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Effect of sulfonating agent and ligand chemistry on structural and optical properties of CuSbS₂ –particles prepared by heat-up method

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Chalcostibite copper antimony sulfide (CuSbS₂) is a promising candidate for application in solar cells. The functionality of CuSbS₂ –particles depends on particle size and morphology, and controlling of these two parameters during synthesis process is of uttermost importance. In this work, CuSbS₂ particles were prepared by a facile heat-up synthesis method to investigate the effect of sulfur source on the structural and properties of CuSbS₂ particles by utilizing sulfur powder (Su) and thiourea (Tu). Different morphologies were observed when Su and Tu were employed. Results demonstrate that the shape uniformity can be improved by applying a coordinating sulfur precursor (Tu). Moreover, nanoplatelet- and nanobrick-shaped particles were obtained by changing the ligand chemistry i.e. using a different combination of oleylamine (OLA), 1-octadecene (ODE), and oleic acid (OL). Band gap calculations show that CuSbS₂ has direct and indirect bandgaps with a small difference of 0.2 eV. Composition analysis of samples obtained from Tu precursor revealed that antimony contents were different resulting in variation of lattice parameter *c*. Moreover, valence band (VB) and conduction band (CB) positions determined by cyclic voltammetry (CV) suggest that this material based on its composition can have dual applications. First, as an absorber in nanocrystalline solar cells and second, as a hole transport material in perovskite solar cells.

Keywords

Copper antimony sulfide, crystal structure, morphology, formation mechanism.

Introduction

Pursuit after new suitable, non-toxic, and abundant semiconductor materials^{1–4} for different applications is a continuous challenge in materials science. In this quest ternary and quaternary semiconductors like CuSbS₂, CuInS₂^{5,6}, CuInSe₂⁷, CuInGaS₂⁸ and Cu₂ZnSnS₄⁹ have gained increasing interest. Among these CuSbS₂ is particularly interesting, but less explored material. Recent studies show that an indium-free CuSbS₂ is a promising p-type material for solar cell and supercapacitor applications^{10–15}. Yang et al.¹² confirmed the p-type conductivity theoretically and experimentally by using density functional theory calculations and Hall effect measurements. They reported a hole concentration of ~10¹⁸

cm^{–3} and hole mobility of 49 cm²/(V.s). Some theoretical simulations and experimental investigations suggest that CuSbS₂ has a direct band gap of 1.38–1.5 eV^{12, 16–19}, while some other studies claim that it has an indirect band gap.^{20, 21} Meanwhile, few studies also report that CuSbS₂ has both direct and indirect band gap with a small difference in energy.^{22–24} Different synthesis methods have been developed to obtain high quality semiconductors. Room temperature²⁵ and high temperature²⁶ synthesis methods have been explored depending on the desired crystal structure, morphology, size, and optical characteristics. For synthesizing of CuSbS₂ particles solvothermal¹⁶, hydrothermal²⁷, mechanochemical²², and hot injection methods^{23, 28, 29} have been reported. Wernick et al.³⁰ prepared this compound by melting the stoichiometric amounts of the component elements in a sealed quartz tube. They reported a single-phase CuSbS₂ with a layer-type structure. In 1999, Su et al.³¹ reported the synthesis of chalcostibite CuSbS₂ particles by a solvothermal route in ethylenediamine solution. An et al.²⁷ prepared CuSbS₂ nanorods by a surfactant-assisted hydrothermal method. Takei et al.²² showed that CuSbS₂ particles could be synthesized by a mechanochemical process, while Ikeda et al.²⁸, Ramasamy et al.²³, Moosakhani et al.^{32, 33} and Yan et al.²⁹ synthesized CuSbS₂ particles by a hot-injection route. Nevertheless, the particles obtained by hydrothermal and solvothermal routes are not of as high quality as those made by a hot injection method and there is a need for more detailed studies to discover all aspects of the crystal growth and reaction mechanism for preparing CuSbS₂. Contrary to the

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typical hot injection method, non-injection synthesis or heat-up synthesis, although been used widely for synthesizing a large range of semiconductors^{34–39}, has thus far not been investigated for synthesizing CuSbS₂ particles. In this method, all the precursors are mixed together and heated controllably to induce the nucleation and growth of the particles. Ligand chemistry and the choice of precursors are the most important considerations in heat-up synthesis because they control nucleation and how the particles evolve over time, i.e., the nature of the solvents and ligands can influence the morphology and crystal structure.^{40, 41}

In this paper, we report a heat-up synthesis of CuSbS₂ by utilizing different sources of sulfur as well as different solvents. Su and Tu were chosen as they have a different nature for participating in the reaction and therefore can cause different results. Tu is a coordinating sulfur precursor that can make a complex with a metallic cation. On the other hand, different combination of solvents and capping agent were employed to evaluate the effect of ligand chemistry with different sulfur sources. OLA, ODE, and OL were employed in our synthesis as a coordinating solvent, non-coordinating solvent, and capping agent, respectively.

