Solvothermal Synthesis of Bi₂O₂CO₃ Nanoplates for Efficient Photodegradation of RhB and Phenol under Simulated Solar Light Irradiation

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Monodispersed Bi₂O₂CO₃ nanoplates with an average width of 320 nm and thicknesses of 50–90 nm were successfully synthesized by a simple solvothermal method in a mixture solution of polyethylene glycol and H₂O. The obtained nanoplates were characterized by means of XRD, FT-IR, SEM and TEM. The effect of surfactant sodium dodecyl benzene sulfonate on the morphology of Bi₂O₂CO₃ product was investigated. Under simulated solar light irradiation, Bi₂O₂CO₃ nanoplates exhibited superior photocatalytic activities towards the degradation of RhB as well as high chemical stability upon cycling photocatalytic test. The nanoplates also showed promising photodegradation ability for eliminating refractory pollutant of phenol. The excellent photocatalytic performance of Bi₂O₂CO₃ nanoplates as compared with P25-TiO₂ endows them as promising high efficiency photocatalysts.

Key Words : Bi₂O₂CO₃, Semiconductor photocatalyst, Solvothermal synthesis

Introduction

Semiconductor photocatalysts have been focused in recent years due to their attractive applications in solar energy conversion and degradation of organic pollutants, which are crucial for sustainable development considering of environmental issues.^{1,2} As a novel kind of photocatalysts, bismuth-containing semiconductors have recently attracted increasingly attention due to their high activities towards the photodegradation of organic dyes as well as good stability.^{3–7} Recently, Xie *et al.*⁸ reported the photocatalytic activity of flower-like hierarchitectures of bismuth subcarbonate (Bi₂O₂CO₃), a commonly-used potent antibacterial agent, under solar light irradiation using rhodamine B (RhB) as a model organic pollutant. The subsequent work were dedicated to the correlation between the photocatalytic performance and structure characteristics of the material, and various morphologies of Bi₂O₂CO₃ have been synthesized, such as nanosheets,⁹ nanotubes,¹⁰ microspheres,^{11,12} and flower-like hierarchitectures.^{13,14} The reported Bi₂O₂CO₃ showed high activities in degrading organic dyes such as methylene blue (MB) and methyl orange (MO), as well as in removing heavy metal ions.

In recent years, two-dimensional (2D) nanomaterials have attracted considerable attention owing to their unique electronic and optical properties, as well as their promising applications in water splitting and environmental purification.^{15–17} Zhu *et al.*¹⁸ developed a simple hydrothermal process to synthesis square Bi₂WO₆ nanoplates, which exhibited high photocatalytic activities under visible light irradiation. Jiang *et al.*¹⁹ selectively synthesized BiOCl single-crystalline nanosheets with exposed {001} and {010} facets *via* a facile hydrothermal route. Zhang *et al.*²⁰ synthesized BiOBr nano-

sheets with thicknesses ranging from 9 to 32 nm by a facile and surfactant-free method, which shown higher photocatalytic activity to RhB under visible-light irradiation.

Bi₂O₂CO₃ is a typical “Sillén” phase, in which Bi-O layers and (CO₃) layers are inter-grown with the plane of the (CO₃) group orthogonal to the plane of the Bi-O layer.^{21,22} The internal layered structure of Bi₂O₂CO₃ would guide the lower growth rate along certain axis compared with that for other axes, to form 2D morphologies such as sheet-like or plate-like products.^{8,23,24} Previous work has demonstrated that Bi₂O₂CO₃ hierarchical structures assembled by nanosheets exhibit high activity towards the photodegradation of RhB as well as the mixed solution of MB and MO, due to their exposed (001) facets.¹² Herein, we reported a facile solvothermal approach to the synthesis of monodispersed Bi₂O₂CO₃ nanoplates with an average thickness of about 70 nm. The as-synthesized Bi₂O₂CO₃ nanoplates exhibited excellent photocatalytic activity towards the degradation of RhB and refractory phenol under simulated solar light (SSL) irradiation.

