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Indium sulfide nanorods from single-source precursor

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Thin films comprised of In_2S_3 nanorods have been prepared on glass substrates by metal-organic chemical vapour deposition using [$Et_2In(S_2CNMe^nBu)$] without either template or catalyst.

Currently, one-dimensional (1D) nanostructure materials have been the focus of much scientific research owing to their unusual properties and their potential applications for the development of nanodevices.[1,2] Several workers have synthesised and characterised nanorods or nanowires of metal chalcogenides or oxides.[3,4] Studies have focused on layered hexagonal structures, such as MoS_2, WS_2, TiS_2 HfS_2 and ZrS_2.[3] Recent reports have indicated that concentric rods can be constructed from non-layered structural materials under appropriate reaction conditions. Systems which have been studied give rise to such materials include; metal oxides (TiO_2,[4] Ga_2O_3, In_2O_3,[5] ZnO[6]) and elemental (Se,[7] Te[8]).

Indium sulfide is a mid band-gap semiconductor which, as is typical for the group 13 chalcogenides, shows a number of forms [*i.e.* InS (Eg = 2.44 eV) and In_2S_3 (Eg = 2.07 eV)].[9] Previously, InS and InSe nanostructures have been reported from the catalysed benzenethiol reactions of $^tBu_3In$ and H_2E (E = S, Se).[10] In the absence of catalysts, the product powders were crystallographically amorphous. It was concluded that the benzenethiol catalyst activates the low energy barrier crystallisation pathways in InE (E = S, Se) syntheses.[10] We reported the preparation of indium sulfide thin films using $R_2InS_2CNEt_2$ (R = Me, Et, Np) as precursors at various growth temperatures.[11] The morphology of films varied with the change of growth temperature and the precursor used.

Indium sulfide thin films have been grown using [$Et_2In(S_2CNMe^nBu)$] as a single-source precursor by aerosol-assisted chemical vapour deposition (AACVD). The compound was prepared by the comproportionation reaction of [$In(S_2CNMe^nBu)_3$] with Et_3In in anhydrous toluene and is a clear liquid at room temperature.†

The as-deposited films were yellow–orange, fairly adherent to the glass substrates.‡ X-ray powder diffraction (XRPD) studies indicated that only tetragonal β-In_2S_3 (JCPDS 25-0390) phase had been deposited showing a preferred orientation along the (109) plane regardless of growth temperatures. (Fig. 1)

The surface morphologies of films were analysed by scanning electron microscope (SEM). It became evident that the morphologies vary noticeably with deposition temperature. Films grown at 325 °C were non-uniform and comprised of clusters of nanorods. With an increase in the deposition temperature to 375 °C, the film consisted of only randomly orientated nanorods (Fig. 2). At 425 °C, considerably increased growth along the length of the nanorods takes place and the average diameter of rods was also increased. At 475 °C, the films gave a mixture of monodispersed and clusters of rods.

Our previous growth studies show that the morphology of films change with the changes in the growth temperature, precursor and the substrate.[11] EDAX analyses of the nanorods showed the In : S ratio to be close to stoichiometric 2 : 3. Similarities in the EDAX profiles at different growth temperatures suggest that the stoichiometry of the films is not greatly affected by the growth temperatures.

β-In_2S_3 films grown at 375 °C were analysed by transmission electron microscopy (TEM) which shows the formation of straight In_2S_3 nanorods (Fig. 3). The average diameter of rods is *ca*. 20 nm and they are *ca*. 400–500 nm in length. A high-resolution TEM image of a single nanorod is given in Fig. 3b and confirms the crystallinity by indicating well-resolved (103) lattice planes. The experimental lattice spacing, 0.66 nm is consistent with the 0.62 nm separation in bulk crystals. Buhro and co-workers have reported the catalysed syntheses of InE (E = S, Se) and the morphological distribution found in the InS precipitates was *ca*. 80–85 % platelets, 13–19 % nanorods and nanotubes and 1–2 % nanorods.[10] Some of the nanoubes and nanospheres appeared to be incompletely closed trough, ribbon and bowl morphologies.

The above results demonstrate that the way to monodispersed In_2S_3 nanorods can be prepared on glass substrates by means of a simple and convenient CVD route from [$Et_2In(S_2CNMe^nBu)$]. To the best of our knowledge, no single-source precursor for the generation of indium sulfide nanorods method has been reported. This new route may open the way to the creation of nanostructures and avoid the use of high temperatures and toxic substances such as

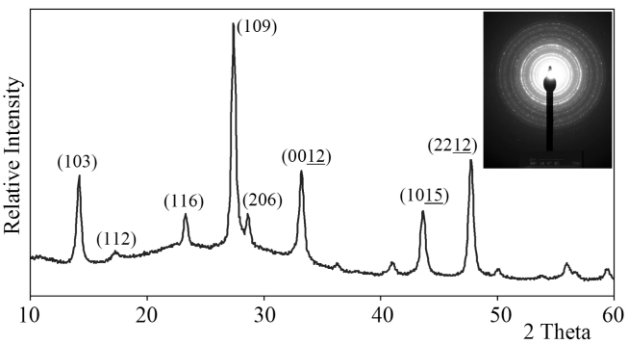

Fig. 1 An XRD pattern of In_2S_3 nanorods grown at 375 °C on amorphous glass substrate. The inset shows an SAED pattern of nanorods at 375 °C.

