Research Article

Synthesis and Characterization of Sb_2S_3 Nanorods via Complex Decomposition Approach

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Received 27 May 2011; Accepted 17 July 2011

Academic Editor: Somchai Thongtem

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Based on the complex decomposition approach, a simple hydrothermal method has been developed for the synthesizing of Sb_2S_3 nanorods with high yield in 24 h at 150°C. The powder X-ray diffraction pattern shows the Sb_2S_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 spectrometric analysis peaks give an atomic ratio of 2:3 for Sb:S. TEM and SEM studies reveal that the appearance of the as-prepared Sb_2S_3 is rod-like which is composed of nanorods with the typical width of 30–160 nm and length of up to 6 μm . High-resolution transmission electron microscopic (HRTEM) studies reveal that the Sb_2S_3 is oriented in the [10-1] growth direction. The band gap calculated from the absorption spectra is found to be 3.29 eV, indicating a considerable blue shift relative to the bulk. The formation mechanism of Sb_2S_3 nanostructures is proposed.

1. Introduction

Recently, metal chalcogenides have attracted considerable attention due to their proven and potential applications in electronic, optical, and superconductor devices. Among these materials, antimony sulfide (Sb_2S_3) is a kind of semiconductor with its interesting high photosensitivity and high thermoelectric power. Antimony sulfide is a layer-structured direct bandgap semiconductor with orthorhombic crystal structure [1]. Sb_2S_3 is considered as a promising material for solar energy due to its band gap which covers the range of the solar spectrum [2]. Sb_2S_3 has been extensively investigated for its special applications as a target material for microwave devices [3], television cameras and switching devices [4], rechargeable storage cell [5], and various optoelectronic devices [6]. Over the past two decades, many methods have been employed to prepare Sb_2S_3 including thermal decomposition [7], solvothermal reaction [8–11], microwave irradiation [12], hydrothermal reaction [13, 14], and vacuum evaporation [15]. Besides an elemental reaction and vacuum evaporation, Sb_2S_3 can be prepared by chemical

routes. SbCl_3 reacts with different sulfide ion sources, such as ammonium sulfide, thiourea, sodium thiosulfate, and thioacetamide as well as with complexing agents in aqueous or nonaqueous solutions [16, 17]. However, most of the as-prepared Sb_2S_3 materials are amorphous, and they need to be annealed at high temperature in air or in N_2 atmosphere in order to crystallize. In addition, crystalline Sb_2S_3 can be obtained directly via two-heater method [18] and liquid-mediated metathetical reactions [19]. But different method has its disadvantage. For the vacuum evaporation and direct elemental reaction methods, it is difficult to obtain exact stoichiometric compositions because of the differences in the vapor pressures of the reaction species. Consequently, exploring a convenient synthesis method is significant [20]. Recently, we have reported a new method via redox mechanism by using starting materials in elemental form [14]. Several morphologies of Sb_2S_3 have been reported, for example, microspheres, microtubes [21], dendrite or feather [22], dumbbell-like [23], and also peanut-shaped superstructures [24]. In this study, Sb_2S_3 nanorods were prepared by complex decomposition approach via hydrothermal method.

FIGURE 1: XRD patterns of the Sb_2S_3 nanorods synthesized at 150°C for 24 h.

FIGURE 2: EDX patterns of synthesized Sb_2S_3 nanorods synthesized at 150°C for 24 h.

2. Experimental

2.1. Synthesis of Sb_2S_3 Nanorods. All the reagents were of analytical grade and were used without further purification. In a typical procedure, 0.4 g CS_2 , 0.6 g EDTA, and 1 g NaOH were added to 50 mL distilled water and stirred well for 20 min at room temperature. Then, 1 mmol of SbCl_3 was added to above mixture and the mixture was transferred into a 100 mL Teflon-lined autoclave. The autoclave was sealed a, maintained at 150°C for 24 h, and cooled at room temperature, naturally. The black precipitate was filtered and washed with dilute chloride acid and water. Then, it was dried at room temperature. Yields for the products were 96%. Finally, the obtained sample was dried at room temperature and used for characterization. The best conditions for this reaction are pH = 10, temperature 150°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 $\text{CuK}\alpha$ radiation

(a)

(b)

FIGURE 3: SEM images of the Sb_2S_3 nanorods in (a) low and (b) high magnifications synthesized at 150°C and 24 h.

FIGURE 4: AFM image of Sb_2S_3 nanorods synthesized at 150°C for 24 h.

($\lambda = 1.5418 \text{ \AA}$). 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

FIGURE 5: (a) TEM image of the Sb_2S_3 nanorods synthesized at 150°C and 24 h (b) HRTEM image and FFT (c) SAED of the Sb_2S_3 nanorods. The SAED zone axis is $[111]$.

FIGURE 6: (a) Excitation spectra and (b) emission spectra of Sb_2S_3 nanorods.

FIGURE 7: UV/Vis spectra of Sb_2S_3 nanorods.

spectroscopy detector). Optical measurements were carried out by a Perkin-Elmer lambda UV/Vis spectrophotometer (model specord 400) and the photoluminescence were done by a perkin-Elmer Ls 55 luminescence spectrometer.

