

Hydrothermal synthesis and photoluminescent properties of stacked indium sulfide superstructures†

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Received (in Cambridge, UK) 12th November 2007, Accepted 15th January 2008

First published as an Advance Article on the web 31st January 2008

DOI: 10.1039/b717512d

Unusual hierarchical stacked superstructures of cubic β -In₂S₃ were fabricated via a facile hydrothermal process in the presence of a surfactant cetyltrimethylammonium bromide CTAB; the 3D superstructures were developed by helical propagation of surface steps from microflakes of 10–20 nm thickness.

The synthesis of organized superstructures or complex architectures based on the assembly of nanoscale building blocks has been the focus of much scientific research owing to their novel collective optical, magnetic, and electrical properties.^{1,2} Many recent efforts have been devoted to fabricating two- and three-dimensional (2D/3D) ordered superstructures based on 0D and 1D nanoscale building blocks, such as nanodots, nanofilaments, nanowires and nanobelts.^{3,4} However, assembly of 2D components into well-defined 3D novel architectures amenable to practical use remains a difficult and demanding scientific task. Very recently, there are several attempts to synthesize 3D complex macroscopic structures based on 2D nanoplates, nanodisks or nanosheets.^{5,6} These self-assembled hierarchical and repetitive superstructures provide a novel approach to bring forth new properties.⁷

Although a large number of diverse semiconductor nanocrystals have been investigated, there are relatively few reports of III–VI semiconductor nanoparticles, such as In₂S₃. Of the three different crystalline forms of In₂S₃, β -In₂S₃ is an n-type semiconductor with a mid-band gap of 2.0–2.3 eV. It has application in preparation of green and red phosphors for the manufacture of picture tubes for colour televisions, dry cells, and so forth.⁸ In addition, it is also a promising candidate for photovoltaic applications, such as solar cells.⁹ Due to these important properties several kinds of techniques have been developed to fabricate β -In₂S₃ with different morphologies, which include a direct reacting of the elements at a high temperature,¹⁰ arrested precipitation method,¹¹ metal–organic chemical vapour deposition (CVD),¹² sonochemical synthesis,¹³ and hydrothermal or solvothermal synthesis.^{14,15} Although the synthesis of β -In₂S₃ has been reported pre-

viously, there has been only few reports on the fabrication of cubic β -In₂S₃.^{13b,14c,d} In this communication, we report the spontaneous formation of novel complex architectures of cubic β -In₂S₃ through a combination of a mild hydrothermal method and surfactant template technique. The 3D complex architectures of β -In₂S₃ composed of stacked arrays of 10–20 nm thickness microflake crystals. To the best of our knowledge, this is the first time that 3D stacked III–VI semiconductor superstructures have been reported.

All chemicals were of analytical grade and were used as received without further purification. In a typical procedure, InCl₃·4H₂O (0.15 g, 0.5 mmol) and CTAB (0.7 g, 2 mmol) were first added to distilled water (10 mL, $\rho = 1 \text{ M}\Omega \text{ cm}$) at room temperature, followed by the addition of thiourea (0.08 g, 1 mmol) under stirring. The resulting solution was transferred into a 18 ml Teflon-lined autoclave. The autoclave was sealed and maintained at 140 °C for 7 h, then air-cooled to room temperature. The products were washed several times with anhydrous ethanol, and finally dried at 50 °C in air.

Fig. 1(a)–(c) show scanning electron microscopy (SEM) images of β -In₂S₃. A large number of β -In₂S₃ stacked superstructures were formed as shown in Fig. 1(a). These superstructures are similar to stacked calcium carbonate (calcite) superstructures consisting of pseudo-hexagonal plates, which were prepared by a microemulsion-based method.^{6c} Here the superstructures are up to more than ten micrometers in length.

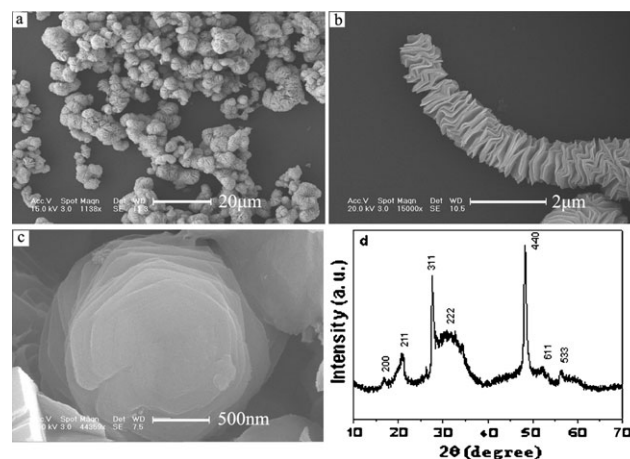


Fig. 1 (a) Low-magnification and (b) high-magnification FE-SEM images of the as-synthesized In₂S₃ stacked superstructures; (c) top-view of stack showing spiral growth pattern of surface steps; (d) XRD pattern of the as-synthesized In₂S₃ products.

