure 5a shows UV-vis DRS of as-prepared  $\text{BiPO}_4$ ,  $\text{Bi}_2\text{S}_3$ , and  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  composites. It reveals that  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  composites have a stronger absorption than that of  $\text{BiPO}_4$  in visible light. The band gap energy can be achieved through the formula [30, 31]. Besides, according to the literature,  $n$  values of  $\text{BiPO}_4$  and  $\text{Bi}_2\text{S}_3$  are 4 [32] and 1 [33], respectively. Therefore, as is shown in Fig. 5b,  $E_g$



**Fig. 5** a UV-vis DRS of  $\text{BiPO}_4$ ,  $\text{Bi}_2\text{S}_3$ , and  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  composites and b the plotting of  $(ah\nu)^{1/2}$  vs.  $h\nu$



**Fig. 6** **a** Photodegradation rate of MB under visible-light irradiation with different samples, **b** photodegradation rate of RhB under visible-light irradiation with different samples

of BiPO<sub>4</sub> and Bi<sub>2</sub>S<sub>3</sub> can be calculated as 4.08 and 1.30 eV. Moreover,  $E_g$  of BB-1, BB-2, and BB-3 are 4.01, 3.93, and 3.81 eV, respectively. Besides, Bi<sub>2</sub>S<sub>3</sub> displays quantum size effect, which may influence the band gap, the position of both CB and VB band. Besides, the band gap shift relative to the bulk can be calculated by the following formula [34, 35]:

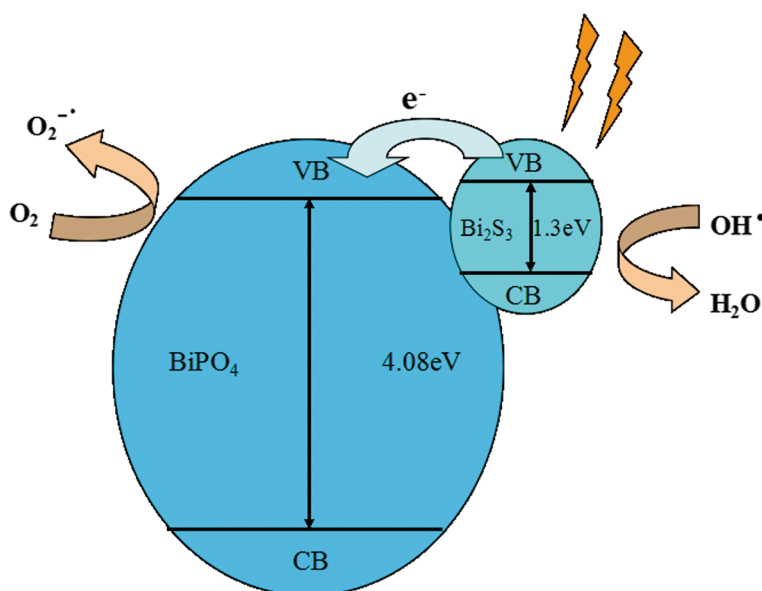
$$\Delta E_g(R) = \frac{h^2}{8m_o R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right),$$

in which  $\Delta E_g(R)$  is the band gap shift,  $h$  is the Planck's constant, and  $R$  is the crystal radius. Besides,  $m_o$  is electron mass and  $m_e^*$  and  $m_h^*$  are the effective masses of electrons and holes, respectively. Then, the size of Bi<sub>2</sub>S<sub>3</sub> nanoparticles attached on the surface of BiPO<sub>4</sub> rods can be calculated as 2.68, 2.72, and 2.78 nm, respectively,

which is much smaller than Bohr excitation radius of 24 nm. Therefore, quantum size confinement can be observed obviously, which influences the band gap, the position of both CB and VB band, etc. These results also support the enhancement of photocatalytic activity.

