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Single-crystalline $Bi_5O_7NO_3$ nanofibers: Hydrothermal synthesis, characterization, growth mechanism, and photocatalytic properties

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ABSTRACT

A new photocatalyst, namely single-crystalline $Bi_5O_7NO_3$ nanofibers, was prepared by a facile hydrothermal method in the presence of Triton X-100 and ammonia. $Bi_5O_7NO_3$ possessing a crystalline sheet morphology could be dissolved and transformed into nanofibers by controlling the reaction time. Samples were characterized by X-ray diffraction, UV–vis diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and high resolution transmission electron microscopy. The $Bi_5O_7NO_3$ nanofiber growth mechanism is discussed in detail. The band gap energy of the as-prepared $Bi_5O_7NO_3$ photocatalyst was about 2.70–2.90 eV. Results of first-principle density functional theory calculations confirmed that $Bi_5O_7NO_3$ had a narrow band gap. They revealed that the conduction band bottom was predominantly composed of Bi 6s, Bi 6p, N 2p and O 2p orbitals, while the valence band (VB) top primarily consisted of Bi 6p, Bi 6s and O 2p orbitals. The as-obtained $Bi_5O_7NO_3$ nanofibers showed good photocatalytic activity and stability for the degradation of Rhodamine B (RhB) under visible light irradiation, which may be ascribed to the highly mobile conduction band (CB) and VB charge carriers.

1. Introduction

In recent years, the design and preparation of novel nano- and microstructured one-dimensional (1D) materials (e.g. tubes, fibers, rods, and whiskers) has attracted much attention because of their unique electronic, optical, and catalytic properties [1–3]. Among these materials, nanofibers have received special consideration due to their high surface-to-volume ratios [4–6]. Nanofibers have been obtained by various methods such as hydrothermal [6], electrospinning [5,7] and sol–gel procedures [8]. The hydrothermal method has been referred to as an environmentally friendly aqueous process [9], and has aroused interest due to the high degree of crystallinity and purity of the resulting product, the ease of which sample shape and size may be controlled, and finally the mild reaction conditions involved [6,9,10]. Triton X-100 is a surfactant which can facilitate the formation of 1D materials. Nanofibers [11,12] and nanorods [13] have been successfully prepared with the aid of Triton X-100.

Bismuth-based photocatalysts (e.g. BiOCl [14], Bi_3TaO_7 [15], Bi_2MoO_6 [16,17], Bi_2WO_6 [18], $BiVO_4$ [19], BiOX (X = F, Cl, Br, I) [20], $Na_{0.5}Bi_{1.5}O_2Cl$ [21] and Bi_5O_7I [22]) have received recent interest due to their high chemical stabilities and visible-light photocatalytic activities, both of which have been ascribed to their unique layered structures. Bismuth oxyhalides all have unique layered structures characterized by $[Bi_2O_2]$ slabs interleaved by slabs of inorganic atoms [20,21].

Kodama [23] synthesized $Bi_5O_7NO_3$ as an intermediate product by thermal decomposition. To date, there are no reports on the preparation of pure $Bi_5O_7NO_3$ nanofibers and their photocatalytic activity.

In the present work, we have synthesized $Bi_5O_7NO_3$ nanofibers by a facile hydrothermal method in the presence of Triton X-100 and ammonia. The influence of reaction conditions on the formation of the $Bi_5O_7NO_3$ nanofibers was systematically investigated, and the obtained nanofibers showed excellent visible-light photocatalytic activity. Furthermore, we have demonstrated a relationship between the electronic structure and photocatalytic activity of the $Bi_5O_7NO_3$ photocatalyst using density functional theory calculations.

2. Materials and methods

2.1. Preparation

$Bi(NO_3)_3{\cdot}5H_2O$, ammonia ($NH_3{\cdot}H_2O$, 25%), NaOH, Triton X-100, terephthalic acid (TA) and 1,4-benzoquinone ($C_6H_4O_2$, BQ) were all of analytical grade and were used without further purification. In a typical process, 1 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was added to 70 mL

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of distilled water, with magnetic stirring used to form a homogeneous solution. A white precipitate appeared immediately after adjusting the pH to 12 using $NH_3{\cdot}H_2O$, and 0.5 mL of Triton X-100 was then added. The reaction mixture was sealed in a 100 mL Teflon-lined stainless steel autoclave, kept at 180 °C for 24 h and then cooled to room temperature. The product was then collected, washed and dried at 60 °C. For comparison, the nanosized Bi_3TaO_7 catalyst was prepared by according to our previous study [15].

2.2. Characterization

The structure and phase composition of samples were analyzed using powder X-ray diffraction (XRD) on a D/MAX-RB powder X-ray diffractometer with Cu Kα radiation. The accelerating voltage and applied current were 40 kV and 80 mA, respectively. Scanning electron microscopy (SEM, JSM-5610LV) and field emission scanning electronic microscopy (FESEM, S-4800) were used to characterize the product morphologies. Morphologies and microstructures were further examined with transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) imaging using a JEM 2100F electron microscope with a 200 kV accelerating voltage. Samples for TEM and selected area electron diffraction (SEAD) analyses were dispersed in ethanol by ultrasonication. UV–vis diffuse reflectance spectra (DRS) were measured using a Shimadzu UV-2550 UV–vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out using an ESCALAB II XPS system with a monochromatic Mg Kα source and a charge neutralizer. Binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon.