Experimental

Materials

We used copper chloride (CuCl, ReagentPlus®, purified, ≥ 95%), antimony chloride (SbCl₃, ACS reagent, ≥ 99%), Su (S, 99.998 % trace metal basis), Tu (ACS reagent, ≥ 99%), OL (Technical grade, 90%), acetonitrile, tetrabutylammonium, hexafluorophosphate, and OLA (Technical grade, 70 %) from Sigma Aldrich. ODE (≥ 95%) was from Fluka and *n*-hexane was purchased from Merck. All the chemicals were used directly without further purification.

Synthesis of CuSbS₂ powder

In a typical synthesis, CuCl (0.5 mmol), SbCl₃ (0.5 mmol), and Tu (1.5 mmol) were dissolved in 10 ml of OLA at a molar ratio of 1:1:3 and backfilled with nitrogen for 1 h at 80 °C. The temperature was increased to 240 °C under N₂ atmosphere and the mixture was maintained at this temperature for 1 h. After completion of the reaction, the solution was cooled down to 60 °C, and the product was dispersed in a mixture of *n*-hexane and ethanol. The resultant dispersion was centrifuged three times at 8000 rpm for 2 min. The precipitate was dried at 60 °C for further characterizations. For preparing samples using Su, it was first dissolved (1.5 mmol) in OLA in an ultrasonic bath to achieve a clear orange solution, the other conditions being similar to the above-mentioned process. The synthesis was carried out by substitution of part of the OLA by ODE and by OL. The reaction conditions are summarized in Table 1.

Measurements and characterization

The crystal structure and phase purity of CuSbS₂ were analyzed by X-ray diffraction (XRD) using PANalytical X'pert Powder Pro diffractometer and Cu-K_α radiation (1.5406 Å) at a voltage setting of 45 kV and a current setting of 40 mA. The morphology and elemental composition of the powders obtained were

studied by Scanning Electron Microscopy (SEM; TESCAN Mira 3) equipped with energy dispersive spectrometer (EDS). The Raman spectra were measured by Labram HR Raman Spectrometer (Horiba Jobin Yvon) applying Argon laser excitation wavelength of 514 nm. The UV-Vis-NIR diffuse reflectance spectrum was recorded using a UV-Vis-NIR Agilent Cary 5000 for band gap calculation. X-ray photoelectron spectra was measured with a Kratos Axis Ultra spectrometer using monochromated Al K_α radiation and charge neutralization. The spectra was acquired using a pass energy of 20 eV, an X-ray power of 225 W and an analysis area of approximately 700 x 300 μm. The C 1s peak of adventitious carbon at 285.0 eV has been used as a charge reference. CV analysis was conducted on an Autolab PGSTAT100 electrochemical workstation using glassy carbon discs as the working electrodes (~ 0.25 cm²), a Pt wire as the counter-electrode and a saturated calomel (SCE) reference electrode. The electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. SCE potential values were converted to the normal hydrogen electrode (NHE) values for further investigations.

Table 2. Summary of reaction conditions in the syntheses.

Sample name	Sulfur source	OLA (ml)	ODE (ml)	OL (ml)
Su-OLA	Su	10	0	0
Su-OLA-ODE	Su	5	5	0
Su-OLA-ODE-OL	Su	4.25	4.25	1.5
Tu-OLA	Tu	10	0	0
Tu-OLA-ODE	Tu	5	5	0
Tu-OLA-ODE-OL	Tu	4.25	4.25	1.5

Results and Discussion

Structural properties and proposed formation mechanisms

XRD patterns of samples obtained by Su and Tu sulfur sources are portrayed in Figs. 1a and b. All the patterns were in good agreement with the orthorhombic CuSbS₂ (ICSD No. 98-017-1051, space group *Pnma*; *a* = 6.018 Å; *b* = 3.7958 Å; *c* = 14.495 Å). The values of lattice parameters are summarized in Table 2. As can be observed the intensity of {111}, {104}, {013}, and {201} reflections were changed in different synthesis conditions, and these changes are more tangible for {104} and {013} peaks. For the Su-OLA sample, the intensity of these reflections is higher than for other samples obtained by Su source. This indicates that decrease of the amount of a coordinating solvent able to react directly with the octa-atomic sulfur ring via autocatalytic reaction to produce linear polysulfide chains result in reduction

Table 1. Summary of SEM characterization and X-ray diffraction measurements of the synthesized powders.

