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Article (Special Issue on Environmental and Energy Catalysis)

Flower-like Bi₂WO₆/ZnO composite with excellent photocatalytic capability under visible light irradiation

Juan Cheng ^a, Yi Shen ^a, Kuan Chen ^a, Xi Wang ^a, Yongfu Guo ^{a,b,*}, Xiaoji Zhou ^a, Renbi Bai ^{a,#}^a Center for Separation and Purification Materials & Technologies, Suzhou University of Science and Technology, Suzhou 215009, Jiangsu, China^b Jiangsu Collaborative Innovation Center of Water Treatment Technology and Material, Suzhou 215009, Jiangsu, China

ARTICLE INFO

Article history:

Received 30 November 2017

Accepted 20 December 2017

Published 5 April 2018

Keywords:

Bismuth tungstate

Zinc oxide

Photocatalysis

Methylene blue

Antibiotics

ABSTRACT

The photocatalytic ability of ZnO is improved through the addition of flower-like Bi₂WO₆ to prepare a Bi₂WO₆/ZnO composite with visible light activity. The composite is characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy with UV–vis diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy and N₂ adsorption-desorption isotherms. After modification, the band gap energy of Bi₂WO₆/ZnO is reduced from 3.2 eV for ZnO to 2.6 eV. Under visible light irradiation, the Bi₂WO₆/ZnO composite shows an excellent photocatalytic activity for degrading methylene blue (MB) and tetracycline. The photo-degradation efficiencies of (0.3:1) Bi₂WO₆/ZnO for MB and tetracycline are approximately 246 and 4500 times higher than those of bare ZnO, respectively, and correspondingly, the photo-degradation rates for the two pollutants are approximately 120 and 200 times higher than those with bare ZnO, respectively. Moreover, the photocatalyst of (0.3:1) Bi₂WO₆/ZnO exhibits a higher transient photocurrent density of approximately 4.5 μA compared with those of bare Bi₂WO₆ and ZnO nanoparticles. The successful recombination of Bi₂WO₆ and ZnO enhances the photocatalytic activity and reduces the band gap energy of ZnO, which can be attributed to the effective separation of electron–hole pairs. Active species trapping experiments display that [O₂]^{•−} is the major species involved during photocatalysis rather than •OH and h⁺. This study provides insight into designing a meaningful visible-light-driven photocatalyst for environmental remediation.

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1. Introduction

The colored organic dyes released from the textile and dye industries into water bodies are hardly biodegradable and can severely damage aquatic ecosystems and aquatic organisms. A recent report has shown that the global annual production of synthetic dyes and pigments has reached over 10⁶ tons. In addition, 5%–15% of the synthetic dyes will usually be lost during

the process of manufacturing and processing, and these waste dyes may be toxic or carcinogenic to aquatic organisms or systems in water [1]. Commonly, synthetic organic dyes used in textile industries (e.g., MB, C₁₆H₁₈N₃SCl, Reactive Orange-16 Dye and C₂₀H₁₇N₃Na₂O₁₁S₃) are considered as allergens, and some are mutagenic and carcinogenic. Moreover, the discharge of industrial wastewater containing synthetic dyes can cause serious contamination at the dumping site [2,3].

* Corresponding author. Tel: +86-512-68092987; E-mail: yongfuguo@163.com

Corresponding author. E-mail: ceebairb@live.com

This work was supported by the National Natural Science Foundation of China (51578354), Six Talent Peaks Program (2016-JNHB-067), Suzhou Science and Technology Bureau (SS201667), and Qing Lan Project and Research Innovation Project for College Graduates of Jiangsu Province (KYCX17_2067).

DOI: 10.1016/S1872-2067(17)63004-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 4, April 2018

So far, a variety of treatment methods, such as chemical precipitation/contaminant separation, coagulation, ozone oxidation, hypochlorite oxidation, electrochemical methods and adsorption, have been used to degrade organic dyes [4–9].

Recently, the use of antibiotics in medicine has considerably improved the treatment efficiency for infectious diseases and has also been widely used in agricultural production. However, with the increasing and extensive use of antibiotics, wastewater containing antibiotics are released into water bodies in large quantities, which has resulted in a serious environmental threat to aquatic and land ecological systems [10]. As one of the most typical antibiotics, tetracycline is widely used in medicine, agriculture and aquaculture. Unfortunately, tetracycline cannot be eliminated by natural environment or biological wastewater treatment technologies [11].

