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Preparation and Morphology Control of Rod-like Nanocrystalline Tin Sulfides via a Simple Ethanol Thermal Route

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Rod-like nanocrystalline tin sulfides with different compositions and phases were obtained via simple ethanol thermal reactions between tin chlorides and thioacetamide at relatively low temperature (100°C for 10 h). It is found that solvents, reaction temperatures, and trace water in the system were important factors in obtaining one-dimensional nanocrystalline tin sulfides. The reaction mechanism has also been investigated. © 2001 Academic Press

Key Words: **tin sulfides; nanorods; ethanol thermal route; thioacetamide; low temperature.**

INTRODUCTION

A number of reviews have illustrated the continuing interest in materials of tin sulfides (1, 2), among which the two most important ones are SnS and SnS_2. Particularly, tin monosulfide has been widely used in semiconductor materials (3), solar cell materials (4), photoconductors (5), photovoltaic materials with high conversion efficiency (6), and commercial semiconductor sensors in environmental industrial, and biomedical monitoring (7). Tin(IV) disulfide also has interesting optical and electrical properties (8, 9), and has potential uses as photoconductors and semiconductors (10). Moreover, the multiple local coordination geometry around a tin center and the catenation ability of sulfur tin allow sulfide-based materials to exist in many forms, such as one-dimensional chains, two-dimensional dense and porous sheets, and three-dimensional open frameworks (1), which enriches tin sulfide chemistry. Other elements, such as copper or silver, can also be incorporated into the tin sulfide structures via the recently developed "soft chemical" synthetic methods to obtain ternary and quaternary materials (11, 12), which show interesting electrical, optical, and adsorption properties (13).

The fabrication of tin sulfides has recently attracted extensive research interest. The preparation of bulk tin chalcogenides (14–18) and the growth of tin sulfide thin films (8, 19–24) have been widely reported. Schleich and co-workers (25–28) prepared a series of amorphous transition metal sulfides by the reactions between metal halides and organic sulfur compounds such as di-*tert*-butyldisulfide (DTBDS), di-*tert*-butylsulfide (DTBS), and *tert*-butylmercaptan (TBMC) at relatively low temperatures. Bonneau and co-workers (29) synthesized a number of transition metal chalcogenides in nonaqueous solutions at room temperature by reactions between anhydrous transition metal chlorides and either lithium sulfide or ammonium hydorgen sulfide. The products had large surface areas, but were poorly crystalline or amorphous. Qian *et al.* (30) adopted a solvothermal route to nanocrystalline β-SnS_2 by the reaction between $SnCl_4$ and anhydrous Na_2S at 150°C in toluene. The manipulations were carried out in dry-box filled with nitrogen; all the raw materials and the solvent toluene must be absolutely anhydrous. The precursor Na_2S was prepared through a complex route.

The control of nucleation and growth of one-dimensional (1-D) nanocrystalline materials is becoming critical, since 1-D nanostructures as building blocks for many novel functional materials are currently the focus of considerable interest (31–35). But as far as we know, almost all the produced tin sulfides easily agglomerated and the morphologies of particles or small clusters were never far from spherical particles. Here we obtained rod-like nanocrystalline tin sulfides through a simple and mild ethanol thermal route, and investigated the reaction conditions systematically. We discovered that crystal shape, size, and composition were strongly influenced by solvents, synthetic temperatures, and precursors.

EXPERIMENTAL

Analytical grade solvents and reagents were purchased from Shanghai Chemistry Co. Ltd.

Appropriate amounts of hydrated tin chloride $SnCl_2 \cdot 2H_2O$ or $SnCl_4 \cdot 4H_2O$ and excessive thioacetamide were

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TABLE 1
Results of XRD, TEM, XPS, and Elemental Analyses under Different Conditions

