

Research Article

Hydrothermal Synthesis of Bi_2MoO_6 Visible-Light-Driven Photocatalyst

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Bismuth molybdate (Bi_2MoO_6) nanoplates were synthesized by the hydrothermal reaction of bismuth nitrate and sodium molybdate as starting materials at 120–180°C for 5–20 h. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, and scanning electron microscopy (SEM) were used to investigate the effect of reaction temperature and length of reaction time on phase and morphologies of the as-synthesized Bi_2MoO_6 samples. In this research, orthorhombic well-crystallized Bi_2MoO_6 nanoplates with the presence of stretching and bending vibrations of MoO_6 and BiO_6 octahedrons were detected, and the Bi_2MoO_6 nanoplates synthesized at 180°C for 5 h exhibit the highest photocatalytic efficiency over 96% within 100 min visible-light irradiation.

1. Introduction

Photocatalysis of semiconductors under sun light energy has attracted worldwide researchers because they can apply it for the splitting of water and the degradation of organic pollutants [1, 2]. Visible-light-driven photocatalysis has accounted for approximately 43% of solar energy, while that of UV radiation has taken up only 5% [1, 3]. Thus it is very urgent to develop new photocatalytic materials responding in the visible light.

Bi_2MoO_6 with 2.9 eV narrow energy gap is typical Aurivillius-phase perovskite with its structure containing perovskite layers ($\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}$) between Bi_2O_2 layers of bismuth oxide family with corner-shared octahedral structure [1, 2, 4]. It was found that Bi_2MoO_6 is very interesting due to its unique physical properties for using as dielectric material, gas sensors, ionic conductors, luminescent material, and photocatalyst for water splitting under visible-light irradiation [1, 4, 5]. There are a number of researchers

studying photocatalytic activities of Bi_2MoO_6 under visible-light irradiation [1, 2, 4–10]. Among them, Bi et al. [6] reported that Bi_2MoO_6 samples were successfully synthesized by a solvothermal process in different types of solvent including water, isopropanol, and ethylene glycol. The visible-light-driven photocatalytic activities for decomposition of rhodamine B (RhB) under visible-light irradiation ($\lambda > 420$ nm) were also investigated. They found that the sample synthesized using glycol as a solvent showed the best performance in the photodegradation of RhB under visible-light irradiation due to the large surface area, unique morphology, and small particle size. Yin et al. [7] reported that cage-like Bi_2MoO_6 hollow spheres were synthesized by a hard-template method and found that Bi_2MoO_6 could degrade phenol under visible-light irradiation. Jung et al. [8] found that the calcination temperature has the influence on the catalytic performance of Bi_2MoO_6 toward the oxidative dehydrogenation of n-butene to 1,3-butadiene under visible-light irradiation.

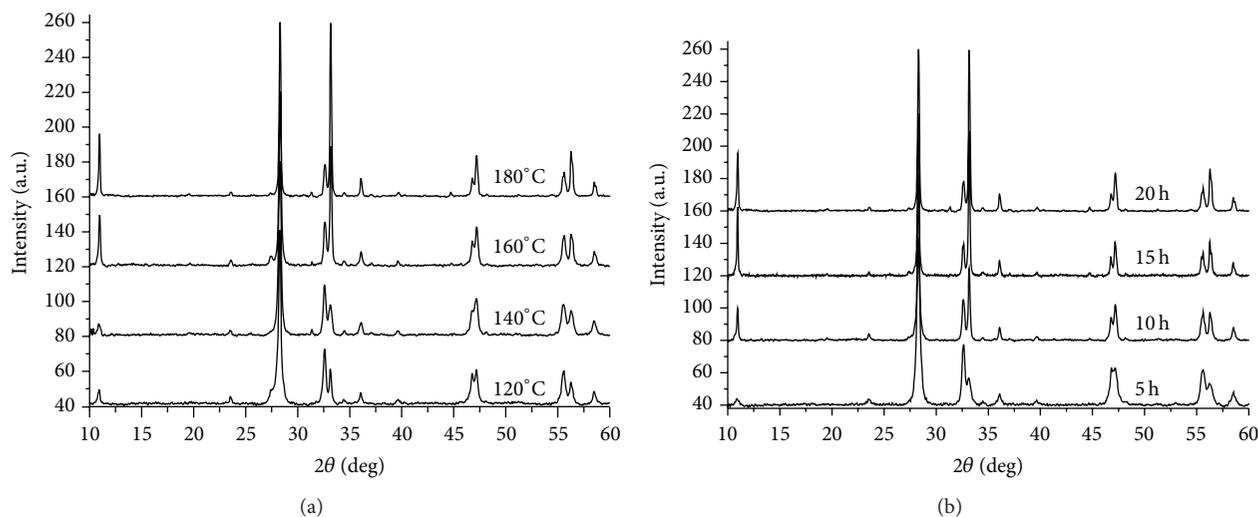


FIGURE 1: XRD patterns of Bi_2MoO_6 synthesized by the hydrothermal method at (a) 120–180 °C for 20 h and (b) 180 °C for 5–20 h.