#### Photocatalytic Activity of Different Samples

The photocatalytic performance of BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction was assessed by photodegradation of MB under visible-light irradiation (Fig. 6a). It can be seen that pure BiPO<sub>4</sub> shows poor photocatalytic ability in degrading MB (40 %). Interestingly, the coupling of BiPO<sub>4</sub> with Bi<sub>2</sub>S<sub>3</sub> leads to notable enhancement MB photodegradation. The MB removal rates are about 50, 80, and 60 %, respectively. Meantime, RhB here is also employed as an organic pollutant to further confirm the photocatalytic activity of BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction. As shown in



**Fig. 7** Schematic illustration of possible electrons and hole transfer mechanism of BiPO<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> heterostructure

Fig. 6b,  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  composites show better photocatalytic activity in the degradation of RhB than that of pure  $\text{BiPO}_4$  and the best photocatalytic property was achieved for BB-2 sample. The enhanced visible-light-driven activity of the heterostructure must be attributed to the synergistic effect between  $\text{BiPO}_4$  and  $\text{Bi}_2\text{S}_3$ . What is more, the quantum size confinement of  $\text{Bi}_2\text{S}_3$  in the visible spectrum also leads to the enhancement of photocatalytic activity. However, the excess  $\text{Bi}_2\text{S}_3$  content in  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  composite will cause their photocatalytic performance to decrease (BB-3). It may be attributed to these reasons: one is reduction of active sites due to the excess  $\text{Bi}_2\text{S}_3$  nanoparticles on the surface  $\text{BiPO}_4$  rod [36]. The other is that excessive narrow band gap  $\text{Bi}_2\text{S}_3$  may lower the separation efficiency of electron-hole pairs and further inhibit the photocatalytic activity [37].

### Possible Photocatalytic Mechanism

The band positions of  $\text{BiPO}_4$  and  $\text{Bi}_2\text{S}_3$  are evaluated based on the equation [38]. Hence, the valence band and conduction band edge potential ( $E_{\text{VB}}$  and  $E_{\text{CB}}$ ) of  $\text{BiPO}_4$  and  $\text{Bi}_2\text{S}_3$  are 4.39 eV, 0.31 eV and 1.43 eV, 0.13 eV, respectively. Therefore, the possible mechanism is shown in Fig. 7.  $\text{Bi}_2\text{S}_3$  nanoparticles absorb the visible light and give rise to electron-hole pairs. The photo-excited electrons in  $\text{Bi}_2\text{S}_3$  CB will transfer to  $\text{BiPO}_4$  rods and holes are left in  $\text{Bi}_2\text{S}_3$  VB, which will decrease recombination rate of photogenerated charge carriers. The electrons in  $\text{BiPO}_4$  CB can rapidly adsorb  $\text{O}_2$  to form  $\text{O}_2^{\cdot-}$ , while the holes can interact with the absorbed  $\text{H}_2\text{O}$  to achieve hydroxyl radicals. After then,  $\text{O}_2^{\cdot-}$  and  $\text{OH}^{\cdot}$  with strong oxidizability can decompose MB (RhB) to generate  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Moreover,  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  heterojunction photocatalysts have a stronger and wider absorption in visible light, which is beneficial to photocatalytic activity.

### Conclusions

In summary, we have synthesized the  $\text{BiPO}_4/\text{Bi}_2\text{S}_3$  heterojunction with a facile two-step hydrothermal method.  $\text{Bi}_2\text{S}_3$  nanoparticles can be in situ formed on the surface of  $\text{BiPO}_4$  rods through ion exchange. As the quantum size confinement of  $\text{Bi}_2\text{S}_3$  in the visible spectrum, it can be used as photosensitizer. When  $\text{BiPO}_4$  rods are modified with  $\text{Bi}_2\text{S}_3$ , the separation of electron-hole pairs could be accelerated and the photoabsorption could be promoted as well. These directly led to the enhancement of photocatalytic activity for the degradation of MB (RhB) under visible-light irradiation, and BB-2 sample exhibits the best photocatalytic property. Degradation rate of MB under visible-light irradiation with BB-2 could reach to 80 % in 3 h, double that of pure  $\text{BiPO}_4$ . Besides, degradation rate of RhB could reach to 99.6 % in 3 h, while it only degraded for 8 % by pure  $\text{BiPO}_4$ .

### Competing interests

The authors declare that they have no competing interests.

### Authors' contributions

The experiments were guided by ML and GY in this work and all the processes were designed by ZW. JG tested and analyzed the dates. YW participated in the discussion and gave useful suggestions. The manuscript was composed by ML. All authors read and approved the final manuscript.

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