This article was downloaded by: [Monash University Library] On: 21 June 2013, At: 23:32 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt20

Preparation of Antimony Sulfide Nanostructures From Single-Source Antimony Thiosemicarbazone Precursors

Jasmine B. Biswal^a & Shivram S. Garje^a

^a Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (East), Mumbai, India

Accepted author version posted online: 03 Dec 2012. Published online: 26 Feb 2013.

To cite this article: Jasmine B. Biswal & Shivram S. Garje (2013): Preparation of Antimony Sulfide Nanostructures From Single-Source Antimony Thiosemicarbazone Precursors, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:4, 461-465

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2012.740747</u>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



Preparation of Antimony Sulfide Nanostructures From Single-Source Antimony Thiosemicarbazone Precursors

Jasmine B. Biswal and Shivram S. Garje

Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (East), Mumbai, India

Antimony sulfide nanostructures have been prepared by the decomposition of antimony(III) chloride thiosemicarbazone precursors, SbCl₃(L), [L = cinnamaldehyde thiosemicarbazone (cinnamtscz) (1) and thiophene-2-carboxaldehyde thiosemicarbazone (thioptscz) (2)] either in a furnace or in solvents (ethylene glycol or diphenyl ether). The as-prepared nanocrystallites were characterized by powder XRD, TEM, and EDAX techniques, and absorption spectroscopy. XRD shows formation of orthorhombic Sb₂S₃ in all the cases. TEM images reveal spherical shaped Sb₂S₃ nanoparticles obtained by pyrolysis method, whereas nearly spherical and rod like morphologies of Sb₂S₃ were observed for the nanoparticles obtained by solvothermal decomposition in diphenyl ether and ethylene glycol, respectively.

Supplemental materials are available for this article. Go to the publisher's online edition of Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry to view the supplemental file.

Keywords antimony sulfide, nanostructures, semiconductors, X-ray diffraction

INTRODUCTION

The inorganic materials, particularly nanomaterials, containing same elements in same stoichiometries but having different morphologies exhibit surprisingly different properties. Therefore, there is an important significance for controlling the morphologies of nanocrystals of a particular material. The design and synthesis of 1D semiconductor nanomaterials and submicron materials with constructive morphologies such as nanotubes, nanorods, nanowires, nanospheres, and nanoribbons have fascinated substantial attention due to their unique electronic, optical, mechanical or magnetic properties, which vary from those of bulk materials.^[1]

Antimony trisulfide (stibnite, Sb_2S_3), an essential member of V_2VI_3 (V = As, Sb, Bi; VI = S, Se, Te) type main group metal

chalcogenides, has been extensively studied due to its interesting photovoltaic properties, high photosensitivity, and high thermoelectric power (TEP), which makes it promising for applications in solar energy conversion,^[2] thermoelectric cooling technologies, and optoelectronics in IR region television cameras with photoconducting targets^[3,4] and write once read many times (WORM) kind of optical storage devices.^[5] Antimony sulfide has also been used as starting material for synthesis of sulfoantimonates of antimony and related compounds.^[6] It is a kind of layer structured direct band gap (1.78–2.5 eV) semiconductor that crystallizes in the orthorhombic system (pbnm space group).^[7] Due to its good photoconductivity and wide range of band gap, it covers the maximum range of visible and IR region of solar energy spectrum.^[2,8,9]

Many approaches have been adopted for the synthesis of Sb_2S_3 including thermal decomposition,^[10] vacuum evaporation,^[11] hydro- or solvothermal synthesis,^[12–15] refluxing,^[16] and microwave treatment of various precursors^[17,18] dissolved in polyols. Recently, few articles wherein single-source precursors, such as antimony xanthates,^[19] dithiocarbamates,^[19,20] dithiophosphates,^[15,19] and thiourea complex of antimony^[21] were used for the synthesis of Sb_2S_3 nanomaterials or thin films have been published.

