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Synthesis and characterization of Bi_2S_3 faceted nanotube bundles

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Abstract

Single-crystalline Bi_2S_3 nanotubes have been prepared by pyrolyzing single-source precursor $Bi(S_2CNEt_2)_3$ at 530 °C. X-ray diffraction (XRD), Raman spectrum, energy-dispersive spectroscopy (EDS) demonstrate that the nanotubes are composed of pure orthorhombic phase Bi_2S_3. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show that the Bi_2S_3 nanotubes have rectangular or polygonal open ends with cross-sectional width of 100–500 nm, and length up to several microns. The nanotubes grow radially from a center toward two or more different directions to form straw-bundle-like morphology. High-resolution (HR) TEM and selected-area electron diffraction (SAED) demonstrate that the nanotubes are single-crystalline and grow along the [001] direction.

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1. Introduction

In recent years, one-dimensional (1D) nanostructures such as nanotubes, nanowires, nanorods and nanobelts have attracted enormous attention due to their potential applications in both mesoscopic research and development of nanodevices [1]. Especially nanotubes possess several different areas of contact (borders, inner and outer surfaces, and structured tube walls) that in principle can be functionalized in several ways such as incorporation of nanorods in nanotubes and generally usage as nanoscale host materials. Currently, the explorations of new fabrication methods for nanotubes have become a subject of a large number of studies [1d–f]. Furthermore, in order to apply nanomaterials to nanoscale machines and devices, it is often necessary to assemble them into well arranged patterns of nanocrystallites. Solid templates, such as porous alumina, polymer membranes and patterned catalysts, are usually required to accomplish highly oriented growth of nanotubes and nanorods [2]. Development of simple, effective and template-free methods for fabricating nanotubes and their well-aligned assemblies is of great importance to nanotechnology and remains a key research challenge.

Bismuth sulfide (Bi_2S_3), a very important semiconductor with a direct bandgap of 1.3 eV, has potential applications in photodiode arrays, photovoltaic converters and thermoelectric cooling devices [3]. For 1D Bi_2S_3 nanostructures, Bi_2S_3 nanorods [4], nanowires [5] and nanoribbons [6] have been extensively studied and a variety of fabrication methods for them have been developed. However, the investigation on Bi_2S_3 nanotubes is quite rare [7]. Furthermore, metal dialkyldithiocarbamate complexes have been used as single-source precursors for preparation of thin films and nanostructures of various metal sulfides [8]. In our present study, novel Bi_2S_3 nanotube bundles were synthesized by using bismuth tris(diethyldithiocarbamate) $[Bi(S_2CNEt_2)_3]$ as a single-source precursor.

2. Experimental

All chemicals were analytically pure and used without further purification. Bismuth tris(diethyldithiocarbamate) $[Bi(S_2CNEt_2)_3]$ was synthesized according to the literature

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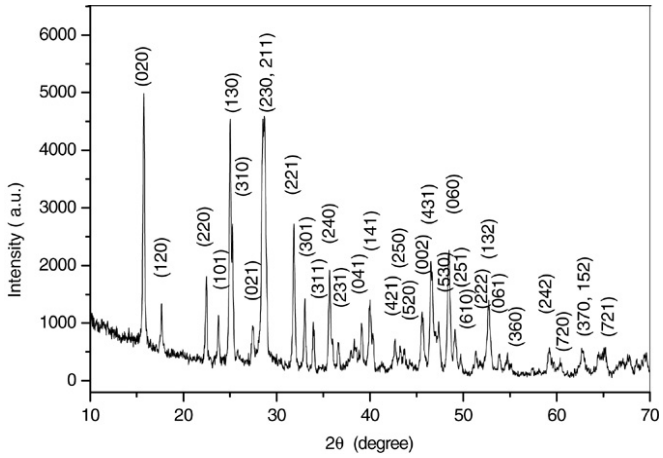

Fig. 1. XRD pattern of the as-synthesized Bi_2S_3 products.

method [9]. In a typical synthesis, the diethylamine (40 mmol) and CS_2 (40 mmol) were added dropwise (in that order) into 20 mL of a methanolic suspension of Bi_2O_3 (6 mmol). The reacting mixture was stirred over 48 h at room temperature. A yellow solid was obtained and then recrystallized from a chloroform/methanol (3:1) mixture. Yield 40%. m.p. 201 °C. The TG–DTA analyses (Perkin-Elmer TG/DTA 6300 thermoanalyser, 10 °C/min heating rate, N_2 atmosphere) showed that the compound decomposed nearly in a single step with the onset at 300 °C and the end at 350 °C. The remanent weight of 41% at 350 °C is consistent with that (39.5%) of the resulting Bi_2S_3 product.

