

Synthesis of SnS nanocrystals by the solvothermal decomposition of a single source precursor

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Abstract SnS nanocrystals (NCs) were synthesized from bis(diethyldithiocarbamate) tin(II) in oleylamine at elevated temperature. High-resolution transmission electron microscopy (HRTEM) investigation and X-ray diffraction (XRD) analysis showed that the synthesized SnS particles are monocrystalline with an orthorhombic structure. The shape and size tunability of SnS NCs can be achieved by controlling the reaction temperature and time, and the nature of the stabilizing ligands. The comparison between experimental optical band gap values shows evidence of quantum confinement of SnS NCs. Prepared SnS NCs display strong absorption in the visible and near-infrared (NIR) spectral regions making them promising candidates for solar cell energy conversion.

Keywords Tin sulfide · Colloidal nanocrystals · Chemical synthesis · Optical properties · Solar energy conversion

Introduction

Among the extensively studied IV–VI semiconductor materials, SnS has attracted particular attention as a low-toxicity [1, 2] photoconductor for the fabrication of

photoelectric energy conversion and near-infrared (NIR) detector materials. Semiconductor SnS has an optical band gap value of 1.1 eV [3], a large optical absorption coefficient of $>10^4 \text{ cm}^{-1}$ [4–6] and a high photoelectric conversion efficiency (up to 25%) [7, 8].

Conventional SnS synthetic techniques have been applied most often for the fabrication of bulk SnS films [4–6, 8–14]. There have been a number of reports of syntheses of nanocrystalline SnS. SnS NCs have been prepared by the reaction of powdered tin with elemental sulfur in a paraffin oil [15] or diglyme [16], and by the solvothermal route using thiourea, thiocyanate, elemental sulfur as sulfur precursors and tin(II) chloride as the tin precursor [17–21]. A more versatile approach to the controlled colloidal synthesis of semiconductor NCs from single source precursors was recently developed for a range of II–VI and IV–VI semiconductor materials [22–24], demonstrating an efficient route to high quality, crystalline nanoparticles. A typical synthetic procedure involves the solvothermal decomposition of preformed single source precursors (metal alkyl xanthates, thiocarbamates and thiocarbonates) in a mixture of coordinating solvents at relatively low temperatures [24]. This particular method has great potential for the production of high-quality SnS NCs with predetermined functionalities.

In this paper, for the first time, we describe a synthetic method for a preparation of SnS NCs from a single source precursor. The synthesis of SnS NCs from bis(diethyldithiocarbamate) tin(II) ($\text{Sn}(\text{Et}_2\text{Dtc})_2$) in oleylamine does not require the use of hazardous materials such as phosphines and volatile organometallic compounds. The crystalline SnS NCs prepared using this new procedure display strong optical absorption in the visible and NIR spectral regions

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making them very attractive for spectroscopic investigations and for incorporation into optical devices.

Experimental

Materials

Tin(II) chloride (99.9%), oleylamine (70%) oleic acid (90%), anhydrous methanol, chloroform and acetone were purchased from Aldrich. Diethylammonium diethyldithiocarbamate and tetradecylphosphonic acid (TDPA) were obtained from Alfa Aesar. The chemicals were used without further purification.

Synthesis

All synthetic steps were conducted inside a nitrogen-filled, dry glove box. Bis(diethyldithiocarbamate) tin(II) was synthesized using a procedure similar to that used elsewhere [13, 14]. Typically, stock solutions of 0.379 g of SnCl_2 and 0.45 g of diethylammonium diethyldithiocarbamate were prepared in 6 ml of anhydrous methanol and purged with argon. With continued stirring, a solution of SnCl_2 was added dropwise to a solution of diethylammonium diethyldithiocarbamate under a stream of argon. White crystals of $\text{Sn}(\text{Et}_2\text{Dtc})_2$ were precipitated, isolated by centrifugation and washed twice with methanol. Resulted $\text{Sn}(\text{Et}_2\text{Dtc})_2$ crystals were dried under vacuum (0.32 g, 40%).

