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Construction of Z-scheme $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite with excellent visible-light photodegradation activity for removal of organic contaminants

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ABSTRACT

Ag_3PO_4 has good potential for use in photocatalytic degradation of organic contaminants. However, the activity and stability of Ag_3PO_4 is hard to sustain because of photocorrosion and the positive potential of the conduction band of Ag_3PO_4 . In this study, A composite consisting of Bi_2WO_6 nanosheets and Ag_3PO_4 was developed to curb recombination of charge carriers and enhance the activity and stability of the catalyst. Formation of a $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite was confirmed using X-ray diffraction, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. Photoluminescence spectroscopy provided convincing evidence that compositing Bi_2WO_6 with Ag_3PO_4 effectively reduced photocorrosion of Ag_3PO_4 . The $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite gave a high photocatalytic performance in photodegradation of methylene blue. A degradation rate of 0.61 min^{-1} was achieved; this is 1.3 and 6.0 times higher than those achieved using Ag_3PO_4 (0.47 min^{-1}) and Bi_2WO_6 (0.10 min^{-1}), respectively. Reactive species trapping experiments using the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite showed that holes, $\cdot\text{OH}$, and $\cdot\text{O}_2^-$ all played specific roles in the photodegradation process. The photocatalytic mechanism was investigated and a Z-scheme was proposed as a plausible mechanism.

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1. Introduction

Environmental hazards pose a great threat to human health and retard social development. The use of solar energy is a good method for dealing with the problems caused by hazardous materials [1–3]. Photocatalysts should: (1) respond to visible-light irradiation, which accounts for the majority of solar energy; (2) have high quantum efficiencies and stabilities; and (3) be produced from safe, cheap, and nontoxic raw materials.

Currently used photocatalysts such as TiO_2 [4–8], ZnO [9,10], ZnS [11], Zn_2GeO_4 [12], and BiPO_4 [13,14] have excellent photocatalytic activities under ultraviolet (UV) irradiation. Although UV radiation, which has high energy, is a highly efficient light source and can excite most semiconductor photocatalysts, it forms only a small part of the solar energy spectrum and is harmful to human health. In recent years, photocatalysts with wide band gaps have been modified and improved by doping [15–17], using surface plasmon resonance (SPR) with noble

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metals [18,19], and constructing heterojunction or solid-solution photocatalysts [20,21]. However, because of the inherent properties of the materials, the improvements are too limited to make the photocatalysts suitable for practical applications. The development of high-efficiency visible-light-driven photocatalysts is therefore important. In recent years, visible-light-driven photocatalysts such as g-C₃N₄ [2,22–25], CdS [26–28], Ag₃PO₄ [29–31], AgX (X = Cl, Br and I) [32], WO₃ [33,34], Bi₂MoO₆ [35], Bi₂WO₆ [36,37], and BiVO₄ [38] have been reported to be good photocatalysts. However, in most cases, photocatalysts that can be excited by visible light do not have high redox capabilities. For example, g-C₃N₄ and CdS, which have strong conduction band (CB) reduction capabilities, have weak valence band (VB) oxidation capabilities. Conversely, Ag₃PO₄, WO₃, and BiVO₄ have strong oxidation but weak reduction capabilities. The development of composite photocatalysts has therefore attracted much attention. Although type-II composite photocatalysts can effectively boost the separation of charge carriers and enhance the photocatalytic activity, the redox capabilities of the individual components of the composite are impaired. The use of Z-scheme photocatalysts provides a feasible solution to this problem [39–43].

Ag₃PO₄, which is responsive to irradiation at wavelengths less than 550 nm but has enhanced light absorption at wavelengths greater than 550 nm because of the SPR effect of Ag nanoparticles, shows excellent photocatalytic activities in the degradation of organic contaminants and oxygen evolution reactions [1,44–47]. Although the holes in the VB of Ag₃PO₄ have enough energy to degrade contaminants and generate hydroxyl radicals (·OH), which are essential for photodegradation, the electrons in the CB cannot be used to produce superoxide anion radicals (·O₂[−]) and further degrade organic pollutants. The electrons in the CB are therefore easily trapped by Ag⁺, and this decreases the stability of the Ag₃PO₄ photocatalytic system. The photodegradation capability of Ag₃PO₄ is several tens of times higher than those of conventional semiconductors such as TiO₂ [2,48], g-C₃N₄ [38,49], Bi₂MoO₆ [50], BiVO₄ [51], and BiOCl [52,53], therefore it is worth optimizing the photocatalytic activity and improving the physicochemical stability of Ag₃PO₄.

