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Research Article

STRUCTURAL ANALYSIS OF Sb_2S_3 NANOCOMPOUNDS SYNTHESIZED FROM MIXTURE OF ANTIMONY(III) CHLORIDE AND S-METHYL-3-PHENYLDITHIOCARBAZATE

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ABSTRACT

Low dimensional nanocompounds of Sb_2S_3 have been achieved from $SbCl_3$ and *s*-methyl-*3*-phenyldithiocarbazate [$C_6H_5NHNHC(S)SMe$] via a facile solvothermal method in ethanol without any surfactants or additives in the reaction mixture. The products have been characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). From this experiment it observed that the rod-shaped Sb_2S_3 nanocrystals, belong to the orthorhombic phase with cell parameters a = 11.295 Å, b = 11.317 Å, c = 3.931 Å. The possible formation mechanism of Sb_2S_3 has also been proposed.

INTRODUCTION

Research on low dimensional nanocrystalline nano materials with their unparalleled size and morphology has been rapidly pursuing because of their strong application in fabrication of optical and electronic devices[1] since the properties of nanocrystalline materials are highly depend on their unique morphology. Binary nanocompounds of group V-VI, e.g. Sb_2S_3 is highly anisotropic, layered structure and is a direct band gap semiconductor that crystallizes in the orthorhombic phase.[2] Sb_2S_3 showed as a potential compound for solar energy conversion because of its unique photoconductivity[3] and has extensive uses in thermo electric cooling technologies and optoelectronics.[4] In literature, so many methods have been discovered for the synthesis of Sb_2S_3 nanocompounds such as solvothermal method,[5] spray pyrolysis[6] and chemical bath deposition[7], sonochemical method[8] and so on. However, conveniently synthesizing crystalline nanocompounds of Sb_2S_3 at low temperature and simple method is still increasing interest to researchers.

Therefore, in this study, I have presented a gentle approach to achieved Sb_2S_3 nanocompounds, which is composed of crystalline Sb_2S_3 nanorods with dimensions of 35 - 150 nm in diameter and 0.4 – 2.0 μm in length via solvothermal process by means of antimony(III) chloride and S-methyl 3-phenyldithiocarbazate [$C_6H_5NHNHC(S)SMe$] in ethanol without any surfactants and additives in reaction mixture.

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MATERIALS AND METHODS

Materials

All the reagents and solvents are of analytical grade and were received from Marck, India. All the chemicals were used without further purification.

The chelating compound s-methyl-3-phenyldithiocarbazate [$C_6H_5NHNHC(S)SMe$] was obtained by adapting the procedure given elswhere.[9] In short, 2.85gm (0.05 mole) of KOH in 30 ml absolute ethyl alcohol with 4.95 ml (0.05 mole) of phenyl hydrazine was taken in a beaker and kept in ice bath with constant stirring to dissolved KOH. Chilled CS_2 (3.02 ml, 0.05 mole) was then added. During starring a light yellow solid mass was formed. The solid, was then dissolved in cold aqueous ethanol and chilled CH_3I (3.1 ml, 0.05 mole) was added slowly with constant stirring. During the addition, a white precipitation was formed. The precipitation was filtered off and washed with water for several times. Crystalline product was obtained by dissolving the product in minimum volume of dichloromethane and slow evaporation. The crystal product was collected after filtration, washed with hexane and dried in air. Anal. Calc. for $C_8H_{10}N_2S_2$: C, 48.45; H, 5.08; N, 14.13; S, 32.34. Found: C, 48.57; H, 4.91; N, 14.57; S, 34.64 %.

Synthesis of Sb_2S_3 nanocompounds

A three-necked round bottom flask (100 ml) was charged with $SbCl_3$ (0.25 g, 1.058 mmol), S-methyl 3-phenyldithiocarbazate (0.217 g. 1.058 mmol) and 50 ml ethanol. The flask was then degassed and filled with nitrogen and reflux at 79 °C for 6 hr.

During heating, the colour of the solution was changed from yellow to orange to black. The black products were collected by centrifugation, washed with water-ethanol mixture (1:1) for several times and dried in vacuum at 60 °C for 24 hr. The obtained product was then used for characterization with XRD and TEM analysis.

Characterization techniques

The elemental analysis of the chelating compound 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 Sb_2S_3 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 ethanol dispersion of Sb_2S_3 on the surface of a carbon-coated copper grid.

RESULT AND DISCUSSION

Reaction between S-methyl-3-phenyldithiocarbazate [$C_6H_5NHNHC(S)SMe$] with antimony(III) trichloride in ethanol generated black Sb_2S_3 nanocompounds.

The crystalline phase of the Sb_2S_3 product were investigated by XRD analysis. XRD pattern of the prepared Sb_2S_3 at 79 °C in ethanol was shown Fig. 1. All diffraction peaks are well indexed to the orthorhombic phase of Sb_2S_3 with cell parameters a = 11.295 Å, b = 11.317 Å and c = 3.931 Å, which are analogous with the values agreed in JCPD file No. 03-065-2432. Sharp peaks and no other peaks related to the impurities were detected, representing that the prepared nanocompounds are crystalline and purely single-phase materials.