For the synthesis of SnS NCs, the mixture of 0.16 g $\text{Sn}(\text{Et}_2\text{Dtc})_2$, 1 ml oleic acid and 6 ml of oleylamine contained in a 50 ml three neck flask (1) was degassed and purged by argon. The solution was heated at 45 °C under an argon flow for about 10 min until $\text{Sn}(\text{Et}_2\text{Dtc})_2$ was completely dissolved. This mixture was injected under vigorous stirring and an argon flow into another flask (2) containing a hot (170 °C or 205 °C) solution of 5 ml of degassed oleylamine and 0.2 g of tetradecylphosphonic acid (TDPA). After the temperature decreased to about 150 °C, resulting from the injection of the precursor, the solution was held for 30 s finally being removed from the reaction vessel with a glass syringe. To increase SnS particles size the reaction was allowed to continue for 3 h at 170 °C. Then the solution was cooled down to room temperature. The resulting dark brown solution containing the SnS nanoparticles was purified to remove unreacted precursors. Purification process included repeated precipitation and dissolution of SnS NCs. In order to precipitate SnS NCs, an appropriate portion of anhydrous acetone was added to the product solution. After

acetone treatment, a flocculate is obtained due to insolubility of SnS NCs in the short chain ketone and then separated by centrifugation. The retrieved flocculate precipitate containing the desired SnS NCs was redissolved in chloroform. The above purification steps were repeated twice. Finally, the purified SnS NCs were redispersed in chloroform.

Characterization

Powder XRD measurements were made using a Scintag X1 powder diffractometer. The samples for XRD analysis were prepared by dropping the solution of NCs onto a silicon substrate. HRTEM analysis was done using a Philips CM20 TEM operating at 200 kV. The samples for TEM investigation were prepared by dropping a solution of washed SnS NCs onto carbon coated copper grids. UV–VIS–NIR absorption spectra were measured at room temperature with a Cary 5000 UV–VIS–NIR spectrometer (Varian).

Results and discussion

Bis(diethyldithiocarbamate) tin(II) (Fig. 1) is a more desirable precursor for the synthesis of high quality semiconductor SnS NCs due to its low cost and low toxicity. As indicated by the thermoanalytical data [13, 14], the substantially complete thermal decomposition of $\text{Sn}(\text{Et}_2\text{Dtc})_2$ with bulk SnS formation occurs at high temperatures (210–360 °C) in a nitrogen atmosphere. Contrary to the thermal decomposition procedure, the solvothermal route gives an additional degree of control over the material particle size and size distribution [21, 25]. SnS NCs have been synthesized by the solvothermal decomposition of single source precursor in a coordinating solvent at elevated temperature. Low-cost and controllable synthetic procedure is highly reproducible with repeated preparations of different batches of samples. This procedure is similar to others published by O'Brian et al. [22, 23] for the synthesis of high quality semiconductor NCs (CdS, ZnS), where less toxic single-molecule organic complexes of heavy metals with dithiocarbamates and

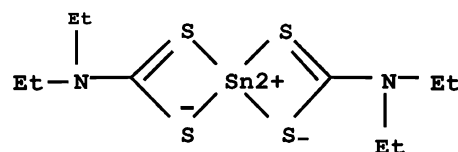


Fig. 1 Bis(diethyldithiocarbamate)tin(II) used as a precursor for SnS NCs synthesis

non-phosphine containing solvents are used. As it was indicated by Efrima et al. [24], Lewis base alkylamine solvents promote the decomposition reaction of metal alkyl xanthates, thiocarbamates and thiocarbonates at relatively low temperatures. Indeed, the heating of the reaction mixture without amines at elevated temperature did not result in SnS formation. By contrast, using hexadecylamine or oleylamine as a reaction solvent promotes $\text{Sn}(\text{Et}_2\text{Dtc})_2$ decomposition at temperature as low as 85 °C. Alkylamines also act as a stabilizing agent for the formed particles permitting control of their size. In the work presented here, the SnS NCs are formed from $\text{Sn}(\text{Et}_2\text{Dtc})_2$ in an oleylamine/oleic acid mixture. The presence of oleic acid in the reaction mixture serves as a ligand and also plays a vital role in the formation of nanoscale tin sulfide by controlling the reactivity of precursors [26, 27].

