Acetic Acid Assisted to Prepare Bi_2MoO_6 with Visible-Light-Induced Activity

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Photocatalysis has been extensively studied and developed. To overcome the visible-light irresponsive hindrance, developing novel materials has become a significant promise. Bismuth-based semiconductors were promising candidates with suitable band gaps, and various bismuth-based semiconductors can be prepared via facile methods. Herein, we report a modified hydrothermal method assisted by adding acetic acid in the precursor to prepare Bi_2MoO_6 with enhanced photocatalytic activity in the degradation of RhB under visible light irradiation. This work provides a new approach to improve photocatalytic activity via adding chemicals in the precursors during the preparation.

Keywords hydrothermal, photocatalysis, Bi_2MoO_6 , acetic acid, RhB

Introduction

Photocatalysis, as one of the advanced oxidation processes, has been extensively studied since 1972.^[1] This technology has been applied in various areas, mainly including hydrogen evolution via water splitting and organic pollutants degradation.^[2–9] As a pioneer photocatalysis material, TiO_2 exhibited various superiorities.^[10] However, its drawbacks are also apparent, especially the visible light-irresponsiveness. Approaches to overcome these hindrances primarily include modification of TiO_2 and development of novel visible light-responsive photocatalysts.

Among these visible light-responsive photocatalysts, bismuth based semiconductor exhibits priorities.^[11–26] Bi-based materials with suitable band gaps can be prepared via a facile method, and their morphologies can be adjusted by changing the preparation conditions. Furthermore, the valence band (VB) of a bismuth-based semiconductor consists of not only O 2p orbitals (generally the only orbital in a VB for metal oxides), but also Bi 6s orbitals. The hybrid orbitals of O 2p and Bi 6s are reported to be beneficial by increasing the mobility of photogenerated carriers.^[27] As one of the Bi-based semiconductors, Bi_2MoO_6 has increasingly drawn the attentions of researchers, owing to its excellent intrinsic properties such as its dielectric nature, its catalytic behavior, and its luminescence.^[28] The band gap of Bi_2MoO_6 was reported in the range of 2.5–2.8 eV,^[29,30] indicating that Bi_2MoO_6 is capable of visible light-driven photocatalytic activity.

Generally, Bi_2MoO_6 was prepared by hydrothermal and solvothermal methods. In this work, we report a new method to prepare Bi_2MoO_6 via a hydrothermal method assisted with acetic acid. It exhibited excellent photocatalytic activity in decomposition of RhB. The preparation conditions including hydrothermal temperature and treatment duration were optimized.

Experimental

Preparation of Bi_2MoO_6

Bi_2MoO_6 was prepared via an acetic acid assisted hydrothermal method. Typically, 1 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in 5 mL acetic acid, and 0.5 mmol of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 30 mL deionized distilled water (DDW). Then, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ solution

was dropwise added into the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution. After stirring for 30 min, the mixture was transferred into a 50 mL autoclave, heated and maintained for designate time. After the autoclave was naturally cooled down to room temperature, the precipitates were filtered out and washed with DDW and ethanol. The precipitates were dried at 60 °C overnight before being collected for further use. The hydrothermal temperatures of 60, 90, 120, 150, 180 and 210 °C and durations of 6, 12, 18, 24, 36, 48 h were selected to optimize the preparation condition. For comparison, Bi_2MoO_6 was also prepared without adding acetic acid.

Characterization

A scanning electron microscopy (FE-SEM, JEOL JSM-7500F) was used to investigate the morphology of prepared samples. Crystal structures were studied by X-ray diffraction (XRD) on a Rigaku Ultima IV Diffractometer with Cu K α radiation ($\lambda=0.15418$ nm) at 40 kV and 44 mA. XRD patterns were recorded at 2θ of 5°–80°. The Fourier Transform Infrared Spectrometer (FTIR) was used via a Cary 630 (Agilent Technologies). Ultraviolet-visible diffuse reflectance spectra (DRS) was observed with a Thermo Evolution 300 spectrophotometer.