No.	Tin salt	Solvent	$T/°C$	t/h	Phase(s)	Morphology	Composition (S/Sn)	Size
1	$SnCl_2 \cdot 2H_2O$	EtOH	60	12	Amorphous SnS + orthorhombic SnS	Spherical	0.95	25 nm
2	$SnCl_2 \cdot 2H_2O$	EtOH	80	10	Orthorhombic SnS	Short rod + spherical	0.98	10 nm × 120 nm 20 nm
3	$SnCl_2 \cdot 2H_2O$	EtOH	100	10	Orthorhombic SnS	Rod-like	0.96	8 nm × 200 nm
4	$SnCl_2 \cdot 2H_2O$	EtOH	≥ 120	8	Orthorhombic SnS	Rod-like	0.99	8 nm × 300 nm
5	$SnCl_2 \cdot 2H_2O$	EtOH + MeOH	100	10	Orthorhombic SnS + hexagonal Sn	Short rod + spherical	0.76	10 nm × 100 nm 25 nm
6	$SnCl_4 \cdot 4H_2O$	EtOH	60	12	Amorphous SnS_2	Spherical	1.98	25 nm
7	$SnCl_4 \cdot 4H_2O$	EtOH	80	10	Hexagonal SnS_2 + amorphous SnS_2	Short rod	2.01	15 nm × 100 nm
8	$SnCl_4 \cdot 4H_2O$	EtOH	100	10	Hexagonal SnS_2	Rod-like	2.02	10 nm × 200 nm
9	$SnCl_4 \cdot 4H_2O$	EtOH	≥ 120	8	Hexagonal SnS_2	Rod-like	1.99	10 nm × 250 nm
10	$SnCl_4 \cdot 4H_2O$	EtOH + MeOH	80	10	Hexagonal SnS_2 + hexagonal Sn_2S_3	Short rod	1.82	10 nm × 150 nm
11	$SnCl_4 \cdot 4H_2O$	EtOH + MeOH	100	10	Hexagonal SnS_2	Short rod	1.48	8 nm × 200 nm

added into a Teflon-lined stainless steel autoclave, which had been filled with ethanol or the mixed solvent ($V_{EtOH}/V_{MeOH} = 3$) up to 80% of the total volume (50 ml). The autoclave was maintained in the temperature range 60–180°C for the proper time, and then cooled to room temperature naturally. The precipitates were collected and washed with distilled water. The final products were dried in a vacuum at 40°C for 1 h.

X-ray powder diffractions (XRD) were carried out on a Rigaku D/max rA X-ray diffractometer equipped with graphite-monochromatized high-intensity (Cu*Kα* radiation ($\lambda = 1.54178$ Å). The accelerating voltage was set at 50 kV, with 100 mA flux at a scanning rate of 0.05°/s in the 2θ range of 10° to 70°. The morphologies and sizes were determined by transmission electron microscopy (TEM). The TEM images were taken with a Hitachi Model H-800 transmission electron microscope with a tungsten filament, using an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII X-ray phtoelectron spectrometer, using Mg*Kα* radiation as the exciting source. Elemental analyses were done by atomic absorption spectroscopy using a Perkin-Elmer 1100B atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Under different reaction conditions, we obtained different solvothermal products (Table 1). Dark-brown nanocrystalline SnS (product **3**) was obtained by the reaction between $SnCl_2 \cdot 2H_2O$ and thioacetamide in ethanol at 100°C for 10 h. Brown hexagonal SnS_2 nanorods (product **8**) were obtained by the reaction between $SnCl_4 \cdot 4H_2O$ and thioacetamide in ethanol at 100°C for 10 h. Orthorhombic Sn_2S_3 nanorods (product **11**) were obtained by the reaction between $SnCl_4 \cdot 4H_2O$ an thioacetamide in the mixed solvent of ethanol and methanol at 100°C for 10 h.

The Phase and Morphology of the Products

The XRD patterns are shown in Fig. 1. Product **3** could be indexed as orthorhombic SnS, with the cell constants of $a = 4.32$ Å, $b = 11.20$ Å, and $c = 3.99$ Å (literature values for SnS (36), $a = 4.30$–4.33 Å, $b = 11.18$–11.21 Å, and $c = 3.98$–4.02 Å). Product **8** was hexagonal SnS_2 with the cell constants of $a = 3.65$ Å, $c = 5.88$ Å, which accorded well with those from a number of X-ray reports (1) ($a = 3.62$–3.65 Å and $c = 5.85$–5.90 Å). Product **11** was orthorhombic Sn_2S_3 with the cell constants of $a = 8.93$ Å, $b = 14.16$ Å, and $c = 3.75$ Å (reported data for Sn_2S_3 (37) $a = 8.80$–8.84 Å, $b = 14.02$ Å, $c = 3.75$–3.77 Å). Some peaks in the XRD patterns, such as (111), (040) in Fig. 1a, (100) in Fig. 1b, and (050) in Fig. 1c, were usually strong, which indicates preferred orientation effects of crystal growth. The TEM micrographs (shown in Fig. 2) also testified that all the above products were rod-like.