Two-dimensional nanomaterials are of interest because of their large specific surface areas, large numbers of reactive sites, and fast separation of charge carriers. They are also convenient for the preparation of composites with large-area heterojunctions [54–56]. Recently, Bi₂WO₆ nanosheets (NSs) have been prepared using a wet-chemical bottom-up route. These Bi₂WO₆ NSs have high activities in photodegradation and CO₂ reduction [57–59]. Bi₂WO₆ can respond to visible-light irradiation and the electrons in the CB are sufficiently negative to participate in photocatalytic reduction. Composites of Ag and Bi have been reported to be useful for preparing high-efficiency stable photocatalysts; this led us to prepare Ag₃PO₄/Bi₂WO₆ [32,35,38,60].

In this work, the successful preparation of Ag₃PO₄/Bi₂WO₆ was confirmed using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). Ultraviolet-visible (UV-vis) diffuse reflectance

spectroscopy (DRS) showed that the composite absorbed light intensely, as in the case of Ag₃PO₄. Photoluminescence (PL) spectroscopy showed that the composite effectively hindered recombination of charge carriers. Ag₃PO₄/Bi₂WO₆ showed enhanced photocatalytic activity. The methylene blue (MB) degradation rate achieved using Ag₃PO₄/Bi₂WO₆ was 0.61 min^{−1}, which is 1.3 and 6.0 times higher than those achieved using Ag₃PO₄ (0.47 min^{−1}) and Bi₂WO₆ (0.10 min^{−1}), respectively. Five successive photodegradation experiments showed that Ag₃PO₄/Bi₂WO₆ had sufficient stability. Reactive species trapping experiments showed that the photocatalytic mechanism was Z-scheme rather than type II.

2. Experimental

2.1. Materials

AgNO₃, NH₃·H₂O, HNO₃, KH₂PO₄, Na₂WO₄·2H₂O, cetyltrimethylammonium bromide (CTAB), and Bi(NO₃)₃·5H₂O were purchased from the Shanghai Chemical Reagent Co., Ltd. (China). L-ascorbic acid, isopropanol (IPA), triethanolamine (TEOA), and MB were purchased from the Sinopharm Chemical Reagent Corp. (China). Double-distilled water was used in the experiments. All the reagents were analytical grade and used without further purification.

2.2. Preparation

Bi₂WO₆ NSs were prepared using a previously reported method [57]. Bi(NO₃)₃·5H₂O (2 mmol), CTAB (0.05 g), and Na₂WO₄·2H₂O (1 mmol) were mixed with deionized water (80 mL) under stirring for 30 min. The mixture was transferred to a 100 mL Teflon-lined autoclave and heated at 120 °C for 24 h. Bi₂WO₆ NSs were obtained by washing six times with deionized water and vacuum freeze-drying for 12 h. AgNO₃ (3.4 g) was dispersed in H₂O (340 mL) and then NH₃·H₂O was added dropwise; the solution changed from clear to brownish black and then to clear again. The pH was adjusted to 7 by dropwise addition of HNO₃. Bi₂WO₆ NSs (0.15 g) were then added under constant stirring for 30 min. The Ag₃PO₄/Bi₂WO₆ composite was obtained by dropwise addition of KH₂PO₄ solution (0.2 mol/L, 35 mL). The Ag₃PO₄/Bi₂WO₆ composite was washed six times with deionized water and vacuum freeze-dried for 12 h. Bulk Ag₃PO₄ was obtained in the same way but without adding Bi₂WO₆ NSs.

2.3. Characterization

XRD patterns were recorded using a Panalytical Empyrean diffractometer with Cu K_α radiation (λ = 1.5406 Å) as the X-ray source. The morphologies and elemental compositions of the prepared samples were investigated using field-emission scanning electron microscopy (FE-SEM; SU8020) with EDS (INCA x-act). XPS was performed using an ESCALAB 250 instrument with Al K_α radiation. UV-vis DRS was performed using a PerkinElmer Lambda 950 UV-vis spectrophotometer. PL spectra were recorded using an FLS920 instrument at an excitation

wavelength of 325 nm.

