

Bismuth Sulfide (Bi_2S_3) Nanorods as Efficient Photodetection Materials

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Abstract. We reported a simple oleylamine-mediated method for preparation of Bi_2S_3 nanorod materials using BiCl_3 and thiourea as reaction precursors. The as-obtained products were characterized by powder X-ray diffraction (XRD), X-ray energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). A photodetection device, which was based on a white light source of xenon lamp and a two-probe method using an electrochemical station, was constructed to evaluate the light responsive property of Bi_2S_3 nanorods. Measurements on current–voltage (I–V) curves and time-dependent photocurrent response under the white-light on–off states indicated that the as-fabricated Bi_2S_3 nanorod photodetector showed clearly enhanced photo-current (photo-conductance), stability and response reproducibility, enabling Bi_2S_3 nanorods to be a promising material for photodetection, optical switch and other photoelectric devices.

Introduction

As one of semiconducting A_2B_3 chalcogenides ($\text{A}=\text{Sb, Bi, As}$, and $\text{B}=\text{S, Se, Te}$), bismuth sulfide (Bi_2S_3) has a bulk narrow direct bandgap of ~ 1.3 eV (953 nm) and large optical absorption coefficient [1]. In recent years, nanosized Bi_2S_3 of various morphologies and sizes has been used as promising materials in photovoltaics (solar cell) [2], photodetection [3-5], photocatalysis [6], photothermal conversion [7], thermoelectrics [8], and so on. In particular, much attention is being paid on one-dimensional (1D) rod-like Bi_2S_3 nanomaterials and their optical and photoelectronic performance. For instance, a variety of preparation methods were explored to obtain Bi_2S_3 nanorods, such as solvothermal or hydrothermal routes [4,9], microwave irradiation [10], colloidal synthesis [2,3,11], and thermalysis of single-source precursors [12]. Meanwhile, it is found that Bi_2S_3 nanomaterials, such as nanorods, nanobelts and nanoflowers, display superior photo-responsibility to visible and near-infrared light and thus have been used in many photoelectric devices, such as photodetectors and optical switches [3-5,13-16].

Herein, a facile oleylamine-mediated method is reported to prepare Bi_2S_3 nanorod materials using BiCl_3 and thiourea as reaction precursors. The crystal phase, the particle size and shape, the chemical composition and the purity of the Bi_2S_3 products were characterized by means of the powder X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and X-ray energy dispersive spectroscopy (EDS). Importantly, the photoresponsive properties of as-obtained Bi_2S_3 nanorods were evaluated by fabricating a photodetection device based on a white light source of xenon lamp and a two-probe method using an electrochemical station. The results of current–voltage (I–V) measurements show that the Bi_2S_3 nanorod photodetector has obviously enhanced photo-current when exposed to white light (400–780 nm), indicating that the as-prepared Bi_2S_3 nanorods are a promising light-active material for photodetectors and optical switch devices.

Experimental Section

Materials preparation. Bismuth chloride (AR), thiourea (AR), oleylamine (OLA, 80–90%, technical grade) and dodecylamine ($n\text{-C}_{12}\text{H}_{25}\text{NH}_2$, 98%) were purchased from Aladdin chemistry Co. Ltd. All chemicals were used as received without further treatments. In a typical procedure, 1 mmol BiCl_3 (0.315 g), 8 mL of OLA and 2 g of dodecylamine were loaded into a two-neck flask. It was heated to 120 °C in a flux reaction under stirring and was kept at this temperature for 25 min. Then, 2 mmol of thiourea (0.152 g) as a sulphur source was added into the flask and the temperature was increased to 180 °C. The reaction was maintained at 180 °C for 1–2 h and naturally cooled to room temperature. The products were precipitated by centrifuging at 8000 rpm, washed with dichloromethane and ethanol 3–4 times, and dried at 50 °C for further characterization.

Structural and property characterization. The crystal phase and purity of the samples was examined by powder X-ray diffraction (XRD) on a D8 Advance diffractometer with graphite-monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$, Bruker-AXS). The analysis softwares of MDI Jade 5.0 and Pcpdftwin 2.3 were used to index the XRD data. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were conducted on a JEM-2100 electron microscope operated at an accelerating voltage of 200 kV. Energy-dispersive X-ray spectroscopy (EDS) was carried out using a GENESIS system (EDAX Inc.), attached to the JEM-2100 microscope. A photodetection device is fabricated to measure the photoresponse properties of as-obtained Bi_2S_3 nanorods. In detail, a concentrated n-hexane solution of Bi_2S_3 nanorods was drop-cast on a glass substrate and two adjacent ITO films severed as conductive electrodes [5,14]. A xenon lamp equipped with a cutoff filter of 400 nm is used as a white light source with an output wavelength range of 400–780 nm. Current–voltage (I–V) characteristics under light and in dark were recorded with a two-probe method using an electrochemical station (CHI660e).