X-Ray Photoelectron Spectrum (*XPS*)

The ratios of tin to sulfur for obtained products were determined by XPS and elemental analyses XPS results were in accord with elemental analyses, which have a variation of less than three elemental percentages. XPS did show some oxygen and carbon contamination on the surface of each product (XPS interrogates the surface ca. 10 atomic layers). The oxygen and carbon were predominantly

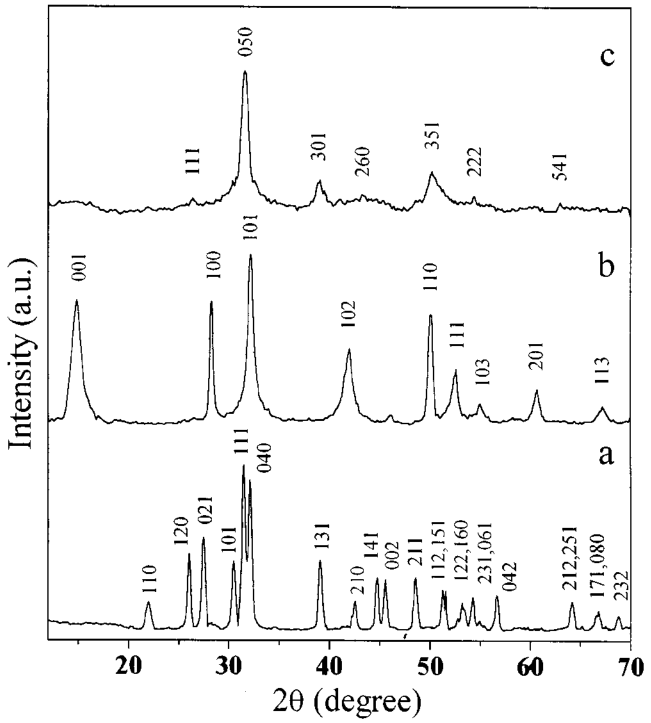

FIG. 1. XRD patterns of samples: (a) product **3**, orthorhombic SnS, (b) product **8**, hexagonal SnS_2, and (c) product **11**, orthorhombic Sn_2S_3.

surface bound, a situation which probably came about by handling and storage of the products in air and not via nanocrystallites themselves. Notably no chlorine was detected by XPS (ca. 0.5 atom percentage detection limit).

The XPS binding energy measurements are shown in Fig. 3. The product SnS had a Sn $3d_{5/2}$ peak at 485.2 eV and an S $2p_{3/2}$ peak at 161.3 eV, which accorded with the Sn $3d_{5/2}$ peak reported for SnS of 485.6 eV (38). The product SnS_2 had an Sn $3d_{5/2}$ peak at 486.1 eV and an S $2p_{3/2}$ peak at 161.5 eV. These values agreed with those for SnS_2 of Sn $3d_{5/2}$ at 486.6 eV and S $2p_{3/2}$ at 161.4 eV (36). The product Sn_2S_3 had Sn $3d_{5/2}$ peaks at 486.3 eV and 485.5 eV, and an S $2p_{3/2}$ peak at 161.4 eV. Notably binding energies of the product Sn_2S_3 corresponded to those for Sn in the oxidation state +4 and +2. So it is thought that Sn_2S_3 was a solid solution of SnS_2 and SnS.

