Preparation of a visible light catalyst of novel Bi$_2$WO$_6$ loaded Ag$_3$PO$_4$ heterojunction and its efficient removal of toluene

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ABSTRACT

Herein, a novel photocatalyst of Ag$_3$PO$_4$/Bi$_2$WO$_6$ was developed via hydrothermal and precipitation method. Its structure and morphology was characterized through XRD, XPS, SEM, TEM, HRTEM, BET, UV-vis DRS, PL, and so on. By employing toluene photodegradation experiment under visible light, the photocatalytic performance of Ag$_3$PO$_4$/Bi$_2$WO$_6$ was proved to be better than Ag$_3$PO$_4$ and Bi$_2$WO$_6$ alone due to the efficient separation of electron-hole pairs. When the molar ratio of Ag$_3$PO$_4$ to Bi$_2$WO$_6$ was 1:2, the degradation rate of toluene could reach 80% within 180 min. This study provided a new idea for the simple preparation of cheap and efficient nanocomposite materials for VOCs degradation by visible light.

1. Introduction

Volatile organic compounds (VOCs) from transportation, industry and household have become major air pollutants and are important factors in the formation of photochemical smog and ozone, posing a serious threat to environmental safety and human health [1]. Aromatic VOCs, such as toluene, are one of the most common VOCs and have complex molecular structures that are toxic and carcinogenic [2]. In recent years, with the increasingly serious energy and environmental problems, the purification of VOCs by semiconductor photocatalysis under visible light irradiation has attracted widespread attention [3–5]. Nonetheless, the preparation of simple, efficient and sustainable photocatalysts with good performance in visible light remains a major challenge in this field. At present, many visible light responsive semiconductor photocatalysts, including Bi$_2$WO$_6$, g-C$_3$N$_4$, Ag$_3$PO$_4$, BiVO$_4$, CeO$_2$, etc., are used to degrade pollutants [6–11]. Bi$_2$WO$_6$, which consists of (WO$_6$)$^{6-}$ octahedral layer and bismuth oxide (Bi$_2$O$_3$)$^{2+}$ layer alternately, has attracted extensive attention in terms of energy conversion and organic pollutants [12–16]. Its layered structure accelerates the separation of charges [17]. Due to its unique characteristics, such as the suitable band gap (2.70 eV), good photo-stability and non-toxicity, it is a promising photocatalytic material. However, the photocatalytic activity of Bi$_2$WO$_6$ is low because of the small visible response range and the easy recombination of electrons and holes (e$^-$/h$^+$), which greatly limits its practical application [18,19]. In order to overcome these shortcomings, researchers usually adopt ion doping, semiconductor catalyst recombination and other means to improve the photocatalytic activity of Bi$_2$WO$_6$, such as Au-Pd/Bi$_2$WO$_6$, Bi$_2$Fe$_2$O$_5$/Bi$_2$WO$_6$, g-C$_3$N$_4$/Bi$_2$WO$_6$, and so on [20–23].

Ag$_3$PO$_4$ has become a research hotspot in the field of photocatalytic materials since Yi et al. synthesized it by the solid phase ion exchange method and successfully applied it to the study of organic wastewater degradation and water decomposition in 2010 [24]. Ag$_3$PO$_4$ is a body-centered cubic structure material with a band gap of about 2.40 eV, absorbs 45% of the visible light in the sunlight and has a quantum efficiency of up to 90% [25]. It has the characteristics of high visible light catalytic activity, high quantum yield and low toxicity, and is an ideal research material in the field of photocatalysis [26]. In addition, the presence of PO$_4^{3-}$ can easily separate the e$^-$/h$^+$ pairs by generating a dipole moment through the interfacial junction electric field [27]. However, the photo-corrosion often happens in Ag containing photocatalysts if the reaction between photoinduced e$^-$ and pollutants adsorbed on the catalyst surface cannot carried out as quick as possible, and Ag$^+$ will be reduced to metallic Ag, which would have side effects on the photocatalytic performances on the Ag$_3$PO$_4$ [28–30]. The above problems can be effectively solved by hybridizing Ag$_3$PO$_4$ with other semiconductors to form heterojunction photocatalysts. Yin et al. prepared Ag$_3$PO$_4$/C$_3$N$_4$ heterojunction material by in-situ precipitation [31]. Under visible light irradiation, the photoexcited e$^-$ on the conduction band (CB) of
Ag₃PO₄ would recombine with the photogenerated h⁺ on the valence band (VB) of C₃N₄, so that the e⁻ and h⁺ remained in the CB of C₃N₄ and the VB of Ag₃PO₄ respectively. The spatial separation of photoinduced carriers was then realized, which was beneficial to the photocatalytic reaction. In addition, there are some other similar composites developed such as g-C₃N₄/MoS₂/Ag₃PO₄, Ag₃PO₄/WO₃, Ag₃PO₄-g-C₃N₄ etc. [32–34].