2.4. Investigation of photocatalytic performance

The photocatalyst (30 mg) was mixed with MB solution (30 mL, 20 mg/L). Light-emitting diode (LED) arrays (active power 50 W, $\lambda = 410$ nm) were used as a solar model. The irradiation time intervals were set at 2 min and the process was repeated five times. After each light irradiation, the absorbance of the MB solution was determined using the clear liquid obtained after centrifuging the mixture. The dominant reactive species affecting MB photodegradation were identified using IPA, L-ascorbic acid, and TEOA as scavengers for $\cdot\text{OH}$, $\cdot\text{O}_2^-$, and holes, respectively. In a typical process [32,61,62], either L-ascorbic acid (150 mg), IPA (20 mmol/L, 5.4 mL), or TEOA (10 mmol/L, 6.1 mL) was added to a mixture of the photocatalyst and MB solution. Radical-trapping experiments were performed using the same method as for the photodegradation experiments.

3. Results and discussion

As shown in Fig. 1, Bi_2WO_6 NSs were prepared using a bottom-up route [57]. When Br^- ions are adsorbed on Bi_2WO_6 seed crystals, coulombic repulsion forces restrain bulk growth of Bi_2WO_6 crystals. This is the key factor in the generation of Bi_2WO_6 NSs. $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ was prepared by in situ growth of Ag_3PO_4 on Bi_2WO_6 NS surfaces. More highly active crystal surfaces were exposed by using $\text{Ag-NH}_3\cdot\text{H}_2\text{O}$ solution to regulate the Ag_3PO_4 growth rate.

In Fig. 2(a), the strong diffraction peaks at $2\theta = 20.93^\circ$, 29.75° , 33.32° , 36.58° , 42.49° , 47.76° , 52.65° , 55.12° , 57.32° , 61.67° , 69.88° , 71.90° , and 73.97° match the (110), (200), (210), (211), (220), (310), (222), (320), (321), (400), (420), (421), and (332) crystal planes of cubic Ag_3PO_4 (PDF #84-0510, $P-43n$, $a = b = c = 6.011$ Å). In Fig. 2(c), the strong diffraction peaks at $2\theta = 28.38^\circ$, 32.87° , 47.21° , 55.96° , 58.58° , 68.80° , 75.99° , and 78.46° are assigned to the (131), (002), (202), (133), (262), (004), (391), and (064) crystal planes of orthorhombic Bi_2WO_6 (PDF #79-2381, $Pca2_1$, $a = 5.43726$ Å, $b = 16.43018$ Å, $c = 5.45842$ Å). All the strong diffraction peaks in Fig. 2(b) can be indexed to a mixture of cubic Ag_3PO_4 and Bi_2WO_6 . However, the diffraction peaks from Bi_2WO_6 are weak because of its low content (about 5 wt% of the composite).

Fig. 3(a)–(c) show SEM images of Ag_3PO_4 , Bi_2WO_6 , and $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$. Ag_3PO_4 consists of particles with sides of length about 1 μm . The size of the Bi_2WO_6 NSs is several micrometres, and the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite retains the

Fig. 1. Schematic diagram of $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ synthesis.

Fig. 2. XRD patterns of Ag_3PO_4 (a), $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ (b), and Bi_2WO_6 (c).

Ag_3PO_4 morphology. Fig. 3(d)–(f) show that all the elements in Ag_3PO_4 , Bi_2WO_6 , and the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite can be detected. The C is derived from the conductive adhesive, and no other impurities can be observed, implying that the samples are pure. The elemental mapping (Fig. 3(g)) shows a homogeneous distribution of Ag, P, O, Bi, and W in the prepared $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite.

In the XPS spectrum in Fig. 4(a), peaks from O, Ag, Bi, W, and P elements can be clearly seen. In Fig. 4(b), the peaks at binding energies of 374.2 and 368.2 eV can be assigned to $\text{Ag } 3d_{3/2}$ and $\text{Ag } 3d_{5/2}$ orbitals, respectively [63]. According to a previous report, the binding energies for Ag^0 are 375.32 and 369.32 eV. In this case, the peaks for Ag^0 could not be obtained by peak fitting, indicating that the Ag^0 content was low [64,65]. In Fig. 4(c), the peaks at binding energies of 532.6 and 531.0 eV correspond to surface-absorbed hydroxyl oxygen and lattice oxygen [66]. In Fig. 4(d), the peak at a binding energy of 133.8 eV is associated with the P 2p orbital of P^{5+} [67,68]. In Fig. 4(e), the peaks at binding energies of 164.6 and 159.6 eV correspond to the Bi $4f_{5/2}$ and Bi $4f_{7/2}$ orbitals, respectively, of Bi^{3+} [69,70]. In Fig. 4(f), the peaks at binding energies of 42.4 and 40.3 eV are indexed to the W $4f_{5/2}$ and W $4f_{7/2}$ orbitals of W^{6+} , respectively [66].

