Synthesis of nano-fibrillar bismuth sulfide by a surfactant-assisted approach

Qing Li b,1, Mingwang Shao b, Ji Wu b, Guihua Yu b, Yitai Qian a,b,*

a Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, PR China
b Department of Chemistry, University of Science and Technology of China, Hefei 230026, PR China

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Abstract

Bi2S3 nanofibers with a diameter less than 10 nm and lengths ranging from 400 to 1000 nm were successfully prepared by a convenient solution route at 90 °C by using BiCl3 and thiourea as the starting materials. The product was characterized by XRD, XPS, and TEM techniques. It was found that anionic surfactant C17H33COOK played an important role in controlling the morphology of the product. The formation of the nanofibers could be well explained by the accordion-like folding mechanism.

Keywords: Bismuth sulfide; Nanofiber; Surfactant; Ethylene glycol

1. Introduction

In recent years, semiconducting chalcogenides have been receiving considerable attention because of their worldwide applications in television cameras with photoconducting targets, thermoelectric and optoelectronic devices, and in IR spectroscopy [1]. Bismuth trisulfide (Bi2S3), an important member of the chalcogenides, is a layered semiconductor that crystallized in the Pbnm orthorhombic space group [2]. Its energy gap is about 1.3 eV [3], which makes it a promising candidate for photovoltaic converters [4,5]. It also finds applications in thermoelectric cooling technologies based on Peltier effect [6].

Conventionally, bismuth sulfide is prepared by direct reaction of bismuth and sulfur vapor in a quartz vessel at high temperature of bismuth dithiocarbamate complexes [7] or metal ethylxanthate [8]. Bismuth sulfide single crystal has been grown by the Bridgman method from a stoichiometric polycrystalline melt [9]. Colloidal suspensions of Bi2S3 were prepared at room temperature with solutions of Bi2(NO3)3 and Na2S·9H2O as the starting materials [10]. Recently, Bi2S3 nanorods have been prepared by the hydro(solvo)thermal techniques [11–13] or by microwave irradiation [14].

In this study, we report the preparation of nano-fibrillar Bi2S3 from ethylene glycol solution at 90 °C in the presence of anionic surfactant C17H33COOK. No complex equipment or other significant energy inputs were needed. The formation mechanism and the role of C17H33COOK played were investigated and were confirmed by the TEM observation.

2. Experimental

Since anhydrous BiCl3 hydrolyzes strongly in an aqueous solution, ethylene glycol was chosen as the solvent. All reagents were of analytic purity and were used as purchased from Shanghai Chemical. The sample was prepared by placing 0.6 g BiCl3, 0.8 g thiourea, and 0.2 g C17H33COOK (potassium oleate) in a conical flask containing 40 ml ethylene glycol. The system was operated continuously for 5 h at 90 °C without stirring. A black-brown precipitate was collected by filtration and was washed with distilled water and anhydrous ethanol. Then, the product was dried in a vacuum at 60 °C for 4 h.
Phase identification was carried out by X-ray diffraction (XRD) technique, using Cu Kα radiation (λ = 1.54056 Å) on an MXP18AHF X-ray diffractometer (MAC Science). X-ray photoelectron spectra (XPS) analysis was performed on a VGESCALAB MKII X-ray photoelectron spectrometer, using MgKα radiation as the excitation source. Morphology and structure information were obtained from transmission electron microscopy (TEM) images, using a Hitachi Model (H-800) transmission electron microscopy at an acceleration voltage of 200 kV.

3. Results and discussion

Fig. 1 is the XRD pattern of the sample obtained at 90 °C for 5 h. All the peaks can be indexed as the orthorhombic lattice of Bi₂S₃ with cell constants a = 11.146, b = 11.299, and c = 3.979 Å, which are close to the reported data (JCPDS 17-320). No peaks attributable to Bi, BiOCl, and Bi₂O₃ were observed. The broadening of the peaks indicates that the grain sizes of the sample are of nanometer scale. The quality and composition of the sample was also characterized by XPS. The binding energies of Bi (4f½, 2), Bi (4f½, 2), and S (2s) were 166.2, 171.6, and 235.6 eV, respectively, which were in good agreement with the literature values [14]. The quantification of the peaks gave the ratio of 2:3.08 for Bi to S. No obvious impurities were detected.

