Research Article

Photoinduced Synthesis of Hierarchical Flower-Like Ag/Bi₂WO₆ Microspheres as an Efficient Visible Light Photocatalyst

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A series of three-dimensional microflower-like Ag/Bi₂WO₆ composites were synthesized through a simple and practical photoreduction process with different photoreduction times. The UV-visible diffuse reflectance spectra indicate that the spectrum of Ag/Bi₂WO₆ is significantly red-shifted compared to pure Bi₂WO₆ microspheres in the visible light region. The photocatalytic activities of the as-prepared samples were evaluated by the decolorization of rhodamine B under visible light irradiation. The photocatalytic reaction rate constants of the Ag/Bi₂WO₆ with a photoreduction time of 20 min was 3.60 times bigger than those of pure Bi₂WO₆. The enhanced photocatalytic activity could be attributed to the synergistic effect of increased light absorption range and the effective separation of photogenerated carriers caused by Ag nanoparticles.

1. Introduction

In the past few decades, photocatalytic degradation of environmental pollutants and photocatalytic hydrogen production have been the concern [1]. Titanium dioxide (TiO₂) has been extensively studied by scholars all over the world for its advantages of low cost, nontoxicity, and high chemical stability. However, TiO₂ has the disadvantage of lower quantum efficiency and inability to absorb visible light; TiO₂-based photocatalysis has not been used for industrial wastewater treatment [2, 3]. It has become a challenge for researchers to develop a visible light-responsive photocatalyst that has both a wide range of light absorption and a low recombination rate of photogenerated charges [4, 5]. Recently, it has been reported that the preparation of a semiconductor heterojunction photocatalyst by coupling another narrow-bandgap semiconductor material can effectively reduce the recombination rate of photogenerated electrons and holes and has been widely used to increase the activity of the photocatalyst [6–8].

With a bandgap width of 2.75 eV, bismuth tungstate (Bi₂WO₆) has received more and more attention due to its excellent photocatalytic properties [9]. However, pure

Bi₂WO₆ has disadvantages of narrower response range of visible light (less than 450 nm) and rapid recombination of photogenerated electron and hole pairs. Therefore, to broaden the response range of visible light and to enhance the photogenerated carriers, separation efficiency of Bi₂WO₆ is very important to improve their photocatalytic properties. In recent years, there have been many attempts to improve the photocatalytic activity of Bi₂WO₆, such as the preparation of a large surface area of the 3D nanostructure Bi₂WO₆ [10] and element doping [11–13]. Due to its high Schottky barrier at the metal-semiconductor interface, the noble metal on the semiconductor surface has been used as an electron acceptor to separate photogenerated electron-hole pairs and to promote interfacial charge transfer processes [14]. Most of the noble metal-semiconductor composite photocatalysts are prepared by in situ photoreduction. The researchers mainly discuss the influence of the precious metal loading, but the influence of photoreduction time is seldom reported. In this dissertation, a series of Ag/Bi₂WO₆ composites with different photoreduction times were synthesized by a simple visible light-driven photoreduction method. The synthesized samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and

transmission electron microscopy (TEM), UV-Vis DRS, and photoluminescence (PL) spectroscopic analysis. The photocatalytic activity and degradation mechanism of the Ag/Bi₂WO₆ composite were studied in detail under visible light irradiation.

2. Materials and Methods

2.1. Preparation of Bi₂WO₆ Microspheres. 2 mmol Bi(NO₃)₃·5H₂O and 1 mmol Na₂WO₄·2H₂O were dissolved in 35 mL deionized water, respectively. After the magnetic stirring for 30 min, the Na₂WO₄ solution was slowly added to the solution of Bi(NO₃)₃ dropwise. Magnetic stirring was continued for 30 min, and the solution was transferred to a 100 mL polytetrafluoroethylene hydrothermal vessel. The hydrothermal reaction was carried out at 180°C for 12 h and formed a pale yellow precipitate and was filtered, washed (deionized water and ethanol each three times), and dried in an oven at 60°C.