Sulfur has a large range of binding energies from 161.7 eV in ZnS (S(-II)) to 171 eV in S(VI) compounds. Binding energies of these tin sulfide nanocrystallites corresponded to that of S(-II). The binding energy of S in the nanocrystalline SnS was among the lowest recorded for sulfur (38). The binding energy of the Sn(IV) nanocrystalline SnS_2 was 0.9 eV greater than that of the Sn(II) nanocrystalline SnS. These results agreed with the fact that there is a variation of 0.8–1.0 eV between the Sn(IV) compound and the Sn(II) analogue found in other studies of tin halides and organometallic compounds (38).

Effects of the Solvent on the Formation of Nanocrystalline Tin Sulfides

In the solvothermal process, ethanol was an important solvent. Tin chlorides ($SnCl_2{\cdot}2H_2O$ and $SnCl_4{\cdot}4H_2O$) and thioacetamide could easily dissolve in ethanol; furthermore,

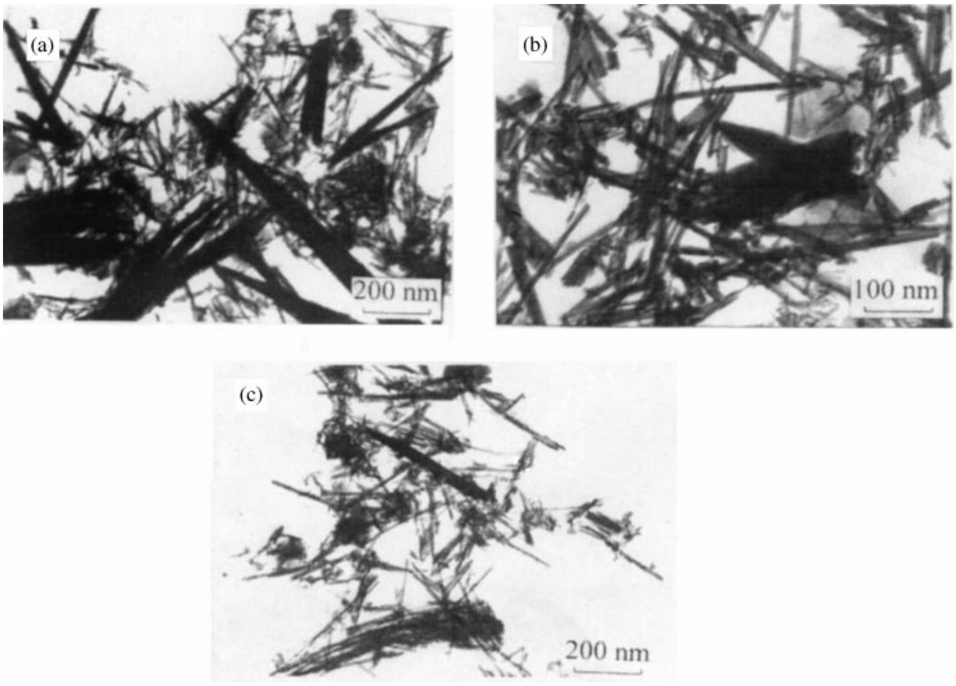

FIG. 2. TEM images of the samples: (a) product **3**, SnS nanorods, (b) product **8**, SnS_2 nanorods, and (c) product **11**, Sn_2S_3 nanorods.

