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Novel photocatalyst, $Bi_2Sn_2O_7$, for photooxidation of As(III) under visible-light irradiation

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ABSTRACT

Nanocrystalline $Bi_2Sn_2O_7$, a visible-light photocatalyst synthesized via a facile hydrothermal route, is used to remove arsenite from aqueous solution for the first time. The as-synthesized $Bi_2Sn_2O_7$ product is characterized by X-ray diffraction, N_2 sorption–desorption, UV–vis diffuse reflectance spectroscopy, transmission electron microscopy, electron spin resonance, X-ray photoelectron spectra, and electrochemistry technology. The results reveal that the sample has an average particle size of approximately 10 nm, a specific surface area of 51.3 m^2/g, and a band gap of 2.88 eV. Moreover, the $Bi_2Sn_2O_7$ nanoparticles exhibit a high photocatalytic activity in the oxidation of As(III) (up to 96.8%) under visible-light irradiation. $^{\bullet}O_2^-$ and h^+ are recognized as the primary active species responsible for As(III) oxidation. Meanwhile, a possible mechanism for the photo-oxidation of As(III) over $Bi_2Sn_2O_7$ is also proposed.

1. Introduction

Arsenic contamination in natural water is posing a great threat to millions of people in many regions of the world [1]. Being a widely distributed element in nature, arsenic can be mobilized into groundwater from soils and ores through both natural process and anthropogenic activities [2,3]. Chronic arsenic poisoning can cause a lot of human health problems through contaminated drinking and agricultural irrigation water. In natural water, most arsenic pollution exists mainly as the As(III) and As(V) oxyanions, arsenite $(AsO_2)^-$ and arsenate $(AsO_4)^{3-}$. In comparison with arsenate, arsenite is much more toxic and mobile in natural waters, and less efficiently removed in adsorption/coagulation processes [4–6]. Therefore, the oxidation of As(III) to As(V) is highly desirable for enhancing the immobilization of arsenic and is required for most arsenic removal technologies [7–9]. Ever since the first report by Rajeshwar in 1999 [8], many efforts have been made on the photocatalytic oxidation of As(III) with TiO_2 under UV light illumination [5,10–14]. However, TiO_2 is active only under UV irradiation ($\lambda < 387$ nm) because of its wide band gap (~3.2 eV), which hinders its further application in the visible light region ($\lambda > 400$ nm).

To improve the efficiency of utilizing solar energy, considerable attentions have been focus on designing the visible-light-driven photocatalysts. TiO_2-based photocatalysts that are sensitive to visible-light have been widely investigated by various strategies, such as doping with metal or non-metal impurities [15–17], coupling with narrow band-gap semiconductors [18] and so on. Nevertheless, through exploitation of new materials, some non-titania-based catalysts have also been synthesized; for example, $BiVO_4$ [19], $Bi_2Si_2O_5$ [20] and some sulfides [21,22] have been found to possess visible-light-driven photocatalytic activity. As a kind of pyrochlore-type stannate, $Bi_2Sn_2O_7$ has received considerable attention due to its wide applications in catalysis and gas sensors [23,24]. The crystal structure of $Bi_2Sn_2O_7$ is constructed of octahedral SnO_6, and these octahedra connect to each other by sharing vertexes. A network of corner-shared octahedra can facilitate the mobility of the charged carriers [25], which may make $Bi_2Sn_2O_7$ a novel material for photocatalysis [26].

In this paper, the nanocrystalline $Bi_2Sn_2O_7$, which synthesized through a facile hydrothermal route, is used for photocatalytic removal of arsenic from aqueous solution. Under visible light irradiation, the $Bi_2Sn_2O_7$ nanoparticles exhibit high photocatalytic activity in the oxidization of arsenite $(AsO_3)^{3-}$ to arsenate $(AsO_4)^{3-}$. The role of the active species during the photocatalytic oxidation of As(III) is also investigated in detail. It is expected that the as-synthesized $Bi_2Sn_2O_7$ nanocrystallite can be used as a promising visible-light photocatalyst for the oxidation and removal of As(III).

2. Experimental

2.1. Catalyst preparation

$Bi(NO_3)_3{\cdot}5H_2O$ and $K_2SnO_3{\cdot}3H_2O$ were used as the starting materials for the syntheses. All reagents are A.R. grade and

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used without further purification. In a typical synthesis, 1.84 g of $Bi(NO_3)_3{\cdot}5H_2O$ (2.5 mmol) and 0.75 g of $K_2SnO_3{\cdot}3H_2O$ (2.5 mmol) were added into 75 mL of deioned water. Under vigorous stirring, the pH value of the mixture was adjusted to 12 by using 2 mol/L KOH and 2 mol/L HCl solution. After stirring for 30 min at room temperature, the mixture was transferred into a Teflon-lined autoclave with a capacity of 100 mL. Then, the autoclave was sealed, heated under autogenous pressure at 180 °C for 24 h, and then cooled down to room temperature naturally. The solid products were isolated by a centrifuge, washed with deionized water and absolute ethanol several times until the total dissolved solid (TDS) value of the supernatant solution is below 10 ppm (measured by a TDS analyzer, HI-98301). Then, the products were dried at 60 °C for further characterization. A series of experiments with varying pH values and hydrothermal temperatures were also carried out to optimize the synthesis condition.