In this paper, Bi_2MoO_6 crystallites were successfully synthesized by the hydrothermal process. Reaction time and temperature can play the role in the Bi_2MoO_6 crystallites via the hydrothermal process. Phase, morphologies, and photocatalytic activities were characterized by X-ray powder diffraction (XRD), Raman spectrophotometry, Fourier transform infrared (FTIR) spectrometry, scanning electron microscopy (SEM), and UV-visible spectrophotometry. The photocatalytic properties of Bi_2MoO_6 crystallites have also been investigated.

2. Experimental Procedures

In a typical procedure, each 0.01 mmol $\text{Bi}(\text{NO}_3)_3$ and each 0.005 mmol Na_2MoO_4 was dissolved into 60 mL deionized water. Subsequently, these two above solutions were mixed together under vigorous stirring, including the pH of the mixture which was adjusted to six. The mixture was stirred for another 30 min and transferred into Teflon-lined stainless steel autoclaves of 150 mL capacity. The hydrothermal process was carried out at 120–180 °C for 5–20 h and the autoclaves were left to cool down to room temperature. Finally the products were synthesized, centrifuged for collection, washed with deionized water and ethanol for several times, and dried in air at 60 °C for 12 h.

X-ray powder diffraction (XRD) patterns were obtained on a Philips PANalytical X'Pert PRO MPD diffractometer using $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.54056 \text{ \AA}$) at a scan rate of $5 \text{ deg}\cdot\text{min}^{-1}$. Raman spectrum was recorded on a HORIBA Jobin Yvon T64000 Raman spectrometer at 50 mW and 514.5 nm wavelength Ar green laser, and FTIR spectrum was recorded on a BRUKER TENSOR 27 Fourier transform infrared (FTIR) spectrometer with KBr as a diluting agent and operated in the range of $400\text{--}4.000 \text{ cm}^{-1}$. Scanning electron microscopic (SEM) images were taken by a JSM-6335F field emission SEM (FESEM, JEOL). UV-visible spectra of

the solutions were obtained using a UV/VIS spectrophotometer (Lambda 25, PerkinElmer).

The photodegradation reaction of rhodamine B (RhB) was carried out in a photochemical reactor under visible light at room temperature. The photochemical reaction system was composed of 150 mg Bi_2MoO_6 catalyst in 10^{-5} M of 150 mL RhB solution. Prior to the UV light irradiation, the RhB solutions containing the photocatalyst were kept in the dark room for 30 min to obtain an adsorption/desorption equilibrium. The photochemical reaction system was irradiated by visible light from Xe-lamp. The sampling analysis was conducted at 20 min interval. The solutions were analyzed by a Lambda 25 spectrometer using a 450 W of Xe-lamp with the wavelength of 554 nm. The decolorization efficiency was calculated by the following formula:

$$\text{Decolorization efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

where C_0 is the initial absorbency of RhB at adsorption equilibrium and C_t is the absorbency of RhB after the sampling analysis within the length of time (t).

3. Results and Discussion

Formation of Bi_2MoO_6 for different temperatures and lengths of reaction time was investigated by XRD. The XRD patterns of the samples synthesized by hydrothermal reaction at 120–180 °C for 20 h are shown in Figure 1(a). XRD patterns of the samples can readily be indexed as pure orthorhombic well-crystallized Bi_2MoO_6 structure with cell parameters of $a = 5.51 \text{ \AA}$, $b = 16.21 \text{ \AA}$, and $c = 5.49 \text{ \AA}$, in good agreement with those of the JCPDS file number 21-0102 [11]. Figure 1(b) shows the XRD patterns of the samples synthesized by hydrothermal method at 180 °C for 5–20 h. All the diffraction peaks can be readily indexed as a pure orthorhombic well-crystallized Bi_2MoO_6 structure of the JCPDS file number 21-0102 [11]. When the length of reaction time or temperature

