

One-pot Hydrothermal Synthesis of Bi₂O₃/BiVO₄ Composites with Highly Efficient Visible-light Photocatalytic Activity

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Abstract. Porous peanut-like Bi₂O₃/BiVO₄ composites with different Bi/V molar ratios have been synthesized by a one-pot hydrothermal synthesis method. The samples were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), UV-vis diffuse reflectance spectra (DRS), Fourier-transform infrared spectra (FTIR) and photoluminescence spectra (PL). Either monoclinic BiVO₄ or monoclinic Bi₂O₃ phase without other impurities was detected in the as-synthesized composite samples. DRS showed that Bi₂O₃/BiVO₄ composites exhibited stronger absorption in the visible range with a steep absorption edge compared with the pure BiVO₄. The PL intensity of the Bi₂O₃/BiVO₄ composites were lower than that of pure BiVO₄. Photocatalytic degradation of Methylene Orange (MO) showed the sample of Bi₂O₃/BiVO₄ composite with Bi:V molar ratio of 1.6:1 exhibited the highest photocatalytic activity and good stability.

Introduction

Over the past few decades, environmental pollution and energy shortages became two very serious problems for human survival with the development of economy. The photocatalytic technology based on the semiconductor was considered as one of the most important approaches to solving the environmental pollution issues and the energy crisis [1]. The traditional photocatalysts such as TiO₂ and ZnO have been studied extensively. Unfortunately, these photocatalysts have relatively weak photocatalytic activity because of their poor photo-quantum efficiency, rendered by the high recombination rate of photo-generated electron-hole pairs and large band gap [2]. It is expected to find new kinds of photocatalysts with high activity under visible-light irradiation. Up to now, a large series of photocatalysts response to visible light were synthesized. Among which, monoclinic scheelite phase BiVO₄ with a band gap of about 2.40 eV has emerged as an outstanding visible-light driven photocatalyst for dematerializing organic pollutants and photocatalytic evolution of O₂ due to its particular electronic band structure and high conduction band energy relative to other visibly active metal oxides semiconductors[3-5]. Nevertheless, the efficiency of the BiVO₄ is still low as a result of its relatively poor light-harvesting ability and rapid recombination of photo-generated electron-hole pairs. So, it is necessary to design an effective strategy to expand the solar spectrum absorption range and improve the photo quantum of BiVO₄ photocatalysts. Great efforts have been proposed to solve these problems, including heterojunction construction, ion doping and loading cocatalysts. Among these methods, fabrication of p-n heterojunction photocatalysts by coupling two semiconductors with appropriate band gap is a well-established strategy to enhance carrier separation. Bismuth oxide (Bi₂O₃), a p-type semiconductor with a band gap of 2.8 eV has attracted increasing attention due to its good photocatalytic oxidative capabilities for O₂ evolution as well as organic substance decomposition under visible light irradiation. Thus, heterostructured Bi₂O₃/BiVO₄ has been studied due to its potential use in the field of pollution remediation and new energy exploitation by Sun, et al [6-8]. However, the synthesis of Bi₂O₃/BiVO₄ heterojunctions with high photocatalytic efficiency remains a challenge. In this study, we demonstrate a facile one-pot synthesis strategy for Bi₂O₃/BiVO₄ hetero-structure with different molar ratios. The as-prepared peanut-like Bi₂O₃/BiVO₄

heterojunction exhibits significantly enhanced photocatalytic activity in degrading the Methylene Orange (MO) under visible light illumination, demonstrating its promising potential use in water pollution remediation.

Experimental

Preparation of photocatalyst

All chemicals used were of analytical grade without further purification. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 were used as the Bi and V sources, respectively. The $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites with molar ratios of nBi:nV from 1.05:1, 1.2:1, 1.6:1 to 2:1 were synthesized via one-pot hydrothermal method. Firstly, quantitative amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 50 mL ethylene glycol to form the homogeneous solution A. 1.2 g NH_4VO_3 was dissolved in 20 mL distilled water to form solution B. Next, Solution B was added to solution A under continuous stirring. Then, the mixtures were transferred into a 100 mL Teflon-lined autoclave, and kept it at 180°C for 12 h. After cooling the autoclave to room temperature, the yellow precipitate was washed with deionized water and dried at 80°C in an oven. Final, the yellow powder were calcined at 450°C for 4.0 h in the tubular resistance furnace. For comparison, pure Bi_2O_3 and BiVO_4 were also prepared in a similar process except for without NH_4VO_3 .

Characterization

The phase purity and compositions of samples were determined by X-ray diffraction (XRD, 6100, Rigaku) with $\text{Cu K}\alpha_1$ radiation scanning from $2\theta=10-80^\circ$ at a rate of $2^\circ \cdot \text{min}^{-1}$. The morphologies and microstructures were analyzed by a field emission scanning electron microscope (JSM-7800F, JEOL). The surface chemical composition was determined by energy dispersive X-ray spectroscopy (EDS, Quantera SXM, Oxford Instruments). The optical properties of the samples were determined using a UV-vis diffuse reflectance spectroscope (DRS, UV-2600, Shimadzu) using BaSO_4 as the reference. The Photoluminescence Spectroscopy (PL) decay curves were obtained by using a F4600 fluorescence spectrophotometer.

