Synthesis, Characterization, and Properties of Nanocrystalline Cu_2SnS_3

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The preparation of nanocrystalline Cu_2SnS_3 at synthetic conditions of low temperature (<180°C) was first reported. Nanocrystalline Cu_2SnS_3 was directly synthesized from the reaction of $CuCl_2 \cdot 2H_2O$ with elemental tin and sulfur through a solvothermal process in ethylenediamine at 140–180°C for 15 h. X-ray diffraction (XRD) patterns, transmission electron microscope (TEM) images, and X-ray photoelectron spectra (XPS) were used to characterize the products. The mechanism of the formation of the Cu_2SnS_3 nanocrystals in the solvothermal process was proposed. The UV–vis absorption spectroscopy and the electric conductivity of products were also studied. © 2000 Academic Press

Key Words: nanocrystals; solvothermal process; multicomponent chalcogenide; Cu_2SnS_3; electric conductivity; ethylenediamine.

1. INTRODUCTION

A number of reviews on multicomponent chalcogenide systems have appeared in many papers which describe the syntheses of new chalcogenide material (1–5). Cu_2SnS_3 belongs to a group of compounds represented by the general formula I_2-IV-VI_3, which are of particular interest due to their potential applications, such as small band-gap semiconductors (6–8), as nonlinear materials (9), and as suitable candidates for photovoltaic cell materials (10). Furthermore, nanocrystalline compounds exhibit special semiconducting properties between macrocrystalline solids and molecular entities. The preparation of nanocrystalline semiconductor has been the focus of intense study in materials science (11).

Traditionally, multicomponent chalcogenides were synthesized by solid-state reaction (12), which requires elevated temperature and inert atmosphere protection and needs a relative long duration. Cu_2SnS_3 can be prepared by a reaction of stoichiometric elements Cu, Sn, and S at 1050°C

(13). Recently, different methods, such as reactive-flux methods (14) at intermediate temperature (about 300–600°C) and solvothermal methods (2) at low temperature ($< 200°C$), have been used to prepare multicomponent chalcogenides. However, those methods are limited to using alkali metal as one of the raw materials (15–17). To our knowledge, no reports have been published about the preparation of Cu_2SnS_3 at synthetic conditions of low temperature or about nanocrystalline Cu_2SnS_3.

The solvothermal pathway, which is carried out at low temperature and does not require organometallic or toxic procurers, has been proved to be a useful technique to prepare nanocrystalline materials (18–20). Use of supercritical ethylenediamine (en: 300–350°C) in the synthesis of metal chalcogenides is known (21). Recently, we have focused on a softer route in which mild solvothermal conditions are applied to reactions in en medium at temperatures generally $<180°C$ (22–24). Under such conditions, both the solubility and the diffusion rate of the solid species are significantly increased compared with the ambient temperature and pressure, and the crystallization process is greatly enhanced. This synthetic route is especially promising for the synthesis of metal polychalcogenides because the very mild solution medium stabilizes the polychalcogen building blocks and allows Q_y^{2-} ($y \geq 2$) ions to incorporate and remain intact in the final structure. We present here a simple solvothermal synthesis of Cu_2SnS_3 nanocrystals in ethylenediamine at temperatures as low as 140°C.

2. EXPERIMENTAL

The compounds Cu_2SnS_3 was synthesized from a stoichiometric mixture of sulfur (0.481 g, 15 mmol), $CuCl_2 \cdot 2H_2O$ (1.721 g, 10 mmol), and elemental tin (0.58 g, 4.9 mmol), all with nominal purity greater than 99.9%. The mixture was loaded into a 100 ml Teflon-lined autoclave, which was then filled with anhydrous ethylenediamine up to 90% of the total volume. The autoclave was sealed and maintained at 140–180°C for 15 h and was then cooled to

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room temperature naturally. The product was filtrated and washed with distilled water and absolute ethanol for several times to remove byproducts. The precipitate was dried in vacuum at 60°C for 4 h.

The obtained products were characterized by X-ray power diffraction (XRD), using a Japan Rigaku D/max-γA X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). A scan rate of 0.05° s^{-1} was applied to record the patterns in the 2θ range of 10–70°. In order to examine the morphology and particle size of the products, a transmission electron microscope (TEM) image was taken on a Hitachi Model H-800 instrument, using an accelerating voltage of 200 kV. Further evidence for the quality and composition of the product was obtained by the X-ray photoelectron spectroscopy (XPS). XPS spectra were collected on an ESCALAB MK II X-ray photoelectron spectrometer, using non-monochromatized Mg$K\alpha$ X-ray as the excitation source. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C_{1s} to 284.60 eV.

The aqueous solution containing Cu_2SnS_3 nanocrystals were placed into silica cuvetts (1 cm) and studied on a Shimadzu UV-365 spectrophotometer, by scanning between 400 and 800 nm. Conductivity measurements of Cu_2SnS_3 were carried out on circular ($2R = 1.2$ cm), cold-pressed nanocrystalline samples by the four-probe method in the temperature range from 18 to 300 K.

