Research Article

Controllable Fabrication of Ordered Mesoporous Bi_2WO_6 and Its High Photocatalytic Activity under Visible Light

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Ordered mesoporous Bi_2WO_6 was fabricated by nanocasting technique using SBA-15 as the template. The effect of the dosage of SBA-15 on the formation of the ordered structure and the photocatalytic ability of mesoporous Bi_2WO_6 was discussed. It was confirmed that the ordered mesoporous structure was obtained as the dosage of SBA-15 was 0.3 g. It was found that, compared to Bi_2WO_6 , the RhB degradation rate with ordered mesoporous Bi_2WO_6 was enhanced under visible light ($\lambda > 400 \text{ nm}$) by the photocatalytic measurements. The enhanced photocatalytic performance of ordered mesoporous Bi_2WO_6 was attributed to its particular ordered mesoporous structure which could increase the light-harvesting efficiency, reduce the recombination of the photogenerated charge carriers, and promote the surface reaction.

1. Introduction

Photocatalytic degradation of organic compounds for the purpose of purifying wastewater from industries and households has attracted much attention in recent years [1]. Heterogeneous photocatalysis is a common advanced oxidation approach for the removal of hazardous organic compounds from wastewater [2–4]. Photocatalysts can harness solar energy to drive useful redox chemistry and therefore are of considerable interest for environmental pollutant treatment [5–7]. Recently, the research of visible-light-driven photocatalysts has drawn the interest of a number of researchers [8–10]. Bi_2WO_6 , with a narrow band gap of 2.7 eV is one of the most attractive materials because of its high stability, nontoxicity, and wide solar response [11–13]. However, just as other photocatalysts, it suffers from the low quantum efficiency. Therefore, some attempts have been devoted to improve the photocatalytic performance of Bi_2WO_6 [14, 15].

Porous materials are of great interest in the application in photocatalysis, owing to their high surface area, which is a basic requirement for an efficient photocatalyst both to enhance the adsorption of photos and reactants and to offer

a large number of reactive sites [16–18]. An ordered porous structure is highly desirable for effective photocatalysis due to their larger surface area and multiple aligned pores, which can further assist the electron/energy transfer within the porous framework [19–22].

The nanocasting pathways developed over the last ten years, which use hard templates to create ordered replicas and provide promising routes for the preparation of mesostructured materials with novel framework compositions. Yang et al. [23–25] have demonstrated that ordered mesoporous silicas, such as two-dimensional (2D) hexagonal ($p6mm$) SBA-15 and three-dimensional (3D) bicontinuous cubic (Ia3d) KIT-6, can be used as a hard template to fabricate various ordered crystalline metal oxides. Nanocasting is processed by filling the void of the template with a precursor of the material, subsequent transform of the precursor to the material, and final removal of the template; a replica structure can be obtained [26]. The quantity rate of template to the precursor can affect the structure and the morphology of the materials.

Herein, taking SBA-15 as the template, ordered mesoporous Bi_2WO_6 was fabricated by nanocasting technique

FIGURE 1: (a) WXR D patterns of Bi_2WO_6 , S_1 , S_2 , and S_3 and (b) LXR D patterns of S_1 , S_2 , and S_3 .

to get enhanced photocatalytic ability under visible light. The effect of the dosage of SBA-15 on the formation of the ordered structure and the photocatalytic ability of mesoporous Bi_2WO_6 was discussed. RhB, a common pollutant in the industry wastewater, was chosen as a test substance to evaluate the photocatalytic performance of the as-prepared samples under visible light.

2. Materials and Methods

2.1. Materials. Tetraethyl orthosilicate (TEOS) was used as the silica source and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123) was used as the surfactant for the preparation of SBA-15. Bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and sodium tungstate dehydrate ($\text{Na}_2\text{WO}_6 \cdot 2\text{H}_2\text{O}$) were used as the bismuth source and the tungsten source, respectively. All reagents were of analytical grade and were used as received.