Experimental

In a typical synthesis procedure, 0.5 mmol of Bi(NO₃)₃·5H₂O was dissolved into 10 mL of polyethylene glycol (PEG 200). Various amounts of sodium dodecyl benzene sulfonate (SDBS) were dissolved into 25 mL of distilled water. The two solutions were fully mixed under magnetic stirring, and then transferred into a Teflon-lined stainless steel autoclave with 50 mL capacity. The reaction temperature was kept at 180 °C for 20 h, then the autoclave was allowed to cooling down to room temperature naturally. The precipitate was collected and washed with distilled water and ethanol for

several times, and then dried at 60 °C in air.

The obtained product was characterized by X-ray diffraction (XRD, Rigaku D/max 2500 diffractometer with Cu K α radiation), scanning electron microscope (SEM, FEI Quanta 200F), transmission electron microscope (TEM, JEOL JEM-2100), and Fourier transform infrared spectrum (FT-IR, Shimadzu IRAffinity-1). UV-vis diffuse reflectance spectrum of the powder samples was recorded on a Shimadzu UV-2550 spectrometer.

RhB and phenol were selected as model pollutants to evaluate the photocatalytic activity of Bi₂O₂CO₃ nanoplates. The detailed experimental setup could be found in previous work.²⁵ The concentrations of RhB and phenol solutions are 1.0×10^{-5} M and 20 mg/L, respectively. The light source is a 300W Xenon lamp (Beijing Aulight, China).

Results and Discussion

Characterization of Bi₂O₂CO₃ Nanoplates. The phase and purity of the as-synthesized product were determined by XRD, and the results were shown in Figure 1. All the diffraction peaks can be perfectly indexed to the tetragonal Bi₂O₂CO₃ with lattice parameters of $a = b = 3.865$ Å, and $c = 13.675$ Å (JCPDS 41-1488). The strong and narrow diffraction peaks indicate that the as-synthesized product has been well crystallized. Compared with the relative intensity of diffraction lines shown in the standard JCPDS card (low panel in Figure 1), the (004) and (006) diffraction intensities of Bi₂O₂CO₃ nanoplates are high, suggesting that the as-prepared products have a preferred (001) orientation. Fourier transform infrared spectrum (FT-IR) of as-synthesized Bi₂O₂CO₃ nanoplates is shown in Figure 2. The carbonate ions possess four internal vibrations: symmetric stretching mode ν_1 , corresponding anti-symmetric vibration ν_2 , the out-of plane bending mode ν_3 and the in-plane deformation ν_4 .^{26,27} The observed peaks centered at 1067, 846 and 820, 1391 and 1468 and 670 cm⁻¹ are associated with the ν_1 , ν_2 , ν_3 , ν_4 vibration modes of the CO₃²⁻ group, respectively. The

Figure 1. XRD pattern of as-synthesized Bi₂O₂CO₃ product. The low panel shows diffraction lines from standard JCPDS card.

Figure 2. FT-IR spectrum of the as-synthesized Bi₂O₂CO₃ product.

absorption peak centered at 1756 cm⁻¹ is assigned to the ($\nu_1 + \nu_4$) mode of the CO₃²⁻ group. In addition, the broad bands centered at 3442 and 2377 cm⁻¹ are assigned to the stretching vibrations of hydroxyl groups.²⁷ The absorption peak centered at 553 cm⁻¹ is attributed to Bi-O stretching mode.

Figure 3(a) and (b) show typical SEM images of Bi₂O₂CO₃ product at different magnifications. Monodispersed nanoplates with an average width of about 320 nm were obtained by current solvothermal method. The thicknesses of Bi₂O₂CO₃ nanoplates range from 50 to 90 nm, as seen from high-magnification SEM image (Figure 3(b)). TEM image shown in Figure 3(c) display the irregular polygon shapes of the nanoplates. The low aspect ratio of Bi₂O₂CO₃ nanoplates results in a few standing plates during both SEM and TEM observations. Selected-area electron diffraction (SAED) pattern of an individual Bi₂O₂CO₃ nanoplate is presented in the inset of Figure 3(c). Indexing of the electron diffraction pattern also suggests the preferred (001) orientation, namely, exposed (001) facet that endow the nanoplates tend to lie on the holy carbon film during TEM observation. Figure 3(d) is

Figure 3. (a, b) SEM images, (c) TEM image, and (d) HRTEM image of the obtained Bi₂O₂CO₃ nanoplates. Inset in (c) is SAED pattern of an individual Bi₂O₂CO₃ nanoplate.

