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Preparation and photocatalytic activity of visible light-sensitive selenium-doped bismuth sulfide

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ABSTRACT

A series of Se-doped Bi_2S_3 photocatalysts are prepared using the hydrothermal method. Selenium is doped into Bi_2S_3 to improve its photocatalytic activity. The obtained products are characterized by X-ray powder diffraction, UV–Vis absorption spectroscopy, X-ray photoemission spectroscopy, and Brunauer–Emmett–Teller surface area analysis. The photocatalytic activities of bare and modified Bi_2S_3 are studied. Se-doped Bi_2S_3 shows high photocatalytic activity during the degradation of methylene blue under visible-light irradiation (λ>400 nm). The effects of different Se contents, synthesis time, temperatures, among others, on photocatalytic activity are discussed. Results show that an appropriate amount of Se dopant can greatly increase photocatalytic activity. Appropriate synthesis times and temperatures are responsible for the obvious increase in photocatalytic activity.

1. Introduction

Over the last few decades, photocatalytic applications of semiconductor materials have attracted great attention. Among the various photocatalytic materials available, metal oxides, such as TiO_2 and ZnO, have been widely investigated and used because they are inexpensive, chemically stable, nontoxic, and possess favorable optoelectronic properties [1–5]. Metal sulfides as photocatalysts have also attracted great interest, and several breakthroughs in their use have been achieved. Many metal sulfides have been reported to have high efficiency in the degradation of organic pollutants under UV irradiation [5–9]. Bismuth sulfide is a typical lamellar-structured semiconductor with a bulk direct bandgap of 1.3 eV. Nanostructures of this material have attracted much attention due to their potential applications in electrochemical hydrogen storage, hydrogen sensors, X-ray computed tomography imaging, biomolecule detection, and as photoresponsive materials. In contrast, however, the photocatalytic properties of Bi_2S_3 have been scarcely reported [10].

In this study, Se-doped nanocrystalline bismuth sulfides are successfully synthesized by a hydrothermal process using Na_2SeSO_3 as the selenium source. Using the photodecomposition of methylene blue (MB) under visible light irradiation as a model, considerable improvements in photocatalytic activity are found for all the Se-doped Bi_2S_3 powders in comparison to P25 and undoped Bi_2S_3 prepared under the same conditions. Characterizations of the structure and chemical states and the doping amount effect of Se-doped Bi_2S_3 are subsequently investigated in detail. Reasons for the improvement of photocatalytic activity are also generally discussed.

2. Experimental

2.1. Chemicals

All chemicals were all of analytical reagent grade quality and used without further purification. Deionized and doubly distilled water were used throughout this study.

2.2. Synthesis of Se-doped Bi_2S_3 photocatalysts

In a typical synthesis, Se-doped Bi_2S_3 was synthesized by a hydrothermal process. A total of 0.01 mol $BiCl_3$ and 0.1 mol $Na_2S{\cdot}9H_2O$ were first dissolved in 40 mL of hydrazine hydrate (N_2H_4, 80 wt.%) to form a clear solution. Then, 0.003 mol Na_2SeSO_3 was added to the above solution under vigorous stirring. After stirring for 15 min, the solution was transferred into a 100 mL autoclave with a Teflon liner. The autoclave was maintained at 180 °C for 12 h and then air-cooled to room temperature. The precipitate was collected and thoroughly washed with deionized water. The as-prepared sample was dried at 80 °C for 3 h in a vacuum oven.

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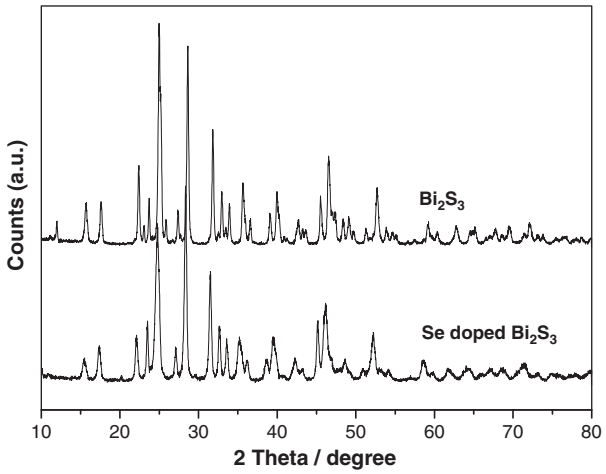

Fig. 1. X-ray diffraction patterns of undoped and Se-doped Bi_2S_3 treated at 180 °C for 12 h (0.003 mol Na_2SeSO_3).

