Time-selective Hydrothermal Synthesis of SnS Nanorods and Nanoparticles by Thiourea Hydrolysis

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SnS nanorods and nanoparticles were synthesized by thiourea hydrolysis in an autoclave at 180 °C within a time window of 2 and 8 h, respectively. In the absence of added structure-directing agent, the nanorods formation was attributed to templating characteristic of ammonium ion produced in situ during hydrolysis.

Nanomaterials of SnS have been gaining a lot of attention in relation to their particle size-dependent electronic and optical properties. It was proved to be an excellent holographic register system in view of its remarkable optical properties,[1] in solar cells for its photoconductive properties,[2] and in photovoltaic devices with high conversion efficiency.[3] Over the decades, several methods, such as chemical vapor deposition, electrodeposition, liquid ammonia, organic template-mediated reaction, solid-state metathesis, sputtering of Sn targets, hydrothermal, mechanochemical, precipitation, ethanol-thermal technique, and spray pyrolysis, were adopted to synthesize tin monosulfide.[4,5] Depending on the experimental conditions, the particle size of the product varied from microporous to nanoparticles and nanorods. Since the particle size is proved to have a significant effect on the physical, chemical, or electronic properties of a material, much emphasis is given in the recent times to prepare SnS material in the nanoscale range. Most of the methods evolved out of this goal involve complicated steps and time-consuming process; the simplest but again time-consuming (20–30 h) method, is the solvothermal route.[5] By this method, nanocrystalline SnS was prepared with different morphologies that include nanowires, nanorods, and nanoparticles by appropriately choosing different alkaline solutions and chelating agents like ethylenediamine and 8-hydroxyquinoline under mild alkali conditions. In this work, we present the synthesis of SnS nanorods and nanoparticles by a difference in time scale under similar hydrothermal conditions of thiourea hydrolysis in the absence of any surfactant and chelating agents. This method is much simpler because the reaction proceeds in a single step without any external addition of alkali and in an autoclave under high temperature and pressure. The present method of synthesis of SnS would be a dream to every industrialist who would like to have the material by a simple and cost-effective technique.

A mixture of $SnCl_2 \cdot 2H_2O$ (0.04 M) and thiourea (0.04 M) in 300 mL of aqueous solution was placed in an autoclave of one-liter capacity. Initial pH was acidic (1.9). The solution was heated to 180 °C for 2 h under continuous stirring. In situ pressure developed was 5 atmospheres. After 2 h, the reaction mixture was allowed to cool down to room temperature, filtered, washed to neutral pH and dried at 120 °C. The final pH was noted to be 5.0. In yet another similar experiment, the reaction time was prolonged to 8 h and the resulting product was analyzed. Powder X-ray diffraction (XRD) data of the samples were obtained using an X-ray diffractometer of Siemens D 5000 with Bragg–Brentano geometry having Cu Kα radiation ($\lambda = 1.5418$ Å). The samples were scanned for 2θ values ranging from 2 to 75°. Transmission electron microscope (TEM) photographs were obtained using Hitachi S520 model.

Figures 1 and 2 present the X-ray powder diffraction pattern and TEM image of the SnS nanorods obtained after 2 h experiment. Figure 3 presents the TEM image of the SnS nanoparticles obtained after 8 h experiment. The XRD patterns of SnS nanorods and nanoparticles can be indexed to the orthorhombic unit cell of SnS (JCPDS cards 39-0354) and in consistent with the earlier report.[5] The nanorods (Figure 2) were not uniform in size and shape. The length of the rods lies in the range of 55–250 nm and the diameter of the rods varies from 10 to 50 nm. From the TEM image in Figure 3, it can be seen that the size of the nanopaticles varies from 3–10 nm. Because of the high surface area and high surface energy, the tendency of nanoparticles to form agglomerates was identified and reported in many papers. Figure 3 shows the dense aggregates (as revealed by darker patches) of very small crystallites while at the edges of dark patches reveals monolayer of SnS particles. The overlapping of monolayers to form multilayered agglomerates occurs at random and does not follow any specific order.

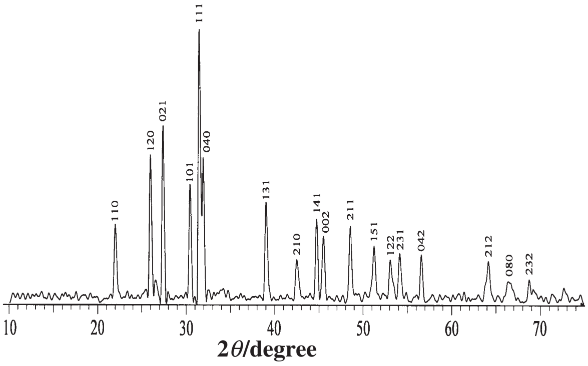

Figure 1. XRD pattern of the SnS nanorods.