Photocatalytic activity testing

Photocatalytic activity of prepared samples was tested through degradation of RhB under visible light irradiation. Specifically, a 500-mL beaker served as the reactor, and the temperature was maintained at 20 °C using a water bath. The visible light irradiation was a 300-W halogen tungsten projector lamp Ushio, wavelength mainly in the range of 310–800 nm) with a UV cut-off (Kenko Zeta, transmittance > 90%) to filter out irradiation with a wavelength below 410 nm. The irradiation intensity on the surface of the solution was measured using a quantum meter (Biospherical QSL-2100, 400 nm < λ < 700 nm) being equal to 1.1×10^{-2} Einsteins $\text{m}^{-2} \cdot \text{s}^{-1}$. In each test, 100 mL of 10 mg/L RhB solution was added to the reactor. The quantity of catalyst that was subsequently added was 1 g/L of reactor solution (0.10 g in 100 mL of solution). The suspensions were magnetically stirred for 30 min before turning on the lamp, in order to obtain an adsorption-desorption equilibrium between RhB and the catalyst. The photocatalytic test was carried out for 60 min, and aliquots were drawn every 10 min, each of which were centrifuged at a rate of

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13,000 rpm for 5 min. The supernatant was then separated and analyzed using a spectrometer at the wavelength of 554 nm. Photocatalytic degradation of phenol with initial concentration of 10 mg/L was also measured. The concentration of phenol was analyzed using a high-performance liquid chromatograph (HPLC, Agilent 1100 series) equipped with a UV-Vis detector. A ZORBAX Eclipse Plus C18 column (4.6×250 mm) was used at a temperature of 60 °C. The detecting wavelength was fixed at 270 nm for the detection of phenol and possible intermediates. The flow phase was composed of methanol (55%, *V/V*) and water (45%, *V/V*) at a flow rate of 0.6 mL/min. The injection volume was set to 25 μ L.

Electronic structure calculation

The quantum-mechanical calculations were performed on the basis of the density functional theory (DFT).^[31] The generalized gradient approximation (GGA) was applied to exchange-correlation effects. The open access software Quantum ESPRESSO was used, which utilizes pseudopotentials to describe electron-ion interactions and to represent electronic wave functions using a plane-wave basis set.^[32] The kinetic energy cut-off was set to 300 eV.

Results and Discussion

Morphology

Morphologies of prepared Bi_2MoO_6 were investigated using SEM as shown in Figure 1. It can be observed plate-like morphology was prepared. With increase of the hydrothermal treatment duration, the size of plate became slightly larger and thicker. It should be noted the thicker the plate is, the longer lifetime required for the separated charge carriers. It means the plate with thicker size may be with lower photocatalytic activity.

Figure 1 SEM images of Bi_2MoO_6 prepared at 120 °C for (a) 6 h, (b) 12 h, (c) 24 h and (d) 48 h.

XRD analysis

Crystal structures of Bi_2MoO_6 samples prepared at different temperature for 24 h and at 120 °C for different duration time were investigated by XRD. As shown in Figure 2, only when hydrothermal temperature increased above or equal to 120 °C, Bi_2MoO_6 with orthorhombic crystal structure [space group: *pbca* (61), PDF card number 72-1524^[33]] can be observed. Meanwhile, with hydrothermal temperature improvement, impurity peaks were increasingly diminished, especially peaks at $2\theta=33.1^\circ$ and 47.2° which are in cor-

respondence with plane (060) and (062), respectively. Specifically, the increase of relative intensity of these peaks with increase of hydrothermal temperature from 120 °C to 210 °C, indicated that the crystal tends to grow in the directions of corresponding planes, mainly including plane (060) and (062) (Figure 4). It is beneficial to form thin nano-plates. As for the effect of hydrothermal duration on the crystal structures of Bi_2MoO_6 , XRD patterns of samples prepared at 120 °C for different time ranging from 6 h to 48 h were performed and shown in Figure 3. Compared to precipitation directly separated out before hydrothermal treatment, Bi_2MoO_6 samples exhibit high crystallinity with sharp and narrow characteristic peaks. It should be noticed that with extension of hydrothermal time, impurity peaks were gradually diminished and completely disappeared for samples hydrothermally treated longer than 18 h. Specifically, improvement of hydrothermal treatment duration is also in favor of orientated growth of the crystal, and forming nano-plates.