2.2. Photocatalyst characterizations

The as-prepared samples were characterized by powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA with Ni-filtered Cu Kα radiation. Data were recorded at a scan step width of 0.02° in the 2θ range of 10–70°. A nitrogen sorption–desorption experiment was carried out at 77 K using an ASAP2020 surface area and porosity analyzer (Micrometrics Instrument). The morphology was further investigated by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) on a JEOL JEM 2010F microscope working at 200 kV. UV–vis diffuse reflectance spectra (UV–vis DRS) of the dry-pressed disk samples were obtained with a UV–visible spectrophotometer (Cary 500 scan spectrophotometers, Varian, USA) using $BaSO_4$ as a reflectance standard. X-ray photoelectron spectroscopy (XPS) analysis was conducted on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 1.2×10^{-9} mbar using an Al KR X-ray beam (1486.6 eV). A conventional three electrode cells using a ZENNIUM electrochemical workstation (Zahner, Germany) was used to determine the flat-band potential (V_{fb}) of the sample. The catalyst sample was deposited on a 1 cm × 1 cm ITO conducting glass served as working electrode, while the Ag/AgCl electrode as the reference electrode and Pt as the counter electrode. The Mott–Schottky plot to evaluate the V_{fb} of the semiconductor space charge region was obtained by measuring impedance spectra at fixed frequency of 1 kHz. Electron spin resonance (ESR) spectra were obtained using Bruker model ESR 300E electron paramagnetic resonance spectrometer equipped with a quanta-Ray Nd:YAG laser system as the irradiation light source. The settings were center field, 3480.00 G; microwave frequency, 9.79 GHz; and power, 5.05 mW.

2.3. As(III) removal experiments

Stock solution (1 g/L) of arsenite [As(III)] was prepared by dissolving 1.734 g of $NaAsO_2$ into 1 L 20% HCl solution. The reaction solutions (2 mg/L AsO_2^-) used for the As(III) removal experiments were made by diluting the stock solution and adjusting the pH value to the neutral state (~7.0) using 1 mol/L NaOH. In a typical As(III) removal experiment, 0.08 g of $Bi_2Sn_2O_7$ was suspended in a 100 mL Pyrex glass vessel which contained 80 mL dilute arsenic solution. The light source was a 300 W halogen lamp (Philips Electronics), which was placed in a cylindrical glass vessel. Two filters were used to cut off the light below 420 nm and above 850 nm to make sure the photoreaction went on under the visible light irradiation. During the experiment, the arsenic solution was stirred magnetically to ensure a good contact of $Bi_2Sn_2O_7$ with the arsenic species.

To examine both the dark adsorption capability and the visible-light photoactivity of $Bi_2Sn_2O_7$, the As(III) removal experiments were conducted with and without the visible light illumination, respectively. For comparison, As(III) solution was also illuminated just by visible light. At the given irradiation time intervals, 1 mL of the suspension was collected, and then centrifuged to remove the photocatalyst. After recovering the photocatalyst by centrifugation, the pH value of the arsenic solution were adjusted to 4 through the dripping of concentrated HCl. Atomic fluorescence spectrometry (PF6, Beijing purkinje general instrument Co., Ltd.) was used to analyze the As(III) content in the reaction solution. And the used photocatalyst was analyzed by XPS to indicate the chemical states of As after the photocatalytic reaction.

3. Results and discussion

3.1. XRD analyses and BET surface areas of the $Bi_2Sn_2O_7$ products

It is well known that the temperature and the pH value play important roles in controlling the crystal phases and sizes of the final products in the hydrothermal process. The XRD patterns of the resultant products through the hydrothermal process at 180 °C for 24 h under different pH values are shown in Fig. 1. For the pH $\geq$ 12, all the diffraction peaks could be readily indexed to a pure cubic phase of $Bi_2Sn_2O_7$ (JCPDS No. 88-0496). However, when the pH value decreases to 10 (curve c), some extra peaks of the tetragonal SnO_2 (JCPDS No. 72-1147) can be found. Further decreasing the pH value to 6, the resultant product turns out to be SnO_2 (curve a). Moreover, the temperature dependence of the resultant products is also investigated when the pH value is fixed at 12. It is found that the $Bi_2Sn_2O_7$ can only be synthesized when the temperature was higher than 180 °C (data no shown here). In this study, therefore, the optimum hydrothermal temperature and pH value are 180 °C and 12, respectively. Furthermore, as shown by curve d, the broadened diffraction peaks of the as-synthesized $Bi_2Sn_2O_7$ indicate a primary crystallite size of approximate 10 nm, calculated from Debye–Scherrer equation based on the main diffraction peak (2 2 2). In addition, BET specific surface area and average pore size of this yellow $Bi_2Sn_2O_7$ powder are found to be 51.3 m^2/g and 12.9 nm, respectively.

3.2. Morphologies of the $Bi_2Sn_2O_7$ products

TEM micrographs reveal that products of $Bi_2Sn_2O_7$ prepared at 180 °C, pH 12, and 24 h of holding time, consist of a large quantity of

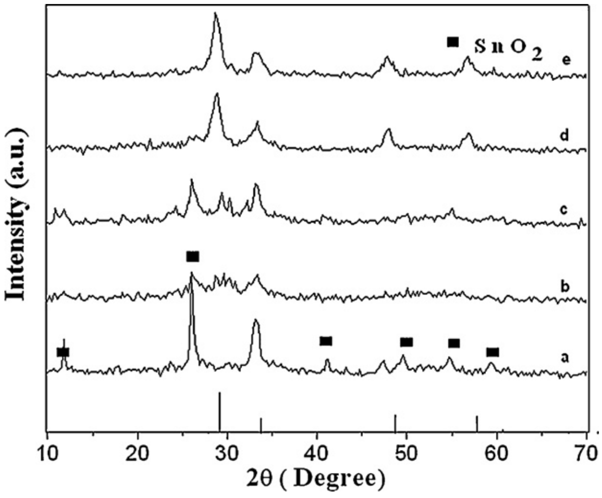

Fig. 1. XRD patterns of the $Bi_2Sn_2O_7$ samples prepared at 180 °C for 24 h with different pH values: (a) 6, (b) 8, (c) 10, (d) 12, and (e) 14.