Research Article

Different Surfactants-Assisted Hydrothermal Fabrication and Photocatalytic Properties of Bi_2MoO_6 for Methylene Blue Degradation under Simulated Sunlight Irradiation

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Bi_2MoO_6 single-crystallites were synthesized by a simple hydrothermal method in the presence of surfactant sodium dodecyl sulfate (SDS), polyvinyl pyrrolidone (PVP), or cetyl trimethyl ammonium bromide (CTAB). The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) techniques. The photocatalytic activities of the as-fabricated Bi_2MoO_6 samples were measured for the degradation of methylene blue (MB) under the Xe light illumination. It is shown that the introduction of surfactant have a crucial influence on the size and morphology of the Bi_2MoO_6 product. Among the as-fabricated Bi_2MoO_6 samples, the ones derived hydrothermally with CTAB showed outstanding photocatalytic activities for the addressed reaction under simulated sunlight irradiation, attributed to the ultrafine nanocrystals and the higher surface areas.

1. Introduction

Recently, many Aurivillius-based compounds [1] have been reported which exhibit interesting properties suitable for photocatalytic applications. Bismuth molybdates have the general chemical formula $\text{Bi}_2\text{O}_3 \cdot n\text{MoO}_3$ where $n = 3, 2$ or 1 , corresponding to the α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, β - $\text{Bi}_2\text{Mo}_2\text{O}_9$, and γ - Bi_2MoO_6 . Among this family, γ - Bi_2MoO_6 with Aurivillius structure is the simplest and probably the most studied example.

It was well known that the microstructure and morphology of photocatalysts are important factors affecting photocatalytic properties [2]. Various synthesis methods of γ - Bi_2MoO_6 have been reported, including hard template method [3], solution combustion method [4], ultrasonic-assisted synthesis [5], citrate complex method [6], coprecipitation method [7], and hydrothermal synthesis [8, 9]. Within them, the hydrothermal route is one of the most effective methods for synthesizing γ - Bi_2MoO_6 nanostructures. This process can be described as a reaction of precursors in a close system in the presence of a solvent. It is possible to control the

shape and size of products by adjusting the processing parameters, such as different solvents and reactants, surfactants, reaction temperature, and time [10–12]. Different surfactants used in this approach were effective to fabricate nanoparticles with controllable phases and morphologies, and thus to affect the property of the product. In this paper, γ - Bi_2MoO_6 is synthesized by a simple hydrothermal method, the influence of surfactants SDS, PVP and CTAB on the microstructure, morphology, and photocatalytic activities of the catalysts is investigated. It is found that the γ - Bi_2MoO_6 synthesized in the presence of surfactant CTAB exhibits an excellent photocatalytic activity in the decomposition of MB under simulated sunlight irradiation (500-W Xe light illumination).

2. Experimental

2.1. Materials. Bismuth nitrate, sodium molybdate, MB, sodium hydroxide, nitric acid, absolute alcohol, SDS, PVP, and CTAB were provided by Sinopharm Chemical Reagent

FIGURE 1: XRD patterns of S1-S4 samples.

Co., Ltd. (Shanghai, China). All chemicals were of analytic grade and used without treating further for purification.

2.2. Preparation of the Bi_2MoO_6 Sample. $\gamma\text{-Bi}_2\text{MoO}_6$ were prepared by a simple hydrothermal synthesis. Briefly, while stirring, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.947 g) was dissolved in 10 mL nitric acid solution (2 mol/L) to form solution A. Then, 0.483 g Na_2MoO_4 was dissolved in 10 mL sodium hydroxide solution (4 mol/L) under stirring to form solution B. Thirdly, solution B was dropwised into solution A to form homogeneous solution C. 0.189 g of SDS, PVP, and CTAB was added into solution C, respectively. The pH = 5 values of the solution were then adjusted with concentrated sodium hydroxide under stirring. After being vigorously stirred for 30 min, the resulting precursor suspension was transferred into a 50 mL capacity Teflon-lined stainless steel autoclave, which was subsequently heated to 180°C and maintained for 22 h. Subsequently, the autoclave was cooled to room temperature naturally. The obtained samples were filtered, washed with deionized water for several times, and dried at 80°C in air. The sample obtained without surfactant was denoted as S1, and the samples obtained by adding SDS, PVP, and CTAB were denoted as S2, S3, and S4, respectively.

2.3. Characterization. X-ray powder diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 X-ray diffractometer (Cu $K\alpha$ source) at a scan rate of $4^\circ/\text{min}$ with the 2θ range from 20° to 80° . The crystal size was estimated from the Scherrer equation, $D = K\lambda/\text{FWHM} \cos \theta$, where D is the crystal size, λ is the wavelength of the X-ray radiation, and K is usually taken as 0.9, FWHM is the full width at half maximum in radian of the sample. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. UV-visible absorption spectra and diffuse reflectance spectra (DRS) were recorded on a Lambda 2500 UV-visible spectrophotometer (Japan island ferry).

2.4. Photocatalytic Degradation of MB Experiment. MB was used as a convenient photostable organic molecule to assay

photochemical activity of $\gamma\text{-Bi}_2\text{MoO}_6$. The prepared $\gamma\text{-Bi}_2\text{MoO}_6$ samples (50 mg) were dispersed into an aqueous solution (100 mL) of MB (10 mg/L^{-1}). The suspension was sonicated for 30 min, followed by stirring in the dark for 120 min to ensure adsorption-desorption equilibrium prior to irradiation. The suspension was then irradiated while stirring by using a 500-W Xe lamp (MAX-302, Asahi Spectra, USA). The initial and final reaction temperatures for MB solution were measured as $25 \pm 3^\circ\text{C}$, respectively. Samples for analysis were taken from the reaction suspension after different reaction time and centrifuged at 3500 rpm for 10 min to remove the particles. The MB concentration from the upper clear solution was analyzed according to the absorption intensity at 664 nm in the measured UV-vis spectra.