Fig. 2(a) shows a typical TEM image of as-synthesized Bi₂S₃ sample. This image reveals that the product consists of uniform fibers. These Bi₂S₃ fibers are curved and tangled together forming bundles or “flower-like” clusters with fibrillar crystallites radiating from the center in a uniform size distribution. From the enlarged part of the fibers (Fig. 2(b)), it can be found that the diameter of the fiber is less than 10 nm while its length ranges from 400 to 1000 nm. The corresponding SAED pattern (Fig. 2(a) inset) shows several diffused rings, indicative of a fine crystallite size character. This is in accordance with the XRD result. When the sample was treated by ultrasonic irradiation for 4 h, no single fiber was observed, indicating a relative stability of these aggregates.

The crystallinity of the product increases with the increase of reaction time. Fig. 2(c) presents the sample obtained after maintaining at 90 °C for 24 h. The product still keeps a “flower-like” pattern though the soft fibers grew into longer straight rods. It’s ED pattern shows that they are well-developed single crystals with their growth along the [010] direction (Fig. 2(c) inset). Temperature was found to have a significant influence on the morphology of the product. When the temperature was below 70 °C, the product was poorly crystallized and showed an irregular lamellar morphology. When the temperature was increased to 130 °C, small dendritic crystallites grew from the major crystal axis.

To examine the growth process of the Bi₂S₃ nanofiber, TEM technique was employed. When the reaction lasted for 2 h, the obtained Bi₂S₃ powders displayed a lamellar shape with many folds on them (Fig. 2(d)). If the reaction time was prolonged to 3 h, bundles of fibers appeared (Fig. 2(e)). TEM images of the products after maintaining for 5 and 24 h had been shown in Fig. 2(a) and (b), respectively. According to these results, the formation of the nano-fibrillar Bi₂S₃ could be well explained by an accordion-like folding mechanism [15]. According to this mechanism, bismuth chloride and thiourea reacted to produce lamellar Bi₂S₃ with many folds on it. After that, the folds on the lamellae agglomerated together. Then, these folds broke and formed Bi₂S₃ nanofibers.

The anionic surfactant C₁₇H₃₃COOK was crucial to the formation of fibrillar Bi₂S₃ nanocrystals. It was reported that C₁₇H₃₃COOK could form threadlike micelles in polyethylene glycol (PEG) [16]. In our synthetic system, the direction of the micelles formed by C₁₇H₃₃COOK and ethylene glycol may also has effect on the formation of the nano-fibrillar pattern. To verify it, further experiments were carried out. When other experimental conditions remained stable but C₁₇H₃₃COOK was absent, the products were not fibrillar Bi₂S₃ crystals. Instead, they consisted of small Bi₂S₃ particles, which had a strong tendency to aggregate to lamellar structure (Fig. 2(f)). We also found in our experiment, when 0.1–0.3 g C₁₇H₃₃COOK was used, the size and the shape of Bi₂S₃ nanofiber kept unchanged. This might be explained by the formation and stabilization of surfactant micelle structure in a certain concentration rate.
4. Conclusions

In summary, nano-fibrillar Bi$_2$S$_3$ with the diameter less than 10 nm and lengths ranging from 400 to 1000 nm were successfully prepared by a convenient solution route at 90 °C. It was found that the micelles formed by C$_{17}$H$_{33}$COOK and ethylene glycol may direct the crystal growth and thus leading to the formation of nano-fibrillar Bi$_2$S$_3$. The formation process could be well explained by the accordion-like folding mechanism. This approach may provide a new convenient route to the production of other metal sulfide nanofibers.

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References