Results and Discussion

The crystal structure and purity of Bi_2S_3 product was characterized by XRD and a typical XRD pattern is shown in Figure 1a. All of the diffraction peaks can be well assignable to the orthorhombic phase Bi_2S_3 with a space group P_{bnm} (JCPDS file No. 17-0320, lattice constants: $a = 11.14 \text{ \AA}$, $b = 11.30 \text{ \AA}$ and $c = 3.981 \text{ \AA}$). No characteristic peaks from impurities were detected. The purity and chemical composition of Bi_2S_3 product were further identified by means of energy-dispersive X-ray spectroscopy (EDS). As shown in Figure 1b, only Cu, C, Bi and S element signals were detected. Cu and C originate from carbon-coated Cu TEM grid used for TEM measurement. Therefore, the EDS spectrum confirms that the sample is only composed of Bi and S. The molar ratio of Bi to S is measured by EDS to be approximately 2:3 (Bi: 37.80%, S: 62.20%), in good match with stoichiometric Bi_2S_3 .

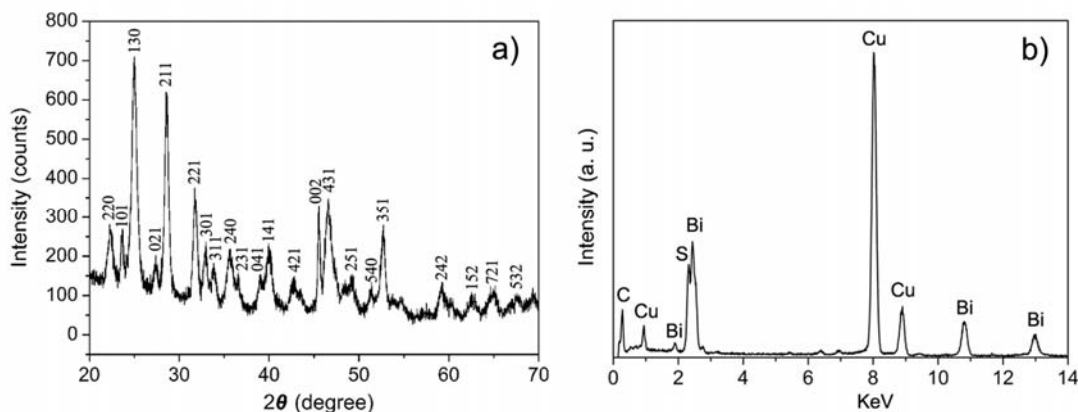


Figure 1. XRD pattern (a) and EDS spectrum (b) of as-prepared Bi_2S_3 nanorods

Figures 2a,b show the TEM images of as-prepared Bi_2S_3 product. A rod-like morphology is measured for the Bi_2S_3 product. It is observed that the length of these nanorods has a large distribution while their diameter has a narrow distribution. The mean diameter of the Bi_2S_3 nanorods

is measured to be ~ 11 nm. More work is needed to achieve Bi_2S_3 nanorods of uniform length and diameter. HRTEM examination (Figure 2c) shows the high crystallinity and single crystal nature of Bi_2S_3 nanorods. In the HRTEM image, the lattice fringes are clearly observed, and their d -spacings are measured to be 0.396 and 0.352 nm with an angle of 90° , corresponding to the spacing of the $\{001\}$ and $\{310\}$ crystal planes of orthorhombic phase Bi_2S_3 , respectively. Also, it can be observed that these nanorods grow along the $[001]$ direction, which is consistent with previous reports for 1D Bi_2S_3 nanostructures [4,5,12].