2.2. Preparation of Ag/Bi₂WO₆ Composites. The Ag/Bi₂WO₆ material with a silver content of 1% by mass was photoreduction synthesized as follows: the weighed amount of AgNO₃ was added to 50 mL of deionized water and stirred in the dark until completely dissolved. Then, 1.0 mmol Bi₂WO₆ was added to the AgNO₃ solution, stirred at room temperature, and irradiated with a 500 W Xenon lamp (irradiance intensity 100 mW/cm²; Institute of Electric Light Source, Beijing) for a certain period of time, and silver ions were photoreduced in situ to form silver nanoparticles on the surface of the Bi₂WO₆ by light irradiation. The reaction was filtered, washed, and dried at 80°C for 12 h to obtain the Ag/Bi₂WO₆ photocatalyst. In order to study the effect of photoreduction time on the photocatalytic activity of Ag/Bi₂WO₆ composites, Ag/Bi₂WO₆ samples with different photoreduction times of 10, 20, 40, and 60 min were labeled as AB-10, AB-20, AB-40, and AB-60, respectively.

2.3. Characterization. Phase analysis of the Ag/Bi₂WO₆ photocatalyst was carried out using an X-ray powder diffractometer (Bruker D8, Germany). The morphology and particle size were analyzed by scanning electron microscopy (Hitachi S-4800, Japan) and transmission electron microscopy (JEOL 2010F, Japan). UV-visible diffuse reflectance spectra were measured on a UV-2550 (Shimadzu, Japan). Photoluminescence fluorescence spectra were measured using a fluorescence spectrometer (Hitachi F-4500, Japan).

2.4. Photocatalytic Activity Test. The photocatalytic activities of the as-synthesized Ag/Bi₂WO₆ were carried out in terms of the degradation of RhB solution. A 500 W Xenon lamp (irradiance intensity 100 mW/cm²; Institute of Electric Light Source, Beijing) with a cutoff filter ($\lambda > 420$ nm) was used as the visible light source. 50 mg of catalyst was dispersed in a beaker of 50 mL RhB solution (1.5×10^{-5} mol/L) or parachlorophenol (4-CP) (1 mg·L⁻¹) and continuously stirred for 30 min in the dark to reach the equilibrium of adsorption-desorption before visible light irradiation. During the irradiation, 3 mL of solution was sampled at certain intervals and centrifuged for analysis. The RhB concentrations in

FIGURE 1: XRD patterns of the pure Bi₂WO₆ and Ag/Bi₂WO₆ composites with different photoreduction times.

the solution were measured by a UV-visible spectrophotometer at the maximum absorption wavelength of RhB of 553 nm (Shanghai Meipuda Instrument Co. Ltd. UV-1600). The 4-CP concentrations in the solution were analyzed by high-performance liquid chromatography (HPLC) using an Agilent 1100 series (Santa Clara, CA, USA) equipped with a UV detector at 280 nm. The mobile phase was composed of 80% methanol and 20% water at a flow rate of 0.5 mL·min⁻¹.

3. Results and Discussion

To characterize the crystalline structure of the samples, the XRD patterns of pure Bi₂WO₆ and Ag/Bi₂WO₆ composites with different photoreduction times were obtained (Figure 1). All of the diffraction peaks observed in the XRD patterns belong to the orthorhombic Bi₂WO₆ (JCPDS number 39-0256) with the unit cell parameters which are $a = 5.456$ Å, $b = 16.435$ Å, and $c = 5.438$ Å [15]. The diffraction angles for pure Bi₂WO₆ and Ag/Bi₂WO₆ composites at 2θ that are equal to 28.3°, 32.8°, 47.0°, 55.8°, and 58.5° can be assigned to 113, 200, 113, 220, 331, and 226 reflections, respectively, of the orthorhombic Bi₂WO₆. The diffraction peaks are strong and sharp, and no other impurity peaks appear, indicating that Ag doping does not change the phase structure of Bi₂WO₆. The absence of Ag diffraction peaks can be attributed to too little Ag nanoparticle content below the detection limit of the instrument.

Figures 2(a) and 2(b) show the SEM images of pure Bi₂WO₆ and Ag/Bi₂WO₆ (20 min). It can be clearly seen that the prepared samples have a three-dimensional flower-like microsphere structure with good dispersion and the diameter of flower-like microspheres is about 2.5–3.5 μm. It is indicated that the nano-Ag particles introduced by photoreduction do not affect the macroscopic morphology of Bi₂WO₆ microspheres. Silver nanoparticles were not observed for the Ag/Bi₂WO₆ microspheres (Figure 2(b)), probably due to the light-induced preparation of silver nanoparticles too small in size. In order to further confirm the presence of silver nanoparticles on the surface of flower-like Bi₂WO₆

FIGURE 2: SEM images of synthetic samples: (a) Bi_2WO_6 ; (b) $\text{Ag}/\text{Bi}_2\text{WO}_6$; (c and e) TEM images of AB-20 and AB-40; (d) HRTEM images of AB-20.

