



Photodegradation of dye pollutants catalyzed by γ -Bi₂MoO₆ nanoplate under visible light irradiation

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ABSTRACT

Nanoplate γ -Bi₂MoO₆ is prepared by hydrothermal method. Using this material as photocatalyst, rhodamine B and methylene blue were efficiently degraded under visible light irradiation. The degradation kinetics, total organic carbon changes, and electron spin resonance detection of active oxygen species were investigated to clarify the degradation process. The experimental results indicated that the target dyes could be facily bleached and mineralized. The formation of active oxygen species of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ is detected, and they are proposed to be responsible for the degradation of the target dyes. The γ -Bi₂MoO₆ catalyst is very stable and can be reused.

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1. Introduction

Photocatalysis offers an advanced technology for the elimination of toxic organic compounds from water [1]. In recent years, the development of visible light photocatalysts has become one of the most important topics in photocatalysis research. Numerous studies have recently been performed to enhance the visible light utilization of TiO₂, which include impurity doping [2], metallization [3], and sensitization [4]. Additionally, some novel complex photocatalysts responsible to visible light have been developed recently [5,6].

Recently, the photocatalytic properties of the bismuth mixed oxides with Aurinillius structure have been studied. Photocatalytic activities of Bi₂WO₆ have been revealed by Kudo and Hiji [7], Tang et al. [8], and Zhang and Zhu [9]. Generally, the molybdates have the same crystalline pattern as the tungstates, implying they can also be used as photocatalyst. Bismuth molybdates have the general chemical formula Bi₂O₃·*n*MoO₃ where *n* = 3, 2 and 1, corresponding to α , β and γ phase, respectively. Such compounds and their mixtures are well-known owing to their good catalytic activities in selective oxidation of light hydrocarbons to produce many useful organic compounds [10]. Kudo et al. found that Bi₂MoO₆ was able to carry out the photocatalytic O₂-evolution

under visible light irradiation [11,12]. However, the Bi₂MoO₆ samples were prepared by solid-state reaction, which was essential to perform at high temperature, and the photocatalytic activities were not high due to large crystal and low surface area. Recently, our studies indicated that γ -Bi₂MoO₆ film fabricated from amorphous complex via dip-coating method exhibited high photocurrent response and photoelectrocatalytic activities in degrading organic contaminants under visible light irradiation [13].

In the present work, γ -Bi₂MoO₆ particles with nanoplate morphology were synthesized through hydrothermal method. It was observed that γ -Bi₂MoO₆ nanoplate can be used as a photocatalyst for the efficient bleaching and mineralization of rhodamine B (RhB) and methylene blue under visible light irradiation. Active oxygen species of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ are detected for the first time, which is insignificant in understanding the photocatalytic process of bismuth mixed oxides. And, a photocatalytic degradation mechanism of RhB/MB over γ -Bi₂MoO₆ was proposed.

2. Experimental

2.1. Catalyst preparation and characterization

γ -Bi₂MoO₆ nanoplates were synthesized through hydrothermal process. All chemicals used were analytic grade reagents without further purification. The start materials were corresponding Na₂MoO₄ and Bi(NO₃)₃ in 1:2 molar ration. The start materials

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(5 mmol Bi) mixed together and added 100 mL deionized water. White precipitates appeared immediately and the beaker was put in ultrasonic bath for 10 min in order to complete the precipitate reaction. Washing for several times, the collected precipitate was added into a 50-mL Teflon-lined autoclave and filled with deionized water up to 80% of the total volume. After that, the autoclave was sealed into a stainless steel tank and treated at 180 °C for 12 h. Then the reactor was cooled to room temperature. Resulting samples were collected and washed with deionized water and dried at 80 °C in air.

