High-efficiency ternary Ag/C@Bi₂MoO₆ photocatalyst: electron transformation, 2,4-dibromophenol degradation and mechanism

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ABSTRACT

A novel Ag nanoparticle modified and carbon layer coated bismuth molybdate (Ag/C@Bi₂MoO₆) composite was successfully synthesized by hydrothermal and ultrasonic methods to attain a high-efficiency route for both reductive dehalogenation and oxidative decomposition of halogenated organics (e.g., 2,4-dibromophenol, 2,4-DBP). The carbon layer was tightly combined with Bi₂MoO₆ by C–O–Bi or C–O–Mo bonds, and the coated carbon layer provided a rapid electron transformation route by its excellent conductivity to enhance the separation of photoexcited charges on the surface of Bi₂MoO₆ according to the transmission emission microscopy, Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and photoluminescence characterizations. The Ag nanoparticles were deposited via the ultrasonic method and built an electric field to aggregate much more electrons on their surface and separate further photoexcited charges from the photoluminescence results. The 2,4-DBP is efficiently degraded by the Ag/C@Bi₂MoO₆ composite under visible-light irradiation, and the 0.5% Ag/C@Bi₂MoO₆ composite demonstrated an extremely removal efficiency of 2,4-DBP (10 mg/L) of 87% within 180 min. The degradation process is started with debromination process in the conduction band by aggregating electrons and followed by the oxidation and mineralization processed in valence band by holes and •OH radicals. This study displays a new approach for halophenols degradation by the heterogeneous photocatalytic process.

Keywords: Visible-light photocatalyst; Bismuth molybdate (Bi₂MoO₆); Carbon layer; Ag; 2,4-dibromophenol

1. Introduction

Halophenols such as 2,4-dibromophenol (2,4-DBP) occurred at high concentrations in freshwater systems, soils, and sediments in the recent decades around the world [1,2]. Advanced oxidation processes (AOPs) technology has been regarded as an important method to degrade and mineralize halophenol contaminants [3,4]. Visible-light induced photocatalytic technology is widely used due to the almost complete mineralization and the low cost with renewable sunlight [5–8]. Bismuth molybdate (Bi₂MoO₆), one of the bismuth contained semiconductor compounds, has attracted a great deal of attention due to the excellent photosensitivity and high photocatalytic activity under visible-light irradiation. Bi₂MoO₆ consists of [Bi₂O₇]₃⁻ layers sandwiched between MoO₄²⁻ sheets and has a band gap energy of 2.2–2.5 eV which is in good agreement with the sunlight spectrum [9,10]. It is well known that the low separation efficiency of photoexcited charge carriers affects the photocatalytic performance of semiconductor photocatalyst [11]. Researchers have tried various methods to improve the photocatalytic
activity of Bi₂MoO₆ including noble metal deposition, metal ion doping, and semiconductor composites [12–14]. Recently, much attention has been paid to the photocatalyst coating with carbon, which can stabilize the catalyst surface and increase the photocatalytic activity. Chen et al. [15] have successfully synthesized carbon-coated ZnIn₂S₄ nanocomposites and found that the carbon coating significantly increases the photocatalytic efficiency and photostability of RhB degradation. In the previous work, we have prepared a carbon-coated Bi₂MoO₆ to enhance the separation efficiency of photogenerated electron–hole pairs and by using low-cost glucose precursors [16,17]. The coated carbon layer on the surface could apply a rapid transmission route for electrons to inhibit the combination of charges and improve photocatalytic activity.

However, the utilization of electrons transmitting from the surface of the photocatalyst is another challenge to improve the charge separation. Noble metals such as gold (Au), silver (Ag), palladium (Pd), and platinum (Pt) could be used as electron traps near the conduction band to facilitate carrier transfer and prevent recombination with valence band holes [18–22]. At the same time, the electric field could be formed by the plasmonic effect of noble metal atoms and accelerate the aggregation of the transmitting electrons. Among all the noble metals, Ag has attracted the great interest of researchers because of its ability to handle organic pollutants over other noble metals and their additional antimicrobial activity [23,24]. Therefore, we conclude that the separated electrons would have a rapid route to an acceptor made up of Ag electrons.

