Preparation and visible light photocatalytic activity of Bi_2O_3/Bi_2WO_6 heterojunction photocatalysts

C Y Yan*, W T Yi*, J Xiong and J Ma

College of Chemistry, Chemical Engineering and Material Science, Zaozhuang University, Zaozhuang, China.

Email: qislycy@163.com; qislywt@163.com

Abstract. The Bi_2O_3 nanorods, flower-like Bi_2WO_6 and Bi_2O_3/Bi_2WO_6 heterojunction composites with the molar ratio of $n_{Bi}:n_W$ from 2:1, 2.5:1, to 3:1 have been synthesized via one-step hydrothermal method and two-step hydrothermal method, respectively. The products are characterized by powder X-ray diffraction (XRD), UV–vis diffuse reflectance spectroscopy (UV-vis DRS), and scanning electron microscopy (SEM). Photocatalytic experiments indicate that such Bi_2O_3/Bi_2WO_6 composite possesses higher photocatalytic activity for RhB degradation under visible-light irradiation in comparison with pure Bi_2O_3 and Bi_2WO_6. The enhancement of the photocatalytic activity of the Bi_2O_3/Bi_2WO_6 heterojunction catalysts can be ascribed to the reduced recombination of the photoexcited electrons and holes during the photocatalytic reaction. The effect of the molar ratio of $n_{Bi}:n_W$ on the catalytic performance of the heterojunction catalysts was also investigated. And the optimal molar ratio of $n_{Bi}:n_W$ is 2.5:1 which was synthesized by one-step hydrothermal method.

1. Introduction

As a free, clean, non-polluting, inexhaustible resource and a domestic energy source, solar energy has been considered one of the most promising renewable energy sources in the world. Photocatalytic reactions are currently studied from the viewpoint of environmental accountability and energy conversion. Heterogeneous photocatalysts offer great potential for decomposing pollutants in air or in solution. In particular, photocatalysts that degrade pollutants under visible light irradiation would have great potential in solar energy applications. The pioneering works done by Kudo et al. found that bismuth tungstate (Bi_2WO_6) exhibited photocatalytic activities for O_2 evolution [1]. Since then, it was reported that Bi_2WO_6 could degrade the organic compound under visible light irradiation [2]. Bismuth tungstate has received more and more attention as a visible-light photocatalyst because of its narrow bandgap (~2.8 eV), chemical inertness, photo-stability, and environmentally friendly features. However, the rapid recombination of photogenerated electronehole pairs seriously impacts its photocatalytic activity of pure Bi_2WO_6. In order to improve the photocatalytic activity of Bi_2WO_6, numerous beneficial ways have been employed, including substitution[3], doping[4], building heterostructure with a narrow-bandgap semiconductor[5], coupling with a carrier[6], and so on[7].

Among these, synthesis Bi_2O_3/Bi_2WO_6 heterojunction photocatalyst could be an effective way to enhance the electrochemical properties, since it is capable of tuning the morphologies into a well-defined structure with various size ranges. Various approaches have been attempted to prepare the Bi_2O_3/Bi_2WO_6 heterojunction photocatalyst. Ge et al synthesized the chrysanthemum-analogous Bi_2O_3/Bi_2WO_6 composite microspheres through a one-step hydrothermal route with the aid of surfactant templates[8]. Recently, Dong and his coworker prepared the Bi_2O_3/Bi_2WO_6 photocatalyst by

a two-step solvothermal process using Bi_2O_3 nanoparticles as modifier and 3D Bi_2WO_6 microspheres as substrate. The heterostructure catalysts are composed of Bi_2O_3 nanoparticles with diameters of about 10–15 nm are tightly grown on the lateral surface of the Bi_2WO_6 microspheres [9]. More recently, Peng et al. reported that a novel one-dimensional (1D) Bi_2O_3 nanorod–Bi_2WO_6 nanosheet p–n junction photocatalyst was prepared by a three-step synthetic route. Bi_2WO_6 nanosheets vertically grew on the Bi_2O_3 rods along the long axial direction[10]. As reported in these previous works, the Bi_2O_3/Bi_2WO_6 microspheres exhibit higher photocatalytic activity than the single phase Bi_2WO_6 or Bi_2O_3 for the degradation of rhodamine B under visible light. Therefore, the photocatalyst with a strong oxidizing potential could be postulated.