Crystallinity of the as-prepared sample was characterized by powder X-ray diffraction (XRD) on Bruker D8-advance X-ray diffractometer at 40 kV and 40 mA for monochromatized Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation. Morphologies of the prepared samples were further examined with transmission electron microscopy (TEM) by a JEM 1010 electron microscope operated at an accelerating voltage of 120 kV. UV–vis diffuse reflectance spectrums (DRS) of the samples were measured by using Hitachi U-3010 UV–vis spectrophotometer. Electron spin resonance (ESR) spectra were obtained using a Bruker model ESP 300 E electron paramagnetic resonance spectrometer equipped with a quanta-Ray Nd:YAG laser system as the irradiation light source ($\lambda = 532 \text{ nm}$). The reagent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), used as the spin trapping agent in the ESR studies, was purchased from the Sigma Chemical Co.

2.2. Degradation experiment

Photocatalytic degradation of RhB/MB over the $\gamma\text{-Bi}_2\text{MoO}_6$ was performed under visible light irradiation of 500 W Xe lamp with the 400 nm cut filter. The reaction cell was placed in a sealed black box whose top was opened and the cut filter was placed to provide visible light irradiation. In each experiment, 0.05 g photocatalysts was added into 100 mL RhB/MB solution ($1 \times 10^{-5} \text{ mol/L}$). After dispersing in ultrasonic bath for 5 min, the dispersions were kept stirred under constant air-equilibrated conditions before and during the irradiation and exposed to visible light irradiation. The concentrations of RhB/MB were determined using Hitachi U-3010 UV–vis spectrophotometer. The mineralization degree of the reaction solution was monitored by measuring the total organic carbon (TOC) content with a Shimadzu TOC 5000A analyzer by directly injecting the aqueous solution after centrifugation.

3. Results and discussion

3.1. Characterization of nanoplate $\gamma\text{-Bi}_2\text{MoO}_6$ photocatalyst

As shown in Fig. 1, the $\gamma\text{-Bi}_2\text{MoO}_6$ samples have square nanoplate morphologies with short edge. The length of the edge is ca. 200 nm. The peaks of the XRD pattern shown in Fig. 2 could be indexed according to $\gamma\text{-Bi}_2\text{MoO}_6$ (JCPDS 21-102), which indicate that the prepared samples were $\gamma\text{-Bi}_2\text{MoO}_6$. Fig. 3 showed a typical diffuse reflection spectrum of prepared $\gamma\text{-Bi}_2\text{MoO}_6$ samples. Steep shape of the spectra indicated that the visible light absorption was not due to the transition from the impurity level but was due to the band-gap transition [14]. For a crystalline semiconductor, it was shown that the optical absorption near the band edge follows the equation [15]: $ah\nu = A(h\nu - E_g)^{n/2}$, where a , ν , E_g , and A are absorption coefficient, light frequency, band gap, and a constant, respectively. From the onset of the absorption edge, the band gap of the nanoplates was estimated to be 2.59 eV, which is narrower than that reported by Kudo and coworkers [12]. The nanoplate morphology may be responsible for the narrower band gap due to the quantum effect. The color of the nanoplates was light yellow, as can be expected from the absorption spectrum. It is suggested that the visible light absorption of $\gamma\text{-Bi}_2\text{MoO}_6$ was due to the transition

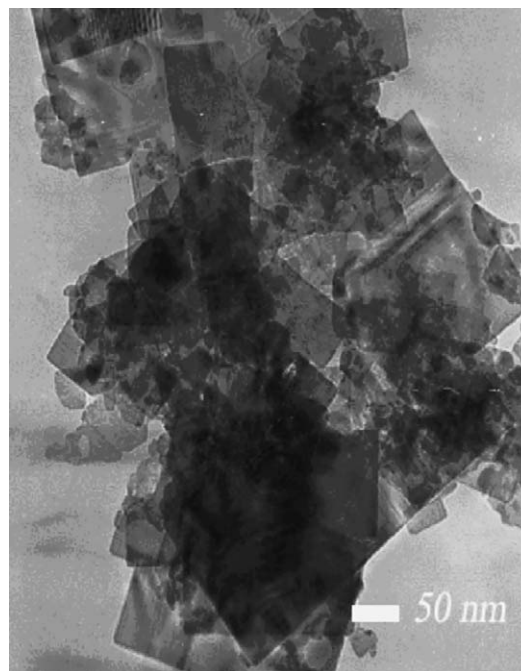


Fig. 1. The morphology of $\gamma\text{-Bi}_2\text{MoO}_6$ samples.

from the valence band consisting of the O 2p orbitals to the conduction band derived from the primary Mo 4d orbitals in MoO_6 octahedra and the secondary Bi 6p orbitals [12].