Photocatalytic activity measurement

Photocatalytic activities of the as-prepared samples were evaluated by degradation of MO under visible light irradiation. A HSX UV-300 Xenon arc lamp with a 400 nm cut-off filter was used as the light source. All experiments were performed in a photoreaction apparatus. For each experiment, 0.20 g photocatalyst was added into 100 mL MO solution with a concentration of $10 \text{ mg} \cdot \text{L}^{-1}$ and pH of 4. Before illumination, the suspensions were stirred in dark for at least 60 min to reach adsorption-desorption equilibrium. Afterwards, quantitative amounts of suspensions were taken out and centrifuged to remove the photocatalyst particles at regular intervals. And then the concentration of the residual solution was determined by a UV-2600 spectrophotometer at the characteristic absorption wavelength 462.5 nm. Recycle tests were also done. The photocatalytic removal ratio R is defined as:

$$R = \frac{A_0 - A}{A_0} \times 100\% = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where, C_0 is the concentration of the MO solution after the adsorption/desorption equilibrium and C is the concentration of the solution after irradiation at different time intervals.

Results and discussion

Crystal structure analysis

Fig. 1 (a) shows the XRD patterns of the as-prepared $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composite with different Bi/V molar ratios obtained by one-pot hydrothermal method. The BiVO_4 and Bi_2O_3 were obtained for the single phase samples. In Fig. 1 (a), it can be seen clearly that the as-prepared pure BiVO_4 samples are in good agreement with the monoclinic BiVO_4 according to the Joint Committee Powder Diffraction Standards (JCPDS file no. 83-1699). The diffraction peaks of BiVO_4 at 29.1° , 34.48° , 35.19° , 46.05° , 47.27° and 58.26° could be indexed to the characteristic peaks (-112), (200), (020), (123), (024) and

(-312) planes of monoclinic BiVO_4 . All the diffraction peaks could be well assigned to either monoclinic BiVO_4 or monoclinic Bi_2O_3 , and no additional impurity phases were found in the diffraction patterns, showing the existence of $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites. Fig. 1 (b) shows the FT-IR spectra of different samples. All the samples show similar FT-IR spectra. The broad bands around $3800\text{--}2500\text{ cm}^{-1}$ and $1620\text{--}1651\text{ cm}^{-1}$ correspond to the stretching vibrations of O-H and bending vibrations of strongly adsorbed water coordinated to the surface of the catalysts, respectively.

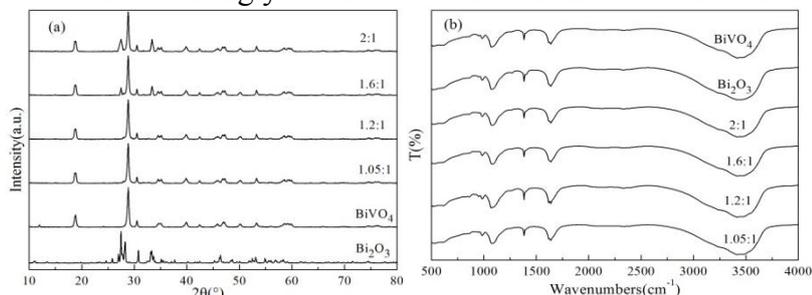


Fig. 1 (a) XRD patterns; (b) FTIR of $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites and pure Bi_2O_3 , BiVO_4 samples

Morphology and EDS characterization

Fig. 2 shows SEM images and EDS analyses of the pure Bi_2O_3 , BiVO_4 , and $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites with Bi:V molar ratio of 1.6:1. As can be seen from Fig. 2 (a), pure Bi_2O_3 has an irregular bulk shape, and the surface is smooth. While pure BiVO_4 presents a hollow peanut-like structure as shown in Fig.2 (b) and the surface is composed of nano-particles with average size of about 100nm. Large amount of pores are distributed on the surface. As for the $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites (Bi:V molar ratio of 1.6:1) in Fig. 2 (c), they also show a peanut-like structure, but the surfaces are more smooth and the pores on the surface are less than that of pure BiVO_4 . All the nano-particles on the surface are uniform, it is speculated that the heterojunctions between Bi_2O_3 and BiVO_4 are formed in the composite. With the porous peanut-like structure, it is easier to harvest the incident light and better access for reactants to the active sites, thus improved photocatalytic activities for the $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composite.

EDS analysis of $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites with Bi:V molar ratio of 1.6:1 is shown in Fig.2 (d). The EDS spectrum showed strong signals from C, O, Bi and V elements without detecting other elements, confirming the presence of O, Bi and V elements on the $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composite surfaces. The atomic distribution percent of the element in $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composite were V 12.9%, Bi 22.4%, O 61.7 %, respectively. And it was close to the ideal value of 1.6: 1 for Bi:V molar ratios.



