Hydrothermal Synthesis and Characterization of SnS_2 Nanocrystals

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(Received June 12, 2001; CL-010553)

Nanocrystalline SnS_2 was synthesized by a hydrothermal reaction between $SnCl_4 \cdot 5H_2O$ and thiourea (NH_2CSNH_2) at 140–200 °C. XRD pattern indicated that the as-prepared sample was β-phase SnS_2. The as-prepared SnS_2 mainly consisted of hexagon slices with average diameter of 30–200 nm. A Raman spectrum of the as-synthesized β-SnS_2 was presented.

Tin disulfide (SnS_2) is a layered semiconductor, which crystallizes with the hexagonal CdI_2 type structure. The optical and electrical properties of SnS_2 have been reported in the literatures.[1–8] The crystal of SnS_2 is highly sensitive in the visible region of the spectrum, and has been used widely studied as a semiconductor and a photoconductor.[8] Conventionally, SnS_2 is synthesized by direct combination of the elements,[9] by the vapor-phase reaction of the halides with hydrogen sulfide,[10–12] and by a solid-state reaction.[13,14] All the above procedures are carried out in sealed tubes or in argon atmosphere and in the temperature range 400–700 °C. In most cases, it is difficult to obtain nanocrysal from those routes.[14] Recently, Bin Hai et al. have reported synthesis of SnS_2 nanocrystals via a solvothermal method at 200–250 °C.[15]

The hydrothermal process is an effective crystallization process. The particle size and distribution, as well as morphology could be well controlled.[16,17] To our knowledge, the synthesis of SnS_2 nanocrystals by a hydrothermal method has not been reported previously. In this paper we report the preparation of nanocrystalline SnS_2 via a hydrothermal process.

The synthesis of SnS_2 was based on the following reaction:

$$SnCl_4 \cdot 5H_2O + 2(NH_2)_2CS \rightarrow 4NH_4Cl + 2CO_2 + SnS_2 + H_2O \quad (1)$$

Analytically pure $SnCl_4 \cdot 5H_2O$ (0.005 mol) and excessive $(NH_2)_2CS$ (0.013 mol) aqueous solution were added to a autoclave of 50-mL capacity. The autoclave was then filled with distilled water up to 85% of the total volume. The autoclave was maintained at 140–200 °C for 10 h and then cooled to room temperature naturally. The precipitate was filtered and washed with distilled water several times. Yellow powders were collected after being dried in vacuum at 70 °C for 4 h.

X-ray powder diffraction (XRD) pattern was obtained on a Rigaku Damax γA X-ray diffractometer with Cu $K\alpha_1$ radiation (λ = 1.54056 Å). The XRD pattern for the SnS_2 sample was shown in Figure 1. All refractions could be indexed as the hexagonal β-SnS_2 phase with cell constants a = 3.640, c = 5.894 Å, which were consistent with the reported value (JCPDS, 23-677). No impurities such as SnO_2 were detected. Figure 1 (inset) shows electron diffraction (ED) pattern of as-prepared SnS_2, indicating that as-prepared SnS_2 is hexagonal phase.

The IR spectra were obtained using a Magna IR-750FT spectrometer. The powders were dispersed in KBr (1.5/150 mg) and

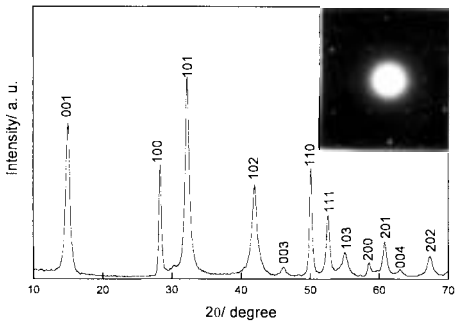

Figure 1. XRD patterns of as-prepared SnS_2 nanocrystals. (Inset) ED pattern of as-prepared SnS_2.

were studied at room temperature. No Sn–O vibrations were detected in the range 500–720 cm^{-1} in the IR spectra of β-SnS_2 formed in distilled water, indicating the absence of tin oxides,[18] which was consistent with the result of XRD.

To provide further evidence for the formation of SnS_2, the samples were also characterized by X-ray photoelectron spectra (XPS). The binding energies for Sn $3d_{5/2}$ (487.0 eV) and Sn $3d_{3/2}$ (495.4 eV) were in good agreement with the observed values in Ag_8SnS_6,[19] demonstrating that only Sn^{4+} existed in SnS_2. The S 2p binding energy, 162.4 eV, was consistent with that of MoS_2.[20] No obvious impurities could be detected in the samples, indicating that the level of impurities was lower than the resolution limit of XPS.

Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscopy, using an accelerating voltage of 200 kV. TEM images of the SnS_2 sample is shown Figure 2. It can be seen that the as-synthesized SnS_2 nanocrystals are hexagonal slices, approximately

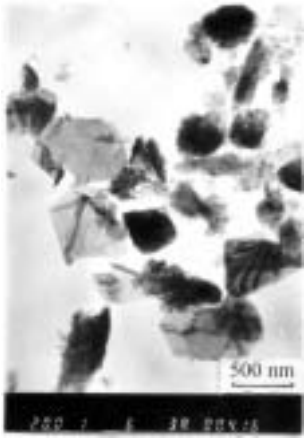

Figure 2. TEM image of nanocrystalline SnS_2 as in Figure 1.

30–200 nm in diameter. Some of them stack each other to form big hexagon.

The influence of reaction temperature and time on the formation of SnS_2 was investigated. It was found that the optimum conditions for the formation of SnS_2 nanocrystal were 140–200 °C for 8–10 h when $(NH_2)_2CS$ was used as sulfur source. If the temperature was lower than 130 °C or the time shorter than 4 h, the yield of SnS_2 was lower and the as-prepared SnS_2 was poorly crystalline. In our hydrothermal process, excessive $(NH_2)_2CS$ played an important role on the formation of SnS_2 nanocrystal. $(NH_2)_2CS$ was hydrolyzed and produced H_2S, which made the reaction to happen under acidic condition. While equivalent $(NH_2)_2CS$ was used, our result showed that the miscellaneous diffraction peaks would be present in the X-ray diffraction patterns.

The effect of different sulfur sources on the formation of nanocrystalline SnS_2 was also studied. $Na_2S{\cdot}9H_2O$ and $(NH_4)_2S$ were used to replace thiourea (NH_2CSNH_2), keeping the other reaction condition identical. The reaction between $SnCl_4{\cdot}5H_2O$ and $Na_2S{\cdot}9H_2O$ could also produce SnS_2. However, the as-prepared SnS_2 was poorly crystalline. Because a reaction between the aqueous solution of $SnCl_4{\cdot}5H_2O$ and $Na_2S{\cdot}9H_2O$ immediately occur at room temperature, yielding a yellow precipitation. XRD indicated that the product was amorphous. The immediate reaction between $SnCl_4{\cdot}5H_2O$ and $Na_2S{\cdot}9H_2O$ is not beneficial in forming nanocrystalline SnS_2. When $(NH_4)_2S$ was used as the sulfur source, because SnS_2 can dissolve in $(NH_4)_2S$ solution,[21] the reaction did not occur.

Raman spectra were recorded on SPEX-1403 spectrometer with 514.5 nm radiation from a 200 mW argon ion laser at room temperature. The Raman spectrum (RS) of β-SnS_2 is illustrated in Figure 3. The spectra show one first-order peak at 312 cm^{-1}. According to the group theory analysis given by Lucovsky et al.,[22] the peak at 312 cm^{-1}, corresponding to A_{1g} mode. The RS of as-prepared SnS_2 shows a slight red-shift in comparison with that of bulk materials(peak at 317 cm^{-1}).[23] The redshift of phonon peaks is due to spatial confinement of phonon modes.[24] This situation is similar to the one recently reported by A. Balandin and coworkers for self-assembled CdS quantum dots[25] and C. R. Wang et al. for BiI_3 nanocrystals.[26] However, the first-order E_g mode (peak at 208 cm^{-1})[22] cannot be observed, which likely results from a nanosize effect.[27] A wide peak between 450 and 750 cm^{-1} (see Figure 3 inset), which only observed in the bulk materials at lower temperature may be attributed to second-order effects.[23, 28]

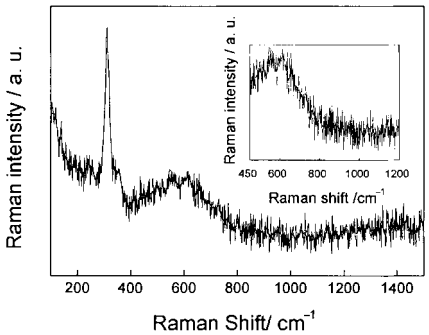

Figure 3. Raman spectrum of as-prepared SnS_2 nanocrystals. Inset is enlargement of the wide peak between 450 and 1200 cm^{-1}.

In summary, SnS_2 nanocrstals were successfully synthesized by a hydrothermal reaction between $SnCl_4{\cdot}5H_2O$ and $(NH_2)_2CS$ at 140–200 °C. The process is simple and easy to control. The as-prepared SnS_2 was characterized by XRD, IR, XPS and TEM. The RS of SnS_2 nanocrystals shows a slight red-shift in comparison with those of bulk materials.

This work was supported by the National Natural Science Foundation of China.

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