3. RESULTS AND DISCUSSION

The XRD patterns of a prepared Cu_2SnS_3 is shown in Fig. 1. All peaks in the pattern correspond to the triclinic phase of Cu_2SnS_3, and the refined cell parameters are in good agreement with the reported data (25). The XRD pattern shows that the products are well crystallized and rather pure. The TEM image in Fig. 2 shows that the as-prepared material particles are ca. 8 nm, which is consistent with the result calculated from the half-width of diffraction peaks of XRD using the Scherrer formula. Because of
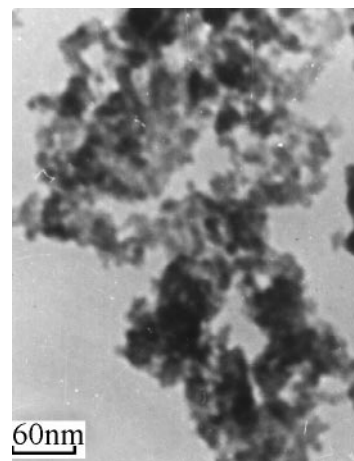

FIG. 2. TEM image of as-prepared nanocrystalline Cu_2SnS_3.

the extremely small dimensions and the high surface energy of the crystals, it is easy for them to aggregate into secondary crystals.

The quality and composition of the samples were also characterized by XPS. The XPS survey spectra shows that no obvious impurities, e.g., chloride ion, elemental tin, or sulfur, could be detected in the samples, indicating that the level of impurities is lower than the resolution limit of XPS (1 at.%). The Cu $2p$ core level spectrum (Fig. 3) illustrates that the observed value of the binding energies for Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are in agreement with the literature values of bulk (26). This means the work function, i.e., the energy needed to remove electrons from the energy levels, is identical for our sample and bulk. However, the full width at half-maximum (FWHM) for peaks Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are 1.9 and 2.4 eV, respectively, which are wider than the reported values for Cu$^+$ (26). This reflects the fact that the surrounding conditions around every atom in our sample are not uniform. Besides, the Cu $2p_{3/2}$ satellite peaks characterizing Cu^{2+}, which are usually centered at about 942 eV (27), are missing in Fig. 3. Therefore, we may conclude that
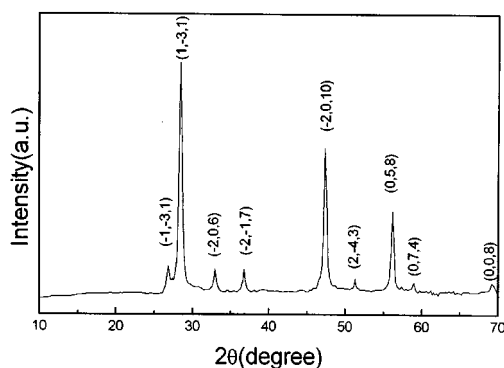

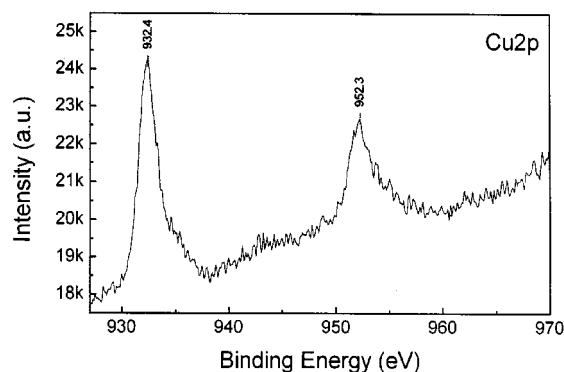**FIG. 1.** XRD pattern of as-prepared nanocrystalline Cu_2SnS_3.

FIG. 3. Cu $2p$ core level XPS spectrum of Cu_2SnS_3.

only Cu^+ exists in this compound. XPS analysis also revealed the normal valence states for S and Sn atoms. The Sn core level spectrum exhibits the binding energies of 486.8 and 495.2 eV, corresponding to $3d_{5/2}$ and $3d_{3/2}$ states, respectively, which are very similar to those observed in SnS_2 (28). The S $2p_{3/2}$ and S $2p_{1/2}$ binding energies, 161.9 and 162.8 eV, respectively, are consistent with those observed in chalcopyrite $CuFeS_2$ (29). The quantification of peaks gives the ratio of Cu:Sn:S of 1.986:1:3.035, in agreement with the EDX and chemical analysis results.

The absorption spectrum of Cu_2SnS_3 nanocrystals is shown in Fig. 4. A minor absorption shoulder peak at 530 nm (2.34 eV) is observed, which can be regarded as an exciton peak. The absorption edge of Cu_2SnS_3 nanocrystals is at ca. 660 nm (1.88 eV), while that of bulk Cu_2SnS_3 is at 1362 nm (0.91 eV) (30) and of film Cu_2SnS_3 at 700 nm (1.77 eV) (31). The large blue shift is associated with a quantum size effect due to confinement of the electron and hole in a small volume. The electric conductivity measurements of Cu_2SnS_3 were performed by the four-probe method. Experimental results are plotted in Fig. 5 as a function of temperature. Data clearly indicate that the product has excellent semiconductor behavior (7).

