Research Article

Hydrothermal Synthesis of Sb$_2$S$_3$ Nanorods Using Iodine via Redox Mechanism

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Crystalline antimony sulfide (Sb$_2$S$_3$) with nanorods morphology was successfully prepared via hydrothermal method by the reaction of elemental sulfur, antimony, and iodine as starting materials with high yield at 180°C for 24 h. Using oxidation reagent like iodine as an initiator of redox reaction to prepare Sb$_2$S$_3$ is reported for first time. The powder X-ray diffraction pattern shows the Sb$_2$S$_3$ crystals belong to the orthorhombic phase with calculated lattice parameters, $a = 1.120$ nm, $b = 1.128$ nm, and $c = 0.383$ nm. The quantification of energy-dispersive X-ray spectrometry analysis peaks gives an atomic ratio of 2 : 3 for Sb : S. TEM and SEM studies reveal the appearance of the as-prepared Sb$_2$S$_3$ is rodlike which is composed of nanorods with the typical width of 50–140 nm and length of up to 4 μm. The PL emission indicates that band gap of Sb$_2$S$_3$ is around 2.50 eV, indicating a considerable blue shift relative to the bulk. A formation mechanism of Sb$_2$S$_3$ nanostructure is proposed.

1. Introduction

Antimony sulfide, a layer-structured direct-band-gap semiconductor with orthorhombic crystal structure, is an important semiconductor with high photosensitivity and high thermoelectric power [1]. In the past few years, main-group metal chalcogenides such as A$_2$B$_3$ (where A = As, Sb, Bi and B = S, Se, Te) as significant semiconductors have received ever-increasing attention. Due to its good photoconductivity, Sb$_2$S$_3$ has received significant attention for potential application in solar energy conversion [2]. It has also been used in switching devices [3], thermoelectric cooling technologies, optoelectronics in the IR region [4, 5], microwave devices [6], and television cameras [7]. Sb$_2$S$_3$ exists in two forms: orange amorphous phase and black orthorhombic modification with a ribbon-like polymeric structure along the [001] direction as building blocks [8]. Each Sb atom and each S atom are bonded to three atoms of the opposite kind within the ribbon-like polymeric structure, forming interlocking Sb$_3$ and SSb$_3$ pyramids. Consequently, amorphous Sb$_2$S$_3$ tends to crystallize into one-dimensional shape to support the stronger intrachain covalent bonds over the relatively weak secondary interchain interaction, during the period of crystallization and lattice arrangement, as what is found in chain-structured trigonal selenium [9]. Over the past two decades, many methods have been employed to prepare Sb$_2$S$_3$ including thermal decomposition [10], solvothermal reaction [11, 12], microwave irritation [13], vacuum evaporation [2], and other chemical reaction approaches. Besides an elemental reaction, Sb$_2$S$_3$ can be prepared by chemical routes, such as sodium thiosulfate and thiocetamide, ammonium sulfide, and thiourea, as well as with complex agents in aqueous or nonaqueous solution. Li et al. [14] have reported a hydrothermal growth of Sb$_2$S$_3$ nanorods without the existence of catalysts or templates. In recent years, the solvothermal method has been applied to synthesize Sb$_2$S$_3$
nanoparticles, nanorods, and microtubular \( \text{Sb}_2\text{S}_3 \) crystals. Polygonal bulk tubular \( \text{Sb}_2\text{E}_3 \) (\( \text{E} = \text{S, Se} \)) crystals and stibnite nanorods were prepared via the solvothermal route by Zheng et al. [15] and Qian et al. [16], respectively. However, in these methods, the reaction temperature was usually high and the products were usually impure. Therefore, the development of facile, mild, and effective methods for creating novel architectures based on nanorods/submicrometer-sized rods or nanoparticles still remains a great challenge. Recently, there has been a strong trend towards the application of solution chemical synthesis techniques to materials preparation, in which the particle size and distribution, phase homogeneity, and morphology of materials could be well controlled [17]. In this study, \( \text{Sb}_2\text{S}_3 \) nanorods were prepared via hydrothermal method by using antimony, sulfur, and iodine in elemental form as raw materials. This is a new route for the preparation of \( \text{Sb}_2\text{S}_3 \) nanomaterials. Elemental iodine is an oxidizing irritant and acts as an initiator material in the reaction of elemental antimony and sulfur. Without iodine, no reaction is occurred. Using oxidation reagent like iodine as an initiator of redox reaction to prepare \( \text{Sb}_2\text{S}_3 \) is reported for the first time.