In this study, Bi₂WO₆ nanosheets were first fabricated via hydrothermal method, and then Ag₃PO₄ nanoparticles were loaded on the obtained Bi₂WO₆ nanosheets by silver ammonia solution in the way of precipitation, and finally Ag₃PO₄/Bi₂WO₆ photocatalyst nanomaterials with Z-scheme heterostructure were synthesized. The morphology and structure were characterized by different analytical methods, such as XRD, XPS, SEM, TEM, HRTEM, BET, UV-vis DRS, PL, and so on. Due to the full contact between Ag₃PO₄ and Bi₂WO₆ in Ag₃PO₄/Bi₂WO₆ nanoparticles, the e⁻/h⁺ separation and electron transfer were improved, and the narrow band gap width of the catalyst improved the optical efficiency. The photocatalytic degradation of toluene by Ag₃PO₄/Bi₂WO₆ under visible light irradiation showed good degradation performance.

2. Experimental

2.1. Chemicals and materials

Bi(NO₃)₃ · 5H₂O, Na₃WO₄ · 2H₂O, cetyltrimethylammonium bromide (CTAB), Na₂HPO₄ · 12H₂O, ethylenediaminetetraacetic acid disodium salt (Na₂-EDTA) were bought from Adams Reagent Co., LTD (Shanghai, China). AgNO₃, NH₄H₂O, HNO₃, isopropyl alcohol (IPA), 1, 4-benzoquinone (BQ), anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used in the experiment were reagent grades and without further purification.

2.2. Preparation of materials

2.2.1. Synthesis of Bi₂WO₆

Bi₂WO₆ was synthesized via the hydrothermal method. Specifically, 0.485 mg Bi(NO₃)₃ · 5H₂O, 0.165 mg Na₃WO₄ · 2H₂O and 0.025 g CTAB were mixed into 40 mL deionized water and stirred for 1 h. The mixed solution was then transferred into 50 mL Teflon-lined autoclave and heated at 160°C for 24 h, followed by cooling at room temperature. Finally, the as-synthesized Bi₂WO₆ was washed alternately with deionized water and ethanol for 5 times, and vacuum freeze-dried for 12 h.

2.2.2. Synthesis of Ag₃PO₄/Bi₂WO₆

The synthesis of Ag₃PO₄/Bi₂WO₆ was as follows. Firstly, AgNO₃ was dissolved in 50 mL deionized water. Second, 2 wt% NH₃·H₂O was added until the color of the solution changed from clear to dark brown and then to transparent again. Third, after adjusting pH to 7 with 1 M HNO₃ solution, Bi₂WO₆ was added into the above solution at the molar ratios of Ag₃PO₄ to Bi₂WO₆ of 1:1, 1:2 and 1:3, and stirred for 30 min. Next, a certain amount of Na₃HPO₄ · 12H₂O was evenly stirred with 20 mL distilled water, and then dropped into the above solution for stirring, centrifugation, washing and freeze-drying. Finally, the sample Ag₃PO₄/Bi₂WO₆ was obtained by grinding.

2.3. Characterization of photocatalysts

X-ray diffractor (XRD, PANalytical, Netherlands X’Pert3 Powder) by Cu Kα radiation (λ = 0.154 nm) was employed for the characterization of the crystal structure of the samples. X-ray photoelectric spectroscopy (XPS, ESCALAB, 250Xi) was characterized with Al Kα (hv = 1486.6 eV) as radiation source to analyze the element composition, valence and so on. A scanning electron microscope (SEM, Japan HITACHI Company, Nova Nano SEM 450) was used to analyze the morphologies of catalysts. Transition electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) studies of materials were obtained using a JEM-2100 F (JEOL, Japan) operated at 200 kV. The specific surface area determination and pore volume and size analysis of the materials were performed via Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively, by using a Beckman Coulter SA3100 (Beckman Coulter, Chaska, MN, USA) analyzer. The optical properties were carried out by UV-vis diffuse reflectance spectra (UV-vis RDS, Shimadzu, UV-2600) and photoluminescence (PL, Japan Branch, JASCO FP-6500).