2.2. Methods

2.2.1. Preparation of Mesoporous Silica SBA-15. The preparation process of SBA-15 referred to the method reported by Zhao and coworkers [27]. About 2 g of P123 was dissolved with 50 mL of deionized water at 35°C followed by addition of 55 g of 4 mol/L HCl solution. After P123 was fully dissolved 4 g of TEOS was added into the solution drop by drop ($\text{TEOS}:\text{P123}:\text{HCl}:\text{H}_2\text{O} = 1:0.017:9.861:137$). The mixture was stirred at 35°C for 24 h before transferring into a Teflon bottle sealed in an autoclave, which was then heated to 100°C for 48 h in an oven. The solid was filtered off, washed three times with deionized water, dried at 100°C for 6 h, and calcined at 600°C for 6 h.

2.2.2. Preparation of Ordered Mesoporous Bi_2WO_6 . Under ultrasonication, 4 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 20 mL of 2 M HNO_3 solution, and then a transparent colorless solution was obtained. Followed 2 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was

added to the solution under ultrasonication for 10 min to form a white solution. Then a certain amount of prepared SBA-15 was added. The samples with 0.15 g, 0.3 g, and 0.6 g of SBA-15 were recorded by S_1 , S_2 , and S_3 , respectively. After complete immersion of the SBA-15, the mixture was put into the electrothermal constant-temperature dry box at 65°C for 18 h to complete filling the Bi_2WO_6 precursor into the void of SBA-15. The dried sample was then converted by calcination at 400°C for 6 h. Finally, the ordered mesoporous Bi_2WO_6 product was obtained with 20 mL of 2 M NaOH solution for 6 h under ambient temperature to eliminate SBA-15. The final product was filtered and washed with distilled water and absolute ethanol. Moreover, the Bi_2WO_6 was obtained as the same process without the addition and removal of SBA-15.

2.2.3. Sample Characterization. Low-angle X-ray diffraction (LXR D) and wide-angle X-ray diffraction (WXR D) spectra were recorded by Rigaku D/MAX-2400 with Cu K α radiation, accelerating voltage of 40 kV, and current of 30 mA. The scanning rate was $8^\circ (2\theta) \text{ min}^{-1}$ and the scanning range was $10\text{--}80^\circ$. Light absorption properties were determined using a UV-vis spectrophotometer (Shimadzu, UV-2450) with a wavelength range of 200–800 nm. The micromorphologies of the samples were observed using a transmission electron microscopy (TEM, JEM-2100(UHR) JEOL). TriStar 3000 was used to examine the N_2 adsorption and desorption properties of the samples at -196°C . Specific surface areas were calculated via the Brunauer-Emmett-Teller (BET) model. Fluorescence (FL) spectra were recorded by fluorescence spectrometer (LS-55, PE).

2.2.4. Measurement of Photocatalytic Activity. The photocatalytic activities of the samples were monitored through the photodegradation of RhB under visible light irradiation. Photocatalytic reactions were conducted in a 100 mL cubic quartz reactor. A 300 W Xe lamp was employed as visible light source. The light was passed through a filter, which should shield any wavelength below 400 nm. In all experiments,

FIGURE 2: N_2 sorption isotherms and pore size distributions (inset) of the Bi_2WO_6 , SBA-15, S_1 , S_2 , and S_3 .

the photocatalyst (0.10 g) was added to 100 mL RhB aqueous solution (5 mg/L). During each photocatalytic experiment, 5 mL of the suspension was collected at predetermined time intervals. The suspension was centrifuged at 9500 rpm for 10 min, and the concentration of RhB in the supernatant was analyzed by measuring the absorbance at $\lambda = 553$ nm with a Shimadzu UV2000 spectrophotometer.