3.2. Photodegradation of dyes under visible irradiation

The degradation reactions were carried out after the establishment of the adsorption/desorption equilibrium by magnetic stirring for 30 min in the dark. After the equilibrium was established, about 5% of RhB was adsorbed on the catalyst. The variations in the concentration of RhB under various conditions are shown in Fig. 4(A). RhB underwent an insignificant degradation under visible light irradiation in the absence of $\gamma\text{-Bi}_2\text{MoO}_6$. However, the visible light irradiation led to rapid degradation of the dye in the presence of $\gamma\text{-Bi}_2\text{MoO}_6$, and the RhB solution was discolored completely within 80 min of irradiation. As a comparison, photodegradation of RhB over P25 was also performed. Seen from Fig. 4(A), it is that degradation of RhB over $\gamma\text{-Bi}_2\text{MoO}_6$

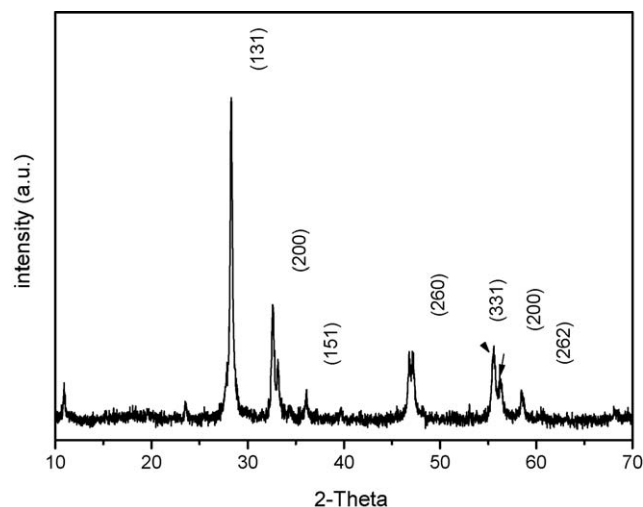


Fig. 2. XRD pattern of series prepared $\gamma\text{-Bi}_2\text{MoO}_6$ samples.

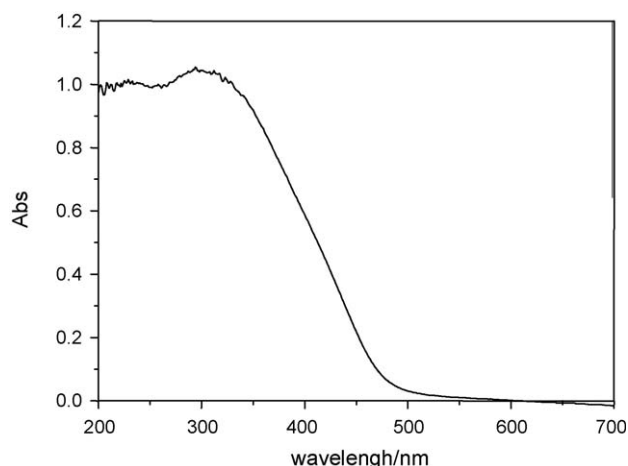


Fig. 3. The UV-vis spectra of γ - Bi_2MoO_6 samples.

nanoplates was clearly faster than that over P25 under same condition. It is worth noting that, during the degradation of RhB, the absorption maximum of the degraded solution with irradiation time exhibited hypsochromic shifts to some extent concomitantly with the cleavage of the conjugated structure, which resulted from the formation and decomposition of a series of *N*-de-ethylated intermediates as reported by Zhao et al. [16]. The photodegradation of MB by the γ - Bi_2MoO_6 nanoplate was also investigated to verify the activity of the photocatalyst. Notably, the MB can also undergo quick degradation in the presence of the γ - Bi_2MoO_6 under visible light irradiation (Fig. 4(B)). Similarly, Bi_2MoO_6 photocatalyst prepared from an amorphous complex precursor followed by