2.4. Photocatalytic experiment

To verify the photocatalytic activity of the as-prepared Ag₃PO₄/Bi₂WO₆, toluene was used as the object of photodegradation under visible light. First, 0.1 g Ag₃PO₄/Bi₂WO₆ was dispersed in a 150 mL quartz reactor filled with gaseous toluene (100 ppm). Then, the mixture was stirred in darkness for 60 min to establish the adsorption-desorption equilibrium. After that, the obtained gas-solid mixture was exposed to the visible light irradiation from a 1000 W Xe lamp (CELHBF1000). In the end, the concentration of toluene and CO₂ was analyzed using a gas chromatograph (Agilent GC 6890 N) equipped with HP-PLOT-Q/HP-Innowax columns and FID/TCD detectors. The degradation rate
and mineralization rate can be calculated by the following formulas, respectively.

\[ Q = \text{Degradation rate (\%)} = 100 \times \left( \frac{C_0 - C}{C_0} \right) \]  

\[ \text{Mineralization rate (\%) } = 100 \times \left( \frac{C_{\text{out}} - C_{\text{in}}}{C_{\text{toluene}} \times Q} \right) \]  

where \( C_0 \) is the concentration of toluene after dark treatment when it reaches adsorption saturation; \( C \) is the concentration of toluene when photocatalysis proceeds to \( t \); \( t \) is the time of photocatalysis; \( C_{\text{out}} \) and \( C_{\text{in}} \) are the concentration of \( \text{CO}_2 \) at the outlet and inlet of the reactor respectively; \( C_{\text{toluene}} \) is the concentration of toluene.

2.5. Reactive species detection

In order to study the photodegradation mechanism of toluene by photocatalysts of \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) reactive species trapping experiments were performed by adding the scavengers such as isopropanol (IPA, hydroxyl radicals -OH scavenger), 4-benzoquinone (BQ, O\(_2^\cdot\) scavenger), and ethylenediaminetetraacetic acid disodium salt (Na\(_2\)-EDTA, h\(^+\) scavenger) to the reaction system. The degradation efficiency of the sample without the capture agents was compared to determine the role of the active group in the photocatalysis.

3. Results and discussion

3.1. Characterization of \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \)

The crystal phase of the samples was measured by XRD characterization. As shown in Figure 1(a), the wide-angle XRD patterns of \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) and \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) (\( n = 1:2 \)) were compared with the standard cards, respectively. The diffraction peaks at 2\( \theta \) = 28.3°, 32.8°, 47.1°, 55.8°, 58.5°, 68.8°, 75.9° and 78.5° matched the (131), (002), (202), (133), (262), (400), (193), and (204) crystal planes of orthorhombic \( \text{Bi}_2\text{WO}_6 \) (JCPDS NO. 30–0256) [35]. The diffraction peaks at 21.7°, 29.7°, 33.3°, 36.5°, 47.8°, 52.6°, 54.9°, 57.2°, 61.8°, 71.8° were assigned to (110), (200), (210), (211), (310), (222), (320), (321), (400) and (421) crystal planes of cubic \( \text{Ag}_3\text{PO}_4 \) (JCPDS NO. 06–0505) [31]. The diffraction peaks of \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) (\( n = 1:2 \)) can well be indexed to the standard cards of \( \text{Bi}_2\text{WO}_6 \) and \( \text{Ag}_3\text{PO}_4 \). Figure 1(b) is the XRD spectra of \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) with different molar ratios. As shown in the figure, as the proportion of \( \text{Bi}_2\text{WO}_6 \) increased, the peaks of \( \text{Bi}_2\text{WO}_6 \) became higher and higher, while that of \( \text{Ag}_3\text{PO}_4 \) became smaller and smaller. Additionally, no other impurity peaks were introduced. The results showed that the high purity \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) composite catalyst was successfully prepared.