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† Electronic supplementary information (ESI) available: XRD pattern of In(OH)₃, EDX pattern, FTIR spectrum, TGA curve and SEM images of indium sulfide prepared under different conditions. See DOI: 10.1039/b717512d

More detailed morphologies of the stacked superstructures are shown in Fig. 1(b) and (c). Fig. 1(b) shows that the products are composed of 10–20 nm-thick flake-like crystals of around 1–2 μm in diameter, and further observation reveals that the flakes are curved with corrugated margins. The individual stacks are structurally intact although they show extensive curling of the microflakes possibly due to drying in the SEM observation, which means the presence of strong interparticle contacts between adjacent lamellae. Fig. 1(c) shows close morphological alignment of flakes, and further confirmed that the superstructures are composed of densely packed layers of microflakes. These microstructures were sufficiently stable that the morphology could not be broken into discrete microflakes, even after a long time of ultrasonication treatment. Significantly, a helical pattern of growth steps on the end faces could be clearly observed in Fig. 1(c). To confirm the chemical stoichiometry of the synthesized products, we performed energy dispersive X-ray spectroscopy (EDX). A representative EDX pattern (ESI[†]) recorded from superstructures revealed that the stacked structures are composed of In, S, C and Br, and the ratio of indium to sulfur atoms is 2 : 3.1 (0.645), which is close to the theoretical 2 : 3 (0.667) ratio expected for In_2S_3 . X-Ray diffraction (XRD) pattern of the product (Fig. 1(d)) shows that the diffraction peaks could be indexed to pure cubic $\beta\text{-In}_2\text{S}_3$ phase (JCPDS Card No. 32-0456).

Further structural characterization of the stacked In_2S_3 nanostructures was performed by TEM and high-resolution TEM (HRTEM). Fig. 2(a) shows a typical TEM image of stacked In_2S_3 and its SAED pattern. The result reveals the highly single crystalline nature of the In_2S_3 microflakes. Fig. 2(b) shows a HRTEM image of a flake-like crystal. The lattice spacing of 0.539 nm corresponds to the (200) planar spacing of cubic $\beta\text{-In}_2\text{S}_3$.

To shed light on the growth process of this novel stacked In_2S_3 superstructures, we studied the samples (obtained at different stages of the reaction under 140 $^\circ\text{C}$ hydrothermal treatment) using SEM and EDX and XRD. After 15 min, a white precipitate was obtained which consists of large-scale uniform nanorod bundles (around 100–200 nm in length) (Fig. 3(a)), and the nanorod bundles consist of individual parallel nanorods with diameters about 20 nm. The EDX pattern (inset of Fig. 3(a)) and XRD pattern (ESI[†]) indicate that the nanorod bundles are $\text{In}(\text{OH})_3$. Further prolonging the reaction time to 3 h in the same reaction system, the colour of obtained products became light yellow, and some cubic crystals together with 3D stacked superstructures composed of microflakes

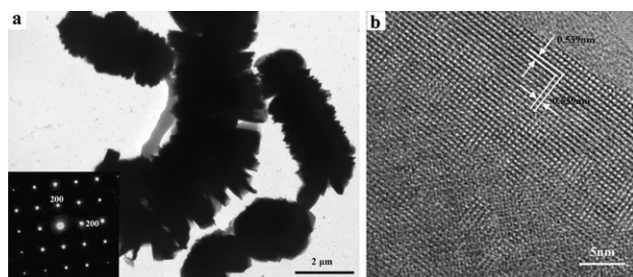


Fig. 2 (a) TEM image of stacked In_2S_3 and its SAED pattern; (b) HRTEM image of the as-prepared $\beta\text{-In}_2\text{S}_3$.