The insets in Fig. 5(a), of color yellow, white, and dark yellow (left to right), correspond to Ag_3PO_4 , Bi_2WO_6 , and the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite, respectively; the colors indicate the differences among the optical properties of these materials. Ag_3PO_4 and Bi_2WO_6 have absorption edges at 527 and 429 nm, respectively. The absorption edge of the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite is almost the same as that of Ag_3PO_4 ; this is attributed to the low Bi_2WO_6 content. Bi_2WO_6 shows almost no response to radiation of wavelength between 429 and 800 nm because the irradiation energy is lower than the excitation energy. Ag_3PO_4 shows a little absorption on irradiation at wavelengths between 527 and 800 nm, which can be ascribed to the SPR effect of Ag nanoparticles. The energy band gaps E_g in Fig. 5(b) were calculated using the following equation:

$$(Ah\nu)^{2/n} \sim h\nu - E_g \quad (1)$$

where $n = 1$ is for a direct semiconductor and $n = 4$ for an indirect semiconductor; A and $h\nu$ stand for the absorbance and irradiation energy, respectively. According to a previous report,

Fig. 3. SEM images of Ag_3PO_4 (a), Bi_2WO_6 (b), and $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ (c) and ED spectra of Ag_3PO_4 (d), Bi_2WO_6 (e), and $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ (f), and SEM image with corresponding elemental mapping images for $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ (g).

Fig. 4. Overview (a) and corresponding high-resolution Ag 3d (b), O 1s (c), P 2p (d), Bi 4f (e), and W 4f (f) XPS spectra of prepared $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite.

Ag_3PO_4 and Bi_2WO_6 are indirect semiconductors. The E_g values for Ag_3PO_4 and Bi_2WO_6 are 2.21 and 2.64 eV, respectively.

$$E_{\text{VB}} = X - E^e + 0.5E_g \quad (2)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \quad (3)$$

where X is 5.96 eV for Ag_3PO_4 and 4.86 eV for Bi_2WO_6 [64,71],

and E^e is a constant (4.5 eV). According to equations (1)–(3), E_{CB} and E_{VB} are 0.36 and 2.57 eV, respectively, for Ag_3PO_4 , and –0.98 and 1.70 eV, respectively, for Bi_2WO_6 .

PL spectroscopy can be used as an indicator of recombination of electron–hole pairs [32,61]. Fig. 6 shows that the main

Fig. 5. (a) UV-vis DR spectra and insets showing photographs of samples of Ag_3PO_4 , Bi_2WO_6 , and $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite; (b) Linear transformation $h\nu - (Ah\nu)^{1/2}$ curves for UV-vis DR spectra.

emission peaks for Ag_3PO_4 , Bi_2WO_6 , and the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite are all centred at about 415 nm. The PL intensities of Ag_3PO_4 and Bi_2WO_6 are high, indicating large quantities of charge carriers, which would recombine in the photocatalyst interior rather than being transferred to the surface to participate in the photocatalytic reaction. This difficulty in achieving highly efficient separation of charge carriers in a single material is consistent with previous reports [72]. The PL intensity of the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite is lower than those of Ag_3PO_4 and Bi_2WO_6 , indicating that fewer charge carriers recombine inside this photocatalyst than in the single materials. This shows that composite construction is an effective method for curbing the recombination of electron-hole pairs.

Fig. 7 shows the N_2 adsorption-desorption isotherms for Bi_2WO_6 , Ag_3PO_4 , and the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite. The Brunauer-Emmett-Teller surface area (A_{BET}) of Ag_3PO_4 is 2.8 m^2/g . When Ag_3PO_4 is coupled with Bi_2WO_6 , the surface area of the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite increases to 10.7 m^2/g because of the large A_{BET} of Bi_2WO_6 (23.4 m^2/g).