XPS was employed to characterize the surface compositions and chemical states of the catalysts. Figure 2(a) shows the elemental composition of \( \text{Bi}_2\text{WO}_6 \), \( \text{Ag}_3\text{PO}_4 \) and \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) (\( n = 1:2 \)). Obviously, the composite catalyst of \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) (\( n = 1:2 \)) showed signals of O, Ag, Bi, P and W, including all the elements of \( \text{Ag}_3\text{PO}_4 \) and \( \text{Bi}_2\text{WO}_6 \). In Figure 2(b), the peaks of \( \text{Bi}_2\text{WO}_6 \) at 164.6 and 159.3 eV were assigned to Bi 4f\(_{5/2}\) and Bi 4f\(_{7/2}\) respectively. Compared with these two peaks of pure \( \text{Bi}_2\text{WO}_6 \), those of \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) (\( n = 1:2 \)) shifted 0.1 eV higher respectively, implying that the valence state of Bi element in \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) (\( n = 1:2 \)) was still +3 [36]. As shown in Figure 2(c), the peaks of W 4f at 35.6 eV (W 4f\(_{5/2}\)) and 37.7 eV (W 4f\(_{7/2}\)) were ascribed to W\(^{6+}\) in \( \text{Bi}_2\text{WO}_6 \) [37]. After the introduction of \( \text{Ag}_3\text{PO}_4 \), these two peaks appeared, respectively, at 35.9 and 38.0 eV, indicating that there was no effect on the valence state of W element of \( \text{Bi}_2\text{WO}_6 \). In Figure 2(d), the peaks at binding energies of 368 eV and 374 eV detected over \( \text{Ag}_3\text{PO}_4 \) could be attributed to the Ag 3d signals of Ag\(^{+}\), corresponding, respectively, to the Ag 3d\(_{5/2}\) and Ag 3d\(_{3/2}\), while these two peaks of Ag\(_3\) PO\(_4/\text{Bi}_2\text{WO}_6 \) were only 0.05 eV higher, respectively, suggesting the presence of Ag\(^{+}\) also on the surface.

Figure 1. (a) XRD patterns of \( \text{Bi}_2\text{WO}_6 \), \( \text{Ag}_3\text{PO}_4 \) and \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) (\( n = 1:2 \)) with standard cards, (b) XRD patterns of \( \text{Bi}_2\text{WO}_6 \), \( \text{Ag}_3\text{PO}_4 \) and \( \text{Ag}_3\text{PO}_4/\text{Bi}_2\text{WO}_6 \) composites with mole ratios of 1:1, 1:2 and 1:3.
of Ag$_3$PO$_4$/Bi$_2$WO$_6$ composite [30,38,39]. Figure 2(e) displays the P 2p$_{3/2}$ peaks of (PO$_4$)$_3^-$ in Ag$_3$PO$_4$ and Ag$_3$PO$_4$/Bi$_2$WO$_6$ which were detected at 133.1 eV and 133.4 eV, respectively [40]. Figure 2(f) exhibits the O 1s spectra of Bi$_2$WO$_6$, Ag$_3$PO$_4$, and Ag$_3$PO$_4$/Bi$_2$WO$_6$. The low binding energy peak at 530 eV was ascribed to the surface hydroxyl oxygen [41]. Compared with Bi$_2$WO$_6$ and Ag$_3$PO$_4$, the peaks of Bi 4f, Ag 3d, P 2p and O 1s in Ag$_3$PO$_4$/Bi$_2$WO$_6$ (n = 1:2) all shifted, mainly because an interfacial electric field formed between the contact surfaces caused the charge to shift after the Fermi energy levels of Bi$_2$WO$_6$ and Ag$_3$PO$_4$ reached equilibrium.

The position of the valence band maximum (VBM) of Bi$_2$WO$_6$ was analyzed by VB-XPS characterization. It can be seen from Figure 3 that it was roughly at 1.91 eV.