Sample name	Morphology	a (Å)	b (Å)	c (Å)
Su-OLA	nanobrick	6.018	3.786	14.522
Su-OLA-ODE	nanoplate	5.970	3.818	14.450
Su-OLA-ODE-OL	nanoplate	6.011	3.794	14.495
Tu-OLA	nanoplate	6.013	3.795	14.543
Tu-OLA-ODE	nanoplate	6.016	3.802	14.508
Tu-OLA-ODE-OL	nanobrick	6.023	3.798	14.501

Figure 1. XRD patterns of CuSbS_2 nanocrystals synthesized with different sulfur sources.

of activated elemental sulfur and change in nucleation and growth rate in preferred orientations. The polysulfide salts decompose to form H_2S , which is available source of sulfur for the reaction.^{42, 43} On the other hand, when sulfur reacts with ODE, thermally activated oxidation of the alkene by sulfur yields a highly reactive H_2S source and a chemically benign side-product 2-tetradecylthiophene.⁴⁴ Because the thiophene molecule has an S atom, the conversion ratio of elemental sulfur cannot be 100%. Fig. 2a outlines the possible reactions resulting in CuSbS_2 using a Su source, OLA, ODE, and OL. When small

amounts of OLA and ODE were replaced by OL as a capping agent, intensities increase in {104} and {013} reflections occurred. Therefore, OL is concluded to promote the formation and crystallization of CuSbS_2 in these orientations. It is generally accepted that deprotonated oleic acid (carboxylate anions, $\text{C}_{17}\text{H}_{33}\text{COO}^-$) can interact selectively with specific crystal facets because of its high electron-donating ability. The carboxylic acid molecules are partially transformed into carboxylate anions according to the following equation:⁴⁵

Figure 2. Schematic representation for the proposed formation mechanism of CuSbS_2 particles with Su sulfur source (a), (b).

Figure 3. Raman spectra of CuSbS₂ powders prepared with different sulfur sources.

Changing the sulfur source to Tu resulted in a different trend. The more intense peaks are related to Tu-OLA-ODE-OL sample. Obviously, using Tu as a sulfur source means that the mechanisms of releasing sulfur for nucleation and growth are different. The intensity of {104} and {013} peaks increased due to the substitution of a non-coordinating solvent with a coordinating one and a capping agent. Interactions between surface cations (Lewis acids) and stabilizing ligands (Lewis

bases) can be characterized in terms of hard and soft acid/base interactions (HSAB).⁴⁶ According to the HSAB theory, Cu⁺ and Sb³⁺ are soft and hard acids, respectively, so the coordinating powers between the metal ions and the hard bases OLA and OL are in the order of Sb³⁺ > Cu⁺. Then Cu⁺ can form a complex with Tu, and antimony is prone to make a complex with oleylamine and oleic acid (hard Lewis bases) (Fig. 2b). Since the Cu–Tu complex is more reactive than antimony complexes, upon heating the mixture the Cu–Tu complex decomposes to form Cu_{2–x}S (x = 0–1).^{47, 48} Subsequently, the Sb–OLA–OL complex decomposes and incorporate into Cu_{2–x}S lattices by ion exchange to produce CuSbS₂ and 3Cu⁺. The released Cu⁺ reacts with extra Tu to form Cu–Tu complex, and the reaction continues until cation exchange finishes. According to this mechanism by reducing the amount of OLA, number of chains around the Sb³⁺ decreases and the decomposition products of antimony complex react easier with Cu_{2–x}S particles. This provides improved growth of crystals in preferred orientations of {104} and {013}. As discussed, replacing a small amount of OLA and ODE with OL can cause selective interaction of carboxylate anions with specific crystal facets and result in increasing the intensity of {104} and {013} diffraction peaks for the Tu-OLA-ODE-OL sample as well.⁴⁹

In order to obtain a more precise assignment of the structure Raman spectra measurements were performed. The Raman peaks detected at 332 cm^{–1} are in agreement with reference data⁵⁰ and confirm the formation of chalcocite (Fig. 3). No

Figure 4. SEM images of powders obtained with Su sulfur source.