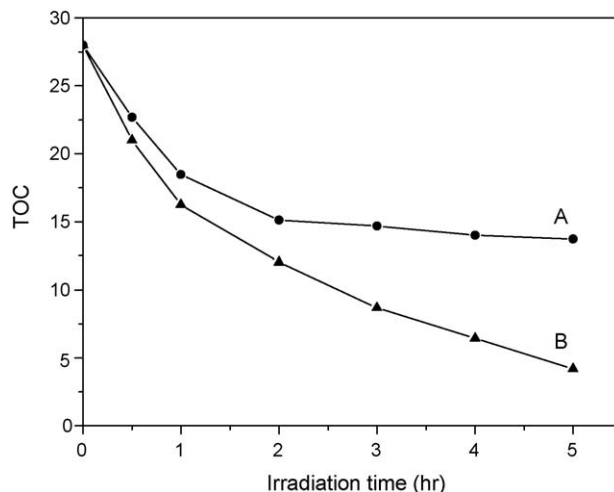


Fig. 5. Temporal change in total organic carbon in the photodegradation of RhB (1×10^{-4} mol/L) in the presence of and γ - Bi_2MoO_6 (A) and TiO_2 (B) photocatalysts under visible light irradiation. Photocatalysts concentration = 0.5 g/L.

calcinations was given. It is clear that the photocatalytic activities of the obtained Bi_2MoO_6 particles are low. The particle size of prepared Bi_2MoO_6 is about 200 nm. The TEM and XRD analysis of the obtained Bi_2MoO_6 particles were given in Supporting information (Fig. 1). Maybe, the separation of electron-hole separation was easier for Bi_2MoO_6 nanoplates and the Bi_2MoO_6 nanoplates have large surface area. All of these points contribute to its high photocatalytic activities.

The mineralization degree of RhB was examined by measuring the decrease in TOC of the reaction solution. TOC variation during