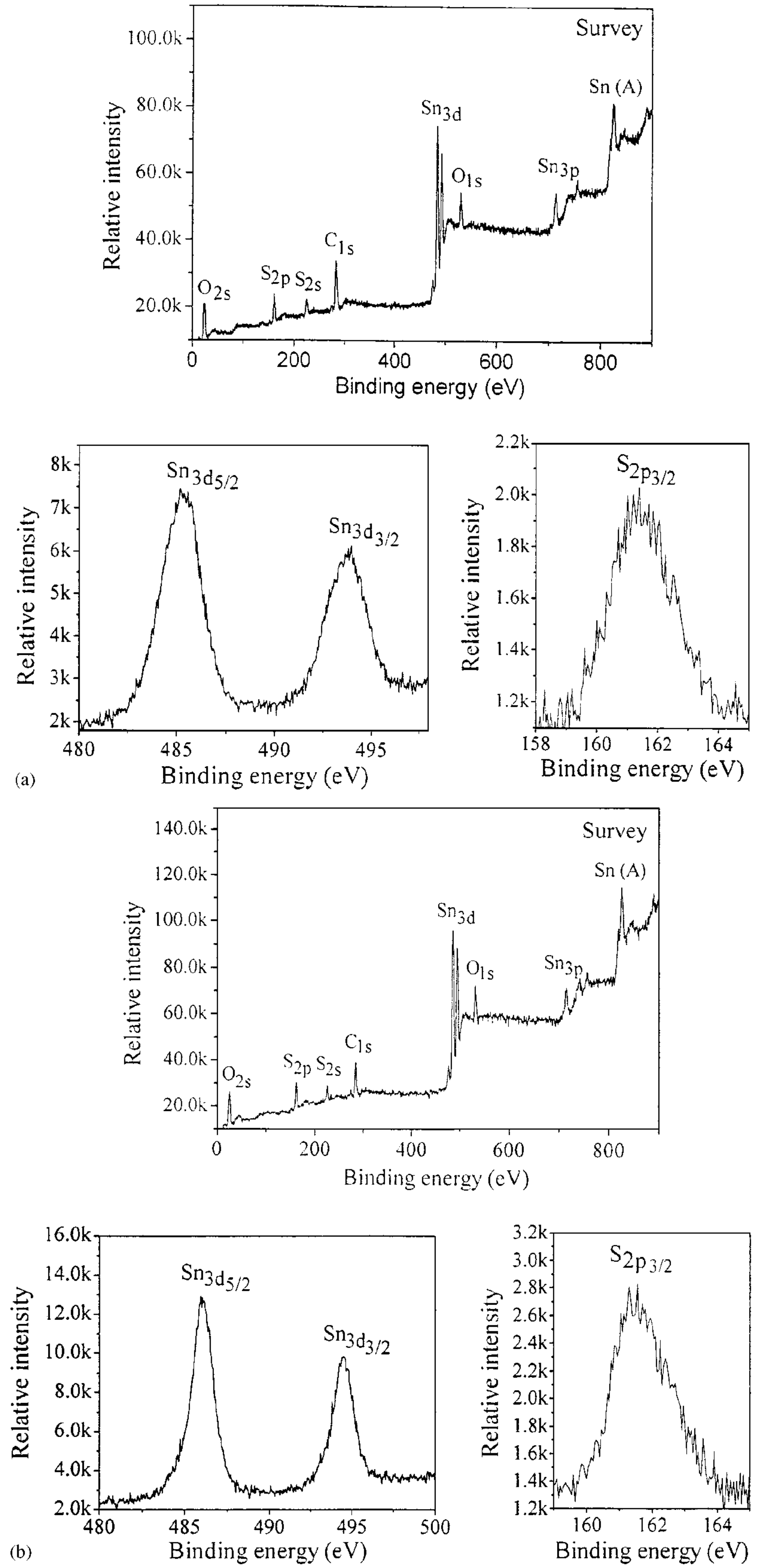

FIG. 3. XPS spectra of the samples: (a) products **3**, nanocrystalline SnS, (b) product **8**, nanocrystalline SnS_2, and (c) product **11**, nanocrystalline Sn_2S_3.

