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Preparation of 2D square-like Bi_2S_3-BiOCl heterostructures with enhanced visible light-driven photocatalytic performance for dye pollutant degradation

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Abstract

A series of Bi_2S_3-BiOCl composites with two-dimensional (2D) square-like structures were prepared via a two-step anion exchange route. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and diffuse reflectance spectra (DRS) were used to investigate the properties of the as-prepared Bi_2S_3-BiOCl heterostructures. The coupling of BiOCl and Bi_2S_3 induced enhanced photoabsorption efficiency and bandgap narrowing. A reactive brilliant red X-3B dye was used as a contaminant to test the photocatalytic activity of the obtained Bi_2S_3-BiOCl samples under visible light irradiation. The sample Bi_2S_3-BiOCl with a mass ratio of 8:4 exhibited the highest photodegradation efficiency, which was six times higher than that of pure BiOCl. In addition, a mechanism for the enhancement of photocatalytic activity is proposed.

Keywords: Photocatalysis; Bi_2S_3; BiOCl; Visible light; Heterostructure

1. Introduction

Photocatalytic technology has been developing quickly since Fujishima and Honda (1972) found that titanium dioxide (TiO_2) photoanodes can induce water splitting. The first attempt at application of photocatalytic technology in the field of organic pollutant degradation was the use of TiO_2 for the photodechlorination of polychlorobiphenyls (Carey et al., 1976). Because of their high reaction speed, stability, low toxicity, and many other advantages, semiconductor photocatalysts have attracted much attention over the past several decades. In recent years, photocatalysts such as TiO_2 (Bianchi et al., 2014; Wang et al., 2014), BiOX (X = Cl, Br, I) (Chen et al., 2013; Ao et al., 2016a, 2016b, 2016c; Qin et al., 2013; Zhang et al., 2013b), and Ag/AgX (X = Cl, Br) (Wang et al., 2012, 2013c) have attracted much attention in this field.

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Bismuth oxyhalide BiOCl has a lamellar structure and strong photocorrosion resistance. BiOCl has been put to many uses, such as pigments (Maile et al., 2005), photoluminescence (Deng et al., 2008), and photocatalysis (Shenawi-Khalil et al., 2011). Much progress has been made. Xiong et al. (2011) prepared square-like BiOCl nanosheets through an environmentally friendly hydrothermal process. At room temperature, Ye et al. (2013) synthesized flower-like BiOCl composed of self-assembled hierarchical nanosheets, which performed well in the degradation of Rhodamine B (RhB). However, wide-bandgap BiOCl shows little response to visible light, which accounts for 45% of solar spectra. This means that BiOCl cannot utilize the solar energy efficiently. The fact that it can only be photo-excited under ultraviolet (UV) irradiation has limited its application to removal of organic pollutants. Major efforts have been made to obtain visible light-driven BiOCl-based photocatalysts (Zhang et al., 2013a; Xia et al., 2013; Wang et al., 2013a; Cao et al., 2013).

Narrow-bandgap Bi_2S_3 has been used to modify TiO_2 (Liu et al., 2017), $Bi_2O_2CO_3$ (Wang et al., 2013b), ZnS (Nawaz, 2017), and some other wide-bandgap photocatalysts (Cheng et al., 2012) in order to improve their performance under visible light irradiation. Cao et al. (2012) synthesized a novel Bi_2S_3-sensitized BiOCl photocatalyst with a rose-like structure, which photodegraded 98.0% of RhB within 2 h under visible light irradiation, much more than BiOCl, Bi_2S_3, or TiO_2 alone. This showed that the combination of Bi_2S_3 and BiOCl can turn BiOCl into a promising visible light-driven photocatalyst (Ferreira et al., 2016; Jiang et al., 2014). However, all the studies mentioned above focused on Bi_2S_3-modified three-dimensional (3D) flower-like structured BiOCl, and no study has focused on the preparation and activity of Bi_2S_3-modified two-dimensional (2D) plate-like structured BiOCl. 2D Bi_2S_3-BiOCl would be highly active under visible light irradiation.