Thiosemicarbazones are significant class of nitrogen- and sulfur-donor ligands and they form complexes with many metals.^[22,23] Usually, sulfur atom is involved in bonding resulting in direct metal–sulfur bond. Hence we thought it worthwhile to use metal thiosemicarbazones as single-source precursors for the preparation of metal-sulfide nanoparticles and thin films. Recently we have reported the utilization of antimony thiosemicarbazones, SbCl₃(L) [L = cinnamaldehyde thiosemicarbazone (cinnamtscz) (1) and thiophene-2-carboxaldehyde thiosemicarbazone (thioptscz) (2)] as single-source precursors for the deposition of Sb₂S₃ thin films by AACVD method.^[24]

Although there are various methods discussed in the literature for preparation of Sb₂S₃ nanorods,^[16,20,25,26] nanoribbons,^[27,28] and nanowires,^[26,29] there is only one report available for the synthesis of Sb₂S₃ nanospheres^[30] to the best of our knowledge. Herein we report the synthesis of Sb₂S₃ nanospheres and nanorods either by solvothermal decomposition of the singlesource precursors in ethylene glycol (coordinating solvent) and diphenyl ether (noncoordinating solvent) or by pyrolysis of

Received 28 February 2012; accepted 11 April 2012.

The authors are thankful to UGC for financial assistance and SAIF, IIT-Bombay, for the EDAX data, TEM images, and SAED patterns. Also thanks are extended to TIFR, Mumbai, for the XRD data.

Address correspondence to Shivram S. Garje, Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (East), Mumbai 400098, India. E-mail: ssgarje@chem.mu.ac.in

single-source precursors in a furnace. The nanostructures were characterized by UV-vis spectroscopy, XRD, EDAX, TEM, and SAED techniques.

EXPERIMENTAL

Materials and Instrumentation

All the solvents used were of analytical grade and the reactions were carried out under oxygen free nitrogen atmosphere. Antimony(III) chloride (S.D. fine) was used after vacuum distillation (73° C/1–2 mm of Hg). The precursors **1** and **2** were synthesized and characterized as discussed previously.^[24]

X-ray diffraction patterns of the materials were recorded using Cu K α radiation on a Philips X'pert PRO PANalytical X-ray diffractometer (TIFR, Mumbai, India) with an accelerating voltage of 45 kV at a scanning rate of 0.05°/s. The compositional analysis of the materials obtained was carried out on EDAX (Inca Energy, model of Oxford, IIT-Bombay, India) with an accumulation time of 100 s. The TEM observations were conducted on a Philips CM 200 microscope with operating voltages between 20 and 200 kV. The TEM imaging and EDAX analyses were carried out at SAIF, IIT-Bombay, India. The absorption spectra were recorded on a UV-2450, UV-Vis Shimadzu spectrophotometer (University of Mumbai, India).

Synthesis of Nanoparticles

Pyrolysis in a furnace

In a small quartz boat a weighed quantity of the precursors (200 mg of 1 and 2 each) were pyrolyzed in a furnace at 350° C for 2 h under nitrogen atmosphere. The furnace was cooled to room temperature and the black material obtained was collected.

Solvothermal decomposition

In a typical experiment, 300 mg of each precursor (1 and 2) and 15 mL of ethylene glycol/diphenyl ether was taken in a round bottom flask. The reaction mixture was refluxed for 2 h under nitrogen atmosphere with continuous stirring. The color of the solution changed to black and the reaction was cooled to room temperature. The grayish black materials obtained were dispersed in methanol and separated by centrifugation.

All the materials obtained were characterized by XRD, EDAX, TEM, and absorption spectroscopy.

RESULTS AND DISCUSSION

In the present investigation, $SbCl_3(cinnamtscz)$ (1) and $SbCl_3(thioptscz)$ (2) were used as single-source precursors for the preparation of antimony sulfide nanoparticles. The precursors were synthesized by simple addition reaction of $SbCl_3$ and corresponding thiosemicarbazone ligand (Eq. 1). They were characterized by elemental analysis, IR, ¹H, and ¹³C {¹H} NMR spectroscopic techniques as discussed in our earlier report.^[24]

$$SbCl_3 + L \xrightarrow{Dry THF} SbCl_3(L)$$
 [1]

where L = thiosemicarbazones of cinnamaldehyde and thiophene-2-carboxaldehyde.