The photocatalytic activities were evaluated by degradation of MB solution (Fig. 8(a)). The photocatalytic activity of the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite was higher than those of Ag_3PO_4

and Bi_2WO_6 , and about 97.5% degradation of the MB solution was achieved within 6 min. The linear relationships between $\ln C_0/C$ and t (Fig. 8(b)) show that the MB degradation curves are in accord with pseudo-first-order kinetics. The degradation rate achieved using $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ was 0.61 min^{-1} , which is 1.3 and 6.0 times higher than those achieved using Ag_3PO_4 (0.47 min^{-1}) and Bi_2WO_6 (0.10 min^{-1}), respectively.

The stabilities of Bi_2MoO_6 , Ag_2MoO_4 , and $\text{Bi}_2\text{MoO}_6/\text{Ag}_2\text{MoO}_4$ 2:1 were evaluated by performing five successive MB degradation experiments. Fig. 9 shows that $\text{Bi}_2\text{MoO}_6/\text{Ag}_2\text{MoO}_4$ 2:1 showed long-term stability, with almost no loss of activity after five cycles. This indicates that the heterojunction benefits not only the photocatalytic activity but also the stability of the photocatalyst.

The main reactive species that affect the degradation of MB using the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite were investigated using various scavengers. L-ascorbic acid, IPA, and TEOA were used as scavengers for $\cdot\text{O}_2^-$, $\cdot\text{OH}$, and holes, respectively. Fig. 10 shows that the degradation efficiency of the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite in the absence of scavengers was 97.5%. Addition of L-ascorbic acid, IPA, and TEOA during the photocatalytic experiments changed the degradation efficiency to 83.6%, 76.2%,

Fig. 6. PL spectra of Ag_3PO_4 , Bi_2WO_6 , and $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite.

Fig. 7. N_2 adsorption-desorption isotherms for Bi_2WO_6 , Ag_3PO_4 , and $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite.

Fig. 8. (a) MB degradation curves under 410 nm LED irradiation; (b) Linear transformations of MB degradation curves.

and 29.2%, respectively. These results show that holes play a key role in photocatalytic degradation of MB, $\cdot\text{OH}$ plays a secondary role, and $\cdot\text{O}_2^-$ has little involvement.

Fig. 11 shows that the photocatalytic mechanism was probably a Z-scheme rather than a typical type-II process. According to the results in Fig. 5(b), the E_g values for Ag_3PO_4 and Bi_2WO_6 are 2.21 and 2.68 eV, respectively. The electrons in the VBs of

Fig. 9. Results of five successive MB degradation experiments using Ag_3PO_4 , Bi_2WO_6 , and $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite.

Fig. 10. Reactive species trapping experiments for $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite.

Ag_3PO_4 and Bi_2WO_6 can be excited to the CBs under visible-light irradiation. The E_{CB} and E_{VB} values for Ag_3PO_4 are 0.36 and 2.57 eV, respectively, and those for Bi_2WO_6 are -0.98 and 1.70 eV, respectively. If the photocatalytic mechanism for the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ system is type II, the electrons in the CB of Bi_2WO_6 will be transferred to the CB of Ag_3PO_4 and holes in the VB of Ag_3PO_4 will be transferred to the VB of Bi_2WO_6 because of the clear electric potential difference. If charge carriers are transferred in this way, the reduction reaction will occur at the CB of Ag_3PO_4 , and the oxidation reaction will occur at the VB of Bi_2WO_6 . The potential of the Ag_3PO_4 CB is 0.36 eV, which is more positive than the potential at which O_2 is reduced to $\cdot\text{O}_2^-$, and the potential of the Bi_2WO_6 VB is 1.70 eV, which is more negative than the potential at which H_2O molecules are oxidized to $\cdot\text{OH}$; this is not in agreement with the results of the reactive species trapping experiments for the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite, shown in Fig. 10. However, if the photocatalytic mechanism is a Z-scheme, the electrons in the CB of Ag_3PO_4 will recombine with holes in the VB of Bi_2WO_6 . The oxidation reaction will occur at the Ag_3PO_4 VB and the reduction reaction will occur at the Bi_2WO_6 CB. The electric potential of holes in the Ag_3PO_4 VB is 2.57 eV, which can oxidize H_2O to $\cdot\text{OH}$. The potential of the electrons in the Bi_2WO_6 CB is -0.98 eV, which can reduce O_2 to $\cdot\text{O}_2^-$. These results are consistent with those shown in Fig. 10. Organic contaminants will be decomposed to H_2O , CO_2 , or other small molecules by the synergistic effect of holes, $\cdot\text{OH}$, and $\cdot\text{O}_2^-$. The recombination of electrons in the CB of Ag_3PO_4 with holes in the VB of Bi_2WO_6 effectively promotes separation of charge carriers and curbs photocorrosion of Ag_3PO_4 ; this is consistent with the results shown in Figs. 8 and 9.