In this study, carbon-coated Bi₂MoO₆ (C@Bi₂MoO₆) was prepared by the addition of glucose as a precursor hydrothermal method. We are confident that the coated carbon layer would show great contrast between the carbon and Bi₂MoO₆ rather than graphene and CNT in our previous study [2,8]. Then Ag deposited C@Bi₂MoO₆ (Ag/C@Bi₂MoO₆) composite was synthesized by an ultrasonic deposition method. The as-prepared Ag/C@Bi₂MoO₆ composite significantly improves the photocatalytic activity under visible-light irradiation. This is mainly attributed to the synergistic effect of noble metal (Ag) and coated carbon layer on the surface of Bi₂MoO₆, which enhances the separation efficiency of photogenerated electron–hole pairs and improves the photocatalytic activity.

2. Experimental

2.1. Synthesis of Bi₂MoO₆

All reagents for synthesis and analysis were analytic grade without further purification, and deionized water was used throughout the experiments. The Bi₂MoO₆ photocatalyst was synthesized via a common method of hydrothermal technique. In a typical procedure, 2.0 mmol Bi(NO₃)₃·5H₂O was dissolved into 10 mL dilute HNO₃ (2 mol/L) (solution A). Secondly, 2.0 mmol (NH₄)₂MoO₄·4H₂O was dissolved into 60 mL of deionized water at 70°C (solution B). Solution A was dropped into solution B with stirring and reacted for 60 min and the pH of the suspension was adjusted to 7.0 using NH₃·H₂O. The resulting mixture was sealed into a 100 mL Teflon-lined stainless steel autoclave and heated at 180°C for 12 h. The products of Bi₂MoO₆ were collected by filtration, washed with deionized water several times, and dried by vacuum at 80°C for 8 h.

2.2. Synthesis of C@Bi₂MoO₆ composites

0.1 g Bi₂MoO₆ was added to 80 mL glucose solution (30 mg/L) with stirring for 30 min, and the mixture solution was sealed into a 100 mL Teflon-lined stainless steel autoclave and heated at 180°C for 6 h. The products of C@Bi₂MoO₆ composites were collected by filtration, washed with deionized water, and dried by vacuum at 80°C for 8 h.

2.3. Synthesis of Ag/C@Bi₂MoO₆ composites

Ag/C@Bi₂MoO₆ composites were synthesized by an ultrasonic method. Typically, 2.5 mL NaBH₄ (0.1 mol/L), 0.2 g as-obtained C@Bi₂MoO₆ composites, and a certain amount of AgNO₃ were added to 100 mL deionized water, and then ultrasonicated for 30 min. The mixture solution was filtrated and dried to obtain the Ag/C@Bi₂MoO₆ composites. The different deposition amount of Ag to Ag/C@Bi₂MoO₆ was controlled to be 0.25%, 0.50%, 1.00%, and 2.00%.

2.4. Characterization

The crystalline phases of the samples were evaluated by X-ray powder diffraction (XRD) on a Bruker D8 Advance diffract meter (Bruker, Germany). The diffraction patterns were determined in the 2θ range of 10°–80° with a Cu Kα source (λ = 1.5418 Å) running at 60 kV and 60 mA. The morphologies and microstructures of the samples were obtained by a scanning electron microscope (SEM, JEOL, JEM 2100). The infrared spectra were examined by a Fourier-transform infrared spectrometer (FTIR, Nicolet Avatar 370). X-ray photoelectron spectroscopy (XPS) measurements were examined via an ESCALAB 250 spectrometer (Thermo Fisher Scientific, UK) with non-monochromatic Al Kα X-rays (1486.6 eV). UV-VIS diffuse reflectance spectra (DRS) were characterized by a UV-VIS spectrophotometer (TU-1901) with BaSO₄ as a reference. The photoluminescence (PL) spectra of the photocatalysts were examined by a fluorescence spectrometer (Hitachi F-4600) with an excitation wavelength of 365 nm.

2.5. Photocatalytic activity

The photocatalytic activities of the samples were evaluated by 2,4-DBP degradation with a visible-light source (λ > 420 nm, 500 W Xe lamp) due to its high occupancy of the sunlight. The as-prepared photocatalyst (0.1 g) was dispersed into 100 mL of 2,4-DBP solution (10 mg/L of 2,4-DBP concentration). Before visible-light irradiation, the mixture was magnetically stirred in the dark for 30 min to reach the equilibrium of adsorption and desorption. The solutions were collected at different time intervals and centrifuged to remove the particles. The obtained solution was analyzed through high-performance liquid chromatography (HPLC) at 280 nm to determine 2,4-DBP concentration.
To capture the corresponding active species, various sacrificial agents were added into the 2,4-DBP solution. Na$_2$C$_2$O$_4$ (5 mmol/L), Cr (VI) (0.5 mmol/L), IPA (5 mmol/L), and TEMPO (2 mmol/L) were employed as the scavengers to capture hole, electron, hydroxyl radical (•OH) and superoxide radical (•O$_2$), respectively.

