Acetic Acid Assisted to Prepare Bi$_2$MoO$_6$ with Visible-Light-Induced Activity

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Photocatalysis has been extensively studied and developed. To overcome the visible-light irresponsible 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$_2$MoO$_6$ 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$_2$MoO$_6$, 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.[2-6] As a pioneer photocatalysis material, TiO$_2$ exhibited various superiorities.[7] 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.[11-15] 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 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 mobilization of photogenerated carriers.[27] As one of the Bi-based semiconductors, Bi$_2$MoO$_6$ 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$_2$MoO$_6$ was reported in the range of 2.5–2.8 eV,[29,30] indicating that Bi$_2$MoO$_6$ is capable of visible light-driven photocatalytic activity.

Generally, Bi$_2$MoO$_6$ was prepared by hydrothermal and solvo-thermal methods. In this work, we report a new method to prepare Bi$_2$MoO$_6$ 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$_2$MoO$_6$

Bi$_2$MoO$_6$ was prepared via an acetic acid assisted hydrothermal method. Typically, 1 mmol of Bi(NO$_3$)$_3$·5H$_2$O were dissolved in 5 mL acetic acid, and 0.5 mmol of Na$_2$MoO$_4$·2H$_2$O were dissolved in 30 mL deionized distilled water (DDW). Then, Na$_2$MoO$_4$·2H$_2$O solution was dropwise added into the Bi(NO$_3$)$_3$·5H$_2$O solution. After stirring for 30 min, the mixture was transferred into a 50 mL autoclave, heated and maintained for desorption. After the autoclave was naturally cooled down to room temperature, the precipitates were collected and washed with DDW and ethanol. The precipitates were dried at 60 °C overnight before being collected for further use. The photocatalytic activity of prepared samples was tested through 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.

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 Kα radiation (λ=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-nL 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 (Biophotonic QSL-2100, 400 nm < λ < 700 nm) being equal to 1.1×10$^{-7}$ Einsteins m$^{-2}$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 withdrawn every 10 min, each of which were centrifuged at a rate of
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 μL.

Electronic structure calculation

The quantum-mechanical calculations were performed on the basis of the density functional theory (DFT).\textsuperscript{[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.\textsuperscript{[32]} The kinetic energy cut-off was set to 300 eV.

Results and Discussion

Morphology

Morphologies of prepared Bi$_2$MoO$_6$ 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](image1)

**Figure 1** SEM images of Bi$_2$MoO$_6$ prepared at 120 °C for (a) 6 h, (b) 12 h, (c) 24 h and (d) 48 h.

XRD analysis

Crystal structures of Bi$_2$MoO$_6$ 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$_2$MoO$_6$ with orthorhombic crystal structure [space group: pbcn (61), PDF card number 72-1524\textsuperscript{[33]}.\textsuperscript{[35]}] can be observed. Meanwhile, with hydrothermal temperature improvement, impurity peaks were increasingly diminished. Relative intensity of characteristic peaks is also orderly changed, especially peaks at $2\theta$=33.1° and 47.2° which are in correspondence 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. For the effect of hydrothermal duration on the crystal structures of Bi$_2$MoO$_6$, 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$_2$MoO$_6$ 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](image2)

**Figure 2** XRD patterns of Bi$_2$MoO$_6$ synthesized under different hydrothermal temperature for 24 h.

![Figure 3](image3)

**Figure 3** XRD patterns of Bi$_2$MoO$_6$ synthesized at 120 °C for different duration.

![Figure 4](image4)

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

Figure 5 shows FT-IR spectra of Bi$_2$MoO$_6$ 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$_2$MoO$_6$. Specifically, the band at 690 cm$^{-1}$ resulted from the asymmetric stretching mode of MoO$_6$ involving vibrations of the equatorial oxygen atoms. 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 1300–1600 cm$^{-1}$ may result from the adsorbed CH$_3$COOH, specifically, the δ CH vibrations of the CH$_3$C=O moiety and coupled ν C–O and δ OH vibrations. 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 °C, peaks at 937 cm$^{-1}$ and 902 cm$^{-1}$ disappeared, further confirming the changes of Bi$_2$MoO$_6$ crystal structure. Based on above analysis, it can be concluded that crystal structure of Bi$_2$MoO$_6$ samples may be influenced by changing hydrothermal temperature and duration time.

Optical properties

The electrical band structure of the relaxed Bi$_2$MoO$_6$ 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$_2$MoO$_6$, indicating the direct bandgap feature. The total and partial density of states (TDOS and PDOS) of Bi$_2$MoO$_6$ 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.  

Diffused reflectance spectrometer (DRS) is performed to detect the optical properties of Bi$_2$MoO$_6$ samples which were prepared at 120 °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):

$$\alpha E_{\text{photon}} = K \left( E_{\text{photon}} - E_g \right)^n$$

where $\alpha$, $K$, $h$, $\nu$ and $n$ 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$_2$MoO$_6$ attributes to direct-transition band gap, so $n=4$. Inset in Figure 8 is plot of $(\alpha E_{\text{photon}})^{1/2}$ vs. $E_{\text{photon}}$. 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.\cite{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.

**Photocatalytic activity test**

Photocatalytic activity of prepared Bi$_2$MoO$_6$ under different conditions was investigated through degradation of RhB under visible light irradiation. As shown in Figure 9, Bi$_2$MoO$_6$ 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 Bi$_2$MoO$_6$ sample with excellent photocatalytic activity in the degradation of RhB under visible light irradiation.

To explore the effect of acetic acid, the photocatalytic activity of Bi$_2$MoO$_6$ 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 Bi$_2$MoO$_6$ assisted by acetic exhibited higher activity in the degradation of RhB. Compared to reported work, the photocatalytic activity of Bi$_2$MoO$_6$ prepared in this work is higher than that prepared by solvothermal method\cite{28} and hydrothermal method.\cite{40} It confirms acetic acid assisted preparation of Bi$_2$MoO$_6$ enhance its photocatalytic activity of degradation of RhB. To further explore the activity of as-prepared Bi$_2$MoO$_6$, 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 Bi$_2$MoO$_6$.
Conclusions

Bi$_2$MoO$_6$ 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$_2$MoO$_6$ 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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References