To assess the suitability of these complexes for the preparation of antimony sulfide, their TG analyses were carried out.^[24] Both the complexes undergo single-step decomposition to afford antimony sulfide. Pyrolysis of SbCl₃(cinnamtscz) (1) and SbCl₃(thioptscz) (2) either in a furnace at 350°C or in solvents such as ethylene glycol and diphenyl ether was carried out to evaluate the potential of these complexes for the preparation of antimony sulfide nanostructures and also assess the difference in morphologies obtained under different conditions. Powder XRD patterns (Figures 1 and S1) of the materials obtained from both the precursors correspond to pure orthorhombic phase of Sb_2S_3 (JCPDS: 75–1310). The sharpness of the XRD peaks indicates the high crystallinity of the samples. The average particle sizes of the materials obtained by decomposition of 1 and 2 in a furnace, in ethylene glycol, and in diphenyl ether estimated from Scherrer's formula are 31, 53, and 26 nm for 1 and 23, 52, and 64 nm for 2. EDAX analyses for the materials obtained from precursor 1 matches with Sb:S ratio of 1:1.47 (in furnace), 1:1.41 (in ethylene glycol), and 1:1.40 (in diphenyl ether) whereas EDAX analyses for the materials obtained from precursor 2 matches with Sb:S ratio of 1:1.30 (in furnace), 1:1.20 (in ethylene glycol), and 1:1.34 (in diphenyl ether).

TEM images (Figure 2) of Sb_2S_3 isolated from the pyrolysis of **1** in a furnace at 350°C and in refluxing diphenyl ether showed agglomerates of spherical nanoparticles with average diameters of 27 and 130 nm, respectively whereas, the material obtained in ethylene glycol revealed the presence of rod like morphology having a width of 135 nm and length of few microns (Figure 2). The diameters of the nanospheres prepared in the present investigations are smaller than the quasinanospheres that were obtained by Sheng et al. using the microemulsion



FIG. 1. XRD patterns of orthorhombic Sb_2S_3 (JCPDS: 75–1310) obtained from $SbCl_3$ (cinnamtscz) (1) by (a) pyrolysis in furnace at 350°C and solvothermal decomposition, (b) in ethylene glycol, and (c) in diphenyl ether.



FIG. 2. TEM images of (a) agglomerates of nearly spherical-shaped Sb_2S_3 nanoparticles, (b) nanorod, and (c) nearly spherical-shaped particles obtained by decomposition of $SbCl_3(cinnamtscz)$ (1) in a furnace at 350°C, in refluxing ethylene glycol and diphenyl ether, respectively (inset shows the SAED patterns of the same).

method.^[30] Bright dotted SAED patterns of Sb₂S₃ nanocrystallites obtained by pyrolysis of **1** in a furnace and in ethylene glycol revealed single-crystalline nature of these materials while SAED of Sb₂S₃ prepared in diphenyl ether showed disclike pattern indicating its polycrystalline nature. The SAED patterns displayed (110), (101), and (211) lattice planes of orthorhombic phase of Sb₂S₃ (JCPDS: 75–1310) for Sb₂S₃ prepared in furnace. Similarly, (101), (230), and (331) lattice planes for Sb₂S₃ prepared in ethylene glycol, and (220), (331) lattice planes for Sb₂S₃ prepared in diphenyl ether were observed. The mismatches between the sizes estimated by XRD and those obtained from TEM are observed because the particle size does not determine the line width directly in XRD.^[31]

The TEM images (Figure S2) of Sb_2S_3 prepared by the pyrolysis of **2** also revealed similar morphologies that were obtained for Sb_2S_3 synthesized from **1**. However, the spherical nanoparticles are well dispersed with an average diameter of 123 nm (furnace) and 270 nm (diphenyl ether) and rods have dimensions of 40 nm in width and the length of few microns (ethylene glycol). Nanorods obtained in ethylene glycol are monodispersed with respect to width. The SAED patterns of these nanostructures showed single-crystalline nature and also lattice planes (110), (111), and (221) (furnace) and (020), (101), and (121) (diphenyl ether) corresponding to orthorhombic phase of Sb_2S_3 (JCPDS: 75–1310).

100 nm

TEM studies revealed that nanomaterials of different morphologies were obtained by the decomposition of precursors **1** and **2** in different experimental conditions. The previous results indicate that the nature of solvent used in solvothermal decomposition method affects the morphology of the product obtained. Yu et al. reported that the difference in dielectric constant of solvents plays an important role in controlling the morphology and particle sizes of the nanocrystals.^[32] In addition to dielectric constant, ethylene glycol being a reducing and a capping agent affects morphologies of nanocrystals depending on the mechanism involved in the formation of nanocrystals. The possible



FIG. 3. Absorption spectra of materials obtained from decomposition of $SbCl_3(cinnamtscz)$ (1) in (a) furnace at $350^{\circ}C$ and (b) in diphenyl ether.