The formation process of nanocrystalline Cu_2SnS_3 may be as follows. As noted in the literature (32), elemental sulfur (S_8) can be activated by nucleophilic attack of a base, such as amine or hydroxide, or through adsorption at electron-rich tin sites present in the surface of the elemental tin particles. In our process, when only tin and sulfur were added into the autoclave and heated at 180°C for 12 h, the final product was determined to be not the binary tin sulfide but the coordination compound of en, tin, and sulfur. When $SnCl_4$ or was used to substitute tin we also got the Cu_2SnS_3 product. Therefore in our process, the sulfur might be activated by tin and en when using tin or $SnCl_2$ as raw material, and the sulfur can only be activated by solvent en when using $SnCl_4$ as raw material. In the solvothermal process, with the increase of temperature and pressure the elemental tin and sulfur solubilize in ethylenediamine and
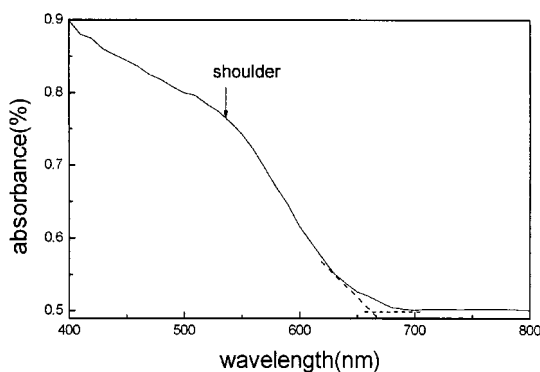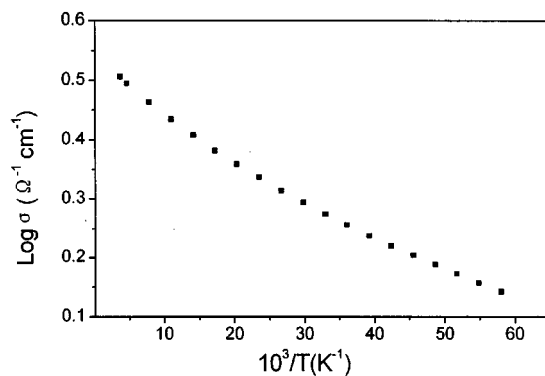
FIG. 5. Electrical conductivity of Cu_2SnS_3 versus temperature.

form some intermediates and then yield various tin(IV) polysulfide-like SnS_4^{4-}, $Sn_2S_6^{4-}$, etc., which might participate in the formation of products. Although the sulfur can be activated only by tin, in our process the solvent plays an important role in the formation of the titled compound nanocrystals.

Ethylenediamine was selected as the optimum solvent due to its special properties, such as strong polarity and strong chelation, which are important to the reaction. In this solvothermal process, Cu^{2+} was reduced to Cu^+, and ethylenediamine can easily chelate Cu^+ and form a stable complex $[Cu(en)_n]^+$ ($K = 10^{10.8}$), thus it effectively deterred the formation of binary copper chalcogenides. Then as temperature and pressure increased, that complex decomposed and released Cu^+. At that time, sulfur had turned into the oligomeric anion $(Sn_2S_6)^{4-}$ which then combined with Cu^+ to form the final product. In a word, the ethylenediamine well protected Cu^+ from being captured by sulfide anions and timely freed it when the oligomeric anion $(Sn_2S_6)^{4-}$ have been formed.

On the other hand, being a strong polar solvent and an absorber to release the excess heat produced in the reaction, ethylenediamine can greatly enhance solubility, diffusion, and crystallization but still provide reaction conditions mild enough to enable molecular building blocks to participate in subsequent formation of the solid-state phase. To confirm the importance of ethylenediamine as a solvent in the formation of the product, the reactions were also performed in other solvents such as benzene and ethanol. The results, which were detected by XRD, showed that no Cu_2SnS_3 but a mixture of copper sulfide and tin sulfide was obtained in those cases.

Optimum conditions for preparing Cu_2SnS_3 nanocrystals are at 140°C for 15 h in the autoclave. Lower temperature or shorter times led to incomplete reaction with decreased yield and crystallinity. In our experiment, when the temperature was lower than 100°C, the reaction could not be initiated. On the other hand, the resultant grains were bigger at higher temperatures or a longer time. When the

FIG. 4. Absorption spectrum of Cu_2SnS_3 nanocrystals.

reaction was carried out at 180°C for 15 h, the grain size reached sizes up to 50 nm. In general, the grain size varied with the reaction temperature and time.

4. CONCLUSION

In conclusion, nanocrystalline Cu$_2$SnS$_3$ with a size of ca. 8 nm can be directly synthesized through solvothermal process in ethylenediamine at temperature as low as 140°C. This solvothermal synthesis method for ternary metal chalcogenides is not only feasible and interesting but also a promising alternative to the traditional techniques usually employed in synthetic chemistry. Solvothermal synthesis can be used to prepare structurally and functionally unique compounds not accessible otherwise.

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