2. Experimental

All the reagents were of analytical grade and were used without further purification. In a typical procedure, 2 mmol \( \text{Sb}, 3 \text{ mmol S}, \) and 1 mmol \( \text{I}_2 \) were added to 50 mL distilled water and stirred well for 20 min at room temperature. Then, the mixture was transferred into a 100 mL Teflon-lined autoclave. The autoclave was sealed, maintained at 180 °C for 24 h, and cooled at room temperature, naturally. The black precipitate was filtered and washed with dilute chloride acid and water. Yields for the products were 95%. Finally, the obtained sample was dried at room temperature and used for characterization. The best conditions for this reaction are pH 12, temperature 180 °C, and time of reaction 24 h. Under other conditions, some impurity is seen in XRD patterns and EDS related to unreacted raw elements or formation of antimony oxides. The crystal structure of the product was characterized by X-ray diffraction (XRD D500 Simens) with CuKα radiation (\( \lambda = 1.5418 \text{ Å} \)). The morphology of materials was examined by a scanning electron microscope SEM (Hitachi S-4200). The HRTEM image and SAED pattern were recorded by a Cs-corrected high-resolution TEM (JEM-2200FS, JEOL) operated at 200 kV. The TEM sample was prepared by using an FIB (Helios Nanolab, FEI). Elemental analysis was carried out using a linked ISIS-300, Oxford EDS (energy dispersion spectroscopy detector).

3. Results and Discussion

Figure 1 shows the XRD pattern of the as-prepared \( \text{Sb}_2\text{S}_3 \). All the peaks in the pattern can be indexed to an orthorhombic phase with lattice parameters \( a = 1.122 \text{ nm}, b = 1.128 \text{ nm} \) and \( c = 0.384 \text{ nm} \). The intensity and positions of the peaks are in good agreement with the values reported in the literature (JCPDS card File: 42-1393). No characteristic peaks are observed for other impurities such as antimony oxides.

In order to further confirm the chemical compositions of these nanomaterials, elemental composition analysis was performed by EDXS. Figure 2 shows a typical EDXA spectrum recorded on single crystals, whose peaks are assigned to Sb and S. The atom ratio of Sb and S are 2:3 according to EDXA. This data indicates that we have obtained pure \( \text{Sb}_2\text{S}_3 \) single crystals.

The morphology of as-prepared \( \text{Sb}_2\text{S}_3 \) at 180 °C and 24 h was examined by SEM indicating the length of nanorods up to 4 μm and 50–140 nm as diameter (Figure 3).

Figure 4(a) shows TEM image of as-prepared \( \text{Sb}_2\text{S}_3 \) nanorods. Also, the typical HRTEM image recorded from the same nanorods is shown in Figure 4(b). The crystal lattice fringes are clearly observed, and average distance between the neighboring fringes is 0.79 nm, corresponding to the [110] plane lattice distance of orthorhombic-structured \( \text{Sb}_2\text{S}_3 \), which suggests that \( \text{Sb}_2\text{S}_3 \) nanorods grow along the [10-1] direction. The SAED pattern of the nanorods indicates its single-crystal nature and long axis [10-1].

To explain the synthesis process, possible chemical reaction involved in the synthesis of \( \text{Sb}_2\text{S}_3 \) could be assigned to iodine and antimony standard electrode potential values.
Figure 3: SEM images of the Sb$_2$S$_3$ nanorods in (a) low and (b) high magnification synthesized at 180°C and 24 h.