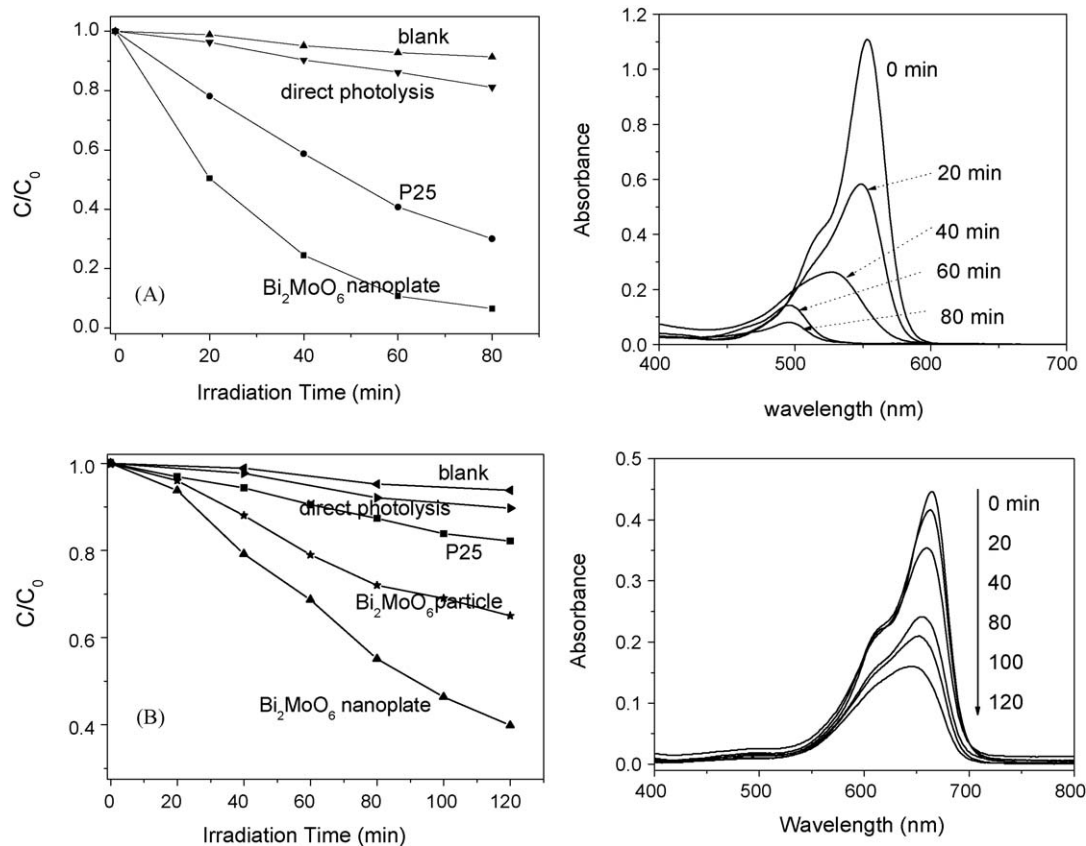


Fig. 4. Degradation kinetics and UV-vis spectral changes of RhB (A) and MB (B) in different reaction systems under visible light irradiation ($\lambda > 400$ nm) (initial concentrations of RhB and MB = 1×10^{-5} M; photocatalysts concentration = 0.5 g/L).

the photodegradation of RhB in the system under visible irradiation is depicted in Fig. 5. To minimize experiment errors, the initial concentration of RhB was promoted from 1.0×10^{-5} to 1.0×10^{-4} mol/L, so the irradiation time needed for complete degradation RhB also increase from 80 min to 5 h. As shown in Fig. 5, under visible light irradiation, the TOC decreased gradually. After irradiation for 5 h, about 85% TOC is removed. However, in the RhB/TiO₂ (P25) system, only 48% RhB is mineralized within 3 h. After that, the TOC remains nearly unchanged. For the RhB/TiO₂ system, once the reaction solution was discolored, there were no substrates to be excited by visible irradiation, which supplied energy for the photodegradation of RhB, and the mineralization process ceased subsequently [16]. These results indicated that RhB solution can not only be discolored but also be mineralized efficiently in the γ -Bi₂MoO₆ nanoplate/RhB system under visible light irradiation. It has been well established that RhB degradation in TiO₂ photocatalytic system was through photosensitization pathway. Thus, it can be concluded that a different degradation process was involved in the γ -Bi₂MoO₆ system.

3.3. Separation and reuse of photocatalysts

An attractive feature of the photocatalyst materials is that inherent structure of the catalyst is stable toward oxidative decomposition and that the photocatalyst can be facily separated from the dispersion by simple centrifugation after reaction, which facilitates the reuse of the catalyst. In addition, as mentioned above, the release of degraded intermediates from the catalyst surface can also prevent the catalyst surface from blocking and poisoning by the intermediates. In our experiments, the stability and reusability of the γ -Bi₂MoO₆ were examined by repetitive use of the catalyst. After RhB was degraded in the first cycle for 60 min, the γ -Bi₂MoO₆ was separated by centrifugation, and then was added again into the same concentration of RhB solution. The decomposition of RhB in the second cycle was nearly as fast as in the first run. As shown in Fig. 6, the five runs of the degradation of RhB showed no significant loss of photoactivity of the catalyst, which indicated the considerable stability of the catalyst under the present conditions.