2.3. Electronic structure calculation

First-principle calculations were carried out using CASTEP software within the generalized gradient approximation (GGA-PBE). The k-point meshes for Brillouin zone sampling were constructed using the Monkhorst–Pack scheme (k-point = 2 × 1 × 4). A plane wave cutoff energy of 340 eV was used.

2.4. Photochemical experiments

The photocatalytic activity of the $Bi_5O_7NO_3$ nanofibers was evaluated by the degradation of Rhodamine B (RhB) solution under visible light irradiation (300 W Dy lamp with a 420 nm cutoff filter), and the reaction temperature was held constant at 25 °C. Reaction solutions were prepared by adding 0.075 g of the nanofibers to a 50 mL RhB solution (5 mg/L). Solutions were magnetically stirred in the dark for 5 min to disperse the catalyst. After various irradiation times, 5 mL aliquots were collected and centrifuged to remove the photocatalyst particles. The concentration of the RhB aqueous solution was determined by its absorbance at 553 nm using a UV–vis spectrophotometer (Unico UV-2102PC, Shimadzu). The total organic carbon (TOC) was measured via a multi N/C 2100 TOC analyzer (Analytic Jena AG). The photocatalytic stability of the $Bi_5O_7NO_3$ nanofibers was evaluated by recycling and reusing the catalyst three times for the degradation of RhB under the same conditions. For comparison, the Bi_3TaO_7 catalyst was used to degrade RhB under the same conditions.

3. Results and discussion

3.1. Formation mechanism of $Bi_5O_7NO_3$ nanofibers

The XRD pattern of the precursor white precipitate prior to hydrothermal reaction is shown in Fig. 1a. Diffraction peaks could be indexed to JCPDS 76-2478 (Bi_2O_3) and JCPDS 01-0898 ($Bi(OH)_3$), and revealed that the precursor was a mixture of Bi_2O_3 and $Bi(OH)_3$.

To understand the role of ammonia, the solution pH was adjusted to 12 using NaOH instead of $NH_3{\cdot}H_2O$, with the $Bi_5O_7NO_3$ nanofibers then prepared according to the procedure described above. Fig. 1b shows that the product obtained via use of NaOH was impure. The formation of pure $Bi_5O_7NO_3$ nanofibers was ascribed to the presence of ammonia which acted as a nitrogen source for the synthesis of $Bi_5O_7NO_3$.

Reaction temperature also had an important effect on $Bi_5O_7NO_3$ formation. Fig. 2 shows XRD patterns for samples prepared at different reaction temperatures. Pure $Bi_5O_7NO_3$ was obtained at temperatures above 160 °C. Diffraction peaks of the product broadened upon increasing the reaction temperature from 160 °C to 180 °C, and then sharpened upon further increasing to 200 °C. The

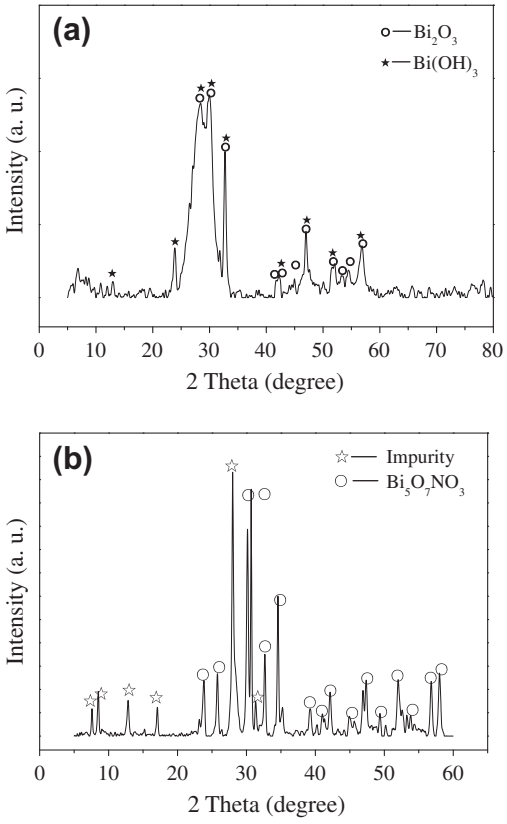

Fig. 1. XRD patterns of (a) the precursor white precipitate, and (b) the hydrothermal product using NaOH instead of $NH_3{\cdot}H_2O$.

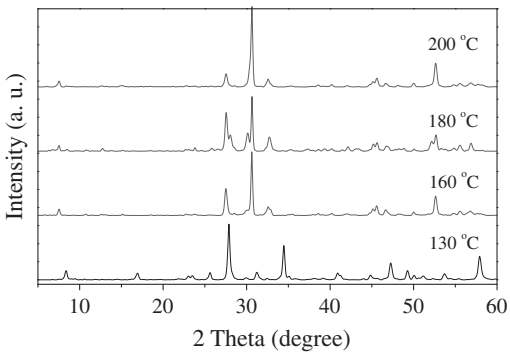

Fig. 2. XRD patterns of samples obtained under typical reaction conditions at different temperatures: (a) 130 °C; (b) 160 °C; (c) 180 °C and (d) 200 °C.