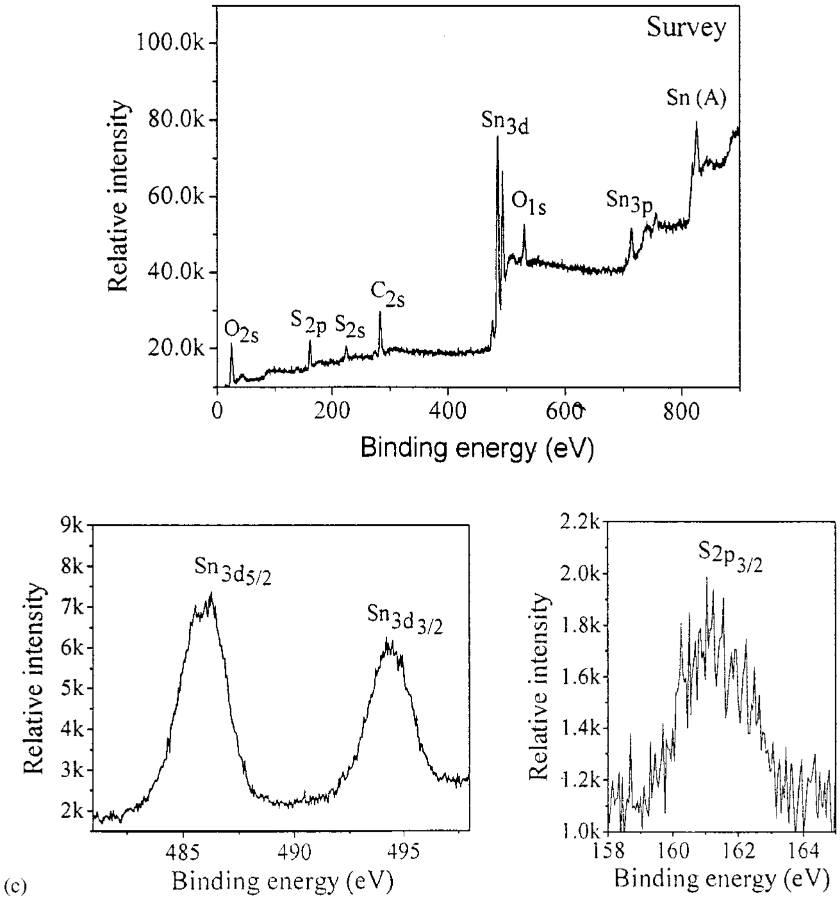

FIG. 3—*Continued*

ethanol and water were always mutually soluble. Thus, tin ions Sn^{2+} or Sn^{4+} and sulfur source thioacetamide were homogeneously dispersed in the mutually soluble solvent of ethanol and trace water from hydrated tin chloride; subsequently thioacetamide would react with trace water (39), shown by Eq. [1].

$$CH_3CSNH_2 + 2H_2O \rightarrow CH_3COONH_4 + H_2S \quad [1]$$

$$Sn^{2+} + H_2S \rightarrow SnS + 2H^+ \quad [2]$$

$$Sn^{4+} + 2H_2S \rightarrow SnS_2 + 4H^+. \quad [3]$$

H_2S was produced slowly and reacted with tin ions to homogeneously form in sulfides. It is obvious that the water from the precursor hydrated tin chlorides was used up to form the corresponding tin sulfides. In addition, the system was weakly acidic due to hydrolysis of thioacetamide, so tin oxides and hydrates would not form, which was helpful to the formation of pure tin sulfides.

Methanol was a reducing solvent. At certain temperature (for example 100°C), methanol could reduce tin(II) to elemental tin, and tin(IV) to tin(II), as shown in Table 1. The product Sn_2S_3, obtained by the reaction of $SnCl_4{\cdot}4H_2O$ and thioacetamide at 100°C for 10 h in the mixed solvent of ethanol and methanol, could be thought to be a solid solution of SnS and SnS_2, proved by XPS results in Fig. 3c. The tin spectroscopy showed tin(II) (485.5 eV) and tin(IV) (486.3 eV).

Effects of Reaction Temperatures on the Quality of Nanocrystalline Tin Sulfides

The temperature was found to play an essential role in the formation of rod-like nanocrystalline tin sulfides. It was found that to form nanocrystalline tin sulfides, the reaction temperature could not be lower than 80°C (close to boiling point of ethanol). Below 80°C, there were some amorphous components; higher temperatures helped crystal formation. In addition, the temperature affected morphologies and sizes of nanocrystalline tin sulfides. Table 1 shows that at relatively low temperature $\leq 80°C$, the oriented growth of tin sulfide nanocrystallites was not obvious; the products displayed spherical and short rod-like morphologies. At higher temperature, the obtained tin sulfide nanocrystallites were longer nanorods with obvious orientation. However, at too high temperature ($> 200°C$), the oriented growth was not obvious, and only coarse crystallites could be obtained.