Fig. 2 (a) SEM image of pure Bi_2O_3 ; (b) SEM image of pure BiVO_4 ; (c) SEM image of 1.6:1 $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites; (d) EDS analysis of 1.6:1 $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites

UV-vis DRS and PL analyses

Fig. 3 (a) shows the UV-vis diffuse-reflectance spectra of pure BiVO_4 and the as-synthesized $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composite. As shown in Fig. 3 (a), in contrast with the pure BiVO_4 samples which exhibit a little stronger absorption in the visible range with a steep absorption edge due to the intrinsic transition between the valence band and the conduction band, $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ nano-composite has a non-steep absorption edge, which could be ascribed to the formation of heterojunction. Furthermore, it is found that the $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composite exhibited broad background absorbance in the visible region, which may be attributed to surface defect states or the room-temperature exciton absorption in the semiconductor.

PL emission is closely related to the recombination of excited electrons and holes, revealing interfacial charge transfer dynamics [9]. Illustrated in Fig. 3 (b) are the room temperature PL spectra of pure BiVO_4 and $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites recorded with a 400 nm laser source. The PL spectra of pure BiVO_4 and $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites show peaks at 457nm. However, the peak intensity of BiVO_4 is much more intense than those of the $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites. And the sample with Bi:V molar ratio of 1.6:1 showed the lowest intensity, indicating the separation of photogenerated electron-holes pairs, leading to enhancement of photocatalytic activity.

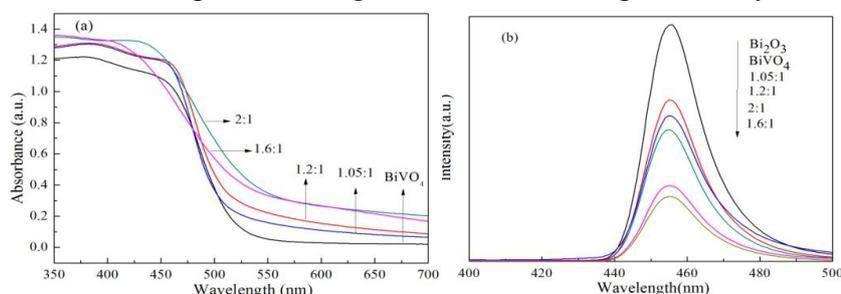


Fig.3 (a) UV-vis DRS spectra; (b) PL spectra of different samples

Evaluation of photocatalytic activity

The photocatalytic activity of the samples was evaluated by the degradation of methyl orange (MO) in aqueous solution under visible light irradiation. The absorbance of the characteristic absorption wavelength at 462.5 nm with time is shown in Fig. 4 (a). It is clear the absorbance decreases gradually with time. The photocatalytic activity comparison of different samples was shown in Fig. 4 (b). Pure BiVO_4 and Bi_2O_3 showed relatively low activity under visible light irradiation.

After 120 min of visible light irradiation, the degradation rates of MO over pure BiVO_4 and Bi_2O_3 were only 19.4% and 11.3%, respectively. In an obvious contrast, the $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ showed a relatively sharp increase in MO degradation, and the $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composite with Bi:V molar ratio of 1.6:1 showed the highest photocatalytic removal rate, reaching 81.2% in 120min. One hour cycle test showed the sample of 1.6:1 had good stability as shown in Fig.4 (c).

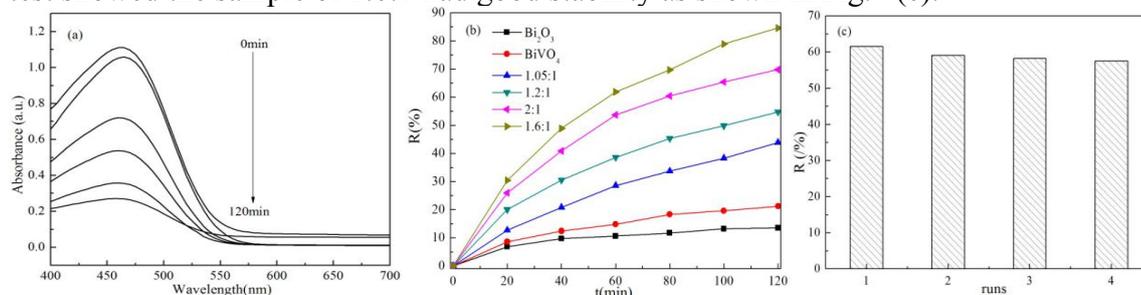


Fig. 4 (a) UV-vis absorption spectra of MO with photocatalytic degradation; (b) Photocatalytic degradation of MO by different samples under visible light irradiation; (c) Recycle test of $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composite with Bi:V molar ratio of 1.6:1

Conclusion

Porous peanut-like $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ heterojunctions with different Bi/V molar ratios were synthesized via a one-pot hydrothermal synthesis method. Either monoclinic BiVO_4 or monoclinic Bi_2O_3 was detected by the XRD. No additional impurity phases were found. $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composites showed stronger DRS absorption in the visible range with a steep absorption edge compared with the pure BiVO_4 . The sample with Bi:V molar ratio of 1.6:1 showed the lowest PL intensity. Photocatalytic degradation of MO showed the sample of $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ composite with Bi:V molar ratio of 1.6:1 exhibited the highest photocatalytic activity and good stability.

Acknowledgments

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