XRD analysis verified the formation of highly crystalline SnS NCs (Fig. 2). The reflections were indexed and assigned to SnS of orthorhombic structure with the lattice parameters $a = 0.4328$ nm, $b = 0.1119$ nm, and $c = 0.3978$ nm (JCPDS 39-354, Herzenbergite). Some small additional peaks from trace impurities were observed as well. The broadening of the XRD peaks is naturally associated with the formation of NCs. Representative TEM micrographs of SnS NCs, synthesized from the single source precursor at various conditions are shown in Fig. 3. The SnS NCs synthesized by this solvothermal procedure were polydisperse in size. A hierarchy of coagulated

NCs could be explained by insufficient surface passivation, leading to aggregate formation [28]. The dimensions of SnS NCs were in a range of 5–200 nm depending on synthetic conditions. Fast nucleation and growth led to the formation of small (5–10 nm) NCs (Fig. 3a, c), whereas prolonged heating caused big NCs to be grown (Fig. 3b). As may be seen clearly in the TEM images, the shape of the SnS NCs seems to be dependent on the nature of the stabilizing agents used in addition to the thermal conditions of the preparation. Isotropic and anisotropic growth of SnS NCs is achieved by use of different capping molecules. As indicated in Fig. 3 (a–c), the chemical nature of stabilizing agents can significantly affect the surface energy of the different facets of growing SnS NCs, leading to the formation of rod-like (Fig. 3a), polygonal (Fig. 3b) or spherical morphologies (Fig. 3c, d) of semiconductor nanomaterials [28, 29]. Addition of TDPA to the reaction mixture as a cosurfactant terminates anisotropic growth of SnS inducing the formation of spherical NCs (Fig. 3c, d). The morphology of non-spherical NCs depends more on the surface energies of the specific crystalline faces, whereas spherical morphology corresponds to the lowest surface energy for small NCs, which have a large atomic surface/volume ratio [28]. Additionally, the existence of lattice planes on HRTEM images of these particles stretching through entire NCs (Fig. 3d) confirms the high crystallinity of the samples, even though the size distribution is broad.

Fig. 2 Powder X-ray diffraction pattern of SnS nanoparticles with reflections indexed for Herzenbergite (JCPDS 39–354)