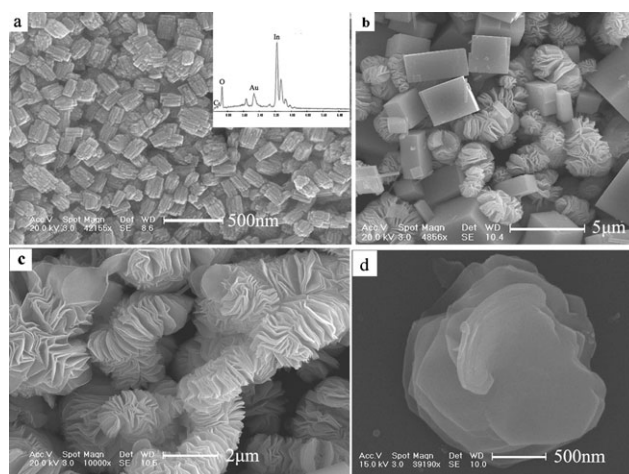


Fig. 3 (a) FE-SEM image and the corresponding EDX pattern of as-synthesized samples obtained by hydrothermal treatment for 15 min; FE-SEM images of the as-formed products collected by hydrothermal reaction for (b) 3 h and (c) 7 h at 140 $^\circ\text{C}$; (d) FE-SEM image of an early stage flake-like crystal showing spiral outgrowth.

were observed in the products as shown in Fig. 3(b). EDX patterns recorded from the cubic crystals and stacks samples show that they are $\text{In}(\text{OH})_3$ and In_2S_3 , respectively, indicating In_2S_3 began to form accompanied by the decomposition of thiourea at this time. The complete conversion to 3D hierarchical stacked In_2S_3 superstructures composed of thin microflakes can be achieved after 7 h of hydrothermal treatment as evidenced by the disappearance of cubic crystals of $\text{In}(\text{OH})_3$ as shown in Fig. 3(c).

SEM investigations on the early stages of development of the stacked superstructures as shown in Fig. 3(d) confirmed that the nascent crystals were in the form of discrete microflakes, which developed by spiral growth from the end faces to form 3D superstructures along the direction perpendicular to the surfaces. Although further investigation is necessary to elucidate the mechanism of the growth of the 3D stacked superstructures, we believe that the strong physical interactions between the organic molecules and the inorganic sheets are responsible for the formation of stacked microstructures, which can be confirmed by EDX analysis and FT-IR spectrum of the stacked product (ESI[†]). The mechanism resembles that of the microemulsion process proposed for the growth of calcium carbonate stacked superstructures by the group of Mann,^{6c} which proposed that the stacks develop by helical propagation of surface steps from a primary sheet-like single crystal.

We also carried out photoluminescence (PL) studies to investigate the optical properties of the stacked In_2S_3 superstructures. The stacks composed of thin microflakes showed good luminescence compared with the non-luminescent behavior of bulk In_2S_3 .¹⁶ Under excitation at 350 nm, a strong emission at ~ 436 nm and a relatively weak emission at ~ 545 nm were observed as shown in Fig. 4. The strong blue luminescence at ~ 436 nm can be attributed to the presence of several deep trap states or defects in the structure. The weak green luminescence at ~ 545 nm may be an emission from the indium interstitial sites, which corresponds to the report of Chen *et al.*¹⁷

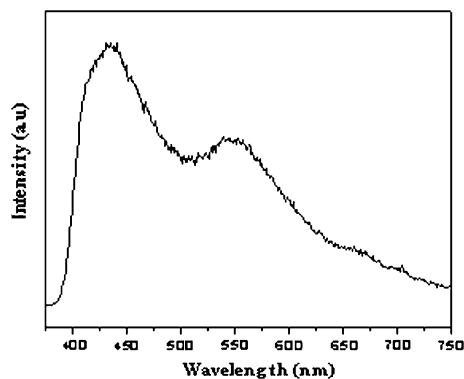


Fig. 4 Room-temperature PL emission spectrum of In_2S_3 stacked superstructures (the intensity scale is linear).

In summary, novel hierarchical stacked superstructures of cubic $\beta\text{-In}_2\text{S}_3$ have been synthesized in high quality and yield via a facile hydrothermal process in the presence of CTAB with thiourea as sulfur source. To the best of our knowledge, this is the first example to prepare stacked superstructures of III–VI compounds, which are expected to show particular physical properties. Our study may provide a new method for direct growth of 3D stacked superstructures and related materials.

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 20490210, 20631040, 20602035 and 20610102007) and the MOST of China (Grant Nos. 2006CB601103, 2006DFA42610). Dr Yan Xing gratefully acknowledges the special starting research fund of K. C. Wong Education Foundation, Hong Kong (2007), the 40th China Postdoctoral Science Foundation and Training Fund of NENU'S Scientific Innovation Project (No. NENU-STC07004).

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