3. Results and discussion

3.1. Crystalline structure and morphology

The as-prepared Bi$_2$MoO$_6$ photocatalyst is identical to orthorhombic according to the XRD patterns (Fig. 1), and the main diffraction peaks of composites were identical to the orthorhombic phase (JCPDS No. 76-2388) [25,26]. The peaks of carbon are not observed in XRD patterns of the C@Bi$_2$MoO$_6$ and Ag/C@Bi$_2$MoO$_6$ composites, indicating that the amorphous carbon is present in these composites. The significant peaks of Ag were hardly observed in the XRD patterns of composites, and it suggests that Ag has a high dispersion and low concentration in the composites [27]. The intensities of the diffraction peaks of Bi$_2$MoO$_6$ are gradually weaker by increasing the deposition of Ag, indicating that Ag deposition affects the crystalline structure of Bi$_2$MoO$_6$ photocatalyst.

The Ag/C@Bi$_2$MoO$_6$ composite is composed of irregular sheets with a thickness of about a hundred nanometers, which is the bulk of Bi$_2$MoO$_6$ in the composite, as shown in Fig. 2a. The EDX spectrum of the 0.50% Ag/C@Bi$_2$MoO$_6$ composite linked to SEM in Fig. 2b shows that C and Ag elements are coated in the surface of the composite. To further confirm the existence of carbon and Ag, the elemental mapping image of the 0.50% Ag/C@Bi$_2$MoO$_6$ composite was measured and is shown in Fig. 2c1–c4. The C, Bi, Mo, and Ag elements are uniformly distributed on the surface of the composite. It suggests that the C layer generated by the hydrothermal method is very thin, and the Ag nanoparticles dispersed more tenuously than C on the surface of the composite. Ag nanoparticles have a diameter of about 10–20 nm and are grown on the surface of the composite, which can be seen in TEM images as shown in Fig. 3a and b. The distinct lattice fringes of $d = 0.204$ nm and 0.236 nm in the high-resolution TEM image in Fig. 3c match with the crystallographic planes of Ag (200) and (111), respectively [28]. Also, the lattice fringes of $d = 0.316$ nm are found and assigned to the (131).
plane in the orthorhombic phase of Bi$_2$MoO$_6$. However, we cannot observe the carbon layer on the outer edge of the Bi$_2$MoO$_6$ sheets due to the layer is too thin to confirm. In the SAED pattern of the 0.50% Ag/C@Bi$_2$MoO$_6$ composite, as shown in Fig. 3d, the crystallographic planes of Ag (200) and Bi$_2$MoO$_6$ (111) have also appeared.

3.2. Surface structure and photoexcited properties

The surface element chemical composition of the photocatalyst is investigated by XPS spectra. The survey XPS spectrum of 0.5% Ag/C@Bi$_2$MoO$_6$ composite is shown in Fig. 4a, and we can find the C 1s and Ag 3d peaks (inset) in the composite. The obtained high-resolution spectrum for Mo 3d is shown in Fig. 4b, and the peaks at 235.2 and 232.0 eV are related to Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ of MoO$_4^{2-}$ in Bi$_2$MoO$_6$ photocatalyst, respectively. The obtained high-resolution C 1s spectrum is shown in Fig. 4c, and the asymmetric peak around 282~288 eV could be fitted to four peaks at about 287.0, 284.9, 283.6, and 283.2 eV. The peaks at 287.0 eV and 283.2 eV correspond to the C–O bond and the C=C bond, respectively [29]. The peak at 283.6 eV corresponds to Mo–O–C bond and the Bi–O–C bond formed between Bi$_2$MoO$_6$ and the carbon layer. It indicates that there is a formation of the metal–O–C bond between carbon and [Bi$_2$O$_2$Mo$_6$]$_2^+$ structure in the 0.5% Ag/C@Bi$_2$MoO$_6$ composite [30]. As indicated in Fig. 4d, the asymmetric peak around 527–532 eV of O 1s could be fitted to four peaks at about 529.9, 528.8, 528.3, and 531.4 eV. The peaks at 529.9 and 528.8 eV correspond to the C=O bond and Mo–O bond in 0.5% Ag/C@Bi$_2$MoO$_6$ composite, respectively. The peaks at 528.3 and 531.4 eV correspond to Mo–O–C bond and the Bi–O–C bond, respectively [17]. The obtained high-resolution spectrum of Ag 3d is shown in Fig. 4e. The peaks at 372.5 and 366.4 eV are related to Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ of Ag in composite, respectively. The interval between the two peaks is 6.1 eV, which confirms that Ag exists in a metal state, but Ag cannot be detected by XRD due to its high dispersion [31]. Generally, the carbon layer can tightly bind to Bi$_2$MoO$_6$ with the formation of C–O–Bi and C–O–Mo bonds on the surface of the composite, and Ag is the major chemical state of Ag nanoparticles.