The synthesis of Bi_2S_3 faceted nanotube bundles was carried out in a quartz tube mounted inside a horizontal tube furnace using $Bi(S_2CNEt_2)_3$ as a single-source molecular precursor. In a typical experiment, the single-source precursor (∼300 mg) was placed at the upstream side of the furnace and a silicon wafer as substrate was positioned downstream 5 cm away from the precursor. The quartz tube was purged with high-purity N_2 for 1 h prior to heating to remove any oxygen in the tube. The deposition reaction was conducted at atmospheric pressure with a flow of high-purity N_2 (30 sccm) and the run-time was 2 h. The temperatures of the precursor and the substrate were *ca.* 480 and 530 °C respectively during deposition. The resulting substrate was collected after the furnace was cooled to room temperature. Yellowish-gray product was observed on the silicon wafer and was used directly for scanning electron microscopy (SEM, JSM-840A), energy-dispersive spectrometry (EDS, attached to SEM), and X-ray diffraction (XRD, D/Max-RA) measurements. The product was suspended in ethanol and then transferred onto TEM grids for transmission electron microscopy (TEM, JEM-200CX) and

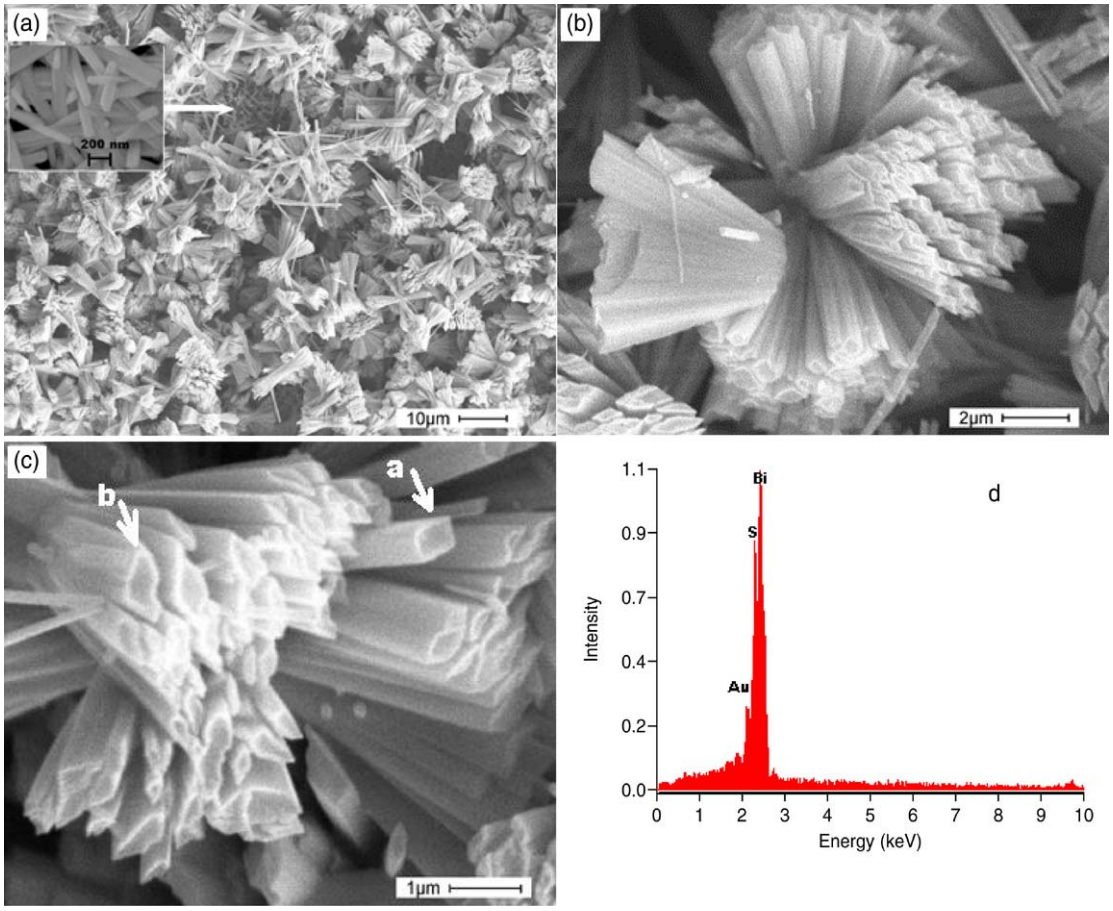

Fig. 2. SEM images of the as-prepared Bi_2S_3 nanotubes. (a) Large area of the nanotube bundles, inset is a magnified view of the zone indicated by the arrow. (b) A typical nanotube bundle. (c) Local view of the nanotube bundle showing the open ends. (d) EDS spectrum of the nanotubes.