3. Results and Discussion

A typical XRD of the as-prepared Sb_2S_3 is shown in Figure 1. All the peaks in the pattern can be indexed to an orthorhombic phase with lattice parameters $a = 1.122$ nm, $b = 1.128$ nm, and $c = 0.384$ 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, or SbOCl .

Figure 2 shows a typical EDXA spectrum recorded on single crystals, whose peaks are assigned to Sb and S. The EDX analysis of the product confirms the ratio of Sb/S to be 2:3, as expected. According to EDX analysis, no impurity such as elemental antimony, antimony oxides or SbOCl is observed.

The crystal size (CS) is calculated from X-ray diffraction patterns using Scherrer's formula ($\text{CS} = K\lambda/\beta \cos \theta$, where β is the full width at the half maximum of peak corrected for instrumental broadening, λ is the wavelength of the X-ray and K is Scherrer's constant) [25]. The grain size was

SCHEME 1: Possible chemical reaction in the synthesis of Sb_2S_3 nanorods.

22 nm. The morphology of the prepared Sb_2S_3 was examined by scanning electron microscopy. SEM images with different magnification shows that the length of Sb_2S_3 nanorods is up to $6\ \mu\text{m}$ and 30–160 nm as diameter (Figures 3(a) and 3(b)).

Also, Figure 4 shows atomic force microscopic image of as-prepared Sb_2S_3 with rod like structure and phase homogeneity.

Figure 5(a) shows TEM image of as-prepared Sb_2S_3 nanorods. Also, the typical HRTEM image recorded from the same nanorods is shown in Figure 5(b). The crystal lattice fringes are clearly observed and average distance between the neighboring fringes is 0.79 nm, corresponding to the $[1\ 1\ 0]$ plane lattice distance of orthorhombic-structured Sb_2S_3 , which suggests that Sb_2S_3 nanorods grow along the $[1\ 0\ -1]$ direction. The SAED pattern of the nanorods indicates that its single-crystal nature and long axis is $[1\ 0\ -1]$ (Figure 5(c)).

To explain the synthesis process, possible chemical reaction involved in the synthesis of Sb_2S_3 could be listed in Scheme 1.

First, EDTA was reacted with CS_2 in water for 12 h to give a clear solution, which was precipitated in ethanol. The product was recrystallized in methanol: chlorophorm (1 : 1) mixture and characterized by FTIR spectroscopy. This is a thiocarbonate ester of EDTA, which seems to act as a ligand to form an intermediate complex of Sb^{3+} , as confirmed by similar FTIR spectroscopy. Such an intermediate complex is isolated by heating of a reaction mixture of CS_2 , EDTA, NaOH , and SbCl_3 in water under hydrothermal condition for 1 h. The resultant mixture was filtered and the obtained precipitate was identified by FTIR spectroscopy.

Comparison of the FTIR spectra shows that the same bands indicate some shift due to the complexation of the ligand. The line positions (in cm^{-1}) of $\nu = 691$ C–S stretching, $\nu = 1174$ esteric band, $\nu = 1250$ C–N stretching (tertiary amine) in case of ligand shifts to $\nu = 888$ C–S stretching, $\nu = 1119$ esteric band, $\nu = 1283$ C–N stretching (tertiary amine) due to complexation. After 24 h exposing to heat and pressure, the resultant Sb^{3+} complex will be degraded completely to form the Sb_2S_3 compound. The

EDX result (see Figure 2) shows that no organic compound remains in the sample. In semiconductors, band gaps have been found to be particle-size dependent and increase with decreasing of particle size [26]. As Sb_2S_3 is a narrow band gap semiconductor (E_g is 1.7 eV for bulk), with decreasing in diameter into nanoscale, novel optical properties may be observed. The photoluminescence (PL) spectrum of synthesized antimony sulfide, shown in Figure 6, has an excitation peak at 390 nm (Figure 6(a)), and the emission peak can be observed at 415, 442 and 475 nm (Figure 6(b)).

The absorption spectra of Sb_2S_3 (prepared by dispersion of Sb_2S_3 nanorods in ethanol) show an intense absorption band at 315 nm with band gap around 3.29 eV (Figure 7). A blue shift phenomena is seen for Sb_2S_3 nanorods.

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

4. Conclusion

In summary, a complex decomposition approach in hydrothermal condition has been developed to prepare Sb_2S_3 nanorods with high yield. The length of the nanorods is up to 6 μm and their diameter is around 30–160 nm. Single crystals could be obtained by increasing of heating time up to 48 h. High-resolution transmission electron microscopic (HRTEM) studies reveal that the Sb_2S_3 is oriented in the [10-1] growth direction. A blue shift was observed in the case of optical absorption and PL, common feature for nanomaterials.

Acknowledgments

This work is funded by the World Class University Grant KRF R32-2008-000-20082-0 of the National Research Foundation of Republic of Korea. Y. Hanifehpour thanks the Council of the University of Tabriz for their invaluable guidance.

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