Figure 4(a-c) show the SEM images of Bi$_2$WO$_6$, Ag$_3$PO$_4$ and Ag$_3$PO$_4$/Bi$_2$WO$_6$ (n = 1:2), respectively. It can be seen that Bi$_2$WO$_6$ was composed of a two-dimensional lamellar structure. Ag$_3$PO$_4$ was consisted of irregular particles with a relatively smooth surface. The morphology of Ag$_3$PO$_4$/Bi$_2$WO$_6$ (n = 1:2) was similar to that of Bi$_2$WO$_6$, but the granular Ag$_3$PO$_4$ was not clearly photographed. Therefore, elemental analysis was performed on the composite material, as shown in the following diagrams in Figure 4(d). The results showed that Ag, P, O, Bi and W elements were uniformly distributed in Ag$_3$PO$_4$/Bi$_2$WO$_6$ (n = 1:2), and no other impurities were found, indicating that the sample was pure. Figure 4(e) shows the TEM image of Bi$_2$WO$_6$ stacked
with lamellar structure and Ag$_3$PO$_4$ was loaded on their nanosheets as irregular particles. The EDS diagram of Figure 4(f) exhibited that Bi, W, O, P, and Ag elements were detected, while no other elements existed. Figure 4(g) displays the HRTEM image of Ag$_3$PO$_4$/Bi$_2$WO$_6$ (n = 1:2). Lattice spacing d of 0.315 nm and 0.167 nm corresponded to the lattice surface (131) of Bi$_2$WO$_6$ and (320) of Ag$_3$PO$_4$, respectively. It indicated that Ag$_3$PO$_4$/Bi$_2$WO$_6$ composite nanomaterial was successfully synthesized and its purity was high, which was consistent with the conclusion obtained by SEM.

Figure 5 shows the nitrogen adsorption-desorption isotherms and BJH pore size distribution curves (inset) of Bi$_2$WO$_6$ and Ag$_3$PO$_4$/Bi$_2$WO$_6$ (n = 1:2), respectively. Typical type-IV adsorption and desorption curves and type H3 hysteresis loops were observed obviously, indicating that the nanomaterials were mesoporous materials. It can be seen from the inset that the pore sizes of both materials were mainly distributed between 2 and 25 nm. The specific surface area of Bi$_2$WO$_6$ and Ag$_3$PO$_4$/Bi$_2$WO$_6$ (n = 1:2) were 23.321 m$^2$/g and 17.696 m$^2$/g, respectively. The introduction of Ag$_3$PO$_4$ did not increase the specific surface area of the composite catalyst, but slightly decreased, which may be because part of the porous structure in Bi$_2$WO$_6$ was blocked by Ag$_3$PO$_4$ nanoparticles.

3.2. Optical absorption properties

The optical properties of Bi$_2$WO$_6$, Ag$_3$PO$_4$ and Ag$_3$PO$_4$/Bi$_2$WO$_6$ composites with different mole ratios were analyzed by UV-vis DRS (Figure 6(a)). As is shown, the
light absorption cutoff sideband of Bi$_2$WO$_6$ was about 470 nm. It has strong absorption in ultraviolet region and certain weak absorption in visible light. The absorption sideband edge of Ag$_3$PO$_4$ was about 530 nm, and the absorption range of visible light was large. As for Ag$_3$PO$_4$/Bi$_2$WO$_6$ composites, it had a red shift phenomenon, and the light absorption range was widened to 470 ~ 530 nm, and presented the characteristic curves of Bi$_2$WO$_6$ and Ag$_3$PO$_4$.

The band gap diagram of Figure 6(b) was calculated according to the Kubelka-Munk formula [42], as shown in the following:

$$a h v = A (h v - E_g)^{n/2}$$  \hspace{1cm} (3)

where $a$ is the absorption coefficient, $h$ is Planck’s constant, $v$ is the light irradiation frequency and $A$ is the absorption constant. By the calculation, the band-gap widths of Ag$_3$PO$_4$ and Bi$_2$WO$_6$ were 2.25 eV and 2.70 eV, respectively.

The approximate band edge position of the catalyst can be roughly deduced according to the empirical equation [43]:

$$E_{VB} = X - E^* + 0.5E_g$$  \hspace{1cm} (4)

$$E_{CB} = E_{VB} - E_g$$  \hspace{1cm} (5)

where $E_{VB}$ is the edge position of valence band, $E_{CB}$ is the edge position of conduction band. $X$ is the electronegativity of the catalyst (Ag$_3$PO$_4$:5.96 eV) [44]. $E^*$ is the energy of a free electron on the hydrogen scale of 4.5 eV. $E_g$ is catalyst band gap energy. By the calculation, the $E_{VB}$ and $E_{CB}$ of Ag$_3$PO$_4$ were 2.57 eV and 0.32 eV, respectively. Combined with the VB-XPS, the $E_{VB}$ and $E_{CB}$ of Bi$_2$WO$_6$ were 1.91 eV and ~0.79 eV, respectively. The details are labeled in Table 1.

