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Very narrow In_2S_3 nanorods and nanowires from a single source precursor

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ABSTRACT

Ultra-thin (< 1.0 nm) nanorods or nanowires of β-In_2S_3were synthesized from the thermolysis of the indium(III) complex of 1,1,5,5-tetra-*iso*-propyl-2-thiobiuret in hot oleylamine.

1. Introduction

One-dimensional (1D) nanostructures such as wires, rods and tubes are proven to be showing enhancement in electrical or thermal transport as compared to zero-dimensional nanostructures [1,2]. These structures (1D) are involved in the fabrication of electronic, optoelectronic and electrochemical devices [2]. Indium sulfide is a semiconductor which exists in different stable forms, specifically, InS, In_2S_3, and In_6S_7 [3]. InS is orthorhombic and In_6S_7 is monoclinic, whereas, In_2S_3 has three different structures: a defect cubic (α-In_2S_3), cubic or tetragonal defect spinel (β-In_2S_3) and layered structure (γ-In_2S_3) [3–5]. β-$In_2S_3$is stable at room temperature and up to 420 °C, with a high degree of vacancies ordering [5,6]. Above 420 °C the In atoms become randomly distributed as the α-In_2S_3 is formed and above 754 °C the trigonal layered structure γ-In_2S_3 becomes the stable phase [7]. The beta form has been used in green or red phosphors for color televisions [8], as buffer layer instead of toxic CdS in $CuInSe_2$-based solar cells [9] and as an electrode material in lithium ion batteries [10]because of its high defects and band gap (2.0–2.3 eV) [11].

Various synthetic methods have been used for the preparation of indium sulfide nanostructures including: hydrothermal [12], solvothermal [10,13], arrested precipitation [14], sonochemical [15] and thermal decomposition in hot coordinating solvent [16]. However, the synthesis of In_2S_3 nanowires and/or nanorods with high aspect ratio is limited. The applicability of indium sulfide nanowires and nanorods can indisputably be augmented if they can be synthesized in narrow size distribution with large surface area. Very few reports are available on the use of single source precursor for the synthesis of monodispersed indium sulfide nanostructures. Although we have previously used single source precursors for the deposition of indium sulfide thin films [17]. Examples of the single source precursor explored for the synthesis of indium sulfide nanoparticles include: $[In(S_2CNEt_2)_3]$ and the polymeric complex $[MeIn(SCH_2CH_2S)]_n$ which produced InS and In_2S_3, respectively [18,19]. Herein we report the facile synthesis of ultra-thin (< 1.0 nm) nanorods or nanowires of β-$In_2S_3$with large

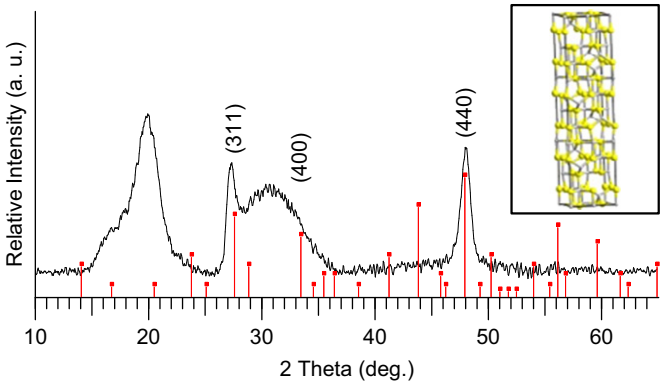

Fig. 1. P-XRD pattern of β-In_2S_3nanorods prepared from a 5 mM solution of the precursor in OLA at 200 °C. Inset shows the crystal structure of β-In_2S_3.

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surface area from the thermolysis of the single source precursor [$In(SON(CN^iPr_2)_2)_3$] [20] in hot oleylamine. To the best of our knowledge this work reports the thinnest indium sulfide nanorods and nanowires to date.

2. Experimental details

All preparations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. The complex was prepared as described in our previous report [20]. A solution of di-*iso*-propylcarbamoyl chloride (1.0 g, 6 mmol) and sodium thiocyanate (0.49 g, 6 mmol) in acetonitrile (25 mL) was heated to reflux with continuous stirring for 1 h, during which time a fine precipitate of sodium chloride formed. The cooled reaction mixture was added to di-*iso*-propylamine (1.49 mL, 12 mmol) followed by stirring for 30 min and addition of indium(III) chloride (0.45 g, 2 mmol) gave the product as white powder which was dried under vacuum for 24 h before use.