It is well known that different methods of synthesis can lead to significant differences in material properties. This work has concentrated on the different synthesis methods of Bi_2O_3/Bi_2WO_6 photocatalyst. The coupled semiconductor photocatalyst was successfully synthesized by one-step hydrothermal method and two-step hydrothermal method, respectively. Their photocatalytic performance were evaluated via photodegradation of Rhodamine B solutions under visible-light irradiation.

2. Methods

2.1 Sample preparation

All chemicals used were analytical grade reagents without further purification. The Bi_2O_3/Bi_2WO_6 photocatalyst with the molar ratio of $n_{Bi}:n_W$ from 2:1, 2.5:1, to 3:1 were synthesized via one-step hydrothermal method as follow steps. First, 5.00mol $Bi(NO_3)_3\cdot5H_2O$ was dissolved in 10mL 10% HNO_3 solution (Solution A) to form the homogeneous solution. 2.50mmol $Na_2WO_4\cdot2H_2O$ was dissolved in 10mL 2mol·L^{-1} NaOH solution (Solution B). Next, Solution B was added to solution A under continuous stirring. Then, the pH value of the resulting white suspension was adjusted to 1.0 with 2mol·L^{-1} NaOH solution. And 0.2g sodium citrate was added into the suspension. Then, the precipitate were transferred into a 50 mL Teflon-lined autoclave, and kept it at 180℃ for 12 h. After cooling the autoclave to room temperature, the yellow precipitate was washed with deionized water and dried at 80℃ in an oven. Final, the yellow powder were calcined at 450 ℃ for 4.5h in the tubular resistance furnace to get different molar ratio Bi_2O_3/Bi_2WO_6 composite materials, and the materials were named as S1, S2, and S3, respectively. For comparison, Bi_2O_3 nanobelts were also prepared in a similar process excepting for without $Na_2WO_4\cdot2H_2O$.

Bi_2O_3/Bi_2WO_6 heterostructures with the molar ratio of $n_{Bi}:n_W$ from 2.5:1 to 3:1 were prepared by two-step hydrothermal method. In a typical reaction, 5mmol of $Bi(NO_3)_3\cdot5H_2O$ solution and 2.50mmol $Na_2WO_4\cdot2H_2O$ solution were prepares as above. Next, 0.62 mmol of Bi_2O_3 nanorods were dispersed into the $Na_2WO_4\cdot2H_2O$ solution to form a suspension. Then dropped the suspension into the $Bi(NO_3)_3\cdot5H_2O$ solution to make a mixture. And 0.2g sodium citrate was added into the above suspension. The mixture was added into the Teflon-lined autoclave. The autoclave was sealed and heated to 180℃ for 12 h. The product was washed with deionized water and ethanol to remove any ionic residual, then dried in oven at 80℃for 8 h. Finally, the Bi_2O_3/Bi_2WO_6 heterostructures by two-step hydrothermal method with molar ratio of $n_{Bi}:n_W$ from 2.5:1 to 3:1 were obtained, and the materials were named as S4 and S5, respectively.

2.2 Characterization

The structures of the products were analyzed using the X-ray diffractometer(XRD, 6100, Rigaku) with Cu $K_{\alpha1}$ radiation at a rate of 5°·min^{-1} in the 2θ ranging from 10 to 80°. The morphologies and microstructures characterizations were performed on the scanning electron microscopy (SEM, JSM-7800F, JEOL). The photoabsorption performance was characterized by a UV–vis diffuse reflectance spectroscopy(DRS, UV-2600, Shimadu), using $BaSO_4$ as the reference.

2.3 Measurement of photocatalytic activities

Photocatalytic activities of as-prepared samples for the degradation of RhB were evaluated under visible light irradiation. A HSX UV-300 Xenon arc lamp with a 420 nm cut-off filter was used as the light source. All experiments were carried out in a photoreaction apparatus. For each experiment, 0.20 g of photocatalyst was added into 100 mL RhB solution with a concentration of 20 $mg \cdot L^{-1}$. Before illumination, the suspensions were stirred in dark for 45min to reach the adsorption–desorption equilibrium. Afterwards, 3.0 mL suspension was withdrawn and centrifuged to remove the photocatalyst particles at regular intervals. And then the concentration of the RhB solution was tested by UV-2600 spectrophotometer at 554 nm. The degradation efficiency is defined as C/C_0, where C_0 is the concentration of the RhB solution after the adsorption/desorption equilibrium established and C is the concentration after various intervals of the irradiation time.