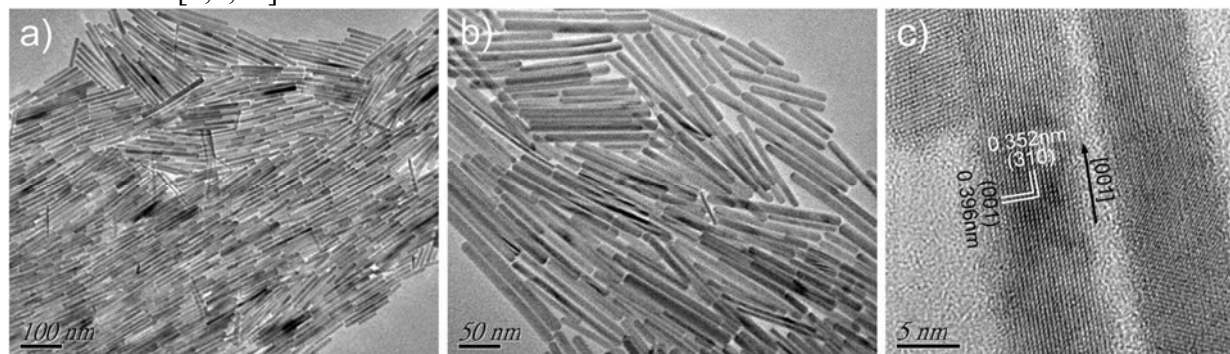


Figure 2. TEM and HRTEM images of Bi_2S_3 nanorods

As is known, Bi_2S_3 has a bulk narrow direct bandgap of ~ 1.3 eV (953 nm) and large optical absorption coefficient [1]. Thus, Bi_2S_3 nanomaterials would possess good light harvesting capability and light-induced electron transport (photoconductive) property [14]. We fabricated a simple light detection device (photodetector) based on the as-prepared Bi_2S_3 nanorods to examine their photoconductive property and photo-response reproducibility. A schematic diagram of the photodetector is shown in Figure 3a, in which the concentrated n-hexane solution of Bi_2S_3 nanorods was drop-cast on a glass substrate and two adjacent ITO films severed as conductive electrodes [5,14]. A xenon lamp is used as a white light source with an output wavelength range of 400–780 nm.

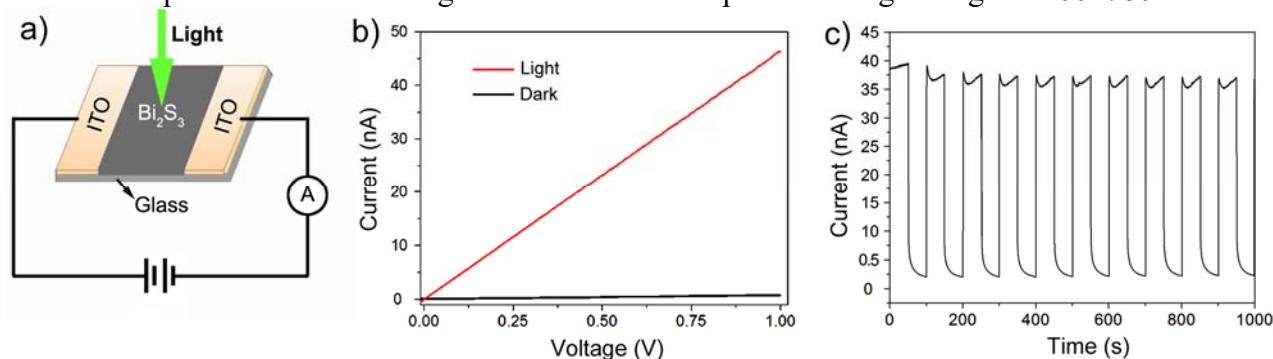


Figure 3. (a) Schematic diagram, (b) Current–voltage (I – V) curves, and (c) Time-dependent response of photocurrent under the on–off states of white light for the Bi_2S_3 nanorod photodetector

The current–voltage (I – V) curves of the photodetector in dark and under illumination of white light were recorded and shown in Figure 3b. In dark, a very weak conductance is observed for the Bi_2S_3 nanorod photodetector. As compared, an obvious increase in photoexcited current was detected upon exposure to the light irradiation. In this experiment, the photon energy of the light is higher than the band gap of Bi_2S_3 (~ 1.3 eV, 953 nm), so the light irradiation excites the electrons from the valence band into conduction band, and increase the charge carrier concentration via direct electron-hole pair generation in Bi_2S_3 nanorod photodetector [16]. Meanwhile, we evaluated the photo-stability and photoresponse reproducibility of photodetector, which are two key factors for high-performance photoelectronic devices. Figure 3c illustrates the time-dependent photocurrent of Bi_2S_3 nanorod photodetector measured at the bias of 1 V when the light source was switched on and off. The on–off responsive cycles can be repeated many times, thereby demonstrating the excellent stability and reproducible capability of the current photodetector [13–16]. In addition, it is found that the photocurrent quickly reaches steady state of maximum value upon light illumination and quickly

returns to normal state under light-off, indicating the fast response characteristic of Bi₂S₃ nanorod photodetector to the light.

Summary

Bi₂S₃ nanorods were prepared via an oleylamine-mediated method, and were characterized by XRD, TEM, HRTEM and EDS. The photoconductive property, photo-stability and response reproducibility of as-prepared Bi₂S₃ nanorods were examined through fabricating a simple photodetector, indicating that Bi₂S₃ nanorods would be an excellent photoresponding materials for photodetectors (or sensors), optical switch and other photoelectric devices.

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