3. Results and Discussion

3.1. XRD Analysis. The XRD technique was used to identify the crystalline phases of the as-prepared $\gamma\text{-Bi}_2\text{MoO}_6$ samples, and the XRD patterns are shown in Figure 1. By comparing the XRD pattern of the standard $\gamma\text{-Bi}_2\text{MoO}_6$ sample (JCPDS PDF# 72-1524 or 71-2086), it can be realized that all of the Bragg diffraction peaks of each as-fabricated bismuth molybdate sample in the 2θ range of 10° – 80° could be well indexed, as indicated in Figure 1 (S1–S4). In other words, all of the $\gamma\text{-Bi}_2\text{MoO}_6$ samples were single-phase and possessed an orthogonal crystal structure, in good consistency with the results reported by other researchers [7, 8, 13]. For four Bi_2MoO_6 samples, there were some discrepancies in peak intensity, indicating that the $\gamma\text{-Bi}_2\text{MoO}_6$ crystallinity was a little different from sample to sample, depending upon the fabrication conditions adopted.

3.2. TEM Analysis. Figure 2 shows the TEM images of the as-prepared $\gamma\text{-Bi}_2\text{MoO}_6$ without or with surfactants. The TEM image in Figure 2(a) shows that bigger $\gamma\text{-Bi}_2\text{MoO}_6$ aggregated particles are composed of sheet-like nanocrystals without any surfactant. In Figure 2(b), the as-prepared $\gamma\text{-Bi}_2\text{MoO}_6$ with SDS is self-organized into a bigger branch-like architecture with irregular morphology. The TEM image in Figure 2(c)

FIGURE 2: TEM images of the various photocatalysts: (a) S1, (b) S2, (c) S3, and (d) S4, respectively.

shows that the $\gamma\text{-Bi}_2\text{MoO}_6$ is composed of nanosheets with different sizes when adding PVP surfactant. Figure 2(d) shows that the TEM images of the $\gamma\text{-Bi}_2\text{MoO}_6$ assisted by CTAB are composed of smaller nanocrystals with thinner sheet-like and regular morphology. It is concluded that surfactants affect the morphology and the particle size of $\gamma\text{-Bi}_2\text{MoO}_6$ during the hydrothermal process.

3.3. Photocatalytic Activities. To demonstrate the photocatalytic activity, MB was chosen as photodegradation target under simulated sunlight irradiation. Figure 3 showed the time-dependent absorption spectra of MB solution during the photodegradation process in the presence of different $\gamma\text{-Bi}_2\text{MoO}_6$ samples (S1–S4). The absorption peaks at 664 nm corresponding to MB diminished gradually as the irradiation time extended. Compared with the absorption peaks in S2 and S1, those in S3 and S4 dramatically decreased and completely disappeared after about 90 min, in particular that in S4. It suggested that S4 exhibited the highest photocatalytic activity among all the $\gamma\text{-Bi}_2\text{MoO}_6$ samples. The variation of

MB concentrations (C/C_0) with irradiation time over the different $\gamma\text{-Bi}_2\text{MoO}_6$ samples was shown in Figure 4, where C_0 and C are the concentrations of MB solution before irradiation and after the irradiation. For comparison, direct photolysis of MB in the absence of $\gamma\text{-Bi}_2\text{MoO}_6$ was performed under the same conditions. It was clearly seen that MB concentration in the absence of the catalysts hardly changed with the increase of irradiation time. The as-synthesized $\gamma\text{-Bi}_2\text{MoO}_6$ products with different surfactants exhibited remarkable variation in photocatalytic activities for MB degradation. Under Xe lamp irradiation within 90 min, the MB photocatalytic degradation ratio (98% and 96.1%) is achieved by S4 and S3 samples, noticeably better photocatalytic activities than the S2 and S1. Among $\gamma\text{-Bi}_2\text{MoO}_6$ products, S4 exhibited superior photocatalytic activity than other products. It was mainly because photocatalytic activities increased with the decrease of the particle size. The probable mechanism is that the surface area of small particle size provides more active sites during the photocatalytic process [14, 15]. The superior activity of S4 might be ascribed to its relatively small particle size by CTAB assisted growth.

FIGURE 3: UV-vis absorption spectra of the MB solution in the presence of various photocatalysts under simulated sunlight irradiation: (a) S1, (b) S2, (c) S3, and (d) S4, respectively.

FIGURE 4: Photocatalytic degradation ratio of MB versus irradiation time by using various photocatalysts.

4. Conclusion

In conclusion, $\gamma\text{-Bi}_2\text{MoO}_6$ was synthesized by a simple hydrothermal method in the presence of surfactants SDS, PVP, and CTAB. The surfactants can affect the particle size, surface area, morphology, and the photocatalytic activity of $\gamma\text{-Bi}_2\text{MoO}_6$. It is also found that surfactant CTAB has a promotive effect on the photocatalytic activity of $\gamma\text{-Bi}_2\text{MoO}_6$ sample, due to the surface area of small particle size providing more active sites during the photocatalytic process. Under a 500 W Xe lamp irradiation, the $\gamma\text{-Bi}_2\text{MoO}_6$ obtained by using CTAB as surfactant can degrade MB 98% in 90 min.

Conflict of Interests

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

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