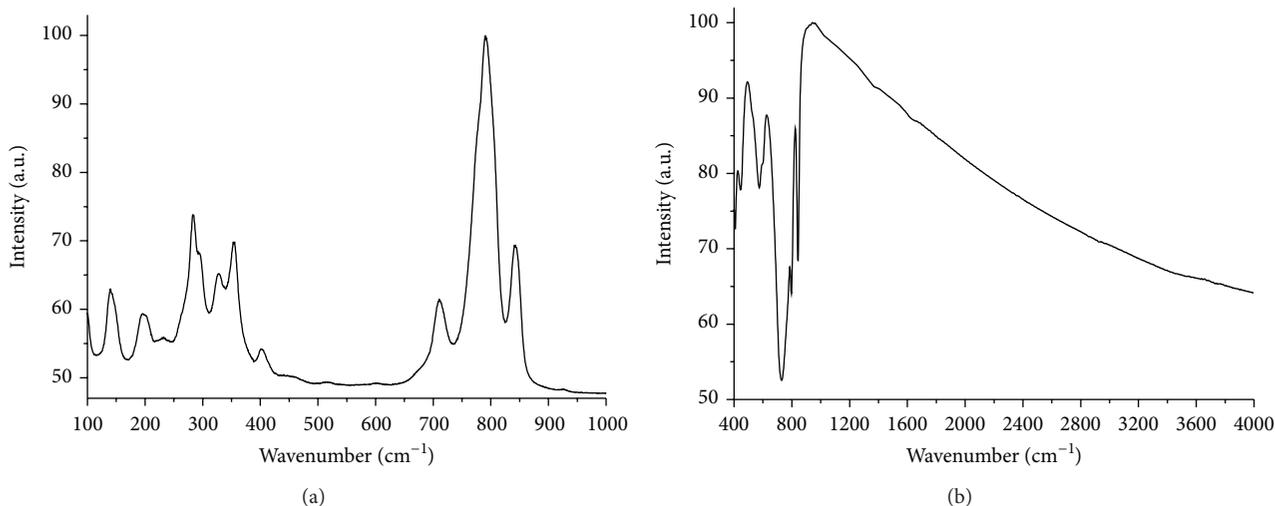


FIGURE 2: (a) Raman and (b) FTIR spectra of Bi_2MoO_6 synthesized by the hydrothermal method at 180°C for 20 h.

was increased, all the diffraction peaks of orthorhombic Bi_2MoO_6 phase were accordingly increased. They implied that the crystalline degree of orthorhombic Bi_2MoO_6 phase was increased. The XRD results indicate that nanostructured Bi_2MoO_6 could be selectively synthesized by adjusting the hydrothermal temperature and length of reaction time.

Raman spectrum of Bi_2MoO_6 sample synthesized by hydrothermal method at 180°C for 20 h is shown in Figure 2(a). The mode below 180 cm^{-1} could be the translation of molybdenum and bismuth atoms. That at 144 cm^{-1} was mainly specified as the lattice mode of Bi^{3+} atoms in the direction normal to the layers. The intense Raman modes near 290 and 280 cm^{-1} are likely to be the E_g bending vibration. Those at 323 , 345 , and 398 cm^{-1} were specified as the E_u symmetric bending. The mode at 712 cm^{-1} was specified as the asymmetric stretching vibration (E_u mode) of the MoO_6 octahedrons relating to the motion of equatorial oxygen atoms joining the MoO_6 octahedrons within the layers. The Raman vibrations at 793 cm^{-1} (A_{1g} mode) and 840 cm^{-1} (A_{2u} mode) were, respectively, specified as the symmetric and asymmetric stretching vibrations of MoO_6 octahedrons relating to the motion of apical oxygen atoms, in the direction normal to the $(\text{Bi}_2\text{O}_2)^{2+}$ layers [12–14].

Figure 2(b) shows the FTIR spectrum of Bi_2MoO_6 sample. The bands at 843 and 797 cm^{-1} were assigned to the asymmetric and symmetric stretching modes of MoO_6 relating to the vibration of apical oxygen atoms. The 734 cm^{-1} mode was attributed to the asymmetric stretching mode of MoO_6 relating to the vibration of the equatorial oxygen atoms. Those at 603 and 570 cm^{-1} corresponded to the bending vibration of MoO_6 . Furthermore, a small band at 454 cm^{-1} was attributed to the stretching and bending vibrations of BiO_6 octahedrons [12, 15].