The nanowires and nanorods were synthesized by thermal decomposition of the single source precursor [$In(SON(CN^iPr_2)_2)_3$]. Thermolysis experiments were carried out under different conditions; using three different concentrations of the precursor (5, 10 and 20 mM) at 200 °C, three different temperatures (200, 240 and 280 °C) at the concentration of 5 mM and different solvent/capping agent combinations. In a typical experiment, oleylamine

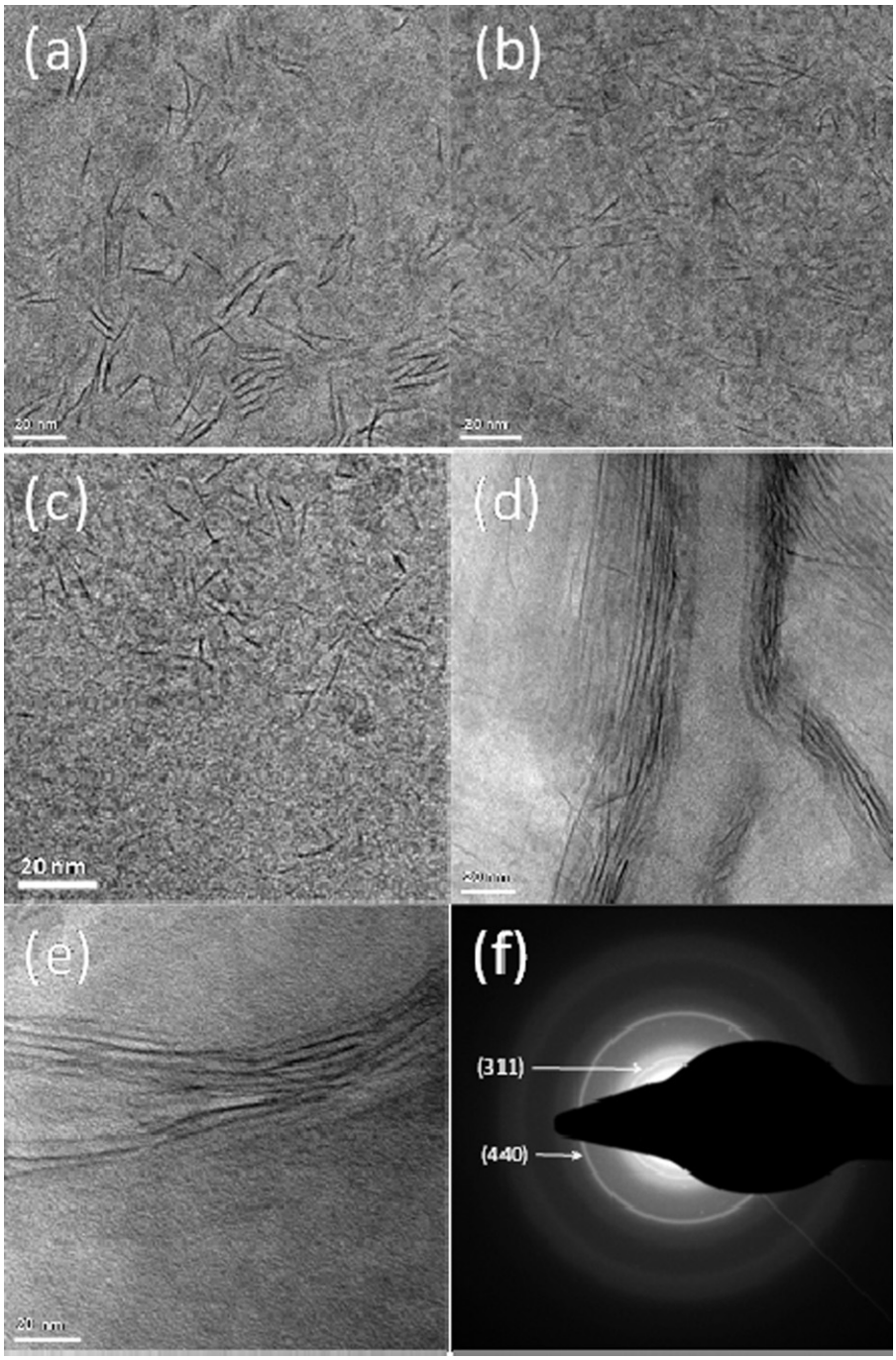

Fig. 2. (a, b, and c) TEM of In_2S_3 nanorods synthesized at 200 °C using 5 mM, 10 mM and 20 mM, respectively. (d and e) TEM of In_2S_3 nanowires synthesized using 5 m M at 240 °C and at 280 °C, respectively. (f) SAED of (d). All scale bars, 20 nm.