mechanisms for the formation of Sb_2S_3 rods by solvothermal decomposition in ethylene glycol can be described in a similar fashion to Yan et al., who proposed a four-step mechanism.^[33] They have used Sb_2O_3 as a source of antimony and Na_2S as sulfur source. It is proposed that ethylene glycol being a good capping agent containing two hydroxyl groups, can hold Sb^{3+} ions tightly in the solution. When the S^{2-} ions are introduced into the former solution, S^{2-} ions rapidly attract to the vicinity of Sb^{3+} ions to form Sb_2S_3 products bounded by ethylene glycol molecules. Under the direction of these surrounded ethylene glycol molecules, the collision of interparticles lead to the formation of oriented neck-like connections along special lattice. Finally, with the prolongation of time, the oriented aggregates of Sb_2S_3 stick to each other by self-assembling and further coalesce together by recrystallization process to form 1D nanowire structure. In contrast to mechanism in ethylene glycol, decomposition of precursor in diphenyl ether involves nucleation followed by the growth of Sb_2S_3 nanostructures. In addition to the nature of solvent, the final shape of the nanocrystal formation also depends on the crystalline phase of the seed at the nucleating stage followed by the other factors for controlling the subsequent growth processes. The key factors include the intrinsic surface energy of different crystallographic surfaces and the choice of the nanocrystal growth regime between thermodynamic and kinetic processes.^[34]

The absorption spectra of the nanomaterials obtained by the pyrolysis of **1** (Figure 3) in a furnace and in diphenyl ether displayed peaks at 246 nm ($\lambda_{onset} = 480$ nm) and 255 nm ($\lambda_{onset} = 450$ nm), respectively. Band gap of these materials estimated by the λ_{onset} values of the respective absorption spectrum are 2.58 and 2.75 eV, respectively. There is considerable shift in band gaps with respect to bulk band gap of Sb₂S₃ (E_g = 1.72 eV) in these materials. The results are comparable to a previous report that showed absorption peaks in the range of 270–300 nm for the rods of an average diameter 75 nm.^[35]

Similarly, absorption spectrum (Figure S3) of the nanospheres afforded by the pyrolysis of **2** in a furnace demonstrated a broad peak at 707 nm. The broadness of the peak indicates the broad distribution of the nanospheres. The absorption spectrum (Figure S3) of nanorods prepared by refluxing **2** in ethylene glycol displayed maximum at 700 nm. The result is consistent with the investigations of Chen et al.^[15] that showed absorption at 704 nm for nanorods of width 45 nm.

CONCLUSIONS

Spherical and rod-shaped nanostructures of phase pure orthorhombic antimony sulfide were successfully synthesized by pyrolysis as well as solvothermal decomposition of antimony(III) thiosemicarbazone precursors. Hence, it was demonstrated that these precursors (1 and 2) can be used to fabricate different morphological nanostructures of Sb_2S_3 by selecting the appropriate experimental parameters such as solvent and temperature.

SUPPLEMENTARY INFORMATION

Figures S1–S3 are the XRD patterns, TEM images, and their SAED patterns (inset) and the absorption spectra of the nanocrystallites obtained by decomposition of precursor **2**.

REFERENCES

- Rao, A.M.; Richter, E.; Bandow, S.; Chase, B.; Eklund, P.C.; Williams, K.A.; Fang, S.; Subbaswamy, K.R.; Menon, M.; Thess, A.; Smalley, R.E.; Dresselhaus, G.; Dresselhaus, M.S. *Science* 1997, 275, 187–191.
- Savadogo, O.; Mandal, K.C. Sol. Energy Mater. Sol. Cells 1992, 26, 117–136.
- Smith, J.D. Arsenic, antimony and bismuth, in Comprehensive Inorganic Chemistry, Pergamon Press, Oxford, 1973, 2.