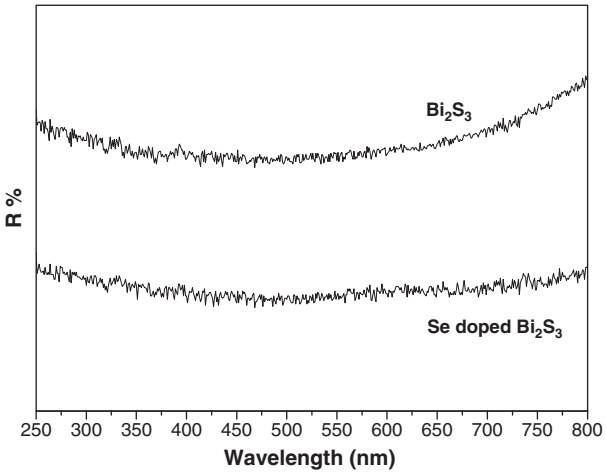

Fig. 2. UV–vis diffuse reflectance spectra of undoped and Se-doped Bi_2S_3 treated at 180 °C for 12 h (0.003 mol Na_2SeSO_3).

2.3. Characterization of Se-doped Bi_2S_3 photocatalysts

The products were characterized by using X-ray diffraction (XRD) recorded on a Rigaku D/max 2500 powder diffractometer equipped with monochromatic high-intensity CuKα radiation (λ = 1.5406 Å). UV/Vis spectra were recorded on a HP8453 spectrophotometer at room temperature. The morphology and size of the as-prepared products were observed by transmission electron microscopy (TEM), using a Hitachi H-7650 transmission electron microscope. The binding energy (BE) of Bi_{4f}, S_{2p} and Se_{3d} was measured by an X-ray photoelectron spectrometer (XPS, Pekin-Elmer PHI5300). In the XPS analysis, the calibration of BE is the standard peak of adventitious carbon (C_{1s}). The BE has been calibrated according to the standard peak of carbon (C_{1s}) in the manuscript. The Brunauer_Emmett–Teller (BET) surface areas (S_{BET}) were measured by N_2 adsorption at −196 °C using an automatic surface area and pore size analyzer (Autosorb-1-MP 1530VP).

2.4. Catalytic activity evaluation

The photocatalytic activity under visible-light irradiation of the Se-doped Bi_2S_3 samples was evaluated by using methylene blue (MB) as the model substrate. In a typical process, 250 mL MB (10 mg/L) aqueous solution and 0.2 g of photocatalyst powder were mixed in a quartz photoreactor. Prior to a photocatalytic reaction, the photocatalyst suspension was sonicated to reach adsorption equilibrium with the photocatalyst in darkness. The above solution was photo-irradiated by using a 300 W Xe lamp (λ>400 nm) as light source under continuous stirring. At a defined time interval, the concentration of MB in the photocatalytic reaction was analyzed by using an UV–vis spectrophotometer at 665 nm.

3. Results and discussion

3.1. Characterization of the Se-doped Bi_2S_3 photocatalysts

The crystalline phases of the undoped and Se-doped Bi_2S_3 were investigated using X-ray diffraction (XRD). The diffraction patterns are depicted in Fig. 1, in which the reflections of both samples were attributed to Bi_2S_3 with an orthorhombic structure (JCPDS Card No. 06-0333). Comparing the diffraction patterns of the undoped and Se-doped Bi_2S_3, we can find that the intensity of the diffraction peaks in Se-doped Bi_2S_3 was lower than that of undoped Bi_2S_3. In addition, it is very clear that all diffraction peaks of the doping sample displaced slightly toward left, which indicating the selenium possibly have doped into the crystal lattice of Bi_2S_3. No reflections of Bi_2Se_3 were found in the XRD patterns, indicating that Se atoms were evenly dispersed in the Bi_2S_3 and did not form any crystalline structures. This can account for the lower diffraction intensity observed in Se-doped Bi_2S_3.

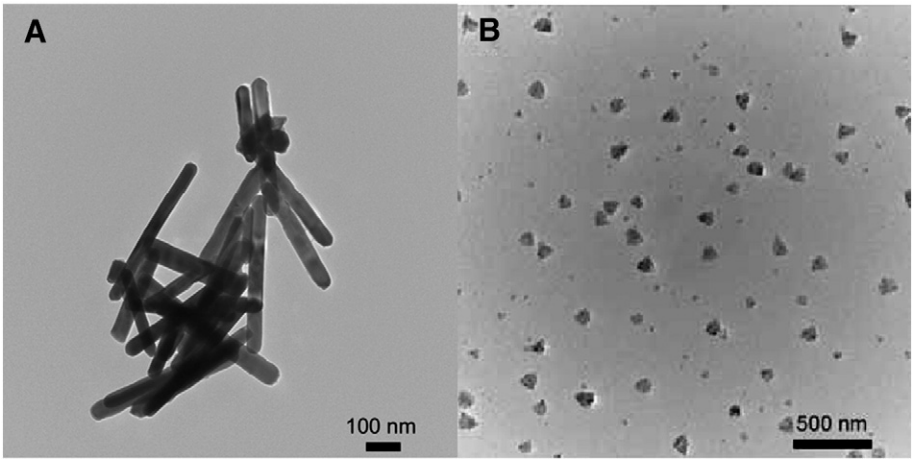

Fig. 3. TEM images of undoped and Se-doped Bi_2S_3 treated at 180 °C for 12 h (0.003 mol Na_2SeSO_3).