

Solvothermal Preparation of Sb_2Se_3 Nanowires

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Crystalline Sb_2Se_3 nanowires with a typical width of 30 nm and length up to 8 μm were synthesized through the reaction between SbCl_3 and elemental selenium with sodium sulfite as reducing reagent in diethylene glycol solution. The composition of the products was identified using EDX and XPS. The possible reaction mechanism was also discussed.

During the past decade, various methods have been reported on the preparation of one-dimensional nanostructured V–VI group semiconductor compounds, such as single-source precursor method,¹ porous alumina templating electrodeposition,² microwave irradiation,³ sonochemical method,⁴ and solvothermal method.^{5,6}

Antimony triselenide, a layer-structured V–VI semiconductor with orthorhombic phase crystal structure, has attracted wide attention due to its good photoconducting properties and high thermoelectric power, which allow possible applications in optical and thermoelectric cooling devices, photo-electrochemical devices, solar selective and decorative coatings.⁷ Many studies have been carried out on the deposition of Sb_2Se_3 thin films by various techniques including electrochemical deposition, spray pyrolysis, laser-induced crystallization and vacuum evaporation.^{7–10} Most recently, solvothermal growth of bulk polygonal tubular Sb_2Se_3 crystals via a solvent-relief-self-seeding process was reported.¹¹ However, to the best of our knowledge, synthesis of one-dimensional Sb_2Se_3 nanocrystals with high aspect ratio has not been reported except for the hydrothermal preparation of Sb_2Se_3 nanorods in hydrazine hydrate media.¹² In this paper, we report the solvothermal synthesis of crystalline Sb_2Se_3 nanowires with high aspect ratio in diethylene glycol media.

In a typical process, 0.005 mol of SbCl_3 was dissolved in diethylene glycol (DEG), then 5 ml ammonia was added under agitation, followed by adding 0.01 mol sodium sulfite and 0.0075 mol Se powder. Finally, the mixture was transferred into a Teflon lined stainless steel container and filled with DEG up to 90% of its capacity, then sealed and maintained at 100–140 °C for 60 h. When the reaction was finished, the products were filtered and washed with water, dilute hydrochloric acid solution and absolute ethanol, respectively, then dried in a vacuum before characterization.

The products were characterized by X-ray powder diffraction using a Rigaku (Japan) D/Max γ -A X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154178$ nm). Figure 1 shows typical XRD patterns of the as-prepared Sb_2Se_3 nanowires obtained at 120 °C and 140 °C, respectively. All the diffraction peaks can be indexed to orthorhombic phase of Sb_2Se_3 (JCPDS 72-1184).

SEM image (Figure 2a) shows the straight Sb_2Se_3 nanowires prepared at 120 °C. The length of the nanowires ranges from 2–8 μm , and their diameter ranges from 20–50 nm, although some

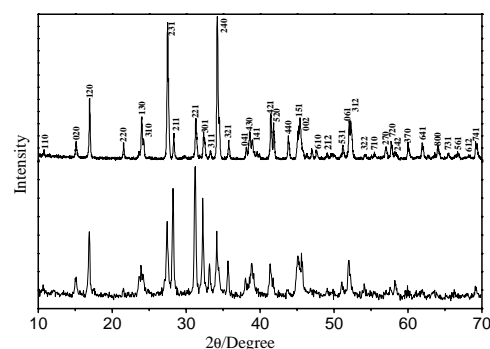


Figure 1. XRD patterns for Sb_2Se_3 samples prepared (a) at 120 °C and (b) at 140 °C

thicker wires (100 nm) have also been observed. Figure 2b shows a typical TEM image of uniform and smooth Sb_2Se_3 nanowires prepared at 120 °C with a width of 30 nm on average. The electron diffraction pattern (inset Figure 2b) indicates that the Sb_2Se_3 nanowires were well crystallized. Sb_2Se_3 nanowires prepared at 140 °C with a width of 50–80 nm and a typical length up to 10 μm