- 4. Arivouli, D.; Gnanam, F.D.; Ramasamy, P. J. Mater. Sci. Lett. 1988, 7, 711–713.
- 5. Arun, P.; Vedeshwar, A.G.; Mehra, N.C. Mater. Res. Bull. 1997, 32, 907–913.
- Schimek, G.L.; Kolis, J.W.; Long, G. J. Chem. Mater. 1997, 9, 2776– 2785.
- Yu, Y.; Jin, C.H.; Wang, R.H.; Chen, Q.; Peng, L.M. J. Phys. Chem. B 2005, 109, 18772–18776.
- Deshmukh, L.P.; Holikatti, S.G.; Rane, B.P.; More, B.M.; Hankare, P.P. J. Electrochem. Soc. 1994, 141, 1779–1783.
- Nair, M.T.S.; Pena, Y.; Campos, J.; Garcia, V.M.; Nair, P.K. J. Electrochem. Soc. 1998, 145, 2113–2120.
- Lalia-Kantouri, M.; Manoussakis, G.E. J. Therm. Anal. 1984, 29, 1151–1169.
- 11. Ghosh, C.; Varma, B.P. Thin Solid Films 1979, 60, 61-65.
- 12. Wang, J.; Li, Y. Mater. Chem. Phys. 2004, 87, 420-423.
- Hu, H.; Liu, Z.; Yang, B.; Mo, M.; Li, Q.; Yu, W.; Qian, Y. J. Cryst. Growth 2004, 262, 375–382.
- Hu, H.; Mo, M.; Yang, B.; Zhang, X.; Li, Q.; Yu, W.; Qian, Y. J. Cryst. Growth 2003, 258, 106–112.
- Lou, W.; Chen, M.; Wang, X.; Liu, W. Chem. Mater. 2007, 19, 872– 878.
- Zhang, R.; Chen, X.; Mo, M.; Wang, Z.; Zhang, M.; Liu, X.; Qian, Y. J. Cryst. Growth 2004, 262, 449–455.
- Chen, D.; Tang, K.; Shen, G.; Sheng, J.; Fang, Z.; Liu, X.; Zheng, H.; Qian, Y. Mater. Chem. Phys. 2003, 82, 206–209.
- 18. An, C.; Tang, K.; Yang, Q.; Qian, Y. Inorg. Chem. 2003, 42, 8081-8086.
- Castro, J.R.; Molloy, K.C.; Liu, Y.; Lai, C.S.; Dong, Z.; White, T.J.; Tiekink, E.R.T. J. Mater. Chem. 2008, 18, 5399–5405.

- Xie, G.; Qiao, Z.-P.; Zeng, M.-H.; Chen, X.-M.; Gao, S.-L. Cryst. Growth Des. 2004, 4, 513–516.
- Yang, J.; Zeng, J.-H.; Yu, S.-H.; Yang, L.; Zhang, Y.-H.; Qian, Y.-T. Chem. Mater. 2000, 12, 2924–2929.
- 22. Padhye, S.; Kauffman, G.B. Coord. Chem. Rev. 1985, 63, 127-160.
- Casas, J.S.; Garcia-Tasende, M.S.; Sordo, J. Coord. Chem. Rev. 2000, 209, 197–261.
- Biswal, J.B.; Sawant, N.V.; Garje, S.S. Thin Solid Films 2010, 518, 3164–3168.
- Li, C.; Yang, X.; Liu, Y.; Zhao, Z.; Qian, Y. J. Cryst. Growth 2003, 255, 342–347.
- 26. Christian, P.; O'Brien, P. J. Mater. Chem. 2005, 15, 4949-4954.
- Yu, Y.; Wang, R.H.; Chen, Q.; Peng, L.-M. J. Phys. Chem. B 2005, 109, 23312–23315.
- Yu, Y.; Wang, R.H.; Chen, Q.; Peng, L.-M. J. Phys. Chem. B 2006, 110, 13415–13419.
- Shen, G.; Chen, D.; Tang, K.; Jiang, X.; Qian, Y. J. Cryst. Growth 2003, 252, 350–354.
- Qing-Sheng, W.; Guo-Xin, Z.; Ya-Ping, D. J. Nanoparticle Res. 2006, 8, 737–742.
- 31. Weller, H. Angew. Chem. Int. Ed. Engl. 1993, 32, 41-53.
- Yu, S.H.; Yang, J.; Han, Z.H.; Zhou, Y.; Yang, R.Y.; Qian, Y.T.; Zhang, Y.H. J. Mater. Chem. 1999, 9, 1283–1287.
- Geng, Z.R.; Wang, M.X.; Yue, G.H.; Yan, P.X. J. Cryst. Growth 2008, 310, 341–344.
- Jun, Y.W.; Lee, J.H.; Choi, J.S.; Cheon, J. J. Phys. Chem. B 2005, 109, 14795–14806.
- Li, C.; Shi, G.; Song, Y.; Zhang, X.; Guang, S.; Xu, H. J. Phys. Chem. Solids 2008, 69, 1829–1834.