IF : 4.547 | IC Value 80.26 VOLUME-6, ISSUE-7, JULY-2017 • ISSN No 2277 - 8160

Original Research Paper Chemistry

GROWTH OF ROD-SHAPED Sb_2S_3 NANO COMPOUNDS UNDER MILD REACTION CONDITION

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ABSTRACT One-dimensional (1D) rod-shaped nano compounds of Sb_2S_3 have been achieved from $SbCl_2$ and S-methyl 3-phenyldithiocarbazate [$C_6H_5NHNHC(S)SMe$] via a simple and mild solvothermal method in ethanol without any surfactants or additives. The products have been characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). From this experiment it showed that the rod-shaped Sb_2S_3 nanocrystals, belong to the orthorhombic phase with cell parameters a = 11.305 Å, b = 11.277 Å, c = 3.952 Å. The probable formation mechanism of rod shaped nano structure of Sb_2S_3 has also been proposed.

KEYWORDS :solvothermal, orthorhombic, nanocrystalline

1. Introduction

Research on one-dimensional (1D) semiconductor nanocrystalline materials with their unique size and morphology has been rapidly exploring because of their potential application in fabrication of optical and electronic devices [1] since the properties of nanocrystalline materials are highly depend on their shape, size and crystalline phase.

Group V-VI binary crystalline compound, e.g. Sb_2S_3 is highly anisotropic and a kind of layered structure parallel to their growth direction and is a direct band gap semiconductor that crystallizes in the orthorhombic phase [2]. Sb_2S_3 is regarded as a promising material for solar energy conversion because of its good photoconductivity [3] and has potential uses in thermo electric cooling technologies and optoelectronics in IR region [4].

There are several methods have been developed for the synthesis of Sb_2S_3 nano materials such as solvothermal synthesis for nanorods [5], nano wires [6] and nano tubes [7], spray pyrolysis [8] and chemical bath deposition [9] for thin films, sonochemical method for micro crystal [10] and so on. However, how to conveniently synthesize crystalline Sb_2S_3 compounds at low temperature and control the morphology through simple method is still increasing research interest to scientists.

Therefore, in this study, we have introduced a simple approach to synthesized Sb_2S_3 nano compounds, which is composed of single crystalline Sb_2S_3 nanorods with dimensions of 40 – 200 nm in diameter and 0.3 – 2.0 µm in length via solvothermal method using antimony(III) chloride and S-methyl 3-phenyldithiocarbazate [$C_6H_5NHNHC(S)SMe$] in ethanol without using any surfactants and additives.

2. Materials and methods

Materials:

All the reagents and solvents are of analytically pure and were purchased from Marck, India. All the chemicals were used without further purification.

S-methyl 3-phenyldithiocarbazate [$C_6H_5NHNHC(S)SMe$] was prepared adapting the procedure given in literature.[11] In brief, 5.61gm (0.1 mole) of KOH in 30 ml absolute ethyl alcohol with 9.91 ml (0.1 mole) of phenyl hydrazine was taken in a 100 ml beaker and kept in a ice bath with constant stirring. When all the solid KOH were dissolved, chilled CS_2 (6.05 ml, 0.1 mole) was added during the period of 45 minutes with constant stirring. The stirring was continued until a light yellow solid mass was formed. The solid, so formed was dissolved in cold 4:6 (v/v) aqueous ethanol. The mixture was again kept in an ice bath and CH_3I (6.2 ml, 0.1 mole) was added drop-wise with constant stirring. During the addition of CH_3I, a white precipitation formed, was filtered off and washed with water for three to four times. White crystalline product was obtained by dissolving the product in minimum volume of dichloromethane and slow diffusion into hexane and was collected after filtration, washed with hexane and dried in air. The compound is confirmed by mass spectroscopy, elemental analysis and ^{1}H-NMR spectroscopy. Anal. Calc. for $C_8H_{10}N_2S_2$: C, 48.45; H, 5.08; N, 14.13; S, 32.34. Found: C, 48.96; H, 5.01; N, 14.18; S, 35.69 %.

Synthesis of rod-shaped Sb_2S_3 nano compounds:

A two necked round bottom flask (50 ml) was charged with $SbCl_2$ (0.5 g, 2.192 mmol), S-methyl 3-phenyldithiocarbazate (0.434 g. 2.192 mmol) and 50 ml ethanol. All the reagents were dissolved by stirring. The flask was then degassed for 10 minutes, filled with nitrogen and boiled at 79 ^{0}C for 12 hr. During heating, the colour of the solution was changed to brick red and finally black. After the completion of the reaction, the black products were collected by centrifugation, washed with water and ethanol (1:1) for several times and dried in vacuum at 60 ^{0}C for 2 hr. The obtained product was then used for characterization with XRD and TEM analysis.