In previous studies, various strategies have been adopted to solve the problem of antibiotic wastewater. Biological removal processes, such as biodegradation by bacteria and fungi, and non-biological processes, including adsorption, hydrolysis, oxidation and reduction, have aroused widespread interest from the research community [12–17]. However, these methods have some inherent defects, including high cost, poor stability and low efficiency, which has limited the application of these technologies. Hence, the development of new technologies or materials to eliminate antibiotic pollution remains as a challenge in the field of environmental chemistry.

The photocatalytic degradation of organic pollutants under visible light or ultraviolet light is an important method, as it can quickly and thoroughly eliminate pollutants without leaving any harmful residue [18]. Semiconductors, which are extensively applied to electronic devices and integrated circuits, have recently been shown to be important photocatalysts in wastewater treatment technology and have been widely studied in the past few decades [19].

Wide band gap semiconductors, such as TiO_2 and ZnO , have been shown to be the most promising photocatalysts of all the semiconductor materials. It has been demonstrated that ZnO is a better photocatalyst than TiO_2 , owing to its wide band gap (3.2 eV) and strong excitation binding energy (~ 60 meV). These characteristics have resulted in a lot of interest from many scholars for their use in electronics, light emitting diodes, gas sensing and photocatalysis [20].

However, ZnO has some inherent flaws, including a rapid recombination of photo-generated electrons and holes, low quantum efficiency, susceptibility to light corrosion, poor light stability, and so forth. These flaws greatly limit the photocatalytic potential and reduce the photocatalytic activity, which therefore limit the application of ZnO in environmental remediation.

Moreover, owing to its wide band gap, ZnO can only be excited by UV light, which only accounts for approximately 5% of the solar spectrum. This results in an ineffective absorption of visible light and low usage rate for sunlight [21]. Therefore, it is a challenging task to obtain a ZnO photocatalyst with both favorable light stability and high photocatalytic activity under visible light by doping or modifying methods, but this has now become a frontier subject in international research [22].

The modification of ZnO with other semiconductors, such as CdS [23], In_2S_3 [24], NiO [25], CdSe [26], PbS [27], Ag_2S [28], Mn_3O_4 [29], Bi_2O_3 [30], Cr_2O_3 [31], Bi_2S_3 [32] and Bi_2WO_6 , is an effective method to generate a large number of electron–hole pairs and enhance the photocatalytic activity of ZnO . The research on Bi-based photocatalysts has long been a hot topic in the field of photocatalysis and many important candidates have been reported, including BiOCl [33], $\text{Bi}_{12}\text{GeO}_{20}$ [34], Bi_2SiO_5 [35] and BiOBr [36]. Among these semiconductors, as inorganic semiconductor nanocrystals, Bi_2WO_6 has received widespread consideration for its nontoxicity, suitable band gap and excellent photocatalytic performance [37–39].

As an efficient material to improve the catalytic properties of photocatalysts, heterojunction photocatalysts can be used to facilitate the separation of photo-excited electron–hole pairs. In general, when p-type and n-type semiconductors are in contact, they form a p–n junction with a space charge region between the interface of the two semiconductors owing to the diffusion of electrons and holes. Therefore, the construction of a semiconductor heterojunction has attracted a lot of attention owing to its effectiveness in improving the photocatalytic activity. Some new findings have been also reported on the semiconductor heterojunction photocatalysts, such as the p–n junctions of $\text{BiOI}/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ [40], $\text{BiVO}_4/\text{BiOI}$ [41] and BiOBr/BiOI [42]. These results provide an important theoretical foundation for this work.

In the present work, a heterojunction catalyst of $\text{Bi}_2\text{WO}_6/\text{ZnO}$ was synthesized by a two-step hydrothermal method. The basic performance and photocatalytic properties were investigated through the degradation of MB and tetracycline. The aim was to improve the photocatalytic efficiency and enhance the conversion for solar energy through reducing the band gap energy of ZnO , increasing the effective separation of electron–hole pairs and promoting the transfer of charge carriers. Moreover, the degradation mechanism of a flower-like $\text{Bi}_2\text{WO}_6/\text{ZnO}$ composite heterojunction photocatalyst was also proposed.

2. Experimental

2.1. Materials

Bismuth nitrate (99.0%), citric acid (99.5%), zinc acetate dihydrate, sodium tungstate, NaOH (96%), HNO_3 (65%–68%), $\text{Na}_2\text{C}_2\text{O}_4$, 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL), methylene blue ($\geq 92\%$) and tetracycline ($\geq 98\%$) were of analytical grade.