SEM images of Bi_2MoO_6 synthesized by different hydrothermal temperatures and lengths of reaction time are shown in Figure 3. The hydrothermal temperature and

reaction time have significant influence on the size and morphology of the products. Figure 3(a) clearly illustrates that Bi_2MoO_6 hydrothermally synthesized at 120°C for 20 h is composed of relatively uniform nanoplates with edge length of 200 nm without detection of other morphologies. The products synthesized at 140 and 160°C for 20 h also show similar morphologies. Figure 3(b) is the SEM image of Bi_2MoO_6 synthesized by hydrothermal method at 180°C for 5 h. The grains are very small in size. Clearly, the formation of nanoplates was almost uniform size distribution. Figure 3(c) shows the SEM image of Bi_2MoO_6 synthesized at 180°C for 15 h, suggesting that the morphology of Bi_2MoO_6 remains as nanoplates with edge length of $0.5\text{ }\mu\text{m}$. Figure 3(d) shows that the product hydrothermally synthesized at 180°C for 20 h is composed of well-defined lamellar structure with dimension in the range of $1 \times 1.2\text{ }\mu\text{m}$. In summary, size of the products was increased when the reaction time and temperature were increased due to Ostwald ripening mechanism.

In this research, RhB was chosen as a representative dye to evaluate the photocatalytic performance of the as-synthesized Bi_2MoO_6 . The UV-visible spectra of RhB aqueous solutions containing Bi_2MoO_6 as a function of visible-light irradiation time are illustrated in Figure 4. The changes can be seen from the UV-visible absorbance. The strong absorption peak of RhB solution at 554 nm steadily decreased and showed the blue-shift to 498 nm of rhodamine during increasing in the length of irradiation time [2, 14]. It is assumed that the RhB was photodegraded to deethylated intermediates under the visible-light irradiation [2, 14, 16]. Further, Bi_2MoO_6 excellently exhibited photocatalytic activity to degrade RhB under visible-light irradiation.

The photodegradation efficiency of Bi_2MoO_6 photocatalyst under visible-light irradiation is shown in Figure 5(a). Under visible-light irradiation, the catalyst shows obvious photocatalytic activities for degradation of RhB. The Bi_2MoO_6 sample synthesized at 180°C for 5 h exhibits the highest activity. The RhB photodegradation efficiency of

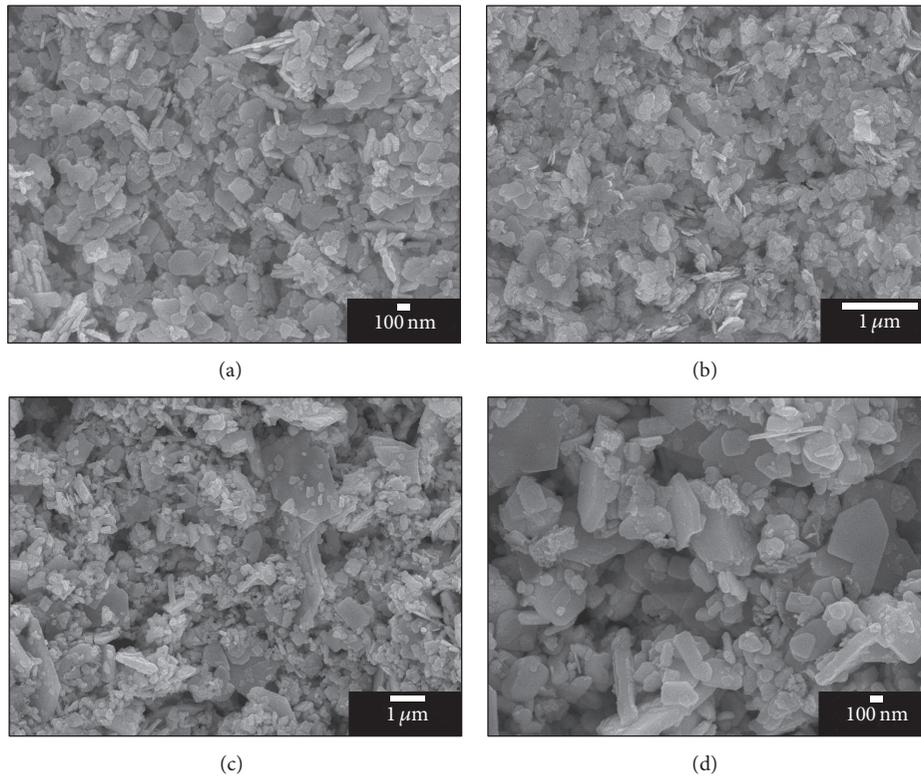


FIGURE 3: SEM images of Bi_2MoO_6 synthesized by the hydrothermal method at (a) 120°C for 20 h, (b) 180°C for 5 h, (c) 180°C for 15 h, and (d) 180°C for 20 h.