Figure 4. (a) UV-vis diffuse reflectance spectrum and (b) plot of the $(ah\nu)^{1/2}$ vs. photon energy ($h\nu$) of Bi₂O₂CO₃ nanoplates.

the high-resolution transmission electron microscope (HRTEM) image of Bi₂O₂CO₃ nanoplates, illustrating the single-crystalline nature of the plates. The well-resolved lattice fringe of 0.371 nm can be assigned to the (011) crystallographic plane spacing of Bi₂O₂CO₃.

The optical absorption characteristic of Bi₂O₂CO₃ nanoplates was evaluated by UV-vis diffuse reflectance spectrum (Figure 4(a)), showing the strong absorption at UV region. The band gap of semiconductors can be estimated according to the equation:

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

where n is determined by the characteristics of the transition in a semiconductor. For Bi₂O₂CO₃, n equals to 4 for indirect transition.^{8,23,24,28} From the onset of the absorption edge (Figure 4b), the band gaps can be estimated from the plot of $(ah\nu)^{1/2}$ versus photo energy ($h\nu$). The band gap of Bi₂O₂CO₃ nanoplates is calculated to be about 3.31 eV. The suitable bandgap makes Bi₂O₂CO₃ sample as a potential photocatalyst for the degradation of organic pollutants under solar light irradiation.

Effect of SDBS Amounts on the Formation of Bi₂O₂CO₃ Nanoplates. The anisotropic growth of Bi₂O₂CO₃ nanoplates might be due to the inherent layer structure,⁸ but its

Figure 5. SEM images of Bi₂O₂CO₃ products synthesized with different amounts of SDBS: (a, b) without SDBS; (c, d) 0.2 g; (e, f) 1.0 g.

Figure 6. XRD patterns of Bi₂O₂CO₃ products synthesized with different amounts of SDBS: (a) without SDBS; (b) 0.2 g; (c) 1.0 g.

morphology also lies on the amount of SDBS. To fully understand the effect of SDBS on the formation of the Bi₂O₂CO₃ nanoplates, experiments with different amounts of SDBS were carried out while keeping other reaction conditions identical. Figures 5 and 6 give SEM images and XRD patterns of Bi₂O₂CO₃ products under different SDBS amounts (0, 0.2 and 1 g). The results indicate that SDBS plays a key role in determining the morphology of Bi₂O₂CO₃ product. In the absence of SDBS, flower-like products with diameter of 5–20 μm rather than monodispersed plates were obtained (Figure 5(a)). High-magnification SEM image (Figure 5(b)) of the sample shows that the flower-like product is composed of nanosheets with thickness of 10–30 nm; and the broaden diffraction peaks of XRD pattern also demon-

Figure 7. (a) Temporal evolution of the absorption spectra of RhB solution in the presence of Bi₂O₂CO₃ nanoplates under SSL irradiation. (b) Changes of RhB solution concentration as a function of irradiation time in the presence of Bi₂O₂CO₃ nanoplates and P25-TiO₂. Blank experiment data is presented as a reference.

strate the nano-size of the building-blocks (Figure 6(a)). In the absence of SDBS, Bi₂O₂CO₃ phase will be formed through the reaction between Bi³⁺ ions and CO₃²⁻ anions originates from air. And the formation of plate-like structures should be related to the slow reaction controlled by Bi-PEG200 complex.²⁹⁻³² With a small amount of SDBS (0.2 g), Bi₂O₂CO₃ nanoplates with irregular shapes were obtained (Figure 5(c) and (d)). The corresponding XRD pattern (Figure 6(b)) also presents the relative high diffraction intensity of (004) and (006) facets, indicating a preferred orientation. Further increasing the amount of SDBS (1.0 g) would produce Bi₂O₂CO₃ nanoplates with small size of *c.a.* 200 nm and thickness of *c.a.* 60 nm (Figure 5(e) and (f)). Therefore, introducing a certain amount of SDBS into the reaction system would promote the formation of Bi₂O₂CO₃ nanoplates. It is widely accepted that organic surfactants in solutions serve as the capping agents, chelating agents or soft templates, which play key roles in the synthesis of micro/nanostructures with different shapes and sizes.³²⁻³⁵

Similar to previous studies, SDBS could adsorb on the

surface of Bi₂O₂CO₃ nanoparticles during the growing process, which changes the growth rate of crystal facets and then tailors the crystal shape, resulting in the final formation of nanoplates. The size decreasing of nanoplates is related to the fact that high amounts of SDBS not only adsorb the crystal face but also increase the viscosity of the reaction solutions.³⁵ Higher viscosity will decrease the diffusion leading to the formation of nanoplates with small sizes.