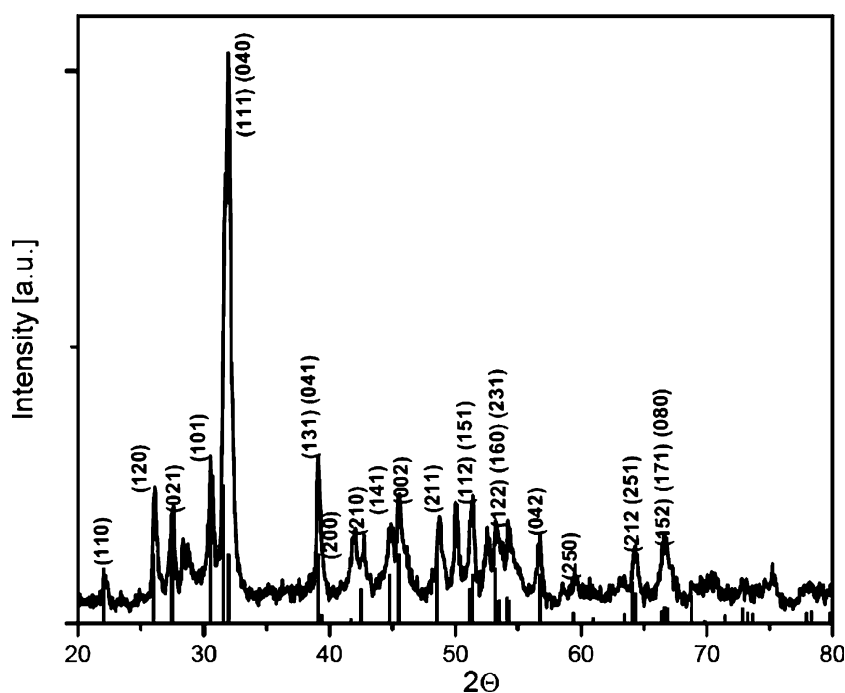
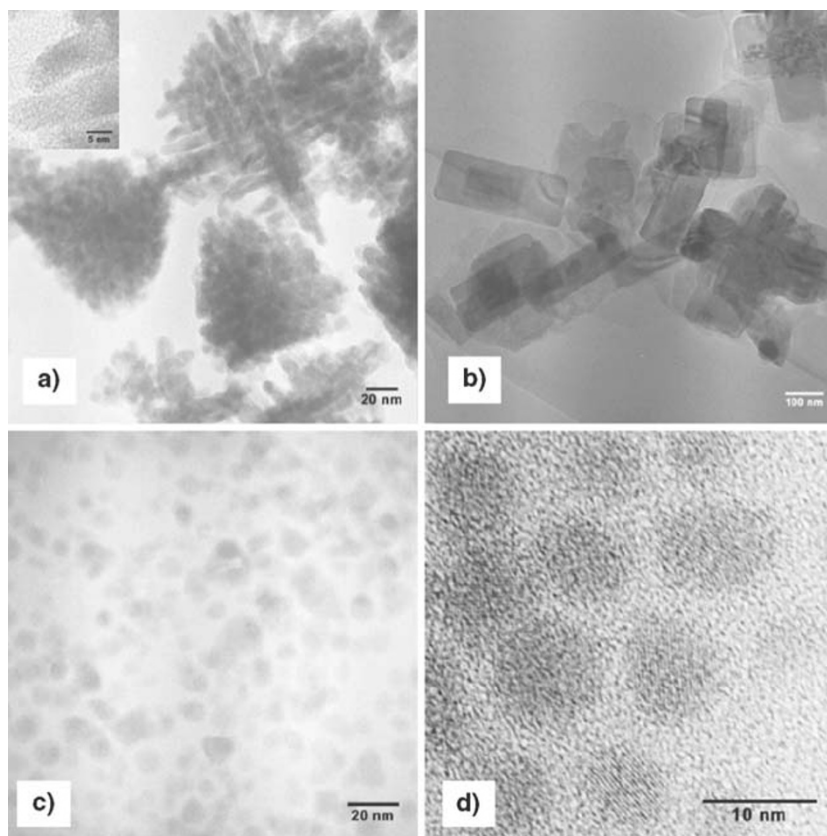


Fig. 3 TEM images of SnS nanoparticles, synthesized in oleylamine/oleic acid mixture at 170 °C for 30 s (a) and 3 h (b); TDPA/oleylamine/oleic acid mixture at 205 °C for 30 s (c) with correspondent HRTEM micrograph of individual SnS nanocrystals (d)



The representative optical absorption spectrum of sub-10 nm SnS NCs synthesized in oleylamine/oleic acid mixture at 170 °C is shown in Fig. 4(a). The absorption coefficient for SnS nanoparticles α , was calculated from the average absorption index (A) as $\alpha = 4\pi A/\lambda$ [4]. The spectral behavior of the absorption coefficient as a function of energy, $h\nu$, is shown in Fig. 4(b). SnS NCs have high absorption coefficient $>10^5 \text{ cm}^{-1}$ in the wavelength range from 400 nm to 800 nm.