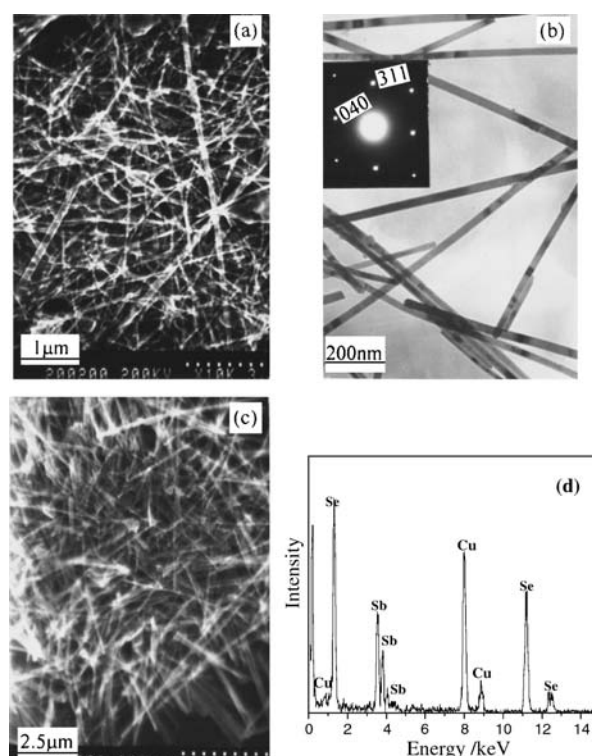
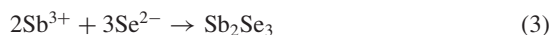
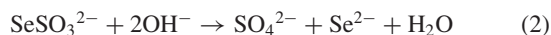


Figure 2. (a) SEM, and (b) TEM images of the sample prepared at 120 °C, (c) SEM image of the sample prepared at 140 °C, (d) EDX spectrum of the Sb_2Se_3 sample.

are shown in Figure 2c. It means that higher temperature leads to the overgrowth of the crystal and produce nanowires with larger diameters.

Energy-dispersive X-ray (EDX) analysis was used to determine the composition of these nanowires. The results (Figure 2d) show that these nanowires are composed of the elements Sb and Se and the ratio of Sb : Se is 1 : 1.43, in agreement with the expected values (the Cu peaks arise from the copper grid). The composition of the sample was further identified by X-ray photoelectron spectra (XPS). The values of the binding energy were calibrated using C1s peak (284.6 eV) as the internal standard. The peak at 53.4 eV corresponds to the Se (3d) transition. Since the position of Sb 3d binding energy (ca. 529 eV) is superposed with that of the O1s binding energy (530 eV) the peaks of Sb 4d were used to detect the binding energy of Sb, and was measured at 33.7 eV. The XPS surface analysis also shows that the selenium ions are ready to be oxidized, in fact, all of the samples are surface-absorbed with carbon and oxygen elements due to exposure to air during the processing of samples.

The solvothermal reaction mechanism of Sb_2Se_3 in DEG could be explained as follows:



First, SeSO_3^{2-} formed by refluxing selenium powder with sodium sulfite, then hydrolyzed slowly in alkaline condition to give Se^{2-} ions.¹³ Finally, the Se^{2-} ions reacted with the Sb^{3+} ions chelated by OH^- to form Sb_2Se_3 . Due to the slow conversion of Se element to Se^{2-} ions and the low free concentration of Sb^{3+} ions, the reaction rate is rather slow, which contributes to the oriented growth and crystallization of the Sb_2Se_3 nanowires. The solvent, DEG, also plays an important role in the formation of Sb_2Se_3 nanowires. Previous investigation had shown that diethylene glycol can efficiently complex and stabilize the surface of the nanoparticles, accordingly, the particles exist almost non-agglomerated in polyol media.¹⁴ The formation of Sb_2Se_3 nanowires indicates that the nucleation and growth of Sb_2Se_3 crystals were well controlled by using DEG as solvent. Confined by solvent molecules the wires' shape is oriented and stabilized, and as a result, uniform size and long length nanowires are obtained.

To make a comparison, the synthesis of Sb_2Se_3 nanowires was also carried out using ethanol, ethylene glycol (EG) and ethylene diamine (en) as solvents. When EG or ethanol was used, some nanoparticles were observed besides Sb_2Se_3 nanowires or nanorods. Upon using en, some unidentified phases besides Sb_2Se_3 phase in the products were also detected by XRD.⁵ It was

found that experimental conditions had much influence on the growth of Sb_2Se_3 nanowires. With no addition of small amount of ammonia, dark red precipitates were found in the products indicating element selenium formed when Na_2SeSO_3 hydrolyzed in acidic condition caused by the hydrolysis of SbCl_3 . The increase of the temperature could result in the enlarged Sb_2Se_3 nanowires, while lower temperature result in the presence of oxide and other impurities being difficult to be identified. Of course, researches including the properties of Sb_2Se_3 nanowires will be the subjects of our future intensive studies

In summary, crystalline Sb_2Se_3 nanowires with a width of 30 nm and length up to 8 μm were prepared in DEG solution via solvothermal route. The low precipitates reaction rates and the solvent are important factors in the oriented growth of Sb_2Se_3 nanowires.

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