Article preview

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Canfieldite Ag_8SnS_6 nanoparticles with high light absorption coefficient and quantum yield

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Highlights

- • Ag_8SnS_6 (STS) nanocubes were prepared using heat-up and hot injection protocols.
- • Phase and shape of nanoparticles were tuned by varying reactants temperature and mole ratios.
- • p-XRD patterns of the STS showed a pure phase orthorhombic crystalline system.
- • STS nanoparticles exhibited high photon absorption and low quantum yield potentials.

Abstract

Canfieldite Ag_8SnS_6 (STS) nanocubes were prepared by the solution decomposition of precursors using heat-up and hot injection protocols employing coordinating solvents (oleylamine - OLA and dodecanethiol - DT) to afford monodispersed silver tin sulfide (STS) nanoparticles. The phase and shape of nanoparticles were tuned by varying reactants' temperature and mole ratios. The powder X-ray diffraction (p-XRD) and transmission electron microscopy (TEM) analysis indicate phase pure orthorhombic

Ag_8SnS_6 nanocrystals with nearly monodispersed particles ranging between 12 and 50 nm. The p-XRD patterns for the STS nanoparticles obtained by the heat-up method exhibited enhanced peak broadening than the hot injection route, accounting for the corresponding quantum confinement effects. Likewise, the (124), (227) and (266) planes of the reflections in OLA/DT capped STS crystals appeared well resolved, indicating that seed growth of a transitional Ag_2S might be involved in the formation of the ternary chalcogenides. The values of the energy bandgap (E_g) were found in the range of 1.16–2.60 eV. At the same time, the STS nanoparticles exhibited high photon absorption and low quantum yield potentials, making them a possible candidate for photovoltaic cells and enhanced photoelectrochemical performance.

Introduction

The recent decades have witnessed the utilization of ternary and quaternary metal sulfides such as (Ag-In-Zn)S, $AgInS_2$, and $Cu(In,Ga)Se_2$ (CIGS), amongst others, as photocatalysts for photoelectrochemical (PEC) water splitting. