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Large-scale synthesis of ultralong Sb_2S_3 sub-microwires via a hydrothermal process

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Abstract

This paper describes an ethylene glycol (EG)-assisted approach to the large-scale ultralong Sb_2S_3 sub-microwires, formed by a simple hydrothermal reaction between $SbCl_3$ and Na_2S in the presence of distilled water. Transmission electron microscopy and scanning electron microscopy studies indicate that these Sb_2S_3 sub-microwires possess a diameter around 200 nm and length up to 100 μm. High-resolution transmission electron microscopy and selected area electron diffraction studies reveal that each Sb_2S_3 sub-microwire is a single-crystal along the [0 0 1] direction. The possible formation mechanism of the sub-microwires was discussed. The effects of volume ratio of EG/water, reaction temperature and the concentration of $CO(NH_2)_2$ on the morphology of Sb_2S_3 sub-microwires were also investigated.

Keywords: A. Nanostructures; A. Semiconductors; B. Chemical synthesis; C. Electron diffraction; C. Electron microscopy

1. Introduction

One-dimensional (1D) nanostructures (wires, rods, tubes and ribbons) are expected to play an important role in fabricating nanoscale devices. As a result, the synthesis and characterization of 1D nanostructure have recently attracted extensive attention from a broad range of researchers [1–5]. In particular, much effort has been devoted to the controlled synthesis of 1D nanostructure from chalcogenides semiconductors due to their interesting physical properties, and their potential applications in fabricating optoelectric and thermoelectric nanoscale devices [6–9]. In the past few years, main-group metal chalcogenides such as $A^{V}{}_2B^{VI}{}_3$ (where A = As, Sb, Bi and B = S, Se, Te) as significant semiconductors have received ever increasing attention [10]. Antimony trisulfide (Sb_2S_3), with an orthorhombic crystalline structure, is an important semiconductor with high photosensitivity and high thermoelectric power [11]. Due to its good photoconductivity, Sb_2S_3 has received significant attention for potential applications in solar energy conversion [12]. It has also been used in thermoelectric cooling technologies and optoelectronics in the IR region [13,14].

To our knowledge, several morphologies of antimony trisulphide, including nanoparticles [15], nanoribbons [16], nanowires [17–19], nanowhiskers [20], microspheres [21] and nanotubular crystals [22], have been fabricated by

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hydrothermal, solvothermal, sonochemical method and chemical vapor deposition. However, how to effectively synthesize Sb_2S_3 crystals and control the morphology via a simple method is still challenging to material scientists. Herein, we report a facile route of hydrothermal synthesis to prepare the large-scale ultralong Sb_2S_3 sub-microwires by using $SbCl_3$ and Na_2S as the raw materials assisted by EG. Compared to the solvothermal synthesis, the advantages of this route preparing Sb_2S_3 sub-microwires lie in its simplicity, high quality, high purity, green and may provide a more promising approach for rationally designing other 1D chalcogenide nanostructures. The products were characterized by using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and high-resolution transmission electron diffraction (HRTEM). The effects on the morphology of reaction temperature, reaction time, the volume ratio of EG/water and the concentration of $CO(NH_2)_2$ were investigated. The possible formation mechanism of Sb_2S_3 sub-microwire has also been proposed.

2. Experiment

All reagents were analytic grade from Shanghai Chemistry Company and used without further purification. $CO(NH_2)_2$ was used as the mineralizer in the experiment. In a typical procedure, 0.346 g $SbCl_3$ were dissolved in 3 mL EG with a continuous stirring, then 10 mL distilled water was added to the solution as sample A. 1.103 g Na_2S were dissolved in 10 mL distilled water as sample B. Then the solution of B was dropped slowly into the A solution under vigorous stirring, and 1.5 M (2.73 g) $CO(NH_2)_2$ was added into the mixture. The resulting mixture was loaded into a 50 mL Telfon-lined stainless-steel autoclave, which was then filled with distilled water up to 70% of the total volume. Finally, the autoclave was sealed and maintained at 120–240 °C for 1–12 h in an oven. After cooling, the resulting solid products were washed with distilled water for several times, and then dried in vacuum at 80 °C for 4 h.

The crystal structures of the resulting products were characterized by X-ray powder diffraction (XRD; Rigaku, D/MAX2550, $\lambda = 1.5406$ Å´). A scan rate of $0.05^\circ\ s^{-1}$ was applied to record the patterns in the 2θ range of 10–70°. The morphologies and sizes of the resulting products were observed by scanning electron microscopy (SEM; Quanta 200, with an accelerating voltage of 20 kV), transmission scanning microscopy (TEM; JEM-3010) and high-resolution transmission electron microscopy (HRTEM; JEM-3010, with an accelerating voltage of 300 kV).

3. Results and discussion

Fig. 1 shows the typical powder XRD pattern of the final products via a hydrothermal synthesis at 240 °C for 12 h. All the peaks in the pattern can be indexed to an orthorhombic phase of Sb_2S_3. The calculated lattice parameters are $a = 1.1220$ nm, $b = 1.130$ nm and $c = 0.3840$ nm, which was in agreement with the reported values (JCPDS-42-1393, $a = 1.122$ nm, $b = 1.131$ nm and $c = 0.3839$ nm). No characteristic peaks are observed for the other impurities such as Sb_2O_3 or SbOCl.

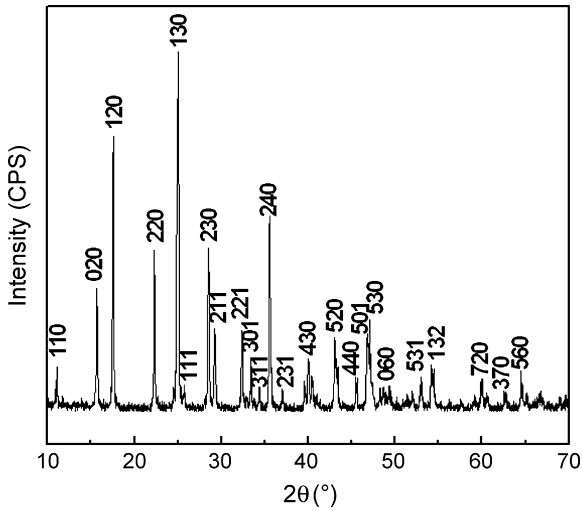

Fig. 1. XRD pattern of the Sb_2S_3 sub-microwires synthesized at 240 °C for 12 h.