[1] Fujishima, A.; Honda, K. Nature 1972, 238, 37.
[2] Fox, M. A.; Dulay, M. T. Chem. Rev. 1993, 93, 341.
[3] Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Chem. Rev. 1995, 95, 69.
[4] Kaneko, M.; Okura, I. Kodansha Springer 2002.
[5] Kobasa, I. M.; Tarasenko, G P. Theor. Exp. Chem. 2002, 38, 255.
[6] Robert, D.; Malato, S. Sci. Total Environ. 2002, 291, 85.
[7] Zhang, K.; Wang, L.; Kim, J. K.; Ma, M.; Veerappan, G; Lee, C.-L.; Kong, K.-j.; Lee, H.; Park, J. H. Energ. Environ. Sci. 2016, 9, 499.
[8] Zhang, K.; Heo, N.; Shi, X.; Park, J. H. J. Phys. Chem. C 2013, 117, 24023.
[9] Huang, Y.; Long, B.; Tang, M.; Rui, Z.; Balogun, M.-S.; Tong, Y.; Ji, H. Appl. Catal. B: Environ. 2016, 181, 779.
[10] Fujishima, A.; Rao, T. N.; Tryk, D. A. J. Photochem. Photobiol. C: Photochem. Rev. 2000, 1, 1.
[11] Meng, X.; Jiang, L.; Wang, W.; Zhang, Z. Int. J. Photoenergy 2015, 2015, 9.
[12] Meng, X.; Zhang, Z. Int. J. Photoenergy 2015, 2015, 12.
[13] Meng, X.; Zhang, Z. J. Photochem. Photobiol. A: Chem. 2015, 310, 33.
[14] Ahmad, A.; Meng, X.; Yun, N.; Zhang, Z. J. Nanomater. 2016, 2016, 10.
[15] Hu, X.; Meng, X.; Zhang, Z. Int. J. Photoenergy 2016, 2016, 8.
[16] Meng, X.; Zhang, Z. Int. J. Photoenergy 2016, 2016, 11.
[17] Meng, X.; Zhang, Z. J. Mol. Catal. A: Chem. 2016, 423, 533.
[18] Meng, X.; Zhang, Z. Appl. Surf. Sci. 2016, 392, 169.
[19] Meng, X.; Zhang, Z. J. Catal. 2016, 344, 616.
[20] Meng, X.; Li, Z.; Zeng, H.; Chen, J.; Zhang, Z. Appl. Catal. B: Environ. 2017, 210, 160.
[21] Meng, X.; Zhang, Z. Mater. Lett. 2017, 189, 267.
[22] Meng, X.; Zhang, Z. Appl. Catal. B: Environ. 2017, 209, 383.
[23] Huang, Y.; Li, H.; Balogun, M.-S.; Liu, W.; Tong, Y.; Lu, X.; Ji, H. ACS Appl. Mater. Inter. 2014, 6, 22920.
[24] Huang, Y.; Li, H.; Fan, W.; Zhao, F.; Qiu, W.; Ji, H.; Tong, Y. ACS Appl. Mater. Inter. 2016, 8, 27859.
[25] Huang, Y.; Fan, W.; Long, B.; Li, H.; Zhao, F.; Liu, Z.; Tong, Y.; Ji, H. Appl. Catal. B: Environ. 2016, 165, 68.
[26] Huang, Y.; Hu, H.; Wang, S.; Balogun, M.-S.; Ji, H.; Tong, Y. Appl. Catal. B: Environ. 2017, 218, 700.
[27] An, H.; Du, Y.; Wang, T.; Wang, C.; Hao, W.; Zhang. J. Rare Metals 2008, 27, 243.
[28] Tian, G.; Chen, Y.; Zhou, W.; Pan, K.; Dong, Y.; Tian, C.; Fu, H. J. Mater. Chem. 2011, 21, 887.
[29] Zhang, L.; Xu, T.; Zhao, X.; Zhu, Y. Appl. Catal. B: Environ. 2010, 98, 138.
[30] Bi, J.; Wu, L.; Li, J.; Li, Z.; Wang, X.; Fu, X. Acta Mater. 2007, 55, 4699.
[31] Kohn, W.; Sham, L. J. Phys. Rev. 1965, 140, A1133.
[32] Paolo, G.; Stefano, B.; Nicola, B.; Matteo, C.; Roberto, C.; Carlo, C.; Davide, C.; Guido, L. C.; Matteo, C.; Ismaila, D.; Andrea Dal, C.; Stefano de G; Stefano, F.; Guido, F.; Ralph, G.; Uwe, G; Christos, G; Anton, K.; Michele, L.; Layla, M.-S.; Nicola, M.; Francesco, M.; Riccardo, M.; Stefano, P.; Alfredo, P.; Lorenzo, P.; Carlo, S.; Sandro, S.; Gabriele, S.; Ari, P. S.; Alexander, S.; Paolo, U.; Renata, M. J. Phys.: Condens. Mat. 2009, 21, 395502.
[33] Pertlik, F.; Zemann, J. Fortschr. Miner Beil 1982, 60, 162.
[34] Li, H.; Liu, C.; Li, K.; Wang, H. J. Mater. Sci. 2008, 43, 7026.
[35] Carrazañ, S. R. G.; Martin, C.; Rives, V.; Vidal, R. Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 1996, 52, 1107.
[36] Trifirò, F.; Hoser, H.; Scharle, R. D. J. Catal. 1972, 25, 12.
[37] Hasan, M. A.; Zaki, M. I.; Pasupulety, L. Appl. Catal. A: Gen. 2003, 243, 81.
[38] Liao, L.-F.; Lien, C.-F.; Lin, J.-L. Phys. Chem. Chem. Phys. 2001, 3, 3831.
[39] Lai, K.; Wei, W.; Dai, Y.; Zhang, R.; Huang, B. Rare Metals 2011, 30, 166.
[40] Li, H.; Li, K.; Wang, H. Mater. Chem. Phys. 2009, 116, 134.