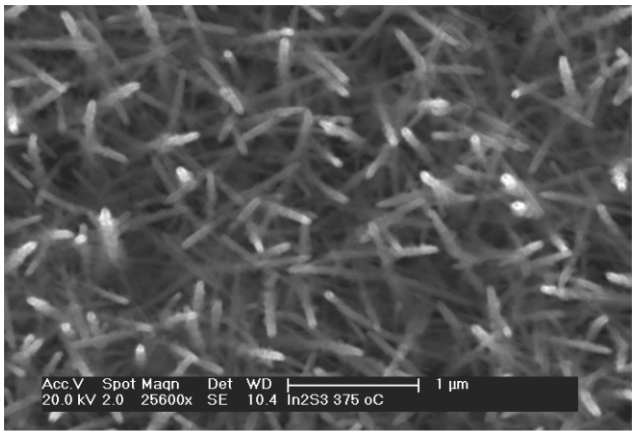

Fig. 2 SEM image of In_2S_3 film at 375 °C.

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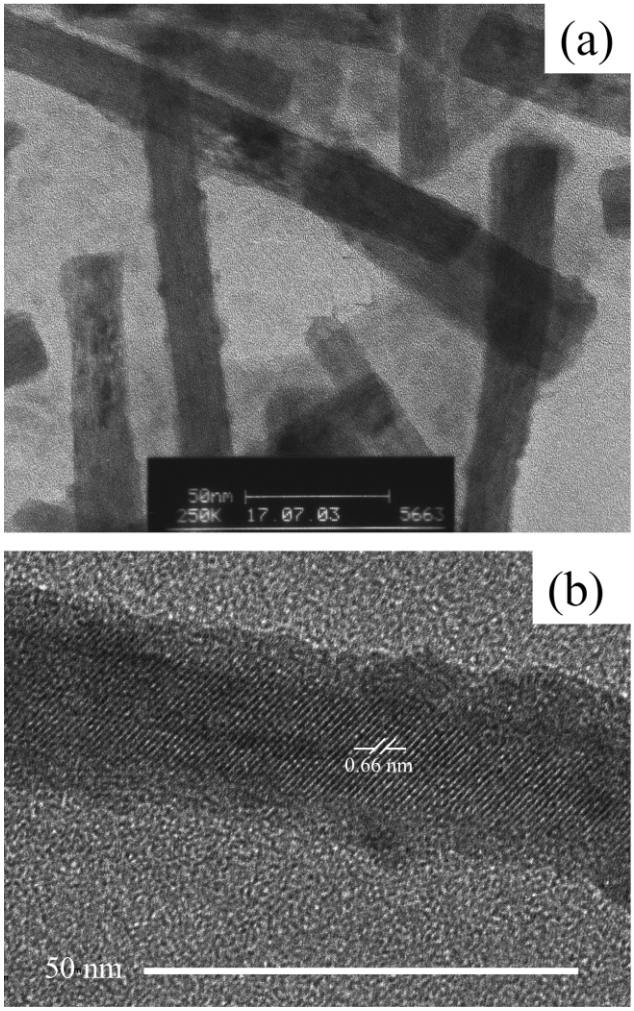

Fig. 3 (a): A typical TEM image of synthesized In_2S_3 nanorods at 375 °C. (b) A HR-TEM image showing a segment of a single straight In_2S_3 nanorod. Interplanar spacing d = 0.66 nm is consistent with the (103) plane.

H_2S. Currently, studies are being carried out on controlling the size of rods supported on metal catalysts such as Au/Fe nanoparticles.

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Notes and references

† $[In(S_2CNMe^nBu)_3]$ was prepared according to the reported method.[12] Toluene (BDH) was distilled over Na-benzophenone and degassed prior to use. All manipulations and reactions were carried out in an inert atmosphere using Schlenk techniques and a vacuum line.

Precursor purity was confirmed by NMR, IR, Mass spectrum and micro-analysis.

‡ The synthesis of nanorods was carried out on glass substrates by AACVD for 2 h, with a constant argon flow rate of 140 sccm by dissolving *ca*. 150 mg of $[Et_2In(S_2CNMe^nBu)]$ in 20 ml dry toluene.[13]

Characterisation: X-ray Powder diffraction studies were conducted on a Bruker D8 AXS diffractometer using monochromated Cu–K_α radiation. Films were carbon coated using Edward's E306A coating system before SEM and EDAX analyses. SEM was carried out on a Philip XL30 FEG and EDAX was preformed on a DX4. TEM analyses were carried on Philips CM200, 200KV DX4EDS. Sample were briefly sonicated in ethanol, which suspended the nanorod material and then a drop of suspension was placed on a TEM grid and allowed to dry.

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