Controllable Growth of Bi$_2$MoO$_6$ Nanoplates by Citric Acid Assisted Hydrothermal Process and Their Photocatalytic Properties

WANG Yi$^{1,\,*}$

$^1$Tianjin Medical College, Tianjin 300222, P.R.China, $^\ast$wangyii_2013@163.com

Abstract. Bi$_2$MoO$_6$ nanoplates with different sizes have been controllably fabricated by citric acid (CA) assisted hydrothermal process. The effects of CA on the morphology of Bi$_2$MoO$_6$ nanoplates have also been investigated. It is found that CA has a critical role in the crystallinity and size of Bi$_2$MoO$_6$ nanoplates. On the basis of XRD analysis and SEM observation of the products, the mechanism for CA assisted hydrothermal synthesis of the Bi$_2$MoO$_6$ nanoplates is discussed. The photocatalytic activity of as-prepared Bi$_2$MoO$_6$ was evaluated by the degradation of RhB dye in water, and the sample prepared when the amount of CA was 2.5mmol exhibited the highest photocatalytic activity.

Keywords: Bi$_2$MoO$_6$; hydrothermal process; citric acid

1 Introduction

Considerable research during the past few years has shown that photocatalytic decomposition of organic pollutants using semiconductors is a potential way of solving environmental issues. In the past few years, TiO$_2$ has been used extensively as photocatalyst for degradation of dyes in wastewater due to its high photocatalytic activity, low cost and nontoxicity. However, TiO$_2$ responds only to the ultraviolet light ($\lambda < 400$ nm) that accounts for only about 4% of the sunlight due to its wide band gap (3.2 eV). This limits the efficient utilization of solar energy for TiO$_2$ photocatalysis. Therefore, considerable effort has been made to design novel materials with narrow band gap.

Bi$_2$MoO$_6$ is one of the simplest members of the Aurivillius oxide family of layered perovskites with the general formula Bi$_2$A$_{n-1}$B$_n$O$_{3n+3}$ (A= Ca, Sr, Ba, Pb, Na, K; B=Ti, Nb, Ta, Mo, W, Fe; and n = number of perovskite-like layers (A$_{n-1}$B$_n$O$_{3n+1}$)$^{\times}$), which are structurally composed of perovskite layers (A$_{n-1}$B$_n$O$_{3n+1}$) between bismuth oxide layers (Bi$_2$O$_2$)$^{1,2}$, Dielectric$^3$, ion conductive$^4$, and catalytic properties$^5$ of this material have attracted attention. Recently, it has also been reported that Bi$_2$MoO$_6$ is a good photocatalyst for water splitting and photodegradation of organic compounds under visible light irradiation$^7$. It is well-known that the photocatalytic activity closely relates with the particle size, surface areas, the efficiency of electron-hole separation, etc., of the photocatalysts. Thus, the synthesis of Bi$_2$MoO$_6$ photocatalysts with controlled microstructure is a subject of considerable research interest.

In this paper, we report the controllable growth of Bi$_2$MoO$_6$ nanostructures by citric acid (CA) assisted hydrothermal process. The photodegradation of Rhodamine B (RhB) was
employed to evaluate the photocatalytic activities of Bi$_2$MoO$_6$. Moreover, the mechanism for the CA assisted hydrothermal synthesis of Bi$_2$MoO$_6$ nanostructures has been discussed.

2 Experimental and Methods

2.1 Synthesis of the Samples

In a typical synthesis, 5.0 mmol of Bi(NO$_3$)$_3$ · 5H$_2$O was dissolved in 15 mL of diluted HNO$_3$ solution, then the weighed amount of citric acid was added to this solution, the amount of CA were 1.0, 2.5, 4.0, 5.0 mmol for samples S1, S2, S3 and S4. Meanwhile, 2.5 mmol Na$_2$MoO$_4$·2H$_2$O was dissolved in 15 mL deionized water. The two solutions were mixed under vigorous stirring and the pH was adjusted to 7.0 by NaOH solution (2M). This precursor solution was poured into a 60 mL Teflon-lined stainless steel autoclave, and then heated at 180°C for 24 h. After the autoclave was cooled to room temperature, the precipitate was separated by centrifugation, washed several times with deionized water and ethanol, and dried in an oven at 80°C for 12 h.