Photocatalytic Performance. It is accepted that 2D nanomaterials possessed excellent photocatalytic performance because of their unique electronic and optical properties. Owing to the band gap and better spectral response of Bi₂O₂CO₃ nanoplates, the sample is used to degrade contaminants under solar light irradiation. Figure 7(a) displays the temporal evolution of absorption spectra of RhB solution in the presence of Bi₂O₂CO₃ nanoplates under SSL irradiation. The characteristic absorption peak of RhB at 553 nm diminishes rapidly within 15 min, suggesting the supervisor photocatalytic activity of Bi₂O₂CO₃ nanoplates as compared with commercial P25-TiO₂ (Figure 7(b)) and previous work.^{8,9}

As for the practical applications in aqueous solution such as waste water purification, the recycling of photocatalysts is

Figure 8. Cyclability of photocatalytic activity of Bi₂O₂CO₃ nanoplates for the degradation of RhB under SSL irradiation.

Figure 9. FT-IR spectrum of Bi₂O₂CO₃ nanoplates after 3 cycles of RhB photocatalytic degradation.

of great significance. The Bi₂O₂CO₃ nanoplates were reused for photodegradation cycle reaction under the same condition, and the results are shown in Figure 8. The efficiency remains the same after 3 cycles. FT-IR spectrum of the cycled sample (Figure 9) is almost the same as that of the pristine nanoplates. These results clearly indicate that Bi₂O₂CO₃ nanoplates are chemically stable as high activity photocatalyst under SSL irradiation.

In view of the practical applications of photocatalysts, a typical refractory organic pollutant, phenol, is selected as another model pollutant to evaluate the potential usage of Bi₂O₂CO₃ nanoplates. As shown in Figure 10(a), the intensity of characteristic absorption peak of phenol at 269 nm decreases gradually with the increase of irradiation time, and the absorbance of phenol decreases by ~100% within 160 min (Figure 10(b)). As a comparison, the degradation ratio of P25-TiO₂ reaches only 40% with identical conditions (Figure 10(b)). This suggests that Bi₂O₂CO₃ nanoplates are rather attractive as a novel photocatalyst towards the degradation of refractory organics.

The superior photocatalytic activity of Bi₂O₂CO₃ nanoplates, as compared with commercial P25-TiO₂, is mainly

attributed to the higher valence band of Bi₂O₂CO₃ structure,^{12,36} namely, 3.31 eV for Bi₂O₂CO₃ vs. 3.2 eV for anatase and 3.0 eV for rutile. The higher band gap means higher oxidation ability of photo-generated holes, which is reasonable that the photocatalytic activity of Bi₂O₂CO₃ is better than that of P25-TiO₂. The other reason is assigned to the exposed (001) facet of Bi₂O₂CO₃ nanoplates, which could supply more oxygen defects to generate electron and vacancy under SSL irradiation.⁸ The nanoscale two-dimensional characteristic also ensures high carrier mobility and large contact area between the photocatalyst and organic pollutants.^{2,6,37,38}

Conclusions

In summary, we have developed a simple solvothermal approach for the synthesis of uniform Bi₂O₂CO₃ nanoplates as a novel photocatalyst. The anisotropic growth of Bi₂O₂CO₃ nanoplates might be due to the inherent layer structure, but suitable amount of SDBS is indispensable for achieving uniform nanoplates. The obtained Bi₂O₂CO₃ nanoplates exhibit high activity towards the photocatalytic degradation of organic pollutants (RhB and phenol) under simulated solar light irradiation, as well as good chemical stability. Thus, the obtained Bi₂O₂CO₃ nanoplates are considered as promising high efficiency photocatalysts for practical applications.

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Figure 10. (a) Temporal evolution of the absorption spectra of phenol solution in the presence of Bi₂O₂CO₃ nanoplates under SSL irradiation. (b) Changes of phenol solution concentration as a function of irradiation time in the presence of Bi₂O₂CO₃ nanoplates and P25-TiO₂. Blank experiment data is presented as a reference.

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