3. Results and discussion

3.1. Structure and morphology

The phase structures of the as-synthesized composites Bi_2O_3/Bi_2WO_6 with the different molar ratios of $n_{Bi}:n_W$ and the pure Bi_2O_3 and Bi_2WO_6 samples were analyzed by XRD, as shown in Figure 1. The sharp diffraction peaks indicate that the samples were well crystallized. Four strong diffraction peaks at 2θ=28.31°, 32.61°, 47.11° and 55.81° can be clearly observed in samples, which can be well-indexed to (103), (200), (220) and (303) planes of the orthorhombic Bi_2WO_6 (JCPDS no.39-0256), respectively. From Figure 1, it can be seen that the XRD patterns for the Bi_2O_3/Bi_2WO_6 composites with various molar ratios of $n_{Bi}:n_W$ S2(the $n_{Bi}:n_W$ molar ratio of 2.5:1 by one-step hydrothermal method), S3(the $n_{Bi}:n_W$ molar ratio of 3:1 by one-step hydrothermal method), S4(the $n_{Bi}:n_W$ molar ratio of 2.5:1 by two-step hydrothermal method), S5 (the $n_{Bi}:n_W$ molar ratio of 3:1 by two-step hydrothermal method) are similar to S1(pure Bi_2WO_6), and no traces of Bi_2O_3 phases are detected in the XRD patterns.

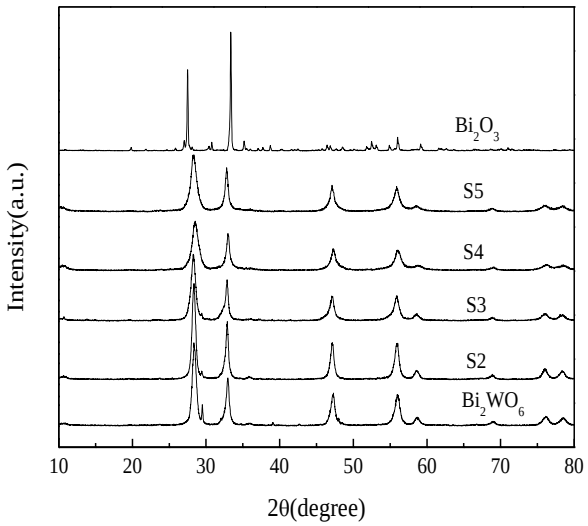

Figure.1 XRD patterns of the as-prepared samples

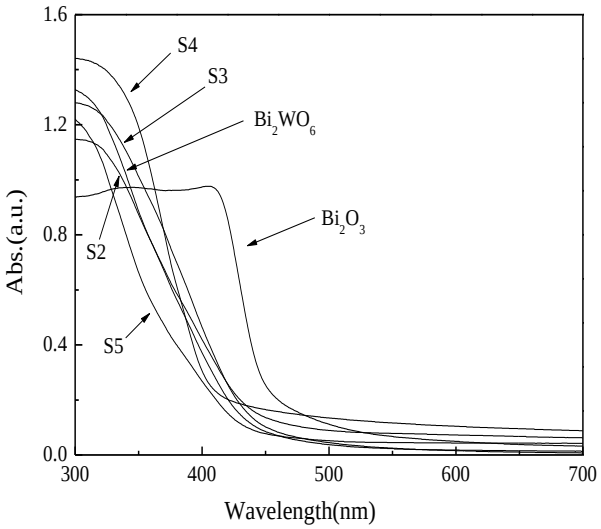

Figure.2 UV-vis DRS of the as-prepared samples

Optical absorption of the Bi_2O_3/Bi_2WO_6 heterojunctions were measured by using an UV-vis spectrometer, as shown in Figure 2. The absorption edges of pure Bi_2O_3 and Bi_2WO_6 are determined to be 455nm and 430 nm, respectively. The absorption edge of Bi_2O_3/Bi_2WO_6 with the different molar ratios of $n_{Bi}:n_W$ were respectively determined to be 438 nm(S2), 440nm(S3), 415nm(S4), 400nm(S5), the value of which lies between those of pure Bi_2O_3 and Bi_2WO_6. The band gaps of pure Bi_2WO_6 and Bi_2O_3/Bi_2WO_6 heterojunctions by one-step hydrothermal method are similar.