FTIR analysis is also an important method to reveal the surface structure of photocatalyst materials. Fig. 4f shows the FTIR spectra of Bi$_2$MoO$_6$, C@Bi$_2$MoO$_6$, and 0.5% Ag/C@Bi$_2$MoO$_6$ composites. The bands at 400~900 cm$^{-1}$ are appeared.
Fig. 4. Survey XPS spectrum (a) and high-resolution XPS spectra of the 0.5% Ag/C@Bi₂MoO₆ (BM) composite with Mo 3d (b), C 1s (c), O 1s (d) and Ag 3d (e), and FTIR spectra (f) of pure Bi₂MoO₆, C@BM and 0.5% Ag/C@BM composite.
in the samples, corresponding to the Bi–O, Mo–O stretching, and Mo–O–Mo bridging stretching modes. The bands at 450 and 582 cm\(^{-1}\) are attributed to Bi–O deformation vibration and stretching vibration, respectively. The bands at 722 and 839 cm\(^{-1}\) are assigned to the asymmetric stretching mode of MoO\(_6\) involving vibrations of the equatorial and apical oxygen atoms, respectively. The bands at 797 cm\(^{-1}\) can be attributed to the stretching mode of MoO\(_6\) involving vibrations of the apical oxygen atoms [32]. The band at 1,622 cm\(^{-1}\) is assigned to the vibration mode of C=C, and the peaks can be found in the spectra of C@Bi\(_2\)MoO\(_6\) and 0.5% Ag/C@Bi\(_2\)MoO\(_6\) composites, indicating the existence of a carbon layer on the surface of the composite.

Bi\(_2\)MoO\(_6\) is a visible light excitable photocatalyst, and the absorption edge at about 480 nm, as shown in the UV-Vis DRS curve in Fig. 5a. The visible light absorption intensity of C@Bi\(_2\)MoO\(_6\) and 0.5% Ag/C@Bi\(_2\)MoO\(_6\) composites are enhanced after carbon layer coating and Ag nanoparticles deposition. It reveals that the introductions of both carbon and Ag have significant effects on increasing the visible light absorption and thus narrowing the bandgap [17].

The PL analysis was carried out to explore the migration, transfer, and recombination of photoexcited electrons and holes of the as-prepared samples. The PL emission at about 470 nm is a feature near edge emission, which is more conducive to the recombination of photoexcited electrons and holes [33]. The PL emission intensity of the 0.5% Ag/C@Bi\(_2\)MoO\(_6\) composite, as shown in Fig. 5b, decreases remarkably compared with the pure Bi\(_2\)MoO\(_6\) and C@Bi\(_2\)MoO\(_6\) suggesting that the recombination of photoexcited electrons and holes was blocked with the deposition of Ag nanoparticles. Therefore, the enhanced separation of photoexcited electrons and holes would be favorable for the quantum efficiency of the 0.5% Ag/C@Bi\(_2\)MoO\(_6\) composite, and improve its photocatalytic activity.

### 3.3. Photocatalytic activities and mechanism

The photocatalytic degradation curves of pure Bi\(_2\)MoO\(_6\), C@Bi\(_2\)MoO\(_6\), and Ag/C@Bi\(_2\)MoO\(_6\) composites during 2,4-DBP degradation under visible light irradiation is shown in Fig. 6a. In dark conditions, C@Bi\(_2\)MoO\(_6\) and Ag/C@Bi\(_2\)MoO\(_6\) composites showed similar adsorption properties, suggesting that Ag deposition could hardly improve the textural properties (The BET surface areas of C@Bi\(_2\)MoO\(_6\) and Ag/C@Bi\(_2\)MoO\(_6\) composites are 5.56 m\(^2\)/g [16] and 5.92 m\(^2\)/g, respectively). The 2,4-DBP has little degradation in photolysis under visible-light irradiation, but its concentration has a remarkable decrease with the addition of C@Bi\(_2\)MoO\(_6\) and Ag/C@Bi\(_2\)MoO\(_6\) photocatalysts. Compared with the C@Bi\(_2\)MoO\(_6\), Ag deposition on the surface of the C@Bi\(_2\)MoO\(_6\) photocatalyst can enhance the photocatalytic activity of the composite, and the 2,4-DBP removal rate reaches 87% within 180 min under visible-light irradiation over 0.5% Ag/C@Bi\(_2\)MoO\(_6\) composite, showing a high performance according to previous research [34]. It demonstrates that 0.5% of the Ag deposition amount is the best one and too less or too many Ag deposition would reduce the photocatalytic activity of the Ag/C@Bi\(_2\)MoO\(_6\) composite.