Formation Mechanism of Tin Sulfide Nanorods

In the ethanol thermal process, the redox did not happen on tin ions. The formation of SnS and SnS_2 only depended on the metathesis reactions between tin ions and H_2S. The difference in the reducibility between ethanol and methanol can be shown by oxidation–reduction potentials:

$$HCHO + 2H_2O + 2e^- \rightarrow CH_3OH + 2OH^- \qquad E^0 = -0.590\,\text{V} \qquad [4]$$

$$CH_3CHO + 2H_2O + 2e^- \rightarrow C_2H_5OH + 2OH^- \qquad E^0 = -0.197\,\text{V}. \qquad [5]$$

The whole reaction proceeded in a sealed autoclave. The formation of tin sulfides improved the acidity strength of the system, which held back thioacetamide hydrolysis and limited the formation velocity of tin sulfides; finally the nucleation and growth of nanocrystalline tin sulfides would be homogeneously carried out. The phase, composition, morphology, and size of the products could be controlled only by selecting appropriate precursor ($SnCl_2 \cdot 2H_2O$ or $SnCl_4 \cdot 4H_2O$), solvent (ethanol or the mixed solvent of ethanol and methanol), and reaction temperature. We obtained orthorhombic SnS or hexagonal SnS_2 by the reaction of $SnCl_2 \cdot 2H_2O$ or $SnCl_4 \cdot 4H_2O$ with thioacetamide in ethanol, respectively, orthorhombic Sn_2S_3 by the reaction of $SnCl_4 \cdot 4H_2O$ with thioacetamide in the mixed solvent of ethanol and methanol at 100°C for 10 h.

All of the above products were rod-like tin sulfide nanocrystallites. The oriented growth of nanocrystalline tin sulfides may be due to trace water in the system and appropriate reaction temperature. At an appropriate temperature (for example, 100°C), the water molecules surrounded by ethanol molecules could go away from tin chlorides and array on chains, due to the hydrogen bonds between them (39, 40). The chain arrangement of water molecules was preferential to the oriented growth of crystalline tin sulfides. So the chains of hydrogen bonds between trace water and ethanol molecules were thought to be important templates to obtain tin sulfide nanorods.

In order to investigate the influence of ethanol on the formation of products, we substituted ethanol with *n*-hexyl alcohol or ethylenediamine. With *n*-hexyl alcohol, only spherical tin sulfides could be obtained, probably because the chains of hydrogen bonds could not form in higher alcohols (39). With ethylenediamine, the reaction system was alkaline, which could not hold back the formation of tin oxides and hydrates. Therefore, ethanol was thought to play an important role in obtaining 1-D tin sulfide nanorods.

CONCLUSIONS

In summary, rod-like nanocrystalline tin sulfides (SnS_2, SnS, Sn_2S_3) were obtained via a simple alcoholic thermal route by the reactions between tin chlorides and thioacetamide at relatively low temperature (100°C). Tin precursor, solvent, reactions temperature, and trace water played important roles in controlling the nucleation and growth of nanocrystalline tin sulfides and obtaining 1-D tin sulfide nanorods with different compositions and phases. This technique is expected to be useful for synthesis of other nanostructured compounds.