The morphologies of the as-synthesized Bi_2O_3/Bi_2WO_6 samples were observed by FE-SEM, as shown in Figure 3. The Bi_2O_3 sample consists of nanorods structures(Figure 3a). Bi_2WO_6 sample

consists of hierarchical structures(Figure 3b). And the Bi_2O_3/Bi_2WO_6 samples contains a mixture of flower-like microstructures. When the Bi_2O_3 nanorods added into the Bi_2WO_6 synthesis process, the nanorods structure vanished and only pure flower-like Bi_2WO_6 microstructures were obtained(Figure 3e and f).

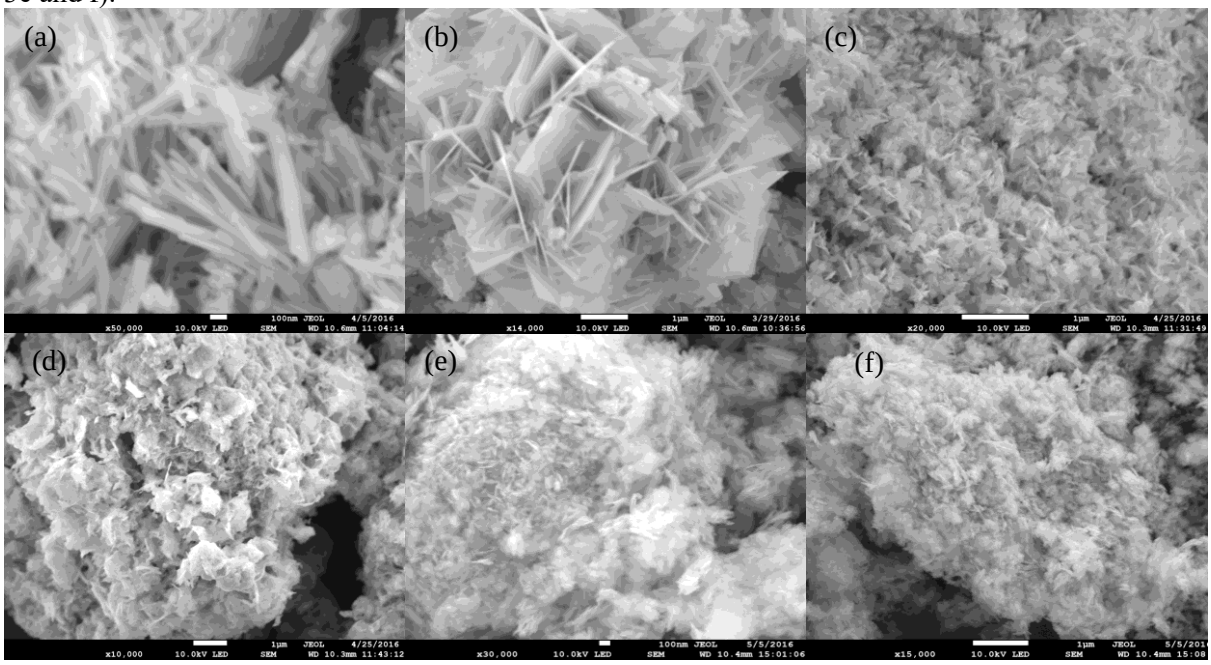

Figure 3 SEM images of Bi_2O_3/Bi_2WO_6 composite microspheres obtained at different methods

(a) Bi_2O_3; (b) Bi_2WO_6; (c) the $n_{Bi}:n_W$ molar ratio of 2.5:1by one step hydrothermal method; (d) the $n_{Bi}:n_W$ molar ratio of 3:1 by one step hydrothermal method; (e) the $n_{Bi}:n_W$ molar ratio of 2.5:1by two-step hydrothermal method; (f) the $n_{Bi}:n_W$ molar ratio of 3:1 by two-step hydrothermal method

Rhodamine-B (RhB) photodegradation in aqueous medium was employed as a probe reaction to test the photoactivity of the as-prepared samples, as shown in Figure 4. The rhodamin B degradation results showed that the Bi_2O_3/Bi_2WO_6 heterojunctions exhibited higher photocatalytic activities than those of pure Bi_2O_3 nanorods and pure Bi_2WO_6 flowers under visible light irradiation. The effect of the molar ratio of $n_{Bi}:n_W$ on the catalytic performance of the heterojunction catalysts was also investigated. And the optimal molar ratio of $n_{Bi}:n_W$ is 2.5:1 which was synthesized by one-step hydrothermal method.