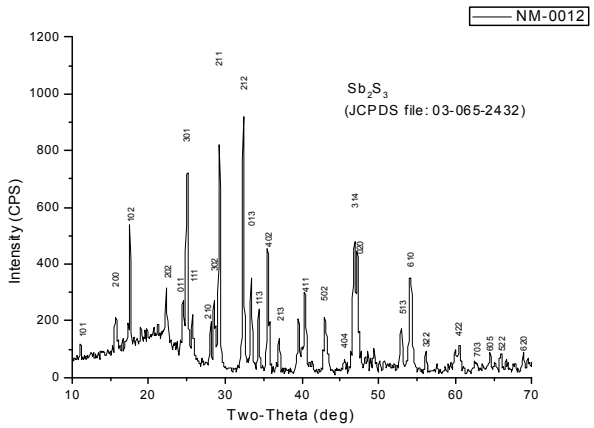

Fig 1 XRD pattern of the prepared Sb_2S_3 compounds obtained in ethanol at 79 °C for 6 hr.

The morphology of the prepared Sb_2S_3 were investigated using transmission electron microscopy (TEM) in Fig. 2. The TEM image shows the prepared Sb_2S_3 is rod-shaped with dimension 35 – 150 nm in diameter and 0.4 – 2.0 µm in length. TEM image of a single nanorod is represented in Fig. 3(a). Fig. 3(c) represents a high resolution TEM (HRTEM) image of Sb_2S_3 nanorod in which crystal lattice fringes are clearly visible which indicated that the Sb_2S_3 are single crystalline in nature. The electron diffraction pattern [Fig 3(b)] was taken from a selected area of the Sb_2S_3 nanorod. The spotty pattern specifies that the prepared compounds are single crystalline. The composition of Sb_2S_3 is examined by EDX (energy dispersive X-ray spectroscopy) analysis (Fig. 4), which shows that the atomic ratio of Sb:S is 1 : 1.56 (the Cu and C peaks are arise from the copper carbon grid).

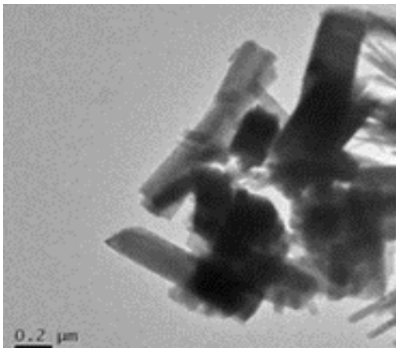

Fig 2 TEM image of prepared Sb_2S_3 nanocompounds prepared in ethanol at 79 °C for 6 hr.

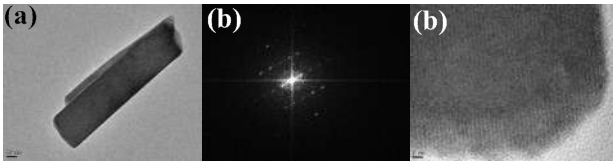

Fig 3 TEM images of Sb_2S_3 at 79 °C (a) nanorods obtain by solvothermal process after 6 hr. (b) SAED pattern of the nanorod and (c) HRTEM image of the nanorod.

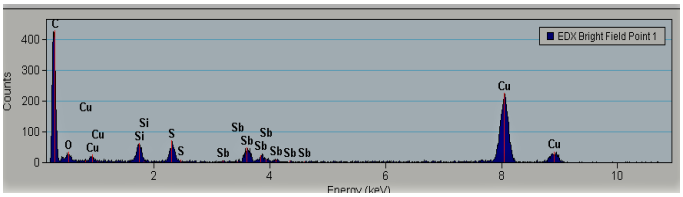

Fig 4 EDX pattern the prepared Sb_2S_3 nanorods obtained at 79 °C for 6 hr (Cu and C peaks are arising from the copper carbon grid.

The experiment is carried out by first $SbCl_3$ and $C_6H_5NHNHC(S)SMe$ were dissolved in ethanol by stirring. At the bigining, no colour changes was seen. In the typical heating at 79 °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, due to the formation of amorphous Sb_2S_3, [10] and then to black, with increasing reaction time (6 hr). This observation pointed out that, in the initial stage of solvothermal process at low temperature, well regulable generation of Sb^{3+} ions from solvated antimony intermediate as well as well controlled release of $S^{=}$, from $C_6H_5NHNHC(S)SMe$,[11] amorphous Sb_2S_3 particles were grownd[12] which converting rod-like shaped when consequently nucleation and preferential growth of crystallization happen simultaneously with time under same reaction condition.

The probable mechanism for the growth of rod-shaped Sb_2S_3 nano structure are anticipated to proceed through two stage process i.e. nucleation or seed generation and crystal growth. In the first stage of reaction, under solvothermal circumstances (source of sulfur, source of antimony, solvent, reaction temperature, reaction time, pressure and so on),[5(a),13] the amorphous particles undergo disruption and generation of large numbers of small nanocrystallites which were acted as nuclei or seeds. In the second stage of the process, as a result of solvothermal ripening, these 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.[14] In the same way, one small rod-like particle after another was generated and then diffuses to larger one maintaining the growing structure under the Sb-S atom chain anisotropy and non-equilibrium growth condition.[12,15]

CONCLUSION

In conclusion, nanocrystalline Sb_2S_3 compounds, having cell parameters a = 11.295 Å, b = 11.317 Å and c = 3.931 Å 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 °C without addition of any surfactants and additives in reaction mixture. At the beginning stage of reaction, amorphous Sb_2S_3 particles were formed. With proceeding reaction time, small nanorods were formed and which were gradually grew onwards on the particles, and finally single crystalline rod-shaped Sb_2S_3 nanocompounds, having dimension of 35 – 150 nm in diameter and 0.4 – 2.0 μm in length. The present synthetic route may have expected to provide an alternative method for the preparation of Sb_2S_3 nanocompounds without using surfactants and additives. Comparing with other method, this method is believed to be more convenient with each of separation and eco-friendly.

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