FIGURE 3: UV-visible diffuse reflectance spectroscopy of the synthetic sample.

microspheres, AB-20 was analyzed using the TEM and HRTEM analysis, which shows that Ag nanoparticles of about 10 nm were distributed on Bi_2WO_6 nanosheets. Figure 2(d) shows that the lattice fringes of Bi_2WO_6 and Ag are clearly visible and correspond to the (113) plane of Bi_2WO_6 and the (111) plane of Ag, respectively. Figure 2(e) reveals that prolonged photoreduction results in excessive silver nanoparticle deposition, which may be detrimental to the rapid separation of photogenerated carriers.

UV-visible diffuse reflectance spectroscopy of pure Bi_2WO_6 and AB-20 was measured using a UV-Vis spectrophotometer with an integrating sphere (Shimadzu, Japan), as shown in Figure 3. All samples have a strong absorption band in the UV-visible region, and absorption is steep up to the edge; this is attributed to the transition of the bandgap level of Bi_2WO_6 rather than to the transition of impurity levels [16]. The band gap energy (E_g) was calculated based on the absorption spectra by the formula [17] $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where h is Planck's constant, ν is the frequency of vibration, α is the absorption coefficient, E_g is the band gap, and A is the proportionality constant. The value of the exponent n denotes the nature of the sample transition, and $n = 0.5$ when assuming a direct allowed transition. According to the results of this analysis, the band gap values of bare Bi_2WO_6 and AB-20 samples were 2.76 and 2.74 eV, respectively. The $\text{Ag}/\text{Bi}_2\text{WO}_6$ nanocomposite exhibited similar E_g to pristine Bi_2WO_6 , which demonstrated that the introduction of Ag had almost no influence on the band gap energy of Bi_2WO_6 . However, the silver-loaded Bi_2WO_6 composite exhibits enhanced light absorption in the visible light region. The enhanced light absorption is due to the surface plasmon resonance (SPR) effect of silver [18]. The plasma peak of silver nanoparticles at about 500 nm is not significantly attributed to the low Ag loading [19]. The silver-supported Bi_2WO_6 composites are more conducive to the visible light absorption compared with the pure Bi_2WO_6 , which maybe contributes to the improvement of the photocatalytic activity.

FIGURE 4: (a, b) Changes in the visible absorption spectra of RhB of AB-20 and pure Bi₂WO₆. (c) Photocatalysis degradation profiles of RhB under visible light irradiation. (d) Kinetic plot of the photocatalysts.

The photocatalytic activities of the pure Bi₂WO₆ and Ag/Bi₂WO₆ were investigated by the photocatalytic oxidation of the cationic dye rhodamine B (RhB). Figures 4(a) and 4(b) show that the photodegradation spectra under visible light were acquired for AB-20 and the pure Bi₂WO₆ after different reaction times. The direct degradation of the conjugated system of the dye can be observed through the decrease in the RhB absorbance at 553 nm. Figure 4(c) shows the RhB photocatalytic degradation curve of the different synthetic samples. It can be seen that the photocatalytic activity of Ag/Bi₂WO₆ prepared at different photoreduction times is superior to that of pure Bi₂WO₆. The photocatalytic activity of Ag/Bi₂WO₆ was also enhanced gradually when the photoreduction time was extended from 10 min to 20 min. This is because the Ag nanoparticle promoted the photoelectron-hole pair separation and interfacial electron transfer. In addition, the surface plasmon resonance of Ag nanoparticles under visible light irradiation also contributes to the absorption of light to enhance the photocatalytic activity [17, 18]. The photocatalytic activity of AB-20 was the best when the photoreduction time was 20 min and the degradation rate of RhB reached 99.2% after 40 min of visible light irradiation. The photocatalytic activity of

Ag/Bi₂WO₆ decreases gradually with the photoreduction time more than 20 min. This may be attributed to the fact that excessive silver nanoparticle deposition promotes the recombination of photogenerated carriers [20] and the excess silver may also cover the active sites of Bi₂WO₆, leading to a decrease in photocatalytic activity.