Characterization techniques:

The elemental analysis of the precursor was performed using FISONS EA-1108 CHN analyzer. Powder X-ray diffraction (XRD) was recorded using a Rijaku Miniplate 600 diffractometer. Transmission electron microscopy (TEM) images and the selected area electron diffraction (SAED) patterns of antimony sulphide nanorods were recorded using a CM 12 PHILIPS along with EDX analyzer at an accelerating voltage 200 kV. The TEM samples are prepared by placing a drop of dilute ethanol dispersion of Sb_2S_3 on the surface of a 200-mesh carbon-coated copper grid.

3. Result and Discussion

The reaction between S-methyl 3-phenyldithiocarbazate [$C_6H_5NHNHC(S)SMe$] with antimony(III) chloride in ethanol produced black Sb_2S_3 nanocompounds.

The phase and crystallographic orientation of the obtained Sb_2S_3 product were examined by XRD analysis. Figure 1 shows the XRD pattern of as-prepared Sb_2S_3 at 79 ^{0}C in ethanol. All diffraction peaks can be well indexed to the corresponding orthorhombic phase of Sb_2S_3 having cell parameters a = 11.305Å, b = 11.277Å and c = 3.952Å, which are comparable with the values given in JCPD file No. 03-065-2432. Sharp peaks and no other peaks related to the impurities like Sb_2O_3 and Sb were detected, indicating that the as-prepared nanocompounds are well crystalline and purely single phase samples.

The size, structure and morphology of as-prepared Sb_2S_3 were examined using transmission electron microscopy (TEM). The TEM image (Figure 2) indicated that the morphology of Sb_2S_3 is rod-like with dimension 0.3 – 2.0 µm in length and 40 - 200 nm in diameter. Figure 3(a) represents the TEM image of a single nanorod. Figure 3(c) represents a high resolution TEM (HRTEM) image of Sb_2S_3 nanorod in which crystal lattice fringes are clearly visible and the observed lattice spacing of about 0.307 nm which indicated that the Sb_2S_3 nanorodes are single crystalline in nature. The electron diffraction pattern [Figure 3(b)] was taken from a selected area of the Sb_2S_3

nanorod. The spotty pattern indicates that the as-prepared samples are single crystalline. The composition of Sb_2S_3 is examined by EDX (energy dispersive X-ray spectroscopy) analysis (Figure 4), which shows that the atomic ratio of Sb:S is 1 : 1.42 (the Cu and C peaks are arise from the copper carbon grid).

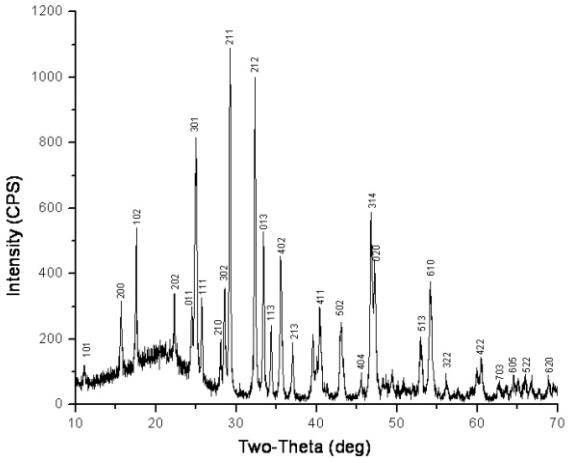

Figure 1. A typical XRD pattern of the as-prepared Sb_2S_3 compounds obtained in ethanol at 79 ^{0}C for 12 hr.

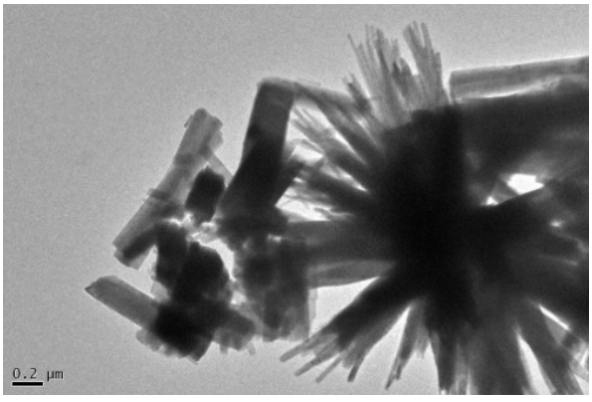

Figure 2. TEM image of Sb_2S_3 nanorodes at 79 ^{0}C for 12 hr.