The Br\(^{-}\) concentration in the degradation process was detected at different time intervals, as shown in Fig. 6b. The Br\(^{-}\) concentration in the degradation solution keeps increasing with the visible-light irradiation time over the C@Bi\(_2\)MoO\(_6\) and Ag/C@Bi\(_2\)MoO\(_6\) composites, indicating a continuous debromination during the 2,4-DBP degradation. The debromination rate of 0.5% Ag/C@Bi\(_2\)MoO\(_6\) composite is 2.8 times that of C@Bi\(_2\)MoO\(_6\) without Ag deposition, suggesting that Ag deposition favors the debromination process of 2,4-DBP. Furthermore, the coated carbon layer and deposited Ag nanoparticles are very stable, and it is confirmed by the recycling test as shown in Fig. 6c. After four repeated degradation tests, the 2,4-DBP removal rates have no significant decrease, showing the practical application stability of the Ag/C@Bi\(_2\)MoO\(_6\) composite.

As we know, degradation means any bond breaking in the structures of the compound. According to the results of removal and debromination rates, the 2,4-DBP removal almost synchronizes with the debromination process, suggesting that the debromination process is the major pathway for 2,4-DBP degradation. The photoexcited electrons...
and holes and the following active radicals, such as •OH and •O$_2^-$, would be likely to contribute to the debromination and degradation process of 2,4-DBP [35]. To reveal the roles of photoexcited radicals, scavenger detecting was used in this study and the results are shown in Fig. 6c. The capture of •O$_2^-$ radical has no obvious change on 2,4-DBP removal rates, demonstrating that the •O$_2^-$ is an invalid radical for 2,4-DBP degradation. When we scavenge the holes and the following •OH radicals, the 2,4-DBP removal rates slightly decrease, indicating that the radicals do not play major parts in the photocatalytic process over the 0.5% Ag/C@Bi$_2$MoO$_6$ composite. However, the 2,4-DBP removal rate is remarkably inhibited due to the photoexcited electrons captured. It suggests that the electronic pathway is dominant within 2,4-DBP removal and the photoexcited electrons play very significant roles in the 2,4-DBP debromination process. Bi$_2$MoO$_6$ is a visible-light generated semiconductor and it has a narrow bandgap with the $E_g$ of 2.2 eV. In the previous work, we have measured the positions of the conduction band (CB) and valence band (VB), and they are +1.0 and +3.2 eV, respectively [33,36]. As shown in Fig. 7, the potential of CB is higher than that of O$_2$/•O$_2^-$, thus the •O$_2^-$ radical would not be generated in CB of Bi$_2$MoO$_6$. It is consistent with the scavenger results in Fig. 6d. The photoexcited electrons and holes are separated on the surface of the Ag/C@Bi$_2$MoO$_6$ composite under the visible-light irradiation and the carbon layer could accelerate the electron transmission to the surface of the composite. At the same time, the electric field would be generated by the plasmonic effect of Ag$_0$ atoms and aggregate much more electrons around the Ag$_0$ atoms [37,38]. The photoexcited electrons have a strongly reductive activity.
to break the C–Br bond in 2,4-DBP structure and they act as the major radicals in the 2,4-DBP debromination process. As the following step, the debromination products would be decomposed and mineralized by the *OH radicals generated from the photoexcited holes.

4. Conclusions

The Ag/C@Bi₂MoO₆ composite photocatalyst was prepared by two steps with hydrothermal and ultrasonic deposition methods. The 0.5% Ag/C@Bi₂MoO₆ composite was proved to be more efficient and reliable in 2,4-DBP photocatalytic degradation under visible-light irradiation. The hydrothermal carbon layer provides a rapid transmission route by its excellent conductivity to enhance the separation of photoexcited charges and the Ag nanoparticles could build an electric field to aggregate much more electrons to reduce the contaminant. The degradation of 2,4-DBP is launched with debromination process in the conduction band by aggregating electrons, and the following oxidation process in valence band would completely mineralize 2,4-DBP by holes and *OH radicals. The result provides new insight into halophenols degradation by the photocatalytic process.

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