2.2. Preparation of photocatalysts

The $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction catalyst was prepared by the following two-step method [43]. The concentration and pH value of a NaOH solution can affect the morphology of as-prepared ZnO . When the concentration and pH of NaOH were 10 mol/L and 13, respectively, the morphology of the synthesized ZnO microspheres were flower-like. Therefore, the synthesis of flower-like ZnO was carried out as follows: zinc

acetate (0.02 mol) and citric acid (0.014 mol) were dissolved in ethanol solution (80 mL, 20%, v/v). The mixed solution was stirred violently and then 10 M of NaOH solution was added to adjust the pH to 13.

The above solution was placed into a Teflon-lined autoclave at 150 °C for 15 h. After cooling, the obtained solid was filtered, washed and then dried at 105 °C. Finally, the production was calcified at approximately 500 °C for 2 h to obtain ZnO nanoparticles.

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.620 g) was dispersed into deionized water (20 mL) and then $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.820 g) and 0.2 mol/L HNO_3 (15 mL) were added dropwise into the solution. The above prepared ZnO samples were added with varied molar ratios of Bi_2WO_6 :Zn = 0.1:1, 0.2:1, 0.3:1 and 1:1 with sonication for 30 min. The above suspension was maintained at 140 °C for 20 h in a Teflon-lined autoclave. After cooling, the obtained materials were filtered, washed and then dried at 60 °C for 12 h to obtain $\text{Bi}_2\text{WO}_6/\text{ZnO}$ samples, marked as (0.1:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$, (0.2:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$, (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ and (1:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ based on the various molar ratios of Bi_2WO_6 and Zn.

2.3. Characterizations

The characterization of photocatalysts was detected by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-vis diffuse reflectance spectroscopy (UV-DRS) and N_2 adsorption-desorption isotherms. SEM (Phenom, USA) and TEM (JEM-2100, Japan) were employed to examine the morphology. The XRD patterns were detected by a Bruker D8 Advance diffractometer. The chemical composition of $\text{Bi}_2\text{WO}_6/\text{ZnO}$ was detected by XPS spectra (Escalab 250Xi, USA). The BET (Brunauer-Emmett-Teller) value was obtained from the N_2 adsorption-desorption isotherms with a BET analyzer (Micromeritic TriStarII 3020, USA). The UV-DRS was measured with a UV-vis spectrophotometer (Shimadzu UV-3600, Japan) from 300 to 800 nm.

2.4. Photocatalytic activity

The performance of $\text{Bi}_2\text{WO}_6/\text{ZnO}$ was measured through degrading MB and tetracycline under visible light. Typically, 50 mg of $\text{Bi}_2\text{WO}_6/\text{ZnO}$ were dissolved in 100 mL of MB solution (10 mg/L) and tetracycline solution (20 mg/L), separately. The solution containing the catalysts was stirred in the dark for 1 h until the adsorption equilibrium was reached. A 500W Xe lamp was applied as the visible light source and equipped with a 420-nm cut-off filter. The solution was then exposed to visible light irradiation and the solution was placed 15 cm from the lamp.

Samples were taken at certain intervals and filtered to remove any suspended substance. Then the supernatant was analyzed by UV-DRS to obtain the residual concentration of MB (664 nm) and tetracycline (350 nm). The degradation efficiency of the photocatalysts was calculated based on the concentration of pollutants at initial equilibrium (C_0 , mg/L) and the re-

sidual concentration (C_t , mg/L) at any time t (min).

2.5. Active species trapping experiments

To probe the photocatalytic mechanism, several active radicals were investigated. Generally speaking, the active species include superoxide radicals $[\text{O}_2]^-$, holes (h^+) and hydroxyl radicals ($\bullet\text{OH}$) [44–46]. In the test, 1.0 mM isopropanol (IPA), $\text{Na}_2\text{C}_2\text{O}_4$ and TEMPOL were added to capture hydroxyl radicals ($\bullet\text{OH}$), holes (h^+) and superoxide radicals $[\text{O}_2]^-$, respectively. Several kinds of scavengers were added into the MB solution and other conditions were the same as for the degradation experiments.

3. Results and discussion

3.1. Morphology and structure

The morphology and structure of the (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction were researched by SEM and high resolution TEM (HR-TEM) [47].