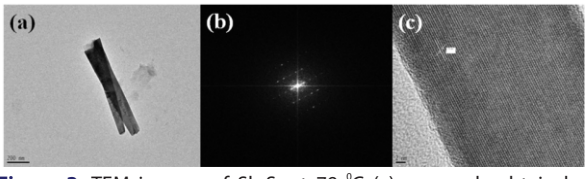

Figure 3. TEM images of Sb_2S_3 at 79 ^{0}C (a) nanorods obtain by solvothermal process after 12 hr. (b) SAED pattern of the nanorod and (c) HRTEM image of the nanorod.

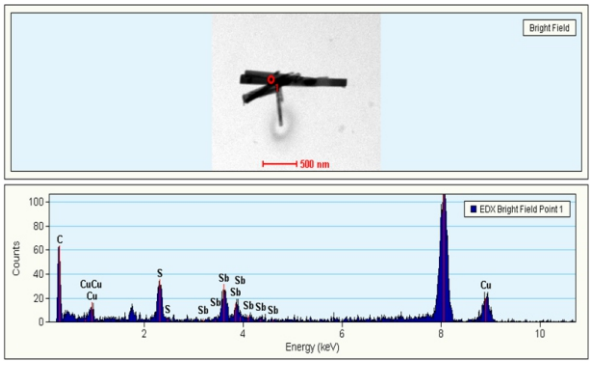

Figure 4. EDX pattern the as-prepared Sb_2S_3 nanorods obtained at 79 ^{0}C for 12 hr (Cu and C peaks are arise from the copper carbon grid).

In this experiment, first $SbCl_3$ and $C_6H_5NHNHC(S)SMe$ were dissolved in ethanol by stirring. In the initial stage, no colour change was observed. In the typical heating process at 79 ^{0}C the colour of the solution first change to yellow, may be due to formation of $Sb[C_6H_5NHNHC(S)SMe]_3$ and then orange red may be due to amorphous Sb_2S_3 [11], and then to black colouration, with increasing reaction time (12hr). These results indicated that, in the early stage of solvothermal process at low temperature, well controlled release of Sb^{3+} ions from solvated antimony intermediate as well as well controlled generation of $S^{=}$, from $C_6H_5NHNHC(S)SMe$ [12], amorphous Sb_2S_3 particles were generated [13] which becoming rod-like structure when subsequent nucleation and preferential growth of crystallization occur simultaneously with time under same reaction condition.

The possible mechanism for the formation of rod-shaped Sb_2S_3 nano structure are expected to proceed through two stages, nucleation or seed formation and crystal growth. In the first stage, under solvothermal conditions (sulfur source, solvent, reaction temperature, reaction time, pressure and so on) [5(a), 14], the amorphous particles underwent disruption and large numbers of small nanocrystallites of Sb_2S_3 which were served as nuclei or seeds, were generated. In the second stage, as a result of solvothermal ripening, these nanocrystalline seeds individually grow preferentially along energetically favorable directions with relatively high concentrations of amorphous Sb_2S_3 and becoming small rod-like through a solid-solution-solid (called SSS) transformation mechanism [15]. Accordingly, one small rod-like particle after another was created and then diffuses to bigger one maintaining the growing structure under the Sb-S atom chain anisotropy and non equilibrium growth condition [13, 16].

4. Conclusion

In summary, orthorhombic phase of Sb_2S_3 nanorods having cell parameters a =11.305Å, b = 11.277Å and c = 3.952Å have been successfully synthesized from S-methyl 3-phenyldithiocarbazate $[C_6H_5NHNHC(S)SMe]$ and $SbCl_3$ via a simple solvothermal process in ethanol at 79 ^{0}C without addition of any surfactants and additives. The experimental results of the as-grown product showed that the crystal structure, shape and size strongly depend on reaction time. At the initial stage of reaction, amorphous Sb_2S_3 particles were generated. With increasing the reaction time, small nanorods were formed and gradually grew onwards on the particles, and finally single crystalline rod-shaped Sb_2S_3 nano compounds, having dimension of 40 – 200 nm in diameter and 0.3 – 2.0 µm in length. The present synthetic route is also expected to provide an alternative method for the preparation of Sb_2S_3 nanocompounds. Comparing with other method, this method is believed to be more convenient with each of separation and eco-friendly.