Figure 2 XRD patterns of Bi_2MoO_6 synthesized under different hydrothermal temperature for 24 h.

Figure 3 XRD patterns of Bi_2MoO_6 synthesized at 120 °C for different duration.

Figure 4 Proposed crystal growth in the directions of plane (060) and (062).

FT-IR

Figure 5 shows FT-IR spectra of Bi_2MoO_6 samples prepared by hydrothermal method with different experimental conditions. The regions of wavelength number ranging from 600 cm^{-1} to 1000 cm^{-1} , are possibly attributed to Bi–O, Mo–O stretching and Mo–O–Mo bridging stretching modes, which can respond to the variation of crystal structure of Bi_2MoO_6 .^[29,34] Specifically, the band at 690 cm^{-1} resulted from the asymmetric stretching mode of MoO_6 involving vibrations of the equatorial oxygen atoms.^[35,36] The absorption peak at around 795 cm^{-1} and 841 cm^{-1} can be attributed to the asymmetric and symmetric stretching mode of MoO_6 involving vibrations of the apical oxygen atoms separately. The absorption bands at 937 cm^{-1} together with a small peak at 902 cm^{-1} may be due to Mo–O stretching modes. Small peaks at the wavelength number range of $1300\text{--}1600\text{ cm}^{-1}$ may result from the adsorbed CH_3COOH , specifically, the δ CH vibrations of the $\text{CH}_3\text{C=O}$ moiety and coupled ν C–O and δ OH vibrations.^[37,38] In Figures 5a and 5b, a minor peak shift of wavelength number at 690 cm^{-1} is observed, indicating the structure variation for MoO_6 octahedra occurred with increase of temperature and duration time. When the hydrothermal temperature improved to $210\text{ }^\circ\text{C}$, peaks at 937 cm^{-1} and 902 cm^{-1} disappeared, further confirming the changes of Bi_2MoO_6 crystal structure. Based on above analysis, it can be concluded that crystal structure of Bi_2MoO_6 samples may be influenced by changing hydrothermal temperature and duration time.

Figure 5 FT-IR spectra of Bi_2MoO_6 samples prepared (a) at different temperature for 24 h and (b) at $120\text{ }^\circ\text{C}$ for different hydrothermal duration time.

Optical properties

The electrical band structure of the relaxed Bi_2MoO_6 is illustrated in Figure 6. The energy zero was set at the top of valence band. The bandgap width (E_g) can be calculated as around 1.910 eV . Moreover,

the valence-band and conduction-band width (W_{vb} and W_{cb}) are 6.65 eV and 2.20 eV , respectively. The band edges are situated at the X point for Bi_2MoO_6 , indicating the direct bandgap feature. The total and partial density of states (TDOS and PDOS) of Bi_2MoO_6 is given in Figure 7, with setting energy zero at top of valence band. O 2p and Bi 6s states contribute to the valence band. Meanwhile, Bi 6p, Mo 4d and O 2p state account for the conduction band. As reported, the well-dispersed Bi 6s orbital facilitates the mobility of photo-generated carriers and narrow the bandgap.^[13,27]

Figure 6 Band structure of Bi_2MoO_6 (The red dash line represents the Fermi level).

Figure 7 Total and partial DOS of relaxed Bi_2MoO_6 .