2.2 Characterization

The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2500 diffractometer with Cu-K$_\alpha$ radiation at a scanning speed of 8°/min ranging from 20 to 60°. The scanning electron microscope (SEM) characterizations were performed on a Nanosem 430 field emission scanning electron microscope. The UV-vis absorption spectra were measured on Shimadzu UV-2550 spectrophotometer using BaSO$_4$ as a reference in wavelength of 200–800 nm.

2.3 Photocatalytic Test

Photocatalytic activity of the obtained Bi$_2$MoO$_6$ samples was investigated by photocatalytic degradation of rhodamine B (RhB) under a 300 W tungsten halogen lamp (Philips Q/YXKC33). 0.1 g of the prepared photocatalyst was added to 100 mL aqueous solution of 1×10$^{-5}$ mol/L RhB. Before illumination, the suspensions were magnetically stirred in the dark for 60 min to ensure the establishment of an adsorption-desorption equilibrium between the photocatalysts and RhB. At given time intervals, 3 mL aliquots were sampled and centrifuged to remove photocatalyst powders. The concentration of centrifugated solution was determined by measuring the absorbance value at approximately 553 nm.
3 Results and Discussion

Fig. 1 XRD patterns of the as-prepared Bi$_2$MoO$_6$ samples

Fig. 1 shows the XRD patterns of the as-prepared Bi$_2$MoO$_6$ samples. All the diffraction peaks can be indexed to Bi$_2$MoO$_6$ (JCPDS No. 21-0102), but with a small impurity that was identified as Mo$_9$O$_{26}$ (JCPDS Card No. 65-1292). It is also found that the intensity of diffraction peaks decreases when the amount of CA exceeds 2.5mmol, indicating crystallinity becomes worse. The average crystallite sizes of the samples were calculated to be 61.7, 50.4, 33.8, 30.3nm for sample S1, S2, S3 and S4, respectively.

Fig. 2 SEM images of Bi$_2$MoO$_6$ samples prepared by hydrothermal method with different amount of citric acid. (a)1.0mmol(b) 2.5mmol(c) 4.0mmol(d) 5.0mmol

Fig. 2 shows SEM images of Bi$_2$MoO$_6$ samples prepared by hydrothermal method with different amount of citric acid. As can be seen, all the products are composed of nanoplates and the dosage of citric acid has a significant impact on the size of the as-synthesized products. The average size of nanoplate decrease with increasing the amount of citric acid. While the amount of citric acid was increased from 1.0mmol to 2.5mmol, the size of Bi$_2$MoO$_6$ nanoplates become smaller and more uniform. When the the amount of citric acid was 4.0mmol, the size of Bi$_2$MoO$_6$ nanoplates futher decrease and aggregate slightly. When the amount of citric acid was further increased to 5.0mmol, nanoplates aggregate compactly together. Based on XRD and SEM results, we suggested that the optimum dosage of citric
acid was 2.5 mmol.

It is well known that citric acid can be used as a complexing agent and can form strong complexes with metal ions through a coordination interaction\textsuperscript{10}. It can also adsorb strongly on metal and mineral surfaces, significantly alter their surface properties and mineral growth behavior. In our experiment, the free Bi\textsuperscript{3+} ion concentration would decrease in solution because Bi\textsuperscript{3+} ions with citrate groups can form complexes, the free Bi\textsuperscript{3+} ion concentration have a great impact on the nucleation and growth rate of Bi\textsubscript{2}MoO\textsubscript{6}, thus, the nucleation and growth rate of Bi\textsubscript{2}MoO\textsubscript{6} can be controlled through changing the amount of citric acid. As the temperature increased during the hydrothermal reaction, the chelation of the Bi\textsuperscript{3+}-citrate complex would be weakened and Bi\textsuperscript{3+} would be released gradually. Therefore, the nucleation and growth of Bi\textsubscript{2}MoO\textsubscript{6} will go through a longer process, which is helpful to form uniform crystals.