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REFERENCES

1. T. Jiang and G. A. Ozin, *J. Mater. Chem.* **8,** 1099 (1998).
2. T. Jiang, A. J. Lough, G. A. Ozin, D. Young, and R. L. Bedard, *Chem. Mater.* **7,** 245 (1995).
3. A. Lopez and A. Ortiz, *Semicond. Sci. Technol.* **9,** 2130 (1994).
4. N. K. Reddy and K. T. R. Reddy, *Rec IEEE Photovoltaic Spec. Conf.* **26,** 515 (1997).
5. J. B. Johnson, H. Jones, B. S. Latham, J. D. Parker, R. D. Engelken, and C. Barber, *Semicond. Sci. Technol.* **14,** 501 (1999).
6. T. Kosugi, K. Murakami, and S. Kaneko, *Mater. Res. Soc. Symp. Proc.* **485,** 273 (1998).
7. T. Jiang, G. A. Ozin, A. Verma, and R. L. Bedard, *J. Mater. Chem.* **8,** 1649 (1998).
8. J. C. Bailar, H. J. Emeleus, R. S. Nyholm, and A. F. Trotman Dickenson, "Comprehensive Inorganic Chemistry." Pergamon Press, Oxford, 1973.
9. B. Palosz, W. Palosz, and S. Gierlotka, *Bull. Mineral.* **109,** 143 (1986).
10. C. Raisin, Y. Bertrand, and J. Robin, *Solid State Commun.* **24,** 353 (1977).
11. B. Li, Y. Xie, J. X. Huang, H. L. Su, and Y. T. Qian, *J. Solid State Chem.* **149,** 338 (2000).
12. B. Li, Y. Xie, J. X. Huang, and Y. T. Qian, *J. Solid State Chem.* **153,** 170 (2000).
13. M. L. E. Moubtassim, C. Bousquet, F. J. Olivier, and J. C. Jumas, *Chem. Mater.* **10,** 968 (1998).
14. R. W. Parry, "Inorganic Synthesis." McGraw-Hill, New York, 1955.
15. J. Morales, J. Santos, J. R. R. Barrado, J. P. Espinos, and A. R. Gonzalezelipe, *J. Solid State Chem.* **150,** 391 (2000).
16. T. Jiang, A. Lough, G. A. Ozin, R. L. Bedard, and R. Broach, *J. Mater. Chem.* **8,** 721 (1998).
17. R. J. Francis, S. J. Price, J. S. O. Evans, S. Obrien, D. Ohare, and S. M. Clark, *Chem. Mater.* **8,** 2102 (1996).
18. I. P. Parkin and A. T. Powley, *Polyhedron* **12,** 2961 (1993).
19. J. A. Sanchez and A. Ortiz, *J. Electrochem. Soc.* **147,** 3708 (2000).
20. A. J. Varkey, *Int. J. Mater. Prod. Technol.* **12,** 490 (1997).
21. S. Kaneko, *Can. Ceram.* **68,** 50 (1999).

22. L. S. Price, I. P. Parkin, M. N. Field, A. M. E. Hardy, R. J. H. Clark, T. G. Hibbert, and K. C. Molloy, *J. Mater. Chem.* **10,** 527 (2000).
23. N. Koteswara Reddy and K. T. Ramakrishna Reddy, *Thin Solid Films* **325,** 4 (1998).
24. L. S. Price, I. P. Parkin, A. M. E. Hardy, and R. J. H. Clark, *Chem. Mater.* **11,** 1792 (1999).
25. D. M. Schleich and M. J. Maartin, *J. Solid State Chem.* **64,** 359 (1986).
26. A. Bensalem and D. M. Schleich, *Mater. Res. Bull.* **23,** 857 (1988).
27. A. Bensalem and D. M. Schleich, *Mater. Res. Bull.* **25,** 349 (1990).
28. M. J. Martin, G. H. Qiang, and D. M. Schleich, *Inorg. Chem.* **27,** 2804 (1988).
29. P. R. Bonneau, R. F. Jarvis, and R. B. Kane, *Inorg. Chem.* **31,** 2127 (1992).
30. X. F. Qian, X. M. Zhang, C. Wang, W. Z. Wang, Y. Yie, and Y. T. Qian, *J. Phys. Chem. Solids* **60,** 415 (1999).
31. H. Dai, E. W. Wong, Y. Z. Lu, and C. M. Lieber, *Nature* **375,** 769 (1995).
32. P. D. Yang and C. M. Lieber, *Science* **273,** 1836 (1996).
33. M. Yazawa, M. Kognchi, and K. Hiruma, *Adv. Mater.* **5,** 577 (1993).
34. S. I. Stupp, *Nature* **380,** 325 (1996).
35. T. J. Trentler, K. M. Hickmar, S. C. Goel, A. M. Viano, P. C. Gibbons, and W. E. Buhro, *Science* **270,** 1791 (1995).
36. C. A. Formstone, E. T. Fitzgerald, P. A. Cox, and D. O'Hare, *Inorg. Chem.* **29,** 3860 (1990).
37. D. Mootz and H. Puhl, *Acta Crystallogr.* **23,** 471 (1967).
38. (D. Briggs and M. Peah, Eds.). Wiley, Chichester, 1990.
39. J. McMurry, "Organic Chemistry." Brooks/Cole, California, 1992.
40. N. S. Akhmetov, "General and Inorganic Chemistry." Mir, Moscow, 1983.