Because the initial concentration of the RhB dye is very small, the photocatalytic degradation of RhB by Ag/Bi₂WO₆ is in accordance with the description of quasi-first-order kinetic equations [21], and the formula is $\ln(C_t/C_0) = -kt$ (C_t and C_0 are the time t RhB solution concentration and initial RhB solution concentration, respectively, and k is the quasi-primary reaction kinetic rate constant). The plot of $-\ln(C_t/C_0)$ versus t is fitted to a straight line, and the fitted slope is the quasi-first-order reaction rate constant k . Figure 4(d) shows the pseudo-first-order linear fit of the photocatalytic degradation reaction of pure Bi₂WO₆ and Ag/Bi₂WO₆ composites synthesized at different photoreduction times. The reaction rate constants of Ag/Bi₂WO₆ composites synthesized at photoreduction times of 10, 20, 40, and 60 min and pure Bi₂WO₆ were 0.0669, 0.08476, 0.07587, 0.04357, and 0.02353 min⁻¹, respectively. The reaction rate constant of Ag/Bi₂WO₆ was the highest when the

FIGURE 5: (a) Photocatalysis degradation profiles of 4-CP under visible light irradiation. (b) Kinetic plot of the photocatalysts.

photoreduction synthesis time was 20 min, which was 3.60 times higher than that of pure Bi_2WO_6 . The photocatalytic results were compared with the already-present related literature; the reaction rate constant of Ag/Bi_2WO_6 synthesized by sonochemical methods [22] or ultrasonic vibration processes [23] was 0.0332 or 0.0279 min^{-1} , respectively. The reaction rate constant of Pt/Bi_2WO_6 [24] using the photoreduction process similar to our synthesis method was 0.035 min^{-1} . Obviously, AB-20 was much more active than Ag/Bi_2WO_6 synthesized by other methods or other metals such as Pt deposited on Bi_2WO_6 using the same method, demonstrating that AB-20 displayed excellent photocatalytic activity.

To further confirm that the photocatalytic activity of Ag/Bi_2WO_6 composites originates from the excitation of the catalysts rather than from the dye sensitization mechanism, the photocatalytic degradation of colorless neutral parachlorophenol (4-CP) over Ag/Bi_2WO_6 composites was also performed (Figure 5). The degradation of 4-CP is extremely slow without photocatalysts after 160 min of reaction, while the degradation efficiency approaches 44.96%, 56.29%, 53.86%, and 47.79% by using AB-10, AB-20, AB-30, or AB-40 as the photocatalyst, respectively (Figure 5(a)). Among these composites, AB-20 exhibits the highest photodegradation efficiency (78.3%), which is much higher than that from Bi_2WO_6 (27.6%). The photodegradation rate constant using AB-20 (0.00664 min^{-1}) is about 2.87 times higher than that using Bi_2WO_6 (0.00231 min^{-1}) (Figure 5(b)).

Photoluminescence (PL) spectra are used to determine the photogenerated carrier recombination, migration, and separation efficiency, as photoluminescence is mainly caused by the recombination of photogenerated electron-hole pairs [25]. The lower the photoluminescence intensity under visible light irradiation, the lower the recombination rate of charge carriers [26]. Figure 6 shows the photoluminescence spectra of pure Bi_2WO_6 and AB-20 samples with an excitation wavelength of 300 nm. Pure Bi_2WO_6 has a broad

FIGURE 6: The photoluminescence spectra of the synthetic sample.

emission peak at 400–560 nm and a strong blue emission peak at 468 nm, attributed to the charge on the hybrid orbital formed by Bi^{6s} and O^{2p} on the Bi_2WO_6 valence band that transferred to the W^{5d} empty conduction band in the WO_6^{2-} complex [27]. It indicates that the recombination probability of photogenerated electron-hole pairs in pure Bi_2WO_6 is much higher, resulting in weaker photocatalytic activity. The PL intensity of silver-supported Bi_2WO_6 composites is much lower than that of pure Bi_2WO_6 , which can effectively inhibit the recombination rate of excited electrons and holes and increase the photocatalytic activity.