On the basis of the experimental results and observations, the possible reactions carried out are proposed as follows:

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\begin{align*}
\text{Bi}(\text{NO}_3)_3 & \leftrightarrow \text{Bi}^{3+} + 3\text{NO}_3^- \\
\text{Na}_2\text{MoO}_4 & \leftrightarrow 2\text{Na}^+ + \text{MoO}_4^{2-} \\
\text{Bi}^{3+} + C_6\text{H}_5\text{O}_7^{3-} & \leftrightarrow C_6\text{H}_5\text{O}_7\text{Bi} \\
C_6\text{H}_5\text{O}_7\text{Bi} & \leftrightarrow \text{Bi}^{3+} + C_6\text{H}_5\text{O}_7^{3-} \\
2\text{Bi}^{3+} + \text{MoO}_4^{2-} + 2\text{H}_2\text{O} & \rightarrow \text{Bi}_2\text{MoO}_6 + 4\text{H}^+ 
\end{align*}
\]

As shown in Formula a, when Bi(NO\textsubscript{3})\textsubscript{3} \cdot 5\text{H}_2\text{O} was added into diluted HNO\textsubscript{3} solution, Bi\textsuperscript{3+} will be produced and MoO\textsubscript{4}\textsuperscript{2-} will be produced when Na\textsubscript{2}MoO\textsubscript{4} dissolves in water (Formula b). After the dissolution of CA, Bi\textsuperscript{3+} was transformed into a C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}Bi as a result of the strong coordination action of Bi\textsuperscript{3+} with citric anions, as shown in formula c. When these two solutions are mixed, a white precipitate of Bi\textsubscript{2}MoO\textsubscript{6} will be immediately produced. The mixture became more and more clear with increasing the amount of CA. When the amount of CA was increased to 5.0 mmol (Bi/CA = 1:1), the mixture became transparent, that is because Bi\textsuperscript{3+} will not directly react with MoO\textsubscript{4}\textsuperscript{2-} to produce the precipitate Bi\textsubscript{2}MoO\textsubscript{6} due to the coordination of Bi\textsuperscript{3+} with citric anions. Under hydrothermal conditions, as the temperature increased, the C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}Bi would gradually decompose and slowly release Bi\textsuperscript{3+}, followed by the reaction with MoO\textsubscript{4}\textsuperscript{2-}, as shown in formulas (d) and (e). Thus, the nucleation and growth process of Bi\textsubscript{2}MoO\textsubscript{6} is tuned during the hydrothermal process. As a result, Bi\textsubscript{2}MoO\textsubscript{6} with smaller size is obtained.
Fig. 3 shows FT-IR spectra of as-synthesized Bi$_2$MoO$_6$ products. The bands at around 843 and 796 cm$^{-1}$ can be assigned as the asymmetric and symmetric stretching mode of MoO$_6$ involving vibrations of the apical oxygen atoms, respectively. The band at 728 cm$^{-1}$ is attributed to the asymmetric stretching mode of MoO$_6$ involving vibrations of the equatorial oxygen atoms$^{11}$. The bands in the 600–400 cm$^{-1}$ range are assigned to Bi-O stretching vibration and deformation vibration.

Optical absorption of the Bi$_2$MoO$_6$ nanoplates was measured by using an UV–vis spectrometer. The UV-vis diffuse reflectance spectra of the as-synthesized Bi$_2$MoO$_6$ samples is shown in Fig. 4. The band gap absorption edge of all these samples is estimated to be about 483 nm, corresponding to a band gap energy of about 2.57 eV. The steep shape of the spectra indicates that the light absorption is not due to the transition from the impurity level but is due to the band-gap transition$^{12,13}$. The band structure of Bi$_2$MoO$_6$
is suggested to be composed of Mo 4d orbitals with Bi 6p orbitals for the conduction band and O 2p orbitals for the valence band. The main orbitals comprising the conduction band are Mo 4d orbitals rather than Bi 6p orbitals. It is revealed that the visible-light absorption of Bi₂MoO₆ was due to the transition from the valence band consisting of the O 2p orbitals to the conduction band derived from the primary Mo 4d orbitals in MoO₆ octahedra and the secondary Bi 6p orbitals.