Fig. 1(a) and (b) show the SEM images of as-prepared ZnO and (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$, respectively, which clearly display that the samples consisted of a flower-like structure with a

Fig. 1. SEM images of ZnO (a) and (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ (b); HR-TEM images of (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ (c, d); EDS pattern of (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ (e).

diameter of 4.0 μm .

To further learn about the detailed structure of $\text{Bi}_2\text{WO}_6/\text{ZnO}$, HR-TEM was employed. The HR-TEM images of (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ clearly indicated the successful synthesis of $\text{Bi}_2\text{WO}_6/\text{ZnO}$, as shown in Fig. 1(c) and (d). In general, when different kinds of semiconductor materials are in close contact, they form p-n junctions at the interface with a space charge region owing to the diffusion of electrons and holes [48].

Fig. 1 shows that Bi_2WO_6 was closely attached onto ZnO to assemble the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction. The HR-TEM images show that the lattice spaces were approximately 0.33 and 0.26 nm, which corresponded to the crystal faces of (131) and (002) for Bi_2WO_6 and ZnO, respectively. Energy dispersive spectroscopy (EDS) analysis (Fig. 1(e)) revealed that the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ sample only consisted of Bi, W, O and Zn elements.

3.2. XRD results

As shown in Fig. 2, all the diffraction peaks of the photocatalysts were pure Bi_2WO_6 and ZnO, which corresponded to homogeneous orthogonal Bi_2WO_6 [JCPDS 39-256] [49] and ZnO [JCPDS 36-1451] [50], respectively. It also shows that no impurity peaks were detected. The main characteristic peaks of Bi_2WO_6 appeared at 28.3° , 32.8° , 47.1° and 56.0° , which corresponded to the (131), (200), (202) and (133) crystal faces of Bi_2WO_6 , respectively [49].

The main characteristic peaks of ZnO appeared at 31.8° , 34.4° , 36.3° , 47.7° , 56.7° and 63.0° , which corresponded to the (100), (002), (101), (102), (110) and (103) crystal faces of ZnO, respectively [50]. Hence, it was clear that the composites of $\text{Bi}_2\text{WO}_6/\text{ZnO}$ were successfully synthesized by the hydrother-

Fig. 2. XRD patterns of the photocatalyst heterojunctions.

mal method.

Compared with pure ZnO and Bi_2WO_6 , with an increasing content of Bi_2WO_6 , the relative peak intensities were changed, which indicated that Bi_2WO_6 could be assimilated into the ZnO lattice to form a $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction. The peak intensities of the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction were clearly related to the molar ratios of Bi_2WO_6 and ZnO.

3.3. Chemical state analysis

Fig. 3(a) shows that the general survey spectra of (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ consisted of the various binding energies of Bi 4f, W 4f, O 1s, Zn 2p and C 1s states. From Fig. 3(b), the two char-

Fig. 3. XPS patterns of the survey scan (a), Bi 4f (b), W 4f (c), O 1s (d) and Zn 2p (e) of (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$.

Fig. 4. UV-visible spectra (a) and band gap values (b) of ZnO and Bi₂WO₆/ZnO.

characteristic peaks of Bi 4*f* with binding energies of 158.8 and 164.1 eV were consistent with Bi 4*f*_{7/2} and Bi 4*f*_{5/2}, respectively [51]. The characteristic peaks located at 37.1 eV and 35.0 eV in Fig. 3(c) corresponded to the +6 oxidation state for W 4*f*_{5/2} and W 4*f*_{7/2}, respectively [51]. The O 1*s* characteristic peaks at 529.6 eV (Fig. 3(d)) corresponded to the O₂⁻ in Bi₂WO₆ crystals [52].

Fig. 3(e) shows the Zn 2*p* spectra with two binding energies of 1044.3 and 1021.2 eV, which correspond to the 2*p*_{1/2} and 2*p*_{3/2} peaks in ZnO, respectively [53]. The XPS data indicated a successful synthesis of the Bi₂WO₆/ZnO photocatalyst, which was in good agreement with the XRD and HR-TEM results.

3.4. DRS property

The UV-DRS patterns are presented in Fig. 4. Compared with the pure ZnO, the absorption wavelengths of Bi₂WO₆/ZnO composites showed a red shift and the absorption wavelengths extended to the visible region from 400 to 500 nm with the increasing content of Bi₂WO₆, as shown in Fig. 4(a). The as-prepared ZnO particles only exhibited a basic absorption band in the UV light region, while Bi₂WO₆/ZnO showed a slight shift to the visible light region owing to the narrower band gap of ZnO compared with that of Bi₂WO₆.