4. Conclusions

In this work, a $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite was successfully prepared. Formation of a composite of Bi_2WO_6 and Ag_3PO_4 effectively curbed recombination of electrons and holes in the photocatalyst. The photocatalytic activity of the $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite was higher than those of Ag_3PO_4 and Bi_2WO_6 . The composite had good stability, with almost no ac-

Fig. 11. Schematic diagram of plausible transfer direction of charge carriers and photocatalytic mechanism.

tivity loss after five successive runs. Reactive species trapping experiments confirmed a Z-scheme photocatalytic mechanism and showed that holes, $\cdot\text{OH}$, and $\cdot\text{O}_2^-$ played specific roles in the photodegradation process. This excellent $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ photocatalyst is expected to have applications in the removal of organic contaminants.

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Graphical Abstract

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Construction of Z-scheme $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite with excellent visible-light photodegradation activity for removal of organic contaminants

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Z-scheme $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6$ composite was successfully constructed by hydrothermal and in-situ growing channels, which exhibited superior photodegradation activity and durable stability under visible irradiation.

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Z-机制磷酸银/钨酸铋复合物的构建及其可见光催化降解有机污染物

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摘要: 环境危害不仅对人类健康构成巨大威胁, 而且也阻碍了经济社会的快速发展. 光催化剂通过利用太阳能来降解污染物为环境问题提供一条理想的途径. 光催化剂的制备应该考虑以下几点: (1) 对可见光响应; (2) 高量子效率和稳定性; (3) 安全、廉价、无毒的原材料. 早期的一些催化剂如二氧化钛、氧化锌、硫化锌、锆酸锌和磷酸铋等在紫外线照射下表现出优秀的光催化活性. 但是紫外光是稀有的, 而且对人体健康有害. 近年来, 对宽带隙半导体的改性如掺杂、贵金属沉积、

构建异质结或固溶体催化剂取得了有效进展。遗憾的是,受限于材料的固有属性,有限的改进仍然不能满足实际应用的需求。因此,探索高效稳定的可见光驱动的光催化剂依然是十分有意义的。

磷酸银在可见光下表现出超强的光催化降解有机污染物和产氧的能力,但是磷酸银容易受到光腐蚀,光催化活性和稳定性很难维持。另外,磷酸银导带上的电子电势较正,这将导致其很难在光催化过程中被利用。而磷酸银导带上电子的积累会抑制其内部电子空穴对的分离,从而对磷酸银的光催化活性和稳定性造成不利影响。

本文选择钨酸铋纳米片与磷酸银复合去抑制电子空穴对的复合和进一步提高磷酸银的活性和稳定性。样品的粉末X射线衍射、能谱和X光电子能谱的分析证实了磷酸银/钨酸铋复合物已经被成功合成。稳态荧光光谱证实了磷酸银/钨酸铋复合物的构建可以作为一种有效抑制电子和空穴对复合的手段。通过对样品进行光催化降解次甲基蓝的实验,我们发现磷酸银/钨酸铋复合材料展现出比磷酸银和钨酸铋更强的光催化活性。其中,磷酸银/钨酸铋光催化降解次甲基蓝的速率为 0.61385 min^{-1} ,这是磷酸银(0.47179 min^{-1})和钨酸铋(0.10270 min^{-1})活性的1.3和6.0倍。同时,磷酸银/钨酸铋表现出耐久的稳定性,在连续五次光降解过程中几乎没有明显的活性损失。进一步通过对磷酸银/钨酸铋复合材料进行光催化活性成分的捕获实验,我们发现空穴、超氧负离子自由基和羟基自由基都发挥了一定的作用。最后,我们讨论了光催化机制,Z-机制光催化机制被认为是合理的。

关键词: 磷酸银; 钨酸铋; 光催化剂; Z-机制; 降解; 可见光

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