2. Experimental setup

2.1. Synthesis

Analytical-grade chemicals have often been used without further purification. In this study, Bi_2S_3-BiOCl composites with different Bi_2S_3 contents were synthesized via a facile two-step anion exchange route at room temperature. First, we prepared white BiOCl nanosheets using the solvothermal method (Xiong et al., 2011). Second, thioacetamide (TAA) was used as the sulfur source to obtain the composites. In the experimental synthesizing of Bi_2S_3-BiOCl composites, 0.26 g of BiOCl nanosheets were added into 25 mL of ultrapure water and sonicated for 10 min to form suspension A. Solution B was obtained after the dissolution of a certain amount of TAA in 25 mL of ultrapure water. Then, solution B was gradually poured into suspension A and stirred for 5 h at room temperature. Finally, the light gray products were obtained; they were washed with deionized water, and dried at 80°C for about 6 h. Four samples were prepared by changing the added amount of TAA. The obtained samples were defined as Bi_2S_3-BiOCl (8:1), Bi_2S_3-BiOCl (8:2), Bi_2S_3-BiOCl (8:4), and Bi_2S_3-BiOCl (8:8), as the added amounts of TAA were 0.009, 0.019, 0.038, and 0.075 g, respectively.

2.2. Characterization

We used X-ray diffraction (XRD) to examine the crystal form and crystallinity of the samples. Field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were utilized to observe the surface morphologies and microstructures of the samples, using a Hitachi S-4800 scanning electron microscope and a Hitachi H-7650 transmission electron microscope, respectively. The absorption ability of catalysts was measured through ultraviolet-visible (UV/Vis) diffuse reflectance spectra (DRS) on a Shimadzu UV3600 spectrometer. The Brunauer-Emmett-Teller (BET) surface area of the samples was obtained with a BET analyzer (ASAP 2020, Micromeritics Instrument Corporation) through N_2 adsorption-desorption isotherms.

2.3. Photocatalytic experiments

The photocatalytic activities of the as-prepared samples were measured through photodegradation of X-3B under visible light ($\lambda \geq 400$ nm, where λ is the wave length) irradiation, a 300 W Xe lamp was used as a light source, and a circulating cooling water system was used to keep the temperature at 12°C. In each experiment, a 0.01-g sample was added to 50 mL of X-3B solution with a concentration of 25 mg/L to form a suspension. In order to reach adsorption-desorption equilibrium, the suspension was ultrasonic-treated for 2 min and further stirred for 30 min in the dark. Under light irradiation, about 1.5 mL of suspension was taken out for examination every 15 min.

3. Results and discussion

The as-prepared Bi_2S_3-BiOCl samples were analyzed through XRD characterization (Fig. 1, where a.u. means arbitrary unit, and 2θ is the diffraction angle) to examine their phase structure, crystal form, and crystallinity. All the diffraction peaks of BiOCl and Bi_2S_3 could be indexed according to the structures of tetragonal BiOCl (JCPDS No. 06-0249) and bulk orthorhombic Bi_2S_3 (JCPDS No. 75-1306), respectively, indicating high crystal purity. No diffraction peaks of Bi_2S_3 were observed in the curves of Bi_2S_3-BiOCl composites. This is probably due to the amorphous structure, high level of dispersity, and small crystallites of Bi_2S_3. The obtained results indicate that the addition of Bi_2S_3 does not cause changes in the crystal phase of BiOCl.

During the preparation process of Bi_2S_3-BiOCl composites, the square-like BiOCl nanosheets with a thickness of 10−25 nm (Fig. 2(a)) were dispersed in the ultrapure water first. Then, through ion exchange, a reaction between Bi^{3+} and TAA occurred over time (the stepwise equations were as follows: $CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S\uparrow$; $2Bi^{3+} + 3H_2S \rightarrow Bi_2S_3\downarrow + 6H^+$). Finally, Bi_2S_3 was dispersed and

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