By comparison, the adsorption of the as-prepared catalysts of Bi₂WO₆/ZnO in the visible light region exhibited a significant

increase owing to the addition of Bi₂WO₆ with a visible light response [54]. The values of the band gap can be calculated using Eq. (1):

$$\alpha = A(h\nu - E_g)^{n/2}/h\nu \quad (1)$$

where α , A and h are the absorption coefficient, constant and Planck's constant, respectively, and E_g , ν and n are the band energy, incident light frequency and constant related to the type of transition, respectively.

Fig. 4(b) shows the Kubelka–Munk transformed reflectance spectra, where the slopes are the values of the band gap energy. The obtained band gap energies of ZnO particles, (0.1:1) Bi₂WO₆/ZnO, (0.2:1) Bi₂WO₆/ZnO, (0.3:1) Bi₂WO₆/ZnO and (1:1) Bi₂WO₆/ZnO solid solutions were 3.2, 2.9, 2.8, 2.6 and 2.9 eV, respectively.

3.5. Porous structure determination

From Fig. 5, all the isotherms conformed to the H3 hysteresis loop in a type IV isotherm [55]. The surface areas (A_{BET}) were estimated by the N₂ isotherms to be 3.81, 195.44 and 18.98 m²/g for the catalysts of ZnO, Bi₂WO₆ and (0.3:1) Bi₂WO₆/ZnO, respectively. The results show that the A_{BET} of (0.3:1) Bi₂WO₆/ZnO was 4.98 times larger than ZnO, which could be attributed to the three-dimensional flower-like structures of Bi₂WO₆/ZnO and large BET value of Bi₂WO₆.

The increase of the A_{BET} could accelerate the enrichment and

Fig. 5. Isotherms of ZnO (a), Bi₂WO₆ (b) and (0.3:1) Bi₂WO₆/ZnO (c).

Fig. 6. Degradation of MB (a) and tetracycline (b) with $\text{Bi}_2\text{WO}_6/\text{ZnO}$ as catalysts.

degradation rate of the target pollutants in the solution. Then, the pore size distributions of the corresponding catalysts were calculated by the BJH method (inset in Fig. 5), which indicated that the average diameters were approximately 5.55 and 18.87 nm for the catalysts of ZnO and (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$, respectively, and these pores were widely distributed. The inter-nanoflake/nanosheet spaces in the as-prepared catalysts may produce the mesoporous feature with widely distributed pores.

3.6. Evaluation of photocatalytic activity

To explore the photocatalytic activity of the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction, the photo-degradations of MB and tetracycline were performed. The activity was first evaluated through the degradation of MB. The concentration changes of MB over time during photo-degradation are shown in Fig. 6(a). The adsorption tests showed that no more than 15% of the MB molecules was adsorbed by the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction when the equilibrium adsorption state was reached under dark conditions.

Under the irradiation of visible light, Fig. 6(a) shows the gradual drop of the MB concentration over the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction, even with less Bi_2WO_6 ((0.1:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$). In

addition, the (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ catalyst possessed the highest photocatalytic efficiency for the degradation of MB.

Tetracycline is a widely used antibiotic substance in planting and breeding areas. However, a large concentration of tetracycline remains in the surface water, groundwater and soil, owing to its limited biodegradation and the inefficiency of traditional water treatment technology, which results in a potential hazard for environment ecological systems [56]. (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ catalyst was used for tetracycline degradation and the results are presented in Fig. 6(b). It was clear that the (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ hybrid material showed the highest photocatalytic activity, compared with the other as-prepared catalysts.

The kinetic behavior of the degradation process can be explained by the kinetic models described by the following equations. Here, the Langmuir-Hinshelwood model was applied under the condition of a millimol concentration of pollutants [57,58]:

$$-\ln \frac{C_t}{C_0} = kt + a \quad (2)$$

where k is the rate constant. The plots of $-\ln(C_t/C_0)$ versus irradiation time of t are shown in Fig. 7. All catalysts were well fitted and had a very high correlation coefficient ($R^2 > 0.94$), as shown in Fig. 7.

Fig. 7. Linear plots of $-\ln(C_t/C_0)$ of MB (a) and tetracycline (b).