Raman peaks of impurity phases, such as Cu_2S , are detectable confirming the purity of the chalcocite phase (CuSbS_2).

from Tu in comparison with Su. This provides control of the nucleation and growth of CuSbS_2 particles leading to shape and

Figure 5. SEM images of powders obtained with Tu sulfur source.

SEM images of the particles synthesized using different sources of sulfur are illustrated in Figs. 4 and 5. It is evident from the images that the morphology of the particles was affected by changes in the reaction conditions. When the Su source was used with OLA, nanobrick-shaped particles resulted. Substitution of half of the solvent with ODE caused nanoplatelets to be formed. This observation suggests that oriented attachment of CuSbS_2 seeds in different directions could have occurred by employing a coordinating solvent and a non-coordinating one along with Su as a sulfur source. As can be seen, a small amount of OL caused formation of smaller particles but decreased shape uniformity of Su-OLA-ODE-OL sample. Moreover, SEM images show that use of ODE and OLA led to improved shape and size uniformity, as less Su was available for the reaction in this case.

Nanoplatelets were obtained with Tu as a sulfur source and OLA and OLA-ODE as the solvent. Apparently, ODE does not affect so much the particle size and shape of the particles, but employing of OL changed the morphology of the particles to nanobricks. It can be argued that deprotonated oleic acid can change the surface energy and lead to different growing rates at different crystallographic directions. On the other hand, considering samples obtained by different sulfur sources, it is obvious that more uniform growth of particles is achieved when using Tu as a source. This can be attributed to the slower release of H_2S

Figure 6. Schematic representation for oriented attachment of the particles.

size uniformity. Furthermore, Tu acts as both a sulfur source and a chelating agent to facilitate the uniform incorporation of sulfur and formation of CuSbS_2 crystallites. The Length and width of the particles obtained were approximately around 290 nm and 233 nm, 310 nm and 290 nm, 526 nm and 236 nm for Tu-OLA, Tu-OLA-ODE and Tu-OLA-ODE-OL, respectively. The possible shape and morphology evolution at different conditions is summarized schematically in Fig. 6a and Fig. 6b.

Figure 7. X-ray photoelectron spectra of a) Sb 3d (and O 1s), b) Cu 2p and c) S 2p regions of Tu-OLA, Tu-OLA-ODE and Tu-OLA-ODE-OL samples.

X-ray photoelectron spectra of Sb 3d, Cu 2p and S 2p regions for Tu-OLA, Tu-OLA-ODE and Tu-OLA-ODE-OL samples are shown in Figure 7. The Sb 3d region has been fitted with two doublet peaks corresponding to Sb^{3+} and Sb^{5+} . For the Sb^{3+} component the resulting $3d_{5/2}$ binding energy of $529.5 \text{ eV} \pm 0.1 \text{ eV}$ and doublet peak separation of $\sim 9.3 \text{ eV}$ corresponds well to that previously observed for CuSbS_2 .^{12, 51} The Sb^{5+} component found at $530.9 \text{ eV} \pm 0.1 \text{ eV}$ with doublet peak separation of $\sim 9.3 \text{ eV}$ can be assigned to oxidized Sb in the form of Sb_2O_5 .^{12, 52} The Sb $3d_{5/2}$ peak overlaps with the O 1s region. Therefore an O 1s component has been added to the fit. It is found at binding energy of $\sim 532 \text{ eV}$ which corresponds to oxygen in Sb_2O_5 ¹² but could contain contributions from e.g. adsorbed oxygen species as well. The Cu 2p spectra are shown in Fig 7b. They show only one doublet peak with $2p_{3/2}$ binding energy of $932.3 \text{ eV} \pm 0.2 \text{ eV}$ and doublet peak separation of roughly 19.9 eV . These observations are consistent with previous reports for Cu^+ in CuSbS_2 .^{12, 51} The absence of peaks around 934 eV and 955 eV and satellite peaks between $940\text{--}945 \text{ eV}$ and $960\text{--}965 \text{ eV}$ confirms that no Cu^{2+} is observed.⁵³ The S 2p region shows two well separated doublet peaks. The main component found at $2p_{3/2}$ binding energy of $161.7 \text{ eV} \pm 0.1 \text{ eV}$ with doublet peak separation of $\sim 1.2 \text{ eV}$ can be assigned to S^{2-} in CuSbS_2 .^{12, 51} The higher binding energy component with a $2p_{3/2}$ binding energy of

roughly 168.7 eV can be assigned to a sulphate species possibly due to surface oxidation of CuSbS_2 .⁵² The XPS results confirm the presence of CuSbS_2 with some oxidation of antimony and sulfur probably originating from the surface region.