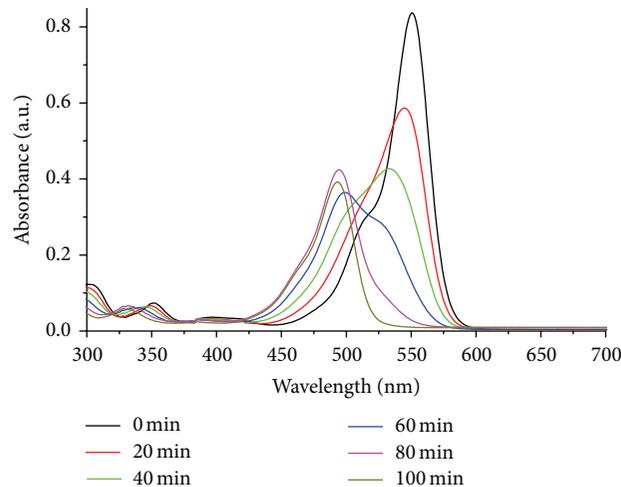


FIGURE 4: UV-visible absorption of RhB in the solutions containing Bi_2MoO_6 nanoplates synthesized at 180°C for 5 h.

Bi_2MoO_6 sample at 180°C for 5 h is over 96% within 100 min of visible-light irradiation. But, for the Bi_2MoO_6 sample synthesized at 120°C and 180°C for 20 h, their activities were over 65% and 74%, respectively. The degradation of RhB is in accordance with the pseudo-first-order kinetics by linear transforming of $\ln(C_0/C_t) = kt$, where C_0 is the initial concentration of RhB, C_t is the concentration of RhB within the length of time t , and k is the kinetics constant [1, 16]. The kinetics plots and the corresponding kinetics constants

were given in Figure 5(b). The kinetics constant for Bi_2MoO_6 synthesized at 180°C for 5 h is the highest at 0.0365 min^{-1} .

4. Conclusions

The effect of reaction temperature and time of photocatalytic nanoplates on phase, morphology, and photocatalytic properties was studied. The XRD patterns were specified as pure orthorhombic well-crystallized Bi_2MoO_6 phase. SEM

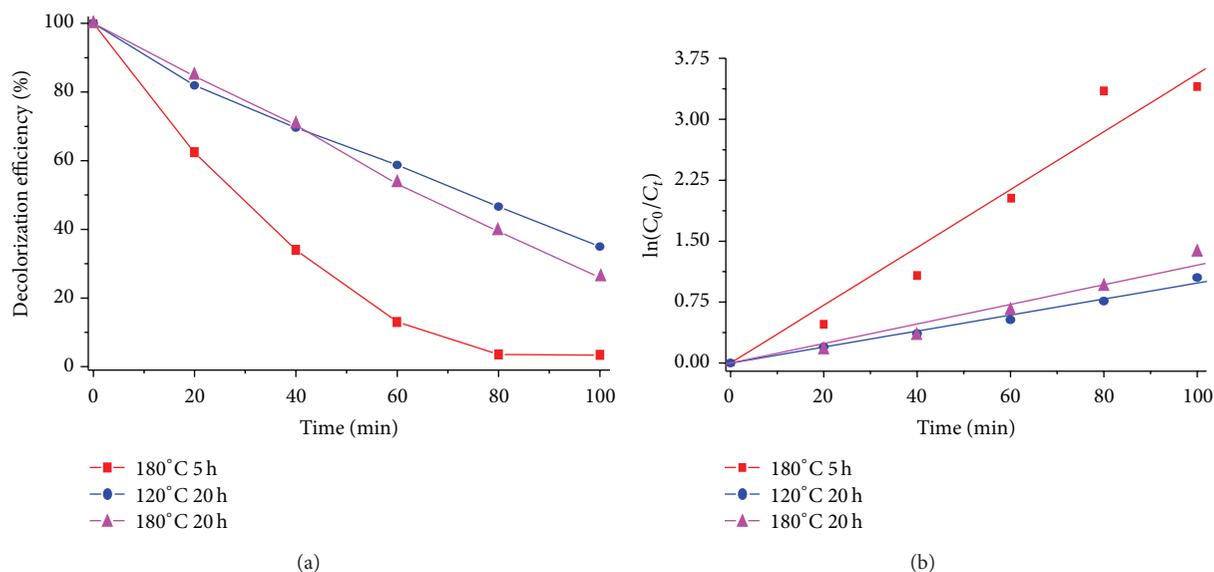


FIGURE 5: Decolorization efficiencies of RhB in the solutions containing Bi_2MoO_6 nanoplates under Xe light irradiation.

analysis showed that the products were nanoplates. The photocatalytic properties of the samples were determined by decomposing the RhB organic dye. In this research, photocatalytic activity of Bi_2MoO_6 nanoplates synthesized at 180°C for 5 h shows 96% degradation of rhodamine B under the Xe light irradiation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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