By a linear fitting of these plots, it could be observed that ZnO had almost no photocatalytic capacity. However, the photo-degradation efficiency and rate of the as-prepared (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ for MB were approximately 246 and 120 times higher than those of ZnO, and for tetracycline were approximately 4500 and 200 times higher than those of ZnO, respectively, which indicated a successful recombination of Bi_2WO_6 and ZnO. The corresponding values for the different catalysts are listed in Tables 1 and 2.

The results indicated that the improved activity of the as-prepared $\text{Bi}_2\text{WO}_6/\text{ZnO}$ could be attributed to the effective separation of the electron-hole pair between Bi_2WO_6 and ZnO.

3.7. Photoluminescence (PL) and photocurrents

PL is a reliable and effective method for evaluating the recombination efficiency of charge carriers [59]. The lower the luminous intensity of photoluminescence is, the lower the recombination rate of photo-generated carriers is, which implies a high efficiency of photocatalysis [60].

Fig. 8 shows that pure ZnO exhibits a strong photoluminescence at 384 nm under an excitation wavelength of 320 nm and at room temperature. Pure Bi_2WO_6 also showed a strong photoluminescence at 427 nm under the same conditions. However, the strength of the emission band of ZnO was significantly reduced after being combined with Bi_2WO_6 . This situation showed that the recombination of Bi_2WO_6 and ZnO could improve the separation efficiency for photoelectron-hole pairs, thereby reducing the recombination rate of electron-hole pairs and facilitating the photocatalytic reaction.

The electrical performance of the as-obtained composite photocatalysts was explored under visible light by determining the photocurrent, where the larger the photocurrent, the higher the separation efficiency of the electron-hole pair [61]. Fig. 9 indicates the photocurrent transient response of ZnO, Bi_2WO_6 and (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction electrodes.

The photocurrent increased sharply and reached a steady state after 160 s upon light illumination. The (0.3:1)

Fig. 8. PL spectra of photocatalysts.

$\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterostructures exhibited a higher transient photocurrent density of approximately 4.5 μA compared with Bi_2WO_6 and ZnO, which indicated an enhanced separation efficiency of the photoelectron-hole pairs.

3.8. Photocatalytic mechanism

To better understand the mechanism of photocatalysis, detection of the main active radical species in the photocatalytic experiments was performed [62]. From Fig. 10(a), TEMPOL, IPA and $\text{Na}_2\text{C}_2\text{O}_4$ exhibited a considerable inhibition for the photo-degradation of MB. The contributions of IPA and $\text{Na}_2\text{C}_2\text{O}_4$ to the degradation of MB were 20.7% and 11.2%, respectively. However, the contribution of TEMPOL reached 64.8%, which was much higher than those of IPA and $\text{Na}_2\text{C}_2\text{O}_4$. The values of the rate constant k for the photo-degradation of MB (Fig. 10(b)) were 0.036, 0.003, 0.012 and 0.017 min^{-1} for no scavenger, TEMPOL, IPA and $\text{Na}_2\text{C}_2\text{O}_4$, respectively.

Based on the above data, it was shown that the photo-degradation of MB over the (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ photocatalyst was mainly dominated by $[\text{O}_2]^-$ radicals (formed by the

Table 1
Photocatalytic results of MB degradation.

Catalyst	Photocatalytic efficiency (%)	Rate constant k (min^{-1})	R^2
(1:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$	75.1	0.0112	0.9908
(0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$	98.4	0.0365	0.9779
(0.2:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$	89.7	0.0185	0.9941
(0.1:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$	80.7	0.0136	0.9987
ZnO	0.4	0.0003	0.9999

Table 2
Photocatalytic results of tetracycline degradation.

Catalyst	Photocatalytic efficiency (%)	Rate constant k (min^{-1})	R^2
(1:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$	82.4	0.0309	0.9468
(0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$	90.0	0.0397	0.9628
(0.2:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$	73.6	0.0235	0.9592
(0.1:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$	79.5	0.0275	0.9591
ZnO	0.02	0.0002	0.9671

Fig. 9. Transient photocurrent response of ZnO, Bi_2WO_6 and (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ samples.

Fig. 10. Photo-degradation of MB (a) and values of the rate constant k (b) over the (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction with several different scavengers.

generation of photo-generated electrons and dissolved oxygen), followed by $\cdot\text{OH}$ and h^+ .