To determine the energy band gap, E_g , and the type of optical transition responsible for this intense optical absorption, the absorption spectrum was analyzed using the equation for the near-edge absorption (Eq. 1) [30].

$$\alpha = \frac{k(h\nu - E_g)^{n/2}}{h\nu} \quad (1)$$

In Eq. 1, k and n are constants and E_g is the band gap energy of the bulk semiconductor. The n value is 4 for indirect-gap materials. Values of the optical band gap for the samples were obtained by the extrapolation of the linear region of the plot of $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) as shown in Fig. 4(c). Clearly, the absorption corresponds to an indirect allowed

transition with an energy gap of 1.6 eV for the nanocrystalline particles, higher than the literature value (1.1 eV) for bulk films of SnS [30, 31]. Calculated the same way band gap value of sub-200 nm SnS particles synthesized by prolonged heating of $\text{Sn}(\text{Et}_2\text{Dtc})_2$ precursor is 1.06 eV which close to reported one for bulk SnS. Since this approach to band gap calculation is not particularly accurate for polydisperse solutions of nanoparticles, these reported bandgap values should be taken as approximate. The increased values of band gap for SnS NCs compared with the bulk material can be explained by quantum confinement of the carriers in semiconductor NCs [32]. When the size of the particles decreases, then quantum confinement leads to a size dependent enlargement of the band gap resulting in a blue shift in the absorbance onset [33], as observed in this work.

In conclusion, for the first time, SnS NCs on a sub-10 nm scale were synthesized from bis(diethylthiocarbamate) tin(II) in oleylamine at elevated temperature. The shape and size tunability of SnS NCs can be achieved by controlling the reaction temperature and time, and the nature of stabilizing ligands. HRTEM investigation and XRD analysis showed that the synthesized SnS particles are monocrystalline with an orthorhombic structure. The synthesized,

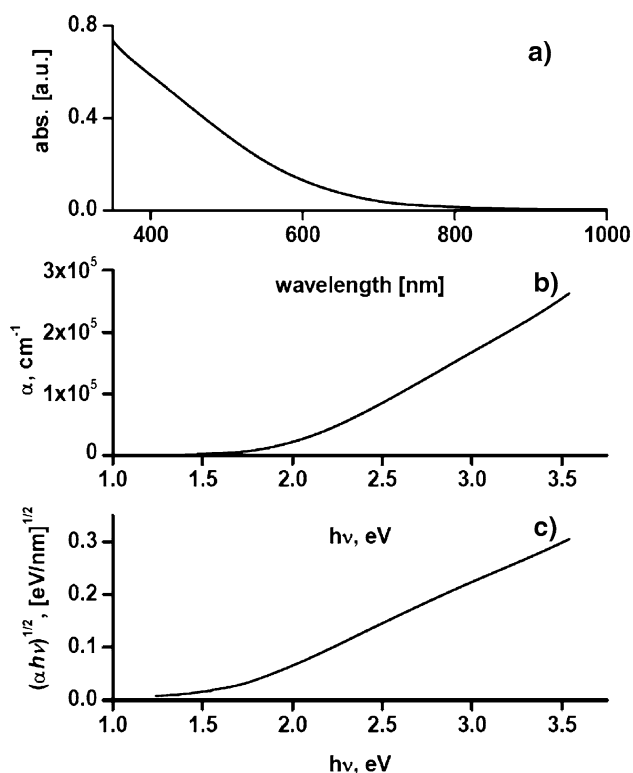


Fig. 4 Optical properties of SnS nanocrystals: optical absorption spectra (a), the dependence of absorption coefficient (α) on photon energy ($h\nu$) (b), the dependence $(\alpha h\nu)^{1/2}$ on photon energy ($h\nu$) (c)

low-toxicity, SnS NCs exhibit strong absorption in the visible-NIR spectral region. The experimental optical band gap values shows the evidence for the quantum confinement of sub-10 nm SnS NCs. These low toxicity SnS NCs may well serve as effective solar energy conversion devices with tunable optical properties and functions. Techniques for improving the monodispersity and refining the optical characteristics are the subject of ongoing investigations.

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