Diffused reflectance spectrometer (DRS) is performed to detect the optical properties of Bi_2MoO_6 samples which were prepared at $120\text{ }^\circ\text{C}$ for 24 h (Figure 8). The photoabsorption occur in the region of UV light and visible-light with wavelength lower than about 490 nm . The steep decrease in the spectrum attributes to the bandgap transition. The UV-Vis photoabsorption property was also simulated and shown in Figure 8. It suggests that much more visible light could be used to activate the photocatalysis. As for the experimental bandgap value, it can be calculated using classical Tauc equation (Equation 1):

$$\alpha E_{\text{photon}} = K(E_{\text{photon}} - E_g)^{\frac{n}{2}} \quad (1)$$

where α , h , ν and K are the absorption coefficient, the Planck constant, the irradiation frequency, and the constant for semiconductors (usually equal to 1), respectively. Constant n depends on the bandgap feature. It is suggested in the electrical structure that Bi_2MoO_6 attributes to direct-transition band gap, so $n=4$. Inset in Figure 8 is plot of $(\alpha E_{\text{photon}})^{1/2}$ vs. E_{photon} . The intercept at the horizontal axis of the tangent line is rightly the bandgap value, which is about 2.5 eV .

The difference between the theoretical and experimental bandgap value is 0.59 eV, which is due to the well-known limitation of GGA. A similar result was also reported.^[39] Although calculated bandgap value could underdetermine the real value, it is still reliable and reasonable to qualitatively analyze the characteristics of the band structure.

Figure 8 DRS of as-prepared Bi₂MoO₆ (red line) with corresponding $(\alpha E_{\text{photon}})^{1/2}$ vs. E_{photon} curves shown in inset, and simulated UV-Vis absorption properties of relaxed Bi₂MoO₆ (blue dash line).

Photocatalytic activity test

Photocatalytic activity of prepared Bi₂MoO₆ under different conditions was investigated through degradation of RhB under visible light irradiation. As shown in Figure 9, Bi₂MoO₆ prepared at 60 and 90 °C, exhibited negligible activity in the degradation of RhB over 60 min. With increase of the treatment temperature, the photocatalytic activity was greatly improved. At 120 °C of the thermal treatment temperature, RhB was completely removed over 60 min. With further increase of the temperature, the activity in the removal of RhB was deteriorated. Similarly, the treatment duration was another significant factor as shown in Figure 10. When the hydrothermal treatment lasted for 24 h, the prepared sample exhibited the best activity in the removal of RhB under visible light irradiation. This phenomenon indicates the optimum hydrothermal treatment temperature and duration existed to prepare a Bi₂MoO₆ sample with excellent photocatalytic

Figure 9 Photocatalytic degradation RhB in the presences of Bi₂MoO₆ prepared at different temperature for 24 h under visible light irradiation.

Figure 10 Photocatalytic degradation RhB in the presences of Bi₂MoO₆ prepared at 120 °C for different time under visible light irradiation.

activity in the degradation of RhB under visible light irradiation.

To explore the effect of acetic acid, the photocatalytic activity of Bi₂MoO₆ samples prepared with and without acetic acid added in the precursor was measured and shown in Figure 11. It can be found the photocatalytic activity of Bi₂MoO₆ assisted by acetic exhibited higher activity in the degradation of RhB. Compared to reported work, the photocatalytic activity of Bi₂MoO₆ prepared in this work is higher than that prepared by solvothermal method^[28] and hydrothermal method.^[40] It confirms acetic acid assisted preparation of Bi₂MoO₆ enhance its photocatalytic activity of degradation of RhB. To further explore the activity of as-prepared Bi₂MoO₆, photocatalytic degradation of a colorless organic, phenol was also measured, and the results were illustrated in inset of Figure 11. It can be found about 10% of phenol were removed over 5 h under visible light irradiation. It further confirms the photocatalytic activity of as-prepared Bi₂MoO₆.

Figure 11 Photocatalytic degradation of RhB in the presence of Bi₂MoO₆ samples prepared with and without acetic acid in the precursor (inset: photocatalytic degradation of phenol in the presence of Bi₂MoO₆ prepared assisted with acetic acid).

Conclusions

Bi_2MoO_6 was successfully prepared using a hydrothermal method assisted by acetic acid. The preparation conditions, including hydrothermal temperature and treatment duration were optimized. It was found when the temperature of 120 °C and the duration of 24 h, prepared Bi_2MoO_6 exhibited the highest activity in the degradation of RhB under visible light irradiation. This work provides a new approach to the improvement of photocatalytic activity via adding chemicals in the precursors during the preparation.

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