To explore the mechanism of the photo-degradation activity of the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction, the relative band positions of Bi_2WO_6 and ZnO were explored. The conduction band (CB) values (E_{CB}) were estimated by Eq. (3) [63].

$$E_{\text{CB}} = X - 0.5E_g + E_0 \quad (3)$$

where E_g , E_0 , and X are the band gap energy of the catalyst, energy of free electrons on hydrogen and electronegativity of a semiconductor, respectively [64]. X values of ZnO and Bi_2WO_6 were obtained to be 5.79 and 6.36 eV and their band gap energies were 3.2 and 2.68 eV [65], respectively.

The E_{CB} values of ZnO and Bi_2WO_6 were -0.31 and -0.84 eV, and the valence band (VB) values (E_{VB}) of ZnO and Bi_2WO_6 were 2.89 and 1.89 eV, respectively. Therefore, it was clear that the values of E_{CB} and E_{VB} of ZnO were all higher than those of Bi_2WO_6 . The calculated results indicated that the modification of ZnO with Bi_2WO_6 benefited the separation of the photo-generated charge carriers.

As shown in Scheme 1, photo-induced electrons and holes were produced when Bi_2WO_6 was excited by visible light. Photo-generated electrons were transferred from the CB of Bi_2WO_6 to the CB of ZnO owing to mutual contact between the two cat-

alysts. Thus, the photo-generated electrons and holes were effectively separated, which resulted in an inhibition for the recombination of electron and holes. Moreover, a large number of electron-hole pairs and other oxidative species were produced during the process of the photocatalytic reactions. Therefore, the photocatalytic efficiency was improved and the pollutants were completely degraded. Thus, the catalysts of $\text{Bi}_2\text{WO}_6/\text{ZnO}$ exhibited an enhanced capability compared with bare ZnO and Bi_2WO_6 [48].

Moreover, as the CB potential of Bi_2WO_6 was more negative than $\text{O}_2/\cdot\text{O}_2^-$ (-0.33 eV), superoxide radical anions ($[\text{O}_2]^-$) were produced from the reaction of dissolved oxygen molecules and electrons (e^-) on the surface of ZnO . Then, the as-produced $[\text{O}_2]^-$ was converted into an hydroxyl radical ($\cdot\text{OH}$) through protonation [66,67]. In addition, the CB potential of ZnO was more positive than $\text{O}_2/\cdot\text{O}_2^-$ (-0.33 eV) but more negative than that of the reaction $\text{e}_{\text{CB}}^- + \text{O}_2 + \text{H}^+ \rightarrow \text{H}_2\text{O}_2$ ($+0.682$ V vs. NHE). Ultimately, the organic pollutants of MB and tetracycline were decomposed effectively by the produced strong oxidizing agent of $\cdot\text{OH}$. The above photo-degradation mechanism could be proposed as follows [68]:

where $[\text{e}^-]$ and $[\text{h}^+]$ refer to the electrons on the CB and holes in the VB, respectively.

4. Conclusions

The efficient heterogeneous junction photocatalyst $\text{Bi}_2\text{WO}_6/\text{ZnO}$ was successfully synthesized through a simple hydrothermal method. After modification, the band gap energy of the ZnO -based photocatalyst was reduced to 2.6 eV from 3.2 eV. Under visible light, the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ composite showed an excellent photocatalytic activity for the degradation of MB and tetracycline. The photo-degradation efficiencies and rates for MB and tetracycline with (0.3:1) $\text{Bi}_2\text{WO}_6/\text{ZnO}$ were hundreds of times higher than those of bare ZnO . The as-prepared (0.3:1)

Scheme 1. Schematic illustration of the electron-transfer process over the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ catalyst.

$\text{Bi}_2\text{WO}_6/\text{ZnO}$ photocatalyst exhibited a higher transient photocurrent density of approximately 4.5 μA compared with bare Bi_2WO_6 and ZnO nanoparticles. The successful recombination of Bi_2WO_6 and ZnO significantly increased the effective separation of electron–hole pairs and correspondingly improved the photocatalytic activity of ZnO . Moreover, the major active species of $[\text{O}_2]^-$ played a key role during the process of photo-degradation. This study suggested that the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ composite was a novel and effective catalyst for contaminated water restoration.