3. Results and Discussion

3.1. XRD Analysis. The measurements of WXR and LXR patterns were performed to identify the crystalline phase and mesoporous ordering of as-prepared samples (see Figure 1). The WXR patterns of Bi_2WO_6 , S_1 , S_2 , and S_3 were shown in Figure 1(a). The crystal forms of the Bi_2WO_6 and mesoporous

FIGURE 3: TEM image of (a) SBA-15, (b) Bi_2WO_6 , (c) S_1 , (d) S_3 , and (e) S_2 and (f) the HRTEM image of S_2 .

Bi_2WO_6 could be identified to the orthorhombic type according to JCPDS card number 73-2020. And no other peaks were found in the spectra of S_1 , S_2 , and S_3 , indicating that no other crystal type was formed, and the template of SBA-15 was completely removed. One obvious peak ($2\theta = 0.80^\circ$) and a little peak ($2\theta = 0.98^\circ$) in the LXR pattern of S_2 could be found, inferring that the periodically ordered structure of S_2 was obtained. However, no ordered mesoporous Bi_2WO_6 was found in S_1 and S_3 , based on the result that there were no obvious peaks in the LXR spectra of them. The results indicated that the dosage of SBA-15 could affect the formation of the ordered mesoporous structure.

3.2. Nitrogen Adsorption-Desorption and TEM Analysis. N_2 sorption isotherms and pore size distributions (inset) of the Bi_2WO_6 , SBA-15, S_1 , S_2 , and S_3 were displayed in Figure 2. The N_2 adsorption/desorption curve of SBA-15 showed a typical

type IV isotherm with the hysteresis loop. Sharp capillary condensation over a narrow relative pressure region indicated the high degree of ordering, corresponding to a mesopore size of 7.7 nm. The SBA-15 had a surface area of $541.8 \text{ m}^2/\text{g}$ and a pore volume of $0.75 \text{ cm}^3/\text{g}$. The isotherms of S_1 , S_2 , and S_3 showed also a type IV curve, indicating a porous feature as shown in Figure 2. And the degree of ordering of S_2 (pore size of 5.1 nm) was higher than that of S_1 and S_3 based on the relative pressure regions of capillary condensation, which was the same as the result of LXR. Furthermore, the particle size of Bi_2WO_6 based on TEM image was about 100–200 nm. The big particle and nonporous structure led to low surface area of Bi_2WO_6 ($20.5 \text{ m}^2/\text{g}$), which was lower than those of S_1 ($38.6 \text{ m}^2/\text{g}$), S_2 ($66.7 \text{ m}^2/\text{g}$), and S_3 ($25.5 \text{ m}^2/\text{g}$). Large surface area could provide more sites for promoted surface reaction.

The ordering degrees of S_1 , S_2 , and S_3 got by the analysis of LXR were certified by TEM images (Figure 3). No ordered

FIGURE 4: (a) UV-vis absorption spectra of Bi_2WO_6 , S_1 , S_2 , and S_3 and (b) calculation of the band gap by Bi_2WO_6 and S_2 by Kubelka-Munk function.

FIGURE 5: FL spectra of Bi_2WO_6 , S_1 , S_2 , and S_3 .

structure was found in S_1 and S_3 , but ordered replicas of SBA-15 were found in S_2 . The HRTEM image of S_2 was presented in Figure 3(f). It could be measured that the d spacing was 0.320 nm, which matched well to the lattice spacing of (113) of orthorhombic type Bi_2WO_6 according to JCPDS card number 73-2020. Furthermore, some big particles with nonporous structure were found in S_1 , and there were some larger pores in S_3 . The ordered porosity of the S_2 resulted from interparticle voids. In the filling process, the pores of SBA-15 were completely filled. After the template was removed, the interparticle would construct the ordered mesoporous structure. SBA-15 dosage of S_1 was only 0.15 g, which was lack of enough pores to make the Bi_2WO_6 particles highly be organized. As a result some particles gathered together. And for the S_3 with 0.6 g SBA-15, there were too much pores for the precursor of Bi_2WO_6 to permeate. The distance of the particles would be larger than the pore size of SBA-15. The Bi_2WO_6 particles maybe gathered after the template was

removed. So many pores may make the Bi_2WO_6 arrange irregularly.