3.4. Involved active oxygen species

ESR spin-trap technique (with DMPO) was used to probe the nature of the reactive oxygen species generated on the surface of

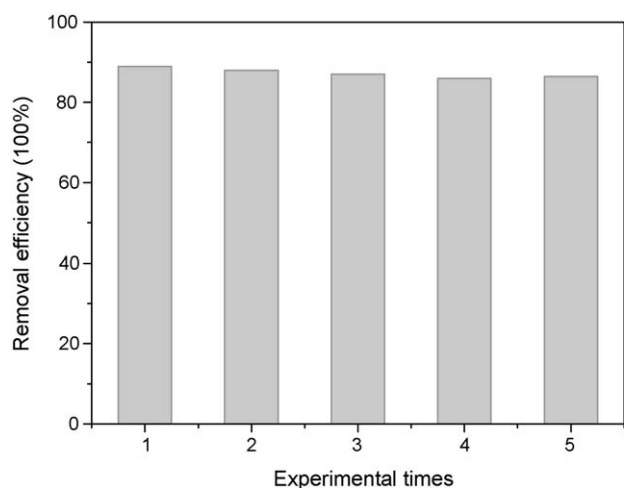


Fig. 6. Removal efficiency of RhB with experimental times in the presence of γ -Bi₂MoO₆ photocatalyst under visible light irradiation.

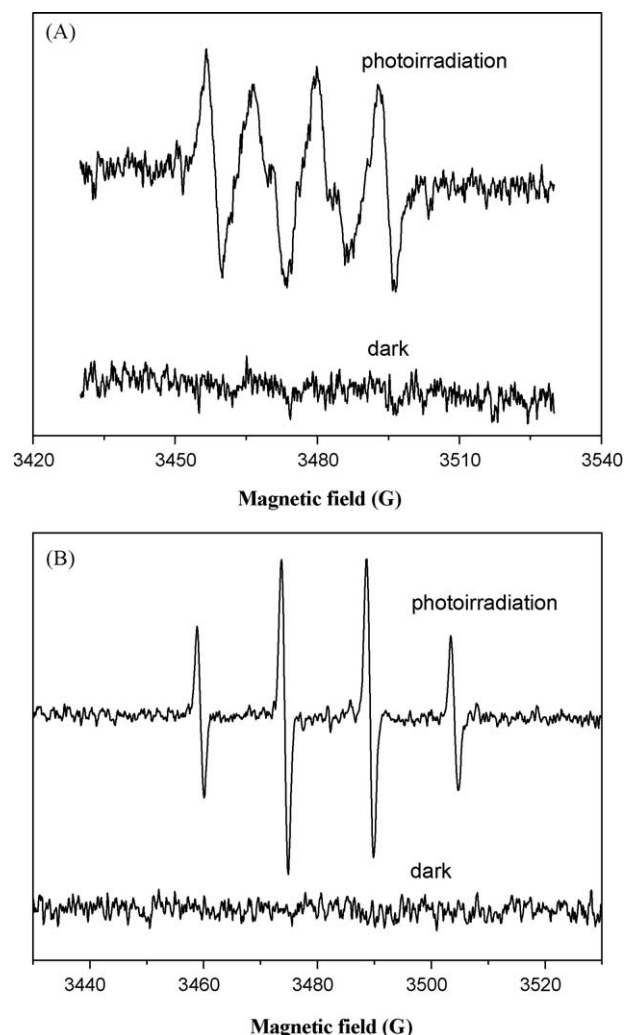


Fig. 7. Spin-trapping ESR spectra of γ -Bi₂MoO₆/DMPO dispersion: (A) ESR signal of the DMPO-•OH adducts under visible light irradiation ($\lambda = 532$ nm); (B) ESR signal of the DMPO-O₂•⁻ adducts under UV light irradiation ($\lambda = 532$ nm).

γ -Bi₂MoO₆ under visible irradiation. A Nd:YAG laser ($\lambda = 532$ nm) was employed to irradiate suspensions containing catalysts. As depicted in Fig. 7, four characteristic peaks of DMPO-•OH were obviously observed in the suspension of γ -Bi₂MoO₆ nanoplates. No such signals were detected in the dark. This means that irradiation is essential to the generation of •OH on the surface of the γ -Bi₂MoO₆. Similarly, DMPO-O₂•⁻ species were detected successfully in the γ -Bi₂MoO₆ suspension under visible light irradiation. The evidence that •OH and O₂•⁻ are produced on the surface of visible illuminated γ -Bi₂MoO₆ provides a solid indication that the catalyst can be efficiently excited by visible light to create electron–hole pairs and the charge separation is maintained long enough to react with adsorbed oxygen/H₂O and to produce a series of active oxygen radicals which finally induce the decomposition of RhB/MB as illustrated in the literature [17,18].