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Graphical Abstract

Chin. J. Catal., 2018, 39: 810–820 doi: 10.1016/S1872-2067(17)63004-3

Flower-like $\text{Bi}_2\text{WO}_6/\text{ZnO}$ composite with excellent photocatalytic capability under visible light irradiation

Juan Cheng, Yi Shen, Kuan Chen, Xi Wang, Yongfu Guo *, Xiaoji Zhou, Renbi Bai *

Suzhou University of Science and Technology; Jiangsu Collaborative Innovation Center of Water Treatment Technology and Material

The $\text{Bi}_2\text{WO}_6/\text{ZnO}$ composite photocatalyst was employed to degrade methylene blue and tetracycline. Under visible light, the $\text{Bi}_2\text{WO}_6/\text{ZnO}$ composite shows excellent photocatalytic activity for methylene blue and tetracycline within a short irradiation time.

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Bi₂WO₆/ZnO: 一种在可见光下具有优良光催化性能的花状新型复合材料

程娟^a, 沈奕^a, 陈宽^a, 汪曦^a, 郭永福^{a,b,*}, 周晓吉^a, 白仁碧^{a,#}

^a苏州科技大学分离净化材料与技术研发中心, 江苏苏州215009

^b江苏高校水处理技术与材料协同创新中心, 江苏苏州215009

摘要: 印染废水具有水量大、色度高、难生化降解、有毒有害物质多等特点; 另外抗生素废水的大量排放对水生和陆地生态系统带来了危害。光催化可有效降解有机物, 因而被广泛研究和应用, 其多以半导体作为光催化剂。ZnO因价廉、无毒、来源广、光催化活性高而广受关注。但是, 由于其带隙较宽, 只能被紫外光激发, 对太阳光的利用率低, 且易发生光腐蚀, 光稳定性较差, 从而大大降低了光催化活性, 不利于其应用。将ZnO与其他半导体复合是改善其光催化活性的最有效方法之一。铋基光催化剂一直是光催化领域的研究热点, 作为无机半导体纳米晶之一, Bi₂WO₆具有无毒性、适当的带隙和优异的光催化性能, 因而得到广泛关注。本文将Bi₂WO₆复合到ZnO上以降低ZnO带隙能, 提高其对太阳能的转换, 降低电子-空穴

的复合几率, 促进电荷转移的有效分离, 从而提高ZnO的光催化性能。

本文采用两步水热法合成了一种异质结的花状 $\text{Bi}_2\text{WO}_6/\text{ZnO}$ 复合材料。通过降解亚甲基蓝(MB)和四环素, 研究了其光催化性能。结果表明, 该 $\text{Bi}_2\text{WO}_6/\text{ZnO}$ 复合材料对MB和四环素具有优异的光催化活性, 对它们的光降解效率分别是纯ZnO的246和4500倍, 相应地, 对这两种污染物的光降解率分别是纯ZnO的120和200倍。活性因子捕获实验结果显示, 超氧自由基在光催化降解过程中起主要作用, 其次是羟基自由基和光生空穴。

采用X射线衍射、透射电镜、扫描电镜、紫外-可见漫反射、 N_2 吸附脱附、X射线光电子能谱、荧光光谱、光电流等方法对材料的形态结构、孔结构、化学组成、带隙能、光吸收性质、载流子复合效率等进行了分析。复合后 $\text{Bi}_2\text{WO}_6/\text{ZnO}$ 的形貌为微米尺寸纳米结构的花状绒球, 直径约为4 μm , 带隙能量从3.2 eV降为2.6 eV。 $\text{Bi}_2\text{WO}_6/\text{ZnO}$ 为介孔结构, 复合后比表面积为原来的4.98倍。所制备的 $\text{Bi}_2\text{WO}_6/\text{ZnO}$ 光催化剂比纯 Bi_2WO_6 和ZnO颗粒具有更高的瞬态光电流密度(约为4.5 μA)。

综上, Bi_2WO_6 和ZnO成功复合形成了异质结, 降低了ZnO的禁带宽度, 促进了电子和空穴的有效分离, 从而提高了其光催化活性。

关键词: 钨酸铋; 氧化锌; 光催化; 亚甲基蓝; 抗生素

收稿日期: 2017-11-30. 接受日期: 2017-12-20. 出版日期: 2018-04-05.

*通讯联系人. 电话: (0512)68092987; 电子信箱: yongfuguo@163.com

#通讯联系人. 电子信箱: ceebairb@live.com

基金来源: 国家自然科学基金(51578354); 江苏省六大人才高峰(2016-JNHB-067); 苏州市科技局科技计划(SS201667); 江苏省青蓝工程和江苏省研究生科研与实践创新计划(KYCX17_2067).

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