Optical and electrochemical properties

Band gap of CuSbS_2 nanocrystals was evaluated with UV-Vis-NIR diffuse reflectance data (Fig. 7a). The calculations were performed using a Tauc equation in the form of $(h\nu F(R))^{1/n}$, where h , ν , and $F(R)$ represent Plank's constant, frequency, and Kubelka-Munk function, respectively. For direct allowed transition $n=1/2$, and for indirect allowed transition $n=2$. The optical band gap values can be obtained by extrapolating the linear region of the $h\nu$ plots. Calculations demonstrate that the direct and indirect band gap values for Tu-OLA, Tu-OLA-ODE, and Tu-OLA-ODE-OL samples are about 1.59 and 1.39, 1.56 and 1.38, and 1.55 and 1.41 eV, respectively. It is worth mentioning that by changing the shape of the particles from nanoplate to nanobrick, no significant change occurred in the band gap values. Moreover, comparison of the indirect and direct values demonstrates a small difference of 0.2 eV suggesting that CuSbS_2 has both direct and indirect band gaps. Ramasamy et al.²³ reported direct and indirect values with a difference of 0.3 eV while Wada and Maeda reported a difference of 0.05 eV.²⁴

Figure 8. Diffuse reflectance spectra (a), direct (b), and indirect (c) band gap estimation of CuSbS_2 nanocrystals prepared by Tu as the coordinating sulfur source.

Common to all cases is that direct band gaps are a little wider than the indirect ones.

Conclusions

Figure 10. CV curves (a) and the energy band positions of the CuSbS₂ particles.

Energy levels are essential parameters for device design and material selection for solar cell applications. Cyclic voltammetry is an effective method for the determination of bandgaps as well as the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of conjugated polymers and organic molecules.⁵⁴ This method has been also used to measure the energy levels in semiconductors as well.^{55, 56} The injection of electrons to the conduction band minimum (CB) generates the reduction current, and the extraction of electrons from the valence band maximum (VB) results in an oxidation current. The energy levels can be calculated from the oxidation onset and reduction onset potentials, respectively. Band gaps from the electrochemical measurements agrees well with the optical ones (summarized in Table 3). VB and CB positions values for Tu-OLA sample differed from those of Tu-OLA-ODE and Tu-OLA-ODE-OL samples. Considering the lattice parameter values (Table 1) and compositions of the particles obtained by EDS (Figure 9), it can be concluded that differences in antimony content are related to the variation in lattice parameter *c*. The differences in energy level values obviously result from differences in composition and interatomic distance.^{57, 58} Comparison of the values of TU-OLA with VB (-3.93 eV) and CB (-5.43 eV) of methylammonium lead iodide suggests its suitability for hole transport material in perovskite solar cells. On the other hand, the energy bands of the two other samples in relation to the VB and CB of titanium dioxide favour their application in nanocrystalline solar cells.

Table 3. Band gaps of CuSbS₂ particles determined by diffuse reflectance spectra and cyclic voltammetry measurements.

Sample name	Direct optical band gap (eV)	Indirect optical band gap (eV)	Electrochemical band gap (eV)
Tu-OLA	1.59	1.39	1.75
Tu-OLA-ODE	1.56	1.38	1.62
Tu-OLA-ODE-OL	1.55	1.41	1.52

Figure 9. EDS results for CuSbS₂ powders.

Pure CuSbS₂ nanocrystals have been synthesized via a heat-up method with Su and Tu sulfur sources. Nanoplatelet- and nanobrick-shaped particles can be obtained by changing the ligand chemistry and sulfur sources. The results show that the nature of the coordinating solvents can strongly influence the crystallographic phase as well as the particle morphology. The slow release of sulfur from Tu provides better control of the nucleation and growth of particles resulting in improved shape and size uniformity. Nevertheless, combination of OLA and ODE with Su leads to nanoplatelets with best shape uniformity. Band gap and energy levels determinations confirm that the values of the band gaps are optimal for the photovoltaic applications and energy levels can be tuned by tuning of antimony content resulting in different lattice parameter. Furthermore, this energy level tuning makes CuSbS₂ to be used as an absorber and a hole transport material in nanocrystalline and perovskite solar cells, respectively.

Conflicts of interest

There are no conflicts to declare.

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