Figure 4: (a) TEM image of the Sb$_2$S$_3$ nanorods synthesized at 180°C and 24 h (b) HRTEM image and SAED (insert) of the Sb$_2$S$_3$ nanorods. The SAED zone axis is [111].

Considering the values of standard electrode potentials of Sb$^{3+}$/Sb ($E_0 = 0.20$ V) and I$_2$/I$^-$ ($E_0 = 0.54$ V), the oxidation reaction between Sb and I$_2$ is possible

\[
\text{Sb}^{3+} + 3e^- \rightarrow \text{Sb} \quad E_0 = 0.20 \text{ V} \quad (1)
\]

\[
\text{I}_2 + 2e^- \rightarrow 2\text{I}^- \quad E_0 = 0.54 \text{ V} \quad (2)
\]

In terms of electrochemistry, since difference of cathodic and anodic standard electrode potentials values is positive, this redox reaction can occur. In aqueous solution, Iodine and I$^-$ form complex of I$_3^-$ which dissolve in water and makes a yellowish solution. The existence of I$^-$ was examined by the formation of red precipitate of Hg$_2$I$_2$

\[
\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-
\]

Disproportion of sulfur in this solution is another possibility. Besides the nature of sulfur, the temperature and pressure of autoclave help to disproportion sulfur

\[
\text{S} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{S}^{2-}
\]

Because the precipitate of Sb$_2$S$_3$ has a great stability ($K_{sp} = 1.7 \times 10^{-97}$), the black precipitate of Sb$_2$S$_3$ is formed as soon
as $S^{2-}$ is produced. Adding Ba$^{2+}$ to the above solution results in white precipitate of $\text{BaSO}_4$

$$\text{Sb}^{3+} + S^{2-} \rightarrow \text{Sb}_2S_3 \quad \text{Ksp} = 1.7 \times 10^{-97} \quad (5)$$

With regard to oxygen standard electrode potential, as long as difference of cathodic and anodic standard electrode potential values is negative, getting electron from it in order to form $S^{2-}$ is impossible

$$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O \quad E_0 = 1.20\,V \quad (6)$$

$$S + 2e \rightleftharpoons S^{2-} \quad E_0 = 0.14\,V \quad (7)$$

During the precipitation of $\text{Sb}_2S_3$, the conditional electrode potential equals $E'_0 = E_0 + 0.06\,\text{PKsp}$, and therefore a reaction of $\text{Sb}^{3+}$ and $S^{2-}$ with high rate rather than primary rate is done. As $\text{Sb}_2S_3$ is a narrow band gap semiconductor (Eg is 1.7 ev for bulk), with decreasing diameter to nanoscale, novel optical properties may be observed [18]. The photoluminescence (PL) spectrum of synthesized antimony sulfide, shown in Figure 5, has an excitation peak at 348 nm (Figure 5(a)), and the emission peak can be observed at 450, 500 nm (Figure 5(b)).

The UV/Vis spectrum (prepared by dispersion of $\text{Sb}_2S_3$ products in ethanol) shows an absorption band at 215 nm with band gap around 2.50 ev which indicates a blue-shift phenomenon, as commonly observed for nanomaterials (Figure 6).

Most of the materials have different structural defects that create defect energy levels between band gaps of material. These defects result in difference between the UV absorption and PL excitation spectra.

4. Conclusion

In summary, a redox reaction approach in hydrothermal condition has been developed to prepare $\text{Sb}_2S_3$ nanorods with high yield at 180°C and 24 h. The length of nanorods is up to $4\,\mu m$, and their diameter is around 50–140 nm. Using iodine as an initiator of oxidation-reduction reaction is reported for the first time. The formation mechanism of $\text{Sb}_2S_3$ based on redox reaction is proposed. In the current process, $I_2$ plays an important role in the formation of $\text{Sb}_2S_3$ nano materials, and other oxidizing agents can be worthwhile for preparing nanostructures in the future. As a common feature for nanomaterials, a blue shift was observed in the case of optical absorption.

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