![Fig.5](image)

**Fig.5** The photodegradation of RhB dye as a function of irradiation time

Fig.5 showed the efficiencies of the photocatalytic degradation in the presence of Bi₂MoO₆ samples, C was the absorption of RhB at the wavelength of 553nm and C₀ was the absorption after the adsorption equilibrium on Bi₂MoO₆ before irradiation. Blank test (RhB without any catalyst) under tungsten halogen lamp exhibited little photolysis. It is clearly seen that the dosage of CA have significant effects on the degradation rate of photocatalysts. When the amount of CA was 2.5mmol, the Bi₂MoO₆ nanoplate possessed the best photocatalytic activity, the amount of CA was further increased, photocatalytic activity decreased.

It is well known that the photocatalytic activities are closely related to their crystallinity and surface areas. A high degree of crystallinity and a large surface area are favorable to the photocatalytic performance due to fewer defects acting as electron–hole recombination centers and more active sites in the photocatalytic process. Compare to sample S1, the sample S2 have smaller particle size, so the surface area of sample S2 maybe higher than that of sample S1, which was advantageous to its photocatalytic activities. The particle size of Sample S3 and sample S4 are smaller than that of sample S2, but their crystallization are not good enough which could be observed from the XRD results, This imperfect crystallization is considered to favorably increase the probability of electron–hole recombination, which is unfavorable to the photocatalytic performance. Therefore, the photocatalytic activities of the samples S3 and S4 decreased and the sample S2 possessed the best photocatalytic activity.

### 4 Conclusions

In conclusion, CA could be used as a complexing agent to control the nucleation and growth rate of Bi₂MoO₆, the amount of CA in CA assisted hydrothermal process have been found to have a significant influence on the morphology of Bi₂MoO₆ nanoplates. The
average size of nanoplate decrease with increasing the amount of CA, which may lead to higher specific surface area and photocatalytic activities, but the crystallinity decreased, which is unfavorable to the photocatalytic activities. Therefore, the amount of CA may have one optimum value, in our experiments, Bi₂MoO₆ prepared when the amount of CA was 2.5mmol exhibited the highest photocatalytic activity. This method has the potential use in preparation of other bismuth compound photocatalysts.

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References

1. Y. Tsunuda, W. Sugimoto and Y. Sugahara, Chem. Mater., 2003, 15, 632-635.
2. J. X. Xia, H. M. Li and Z. J. Luo, Materials Chemistry and Physics, 2010, 121, 6-9.
3. M. Hartmanova, M. T. Le and I. Driessche, Russian Journal of Electrochemistry, 2005, 41, 455-460.
4. R. Murugan, Physical B: Condensed Matter, 2004, 352, 227-232.
5. L. T. Sim, C. K. Lee and A. R. West, J. Mater. Chem., 2002, 12, 17-19.
6. J. C. Lun, H. Kim and Y. S. Kim, Applied Catalyst A: General, 2007, 317, 244-249.
7. J. Q. Yu and A. Kudo, Chemistry Letters, 2005, 34, 1528-1529.
8. H. H. Li, C. Y. Liu and K. W. Li, Journal of Material Science, 2008, 43, 7026-7034.
9. W. Z. Yin, W. Z. Wang and S. M. Sun, Catalysis Communication, 2010, 11, 647-650.
10. D. K. Ma, S. M. Huang and W. X. Chen, J. Phys. Chem. C, 2009, 113, 4369-4374.
11. L. Zhang, T. Xu and X. Zhao, Applied Catalysis B: Environmental, 2010, 98, 138-146.
12. A. Kudo and M. Sekizawa, Chem. Commun., 2000, 15, 1371-1372.
13. A. Kudo and M. Sekizawa, Catal. Lett., 1999, 58, 241-243.
14. Y. Shimodaira, H. Kato and H. Kobayashi, J. Phys. Chem. B, 2006, 110, 17790-17797.
15. J. G. Yu, J. F. Xiong and B. Chen, Journal of Solid State Chemistry, 2005, 178, 1968-1972.