Figure 7 shows the transient photocurrent test pattern of pure Bi_2WO_6 and AB-20 samples tested in 1 M NaOH solution at 300 W xenon lamp illumination. From Figure 7, it can be seen that the photocurrent densities of pure Bi_2WO_6 and AB-20 electrodes are 0.7 and $2.2 \mu A/cm^2$, respectively. The photocurrent density of the Ag/Bi_2WO_6 electrode is higher than that of the pure Bi_2WO_6 electrode. This also shows that

FIGURE 7: Transient photocurrent responses of the synthetic sample.

FIGURE 8: Photocatalytic degradation of RhB by Ag/Bi₂WO₆ with the presence of a capturing agent.

loading a certain amount of Ag can promote photogenerated electron-hole transfer and inhibit rapid recombination of photogenerated charges.

To analyze the photocatalytic reaction mechanism, it is of vital importance to identify the primary active species during the degradation process. Thus, the radical trapping experiments were performed (Figure 8). The capturing agents such as benzoquinone (BQ), triethanolammonium (TEOA), isopropanol (IPA), and sodium azide (NaN₃) with a concentration of 1 mmol/L are commonly used to capture superoxide radical ($O_2^{\bullet-}$), photogenerated hole (h_{VB}^+), hydroxyl radical ($\bullet OH$), and singlet oxygen (1O_2), respectively. When the photocatalytic reaction time is 40 min, the effect of adding TEOA is very significant, the degradation rate of rhodamine B is reduced to 27.38%, and the addition of IPA and NaN₃ had little effect on the degradation of

FIGURE 9: Schematic diagram of the photocatalytic mechanism for the Ag/Bi₂WO₆ composite.

rhodamine B, while the photocatalytic activity of the catalyst was reduced to 48.97% after the addition of BQ. In summary, h_{VB}^+ plays a key role in the photocatalytic degradation process, $O_2^{\bullet-}$ plays a part role in the degradation process, $\bullet OH$ and 1O_2 have no effect, and the order of the active species is $h_{VB}^+ > O_2^{\bullet-} \gg \bullet OH$.

Combined with the radical trapping experiments and relevant literature, the possible photocatalytic degradation mechanism of rhodamine B with the Ag/Bi₂WO₆ composite photocatalyst is speculated as shown in Figure 8. The photocatalysis of Ag/Bi₂WO₆ composites is caused by the effective absorption of visible photons, the electrons (e^-) in the valence band of Bi₂WO₆ (VB) are excited to transition to the conduction band (CB), and holes (h_{VB}^+) are left on the valence band of Bi₂WO₆. Because the conduction band energy level of Bi₂WO₆ is higher than the conduction band energy level of Ag, the electrons can be quickly transferred to the Ag nanoparticles through the Schottky barrier at the metal-semiconductor interface, which is similar to other researchers' studies on the electron transfer from semiconductors to metals [28, 29]. Thus, the recombination probability of the photogenerated electrons in the conduction band (CB) and the photogenerated holes in the valence band (VB) was lessened, as revealed by photoluminescence experiment results and transient photocurrent test. Subsequently, the h^+ stored in the VB of Bi₂WO₆ can directly oxidize RhB, and the photogenerated electrons are quickly captured by molecular oxygen absorbed on the surface of the photocatalyst and generate superoxide radical ($O_2^{\bullet-}$) to further degrade RhB. Therefore, the enhancement of photocatalytic activity of Ag/Bi₂WO₆ is owed to photogenerated holes (h_{VB}^+) and superoxide radical ($O_2^{\bullet-}$), which are consistent with the result of radical trapping experiments (Figure 9).

4. Conclusions

Three-dimensional flower-like Ag/Bi₂WO₆ composites were successfully prepared by a simple photoreduction method. The results of photocatalytic experiments show that Ag/Bi₂WO₆ composites have higher photocatalytic activity than pure Bi₂WO₆. The photocatalytic reaction rate constant of Ag/Bi₂WO₆ composites prepared at a photoreduction time of 20 min was 3.60 times bigger than that of pure Bi₂WO₆.

The excellent photocatalytic performance of Ag/Bi₂WO₆ composites is due to the introduction of silver which results in a synergistic effect of an increase of the light absorption range and an effective separation of photogenerated carriers. The synthesis of this material will help design new high-performance photocatalysts.

Data Availability

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare no conflict of interest.

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