In the case of Bi₂WO₆ photocatalytic degradation of RhB, it was suggested that the direct hole transfers and O₂•⁻ were responsible for the RhB degradation [19]. γ -Bi₂MoO₆ possesses perovskite-like slabs consisting of MoO₆ octahedra of which the structure is often advantageous for photocatalysts [20]. It was estimated by Kudo et al. that the valence band was mainly derived from the O 2p orbitals and the conduction band was derived from the Mo 4d orbitals and the Bi 6p orbitals. The contribution of the Bi 6s orbitals to the valence band formation, as seen in Bi₂WO₆ was not

observed. The different band structure may be responsible for the different photocatalytic mechanism in RhB degradation.

4. Conclusions

The results of this work indicate that γ -Bi₂MoO₆ nanoplate photocatalysts that are responsive to visible light exhibit high photocatalytic activity and good stability and can be simply regenerated. These characteristics indicate the great potential of γ -Bi₂MoO₆ to be used in environmental purification, to promote cleanliness and energy saving. The studies of ESR show that \cdot OH and O^{2•-} were formed under visible light irradiation, which are mainly responsible for the photocatalytic degradation of RhB and MB. Furthermore, the catalyst activity did not change after a series of repeated experiments for the degradation of RhB under experiment conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apsusc.2009.05.010.

References

- [1] D.F. Ollis, E. Pelizzetti, N. Serpone, *Environ. Sci. Technol.* 25 (1991) 1522–1529.
- [2] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293 (2001) 4782.
- [3] E. Bae, W. Choi, *Environ. Sci. Technol.* 37 (2003) 147–152.
- [4] R.W. Fessenden, P.V. Kamat, *J. Phys. Chem. B* 99 (1995) 12902–12906.
- [5] Z.G. Zou, J.H. Ye, K. Sayama, H. Arakawa, *Nature* 414 (2001) 625.
- [6] D.W. Hwang, H.G. Kim, J.S. Lee, J. Kim, W. Li, S.H. Oh, *J. Phys. Chem. B* 109 (2005) 2093.
- [7] A. Kudo, S. Hiji, *Chem. Lett.* 10 (1999) 1103–1104.
- [8] J.W. Tang, Z.G. Zou, J.H. Ye, *Catal. Lett.* 92 (2004) 53.
- [9] C. Zhang, Y.F. Zhu, *Chem. Mater.* 17 (2005) 3537–3545.
- [10] M.M. Bettahar, G. Costentin, L. Savary, J.C. Lavalley, *Appl. Catal. A* 145 (1996) 1.
- [11] J.Q. Yu, A. Kudo, *Chem. Lett.* 34 (2005) 1528–1529.
- [12] Y. Shimodaira, H. Kato, H. Kobayashi, A. Kudo, *J. Phys. Chem. B* 110 (2006) 17790–17797.
- [13] X. Zhao, J.H. Qu, H.J. Liu, C. Hu, *Environ. Sci. Technol.* 41 (2007) 6802–6807.
- [14] A. Kudo, I. Tsuji, H. Kato, *Chem. Commun.* 17 (2002) 1958–1959.
- [15] M.A. Butler, *Appl. Phys.* 48 (1977) 1914.
- [16] C. Chen, W. Zhao, P.X. Lei, J.C. Zhao, N. Serpone, *Chem. -Eur. J.* 10 (2004) 1956–1965.
- [17] A.L. Linsebigler, G. Lu, J.T. Yates, *Chem. Rev.* 95 (1995) 735–758.
- [18] A. Maldotti, A. Molinari, R. Amadelli, *Chem. Rev.* 102 (2002) 3811–3836.
- [19] H. Fu, C. Pan, W. Yao, Y. Zhu, *J. Phys. Chem. B* 109 (2005) 22432–22439.
- [20] H. Kato, A. Kudo, *J. Phys. Chem. B* 105 (2001) 4285.