These results were highly interesting in view of the formation of SnS nanorods in the absence of any structure-directing agent and the subsequent formation of SnS nanoparticles with increase in time duration of hydrolysis. The acidity of experimental solution prior and after hydrolysis suggests that the formation of nanorods has taken place in acidic conditions as against the earlier reports where mild alkaline conditions were of necessity.

Stannic chloride and thiourea upon dissolution in aqueous medium release Cl^- and S^{2-} anions into solution, which turns the solution pH into acidic. When Sn^{2+} ions react with acidic S^{2-} anions from the solution, they form SnS but not SnS_2. This

Figure 2. TEM image of the SnS nanorods obtained after 2 h reaction time.

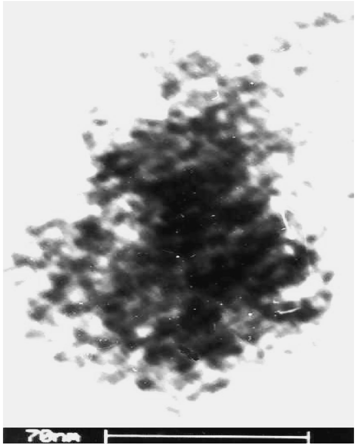

Figure 3. TEM image of the SnS nanoparticles obtained after 8 h reaction time.

implies that there was a reducing atmosphere in the autoclave that prevents the formation of tetravalent tin sulfide and this situation is similar to that of SnO formation by urea hydrolysis in an autoclave, which we reported in our earlier communication. Hence the reactions responsible for the formation of SnS may be written as:

$$SnCl_2{\cdot}2H_2O \xrightarrow{\text{Prior to hydrolysis}} Sn^{2+} + 2Cl^- + 2H^+ + 2OH^- \quad (1)$$

(solution pH = 1.9)

$$Sn^{2+} + 2OH^- + (NH_2)_2C{=}S \xrightarrow[180\,^\circ C]{\text{Hydrolysis}} SnS + CO + NH_4OH \quad (2)$$

$$NH_4OH + 2Cl^- + 2H^+ \longrightarrow NH_4Cl + H_2O + HCl \quad (3)$$

(solution pH = 5)

The formation of SnS nanorods in the absence of externally added structure-directing agent stimulates a lot of interest; the situation is not exactly unusual as there are several instances where the inorganic cations acted as templating agents. In the case of SnS-1 ($Cat_2Sn_3S_7$) and SnS-3 ($Cat_2Sn_4S_9$), the two open-frameworks of tin(IV) thiostannate materials are built entirely of inorganic components with alkali metal cations, Rb^+ and Cs^+ as counter ions. When organic cations are used as charge balancing moieties, sulfur moieties act as cotemplating agents. Hence the cations in the open framework tin chalcogenides appear to have a charge-balancing, space-filling, and structure-directing role, possibly analogous to the templating properties of cations in the synthesis of zeolities and molecular sieves. Various SnS-1 and SnS-3 materials, with different space groups, layer spacing and stacking sequences, have been obtained in the presence of a range of template cations. For example, *tert*-butylammonium, Me_3HN^+, Me_4N^+, $NH_4{}^+$, and Et_4N^+ have all resulted in SnS-1 structure.[6]

On the basis of the above inferences, it can be safely asserted that the $NH_4{}^+$ ion acted as structure-directing agent resulting in the formation of nanorods in a 2 h experiment. On prolonged hydrolysis to 8 h, the 2-D structure was converted to 3-D nanoporous materials. This was an unexpected result as one expects the growth of nanorods with time. This unusual observation leads us to believe that the $NH_4{}^+$ ion indeed acts as the structure-directing agent; as the hydrolysis prolongs, the situation changes. It is possible the $NH_4{}^+$ ions get decompose, thereby destroying the interactions between the templating agent and the tin sulfide matrix which in turn leads to the collapse of SnS nanorod structure. Since the XRD patterns of both SnS nanorods and nanoparticles were the same, it is inferred that there is no change in crystal structure.

To conclude, the time-framed synthesis of SnS nanorods and nanoparticles in a simple single step hydrothermal synthesis was exclusive and economically viable. The need for a structure-directing agent was eliminated, thus making the synthesis much more attractive. Such an easier method to prepare phase-pure SnS material could be a dream to every scientist and industrialist of vested interest.

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