Figure 7 shows the PL spectra of Bi$_2$WO$_6$ and Ag$_3$PO$_4$/Bi$_2$WO$_6$ composites with different mole ratios. It can be seen that all samples have strong absorption peaks at 470 nm, and the peak intensity decreased significantly after the introduction of Ag$_3$PO$_4$. When the ratio of Ag$_3$PO$_4$ to Bi$_2$WO$_6$ was 1:2, the peak intensity reached the lowest. The peak intensity indicated the rate of electron-hole recombination, which suggested that the separation efficiency of photogenerated carriers was significantly improved by the introduction of Ag$_3$PO$_4$ [6]. Both electrons and holes contribute to the photocatalytic reaction, and the high separation efficiency of Ag$_3$PO$_4$ and Bi$_2$WO$_6$ composite will helpful to improve the photocatalytic performance.

3.3. Photocatalytic degradation of toluene

Before the photocatalytic experiment, the catalyst was treated with dark adsorption for 60 min. Figure 8(a) shows the photocatalytic degradation performance of the catalysts for toluene under 1000 W Xenon lamp irradiation for 180 min. It can be concluded that the degradation efficiency of Ag$_3$PO$_4$ and Bi$_2$WO$_6$ was 26% and 45%, respectively, and that was improved after compounding. When the molar ratio of Ag$_3$PO$_4$ to Bi$_2$WO$_6$ was 1:2, the degradation rate reached 80%, which was 1.8 times that of Bi$_2$WO$_6$. Figure 8(b) shows the
The kinetic curve of toluene with time, indicating that the catalysts followed the first-order kinetic equation [45]:

\[ -\ln\left(\frac{C}{C_0}\right) = kt \]  

(6)

where \( C_0 \) is the concentration of toluene after dark treatment when it reaches adsorption saturation, \( C \) is the concentration of toluene when photocatalysis proceeds to \( t \), \( t \) is the time of photocatalysis, and \( k \) is the rate constant of the first-order reaction. The \( k \) value of Ag₃PO₄, Bi₂WO₆, and Ag₃PO₄/Bi₂WO₆ (n = 1:1, 1:2, 1:3) was 0.1007, 0.1989, 0.3026, 0.5381 and 0.2883 \( \text{h}^{-1} \), respectively. It can be seen from Figure 8(c) that the mineralization rate of toluene after 180 min photocatalytic degradation by Bi₂WO₆ and Ag₃PO₄ was 29.73% and 22.8%, respectively. After the combination of Bi₂WO₆ and Ag₃PO₄, the mineralization rate was significantly increased, and the best mineralization rate was about 36.2% when the molar ratio of Ag₃PO₄ to Bi₂WO₆ was 1:2. Furthermore, the \( k \) value of Ag₃PO₄/Bi₂WO₆ was higher than that of some other materials, as shown in Table 2. Therefore, it can be concluded that the prepared Ag₃PO₄/Bi₂WO₆ composite had excellent photocatalytic performance for toluene.

Next, the recycle degradation of toluene by Ag₃PO₄/Bi₂WO₆ (n = 1:2) was carried out under visible light irradiation, and the results are illustrated in Figure 9. As shown, the degradation rates of the seven rounds were 80.0%, 79.8%, 79.6%, 77.6%, 76.0%, 74.3%, and 72.5%, respectively. In the first three rounds of the photocatalytic experiments, the degradation efficiency of the catalyst maintained stable, but gradually decreased from the fourth round. At the end of seven cycles, it decreased by 7.5%, suggesting that the prepared Ag₃PO₄/Bi₂WO₆ (n = 1:2) was high stability.