3.3. Optical Absorption Ability. The photo absorption abilities of the samples were detected by UV-vis absorption spectra, and the results were shown in Figure 4(a). All the samples showed intense absorption in the region from 200 to 450 nm. An obvious red shift of band gap edge was found in the spectra of mesoporous Bi_2WO_6 . The band gaps of Bi_2WO_6 and S_2 were determined to be 2.72 and 2.59 eV, respectively (Figure 4(b)), according to the Kubelka-Munk function

$$\alpha h\nu = A(h\nu - E_g)^{n/2}. \quad (1)$$

Because Bi_2WO_6 is the directly allowed optical transition semiconductor, n in the function equals 1. The narrower band gap of S_2 meant that S_2 could be excited by more photos and had enhanced light absorption ability.

3.4. FL Spectra Analysis. FL analysis was used to reveal the separation efficiency of the photogenerated electrons and holes in semiconductors, and the results were shown in Figure 5. The lower peak indicated lower recombination rate of them. The FL intensity of Bi_2WO_6 was the biggest one, inferring that Bi_2WO_6 had the highest recombination rate of photogenerated charge carriers. The results confirmed that the separation of photogenerated charge carriers could be improved through the construction of mesoporous Bi_2WO_6 , leading to the enhancement of photocatalytic activity. The FL intensity of S_2 got the lowest one among those of mesoporous Bi_2WO_6 , indicating that S_2 should have higher photocatalytic ability.

3.5. Photocatalytic Activity. The variation of RhB concentration (C_t/C_0), where C_t was the concentration of RhB at irradiation time (t) and C_0 is the initial concentration of RhB (5 mg/L) versus t over the photocatalysts, was shown

FIGURE 6: C_t/C_0 of the RhB concentration versus reaction time for (a) photocatalytic degradation with Bi_2WO_6 , S_1 , S_2 , and S_3 under visible light and (b) adsorption with S_2 .

in Figure 6(a). In 30 min, only 23.8% of RhB was removed with Bi_2WO_6 . However, RhB removal rate with S_1 , S_2 , and S_3 was 69.2%, 91.5%, and 39.0%, respectively. The results indicated that the photocatalytic ability of Bi_2WO_6 could be enhanced by constructing mesoporous structure. And the photocatalytic ability of S_2 was higher than those of S_1 and S_3 , inferring that the ordered mesoporous structure could further enhance the photocatalytic performance of Bi_2WO_6 . Because of the ordered mesoporous structure, the harvesting of incident light of S_2 became more efficient; the separation efficiency of photogenerated charge carriers was enhanced. Thus, an increased number of electrons and holes would arrive at the surface of Bi_2WO_6 particles, participating in oxidative reactions with RhB. High surface area could also provide more active sites for oxidative reactions and subsequently promote RhB removal. The adsorption performance of RhB of S_2 was measured, and the result has been presented in Figure 6(b). The removal rate of RhB (26.0%) was largely lower than that in photocatalytic process, indicating that ordered mesoporous Bi_2WO_6 had excellent photocatalytic ability.

4. Conclusions

Ordered mesoporous Bi_2WO_6 was successfully synthesized by nanocasting technique using SBA-15 as the template. The dosage of SBA-15 could affect the formation of ordered structure of mesoporous Bi_2WO_6 . The as-prepared ordered mesoporous Bi_2WO_6 exhibited an excellent photocatalytic decomposition of RhB under visible light irradiation. The high photocatalytic activity could be ascribed to its particularly ordered mesoporous structure which could increase the light-harvesting efficiency, reduce the recombination of the photogenerated charge carriers, and promote the surface reaction. Based on the results got here, it is confirmed that

construction of ordered mesoporous structure can efficiently improve the photocatalytic performance of photocatalysts, and photocatalysts with ordered mesoporous structure will be a promising candidate for the removal of hazardous organic compounds from wastewater.

Conflict of Interests

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

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