Acknowledgements

I am very much thankful to Department of Chemistry, Midnapore College (Autonomous) for Instrumental facilities and CRF, IIT Kharagpur for TEM study. This work is partly supported by minor research project (Grant No. F_PSW 222/15-16) from UGC of India.

References

1. (a) B. O. Dabbousi, M. G. Bawendi, O. Onitsuka, M. F. Rubner, , Appl. Phys. Lett. 1995, 66, 1316. (b) V. L. Colvin, M. C. Schlamp. A. P. Alivisatos, Nature 1994, 370, 354. (c) D. L. Klein,; R. Roth, A. K. L. Lim, A. P. Alivisatos, P. L. McEuen, Nature, 1997, 389, 699.
2. (a) Y. Yu, C. H. Jin, R. H. Wang, Q. Chen, L. M. Peng, J. Phys. Chem. B 2005, 109, 18772. (b) Y. Yu, C. H. Jin, R. H. Wang, Q. Chen, L. M. Peng, J. Phys. Chem. B 2005, 109, 23312. (c) Y. Yu, C. H. Jin, R. H. Wang, Q. Chen, L. M. Peng, J. Phys. Chem. B 2006, 110, 13415.
3. (a) B. Roy, B. R. Chakraborty, R. Bhattacharya, A. K. Dutta, Solid State Commun. 1978, 25, 973. (b) O. Savadogo, K. C. Mandal, Sol.Energy Mater. Sol. Cells 1992, 26, 117.
4. H. M. Hu, M. S. Mo, B. J. Yang, X. J. Zhang, Q. W. Li, W. C. Yu, Y. T. Qian, J. Cryst. Growth 2003, 258, 106.
5. (a) M. S. Mo, Z. Y. Zhu, X. G. Yang, X. Y. Liu, S. Y. Zhang, J. Y. Gao, T. Qian, J. Crystal Growth, 2003, 256, 377. (b) C. Li, X. G. Yang, Y. F. Liu, Z. Y. Zhao, Y. T. Qian, J. Crystal Growth, 2003, 255, 342.
6. G. Z. Shen, D. Chen, K. B. Tang, X. Jiang, Y. T. Qian, J. Crystal Growth, 2003, 252, 350.
7. (a) X. W. Zheng, Y. Xie, L. Y. Zhu, X. C. Jiang, Y. B. Jia, W. H. Song, Y. P. Sun, Inorg. Chem. 2002, 41, 455. (b) Q. Yang, K. B. Tang, C. R. Wang, Y. T. Qian, W. C. Yu, G. E. Zhou, F. Q. Li, J. Mater. Chem. 2001, 11, 257.
8. S. A. Manolache,; A. Duta, Romanian J. of Information Science and Technology, 2008, 11, 109.

9. O. Savadogo, K. C. Mandol, Sol. Energ. Mat. Sol. C, 1992, 26, 117.
10. J. H. Zhang, Z. Chen, Z. L. Wang, N. B. Ming, J. Mater. Res. 2008, 8, 1804.
11. J. Yang, J. H. Zeng, S. H. Yu, L. Yang, Y. H. Zhang, Y. T. Qian, Chem. Mater., 2000, 12, 2924.
12. (a) P. Bera, C. H. Kim, S. I. Seok, polyhedron, 2008, 27, 3433.
13. N. Maiti, S. H. Im, Y. H. Lee, S. I. Seok, ACS Appl. Mater. Interface. 2012, 4(9), 4787.
14. (a) H. Hu, Z. Liu, B. Yang, M. Mo, Q. Li, W. Yu, Y. Qian, J. Crystal Growth, 2004, 262, 375. (b) S. W. Sheldrick, M. Wachhold, Angew. Chem. Int. Ed. Engl. 1997, 36, 207 (c) R. Zhang, X. Chen, M. Mo, Z. Wang, M. Zhang, X. Liu, Y. Qian, J. Crystal Growth, 2004, 262, 449 and references therein.
15. B. Gates, Y. Yin, Y. Xia, J. Am. Chem. Soc. 2000, 122, 12582.
16. (a) G. Y. Chen, B. Dneg, G. B. Cai, T. K. Zhang, W. F. Dong, W. X. Zhang,; A. W. Xu, J. Phys. Chem. C, 2008, 112, 672. (b) J. Yang, J. H. Zeng, S. H. Yu, L. Yang, Y. H. Zhang, Y. T. Qian, Chem. Mater, 2000, 12, 2924.
17. D. Attanasio, V. Fares, P. Imperatori, G. Mattogno, F. Tarli, J. Chem. Soc., Dalton Trans., 1988, 1217.