### Table 1. Band gap structure of the catalysts.

| Catalyst       | \( E_g/\text{eV} \) | \( E_{\text{opt}}/\text{eV} \) | \( E_{\text{cal}}/\text{eV} \) |
|----------------|----------------------|---------------------------------|-------------------------------|
| Ag₃PO₄         | 2.25                 | 2.57                            | 0.32                          |
| Bi₂WO₆         | 2.70                 | 1.91                            | -0.79                         |

### 3.4. Photocatalytic mechanism discussion

Radical trapping experiments were carried out to understand the reaction mechanism of toluene degradation photocatalyzed by Ag₃PO₄/Bi₂WO₆ (n = 1:2) under visible light. BQ, IPA, and Na₂-EDTA were used as -OH, -O₂⁻ and \( \text{h}^+ \) capture agents, respectively (Figure 10(a)). It showed that the degradation rate of toluene by Ag₃PO₄/Bi₂WO₆ (n = 1:2) was 80% after 180 min irradiation under 1000 W Xenon lamp without trapping agent, and it was 68%, 59% and 30% after BQ, IPA and Na₂-EDTA were added, respectively. Obviously, \( \text{h}^+ \) played a key role in the photocatalytic degradation of toluene, followed with -OH and -O₂⁻. In conclusion, the photocatalytic mechanism of Ag₃PO₄/Bi₂WO₆ may be a Z-scheme rather than typical type-II heterojunction, as shown in Figure 10(b). It is known that the construction of Z-scheme heterojunctions is quite helpful for spatial separation of the photogenerated carriers and is considered as an effective way to improve the photocatalytic performance of the original semiconductors [23]. The reducing semiconductor with a high reduction potential and the oxidizing semiconductor with a high oxidation potential were assembled with
transferred to CB of Ag$_3$PO$_4$ due to potential difference. If the charge carriers were transferred in this way, a reduction reaction would take place on CB of Ag$_3$PO$_4$ and an oxidation reaction on VB of Bi$_2$WO$_6$. In this way, the CB potential of Ag$_3$PO$_4$ was more positive than that of O$_2$ reduced to -O$_2$-, and the VB potential of Bi$_2$WO$_6$ was more negative than that of H$_2$O oxidized to -OH, which was inconsistent with the free radical trapping experiment in Figure 10(a). However, if the photocatalytic mechanism of Ag$_3$PO$_4$/Bi$_2$WO$_6$ composite was Z-scheme, the oxidation reaction would take place on Ag$_3$PO$_4$ VB and the reduction reaction on Bi$_2$WO$_6$ CB. The h$^+$ potential in Ag$_3$PO$_4$ VB was 2.57 eV, which can oxidize H$_2$O to -OH. The e$^-$ potential in Bi$_2$WO$_6$ CB was −0.79 eV, which can reduce O$_2$ to -O$_2$-. Thus, the recombination of the CB e$^-$ of Ag$_3$PO$_4$ with the VB h$^+$ of Bi$_2$WO$_6$ effectively improved the e$^-$/h$^+$ separation of the composite and inhibited the photo-corrosion of Ag$_3$PO$_4$ [43]. Under the synergistic action of -O$_2$-, h$^+$ and -OH, organic pollutants were finally photodegraded into H$_2$O and CO$_2$. Summary, Z-scheme mechanism was employed for photocatalytic degradation of toluene by Ag$_3$PO$_4$/Bi$_2$WO$_6$.

4. Conclusions

In this work, Bi$_2$WO$_6$ was prepared by the hydrothermal method and Ag$_3$PO$_4$ was then loaded on it by silver ammonia precipitation method. It can be found that the irregular Ag$_3$PO$_4$ nanoparticles were dispersed on the surface of Bi$_2$WO$_6$ nanoflakes by the morphology
characterization. From UV-vis DRS and PL study, it can be seen that the light absorption range of the composite catalyst was enlarged and the recombination rate of photogenerated carriers was decreased. The photocatalytic performance of the obtained Ag3PO4/Bi2WO6 composite with different molar ratios of Bi2WO6 and Ag3PO4 was studied by the photocatalytic degradation of toluene under visible light. When the molar ratio of Ag3PO4 to Bi2WO6 is 1:2, the degradation rate of toluene reaches 80% in 180 min and the mineralization rate was about 36.2%. In conclusion, this work provided a simple synthesis way to develop a desirable photocatalyst for the removal of harmful VOCs pollutants in practical applications.

Disclosure statement
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