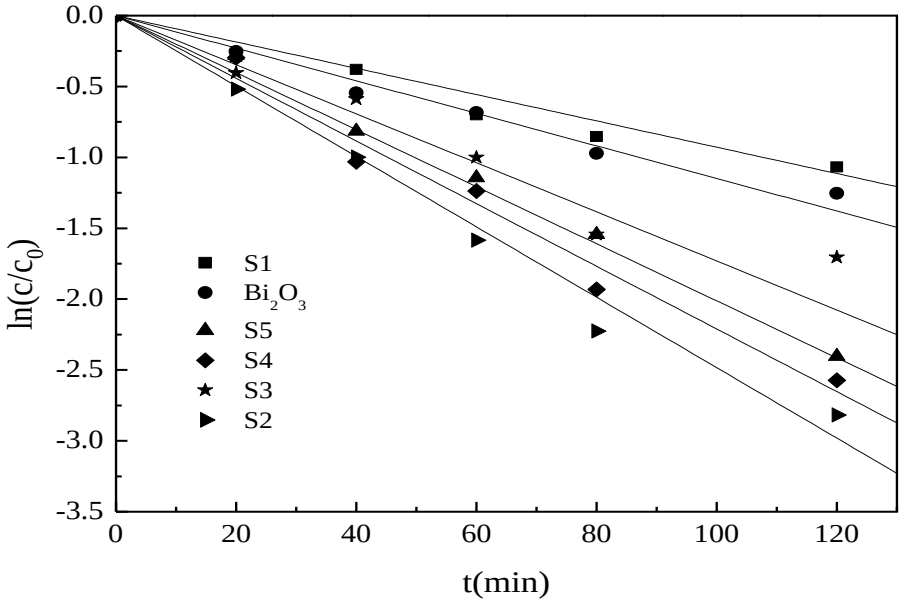

Figure 4 Photocatalytic degradation of RhB over the as-prepared samples

4. Conclusions

A series of Bi_2O_3/Bi_2WO_6 heterojunctions photocatalyst with different molar ratios of $n_{Bi}:n_W$ were synthesized via one-step hydrothermal method and two-step hydrothermal method. XRD results revealed that the Bi_2O_3/Bi_2WO_6 composites were similar to orthorhombic Bi_2WO_6. All photocatalysts prepared exhibited photocatalytic activity upon the irradiation by visible light. A molar ratio of $n_{Bi}:n_W$ of 2.5:1 which was synthesized by one-step hydrothermal method was the optimum condition for the preparation of the best performing Bi_2O_3/Bi_2WO_6 heterojunctions photocatalysts by the decolorization of RhB . The enhancement of the photocatalytic activity of the Bi_2O_3/Bi_2WO_6 heterojunctions structures can be ascribed to strong visible light absorption and the effective separation of photogenerated electrons and holes by the internal electrostatic field in the junction region.

Acknowledgments

This work was financially supported by Natural Science Foundation of Shandong Province (No.ZR2014BQ025), the Science and Technology Research Program of Shandong Province (No.2015GGX107003).

References

[1] Kudo A and Hijii S 1999 *Chem. Lett.* **28** 1103.
[2] Fu H, Pan C, Yao W and Zhu Y 2005 *J. Phys. Chem. B* **109** 22432.
[3] Finlayson A P, Tsaneva V N, Lyons L, Clark M and Glowacki B A 2006 Phys. Status Solidi (a), **203** 327.
[4] Huang H, Liu K, Chen K, Zhang Y, Zhang Y and Wang S. 2014 *J. Phys. Chem. C* **118** 14379
[5] Xiang Y, Ju P, Wang Y, Sun Y, Zhang D and Yu J 2016 *Chem. Eng. J.* **288** 264.
[6] Tian Y, Chang B, Lu J, Fu J, Xi F and Dong X 2013 *ACS Appl. Mater. Inter.* **5** 7079.
[7] Yu Y N, Lu S Y and Bao S J 2015 *J. Nanopart. Res.* **17** 1.
[8] Ge M, Li Y, Liu L, Zhou Z and Chen W 2011 J. Phys. Chem. C **115** 5220.
[9] Dong Z, Mao J, Wang D,Yang M and Ji X 2011 J. Solid State Chem. **184** 1977.
[10] Peng Y, Yan M, Chen Q, Fan C, Zhou H and Xu A 2014 *J. Mater. Chem. A* **2** 8517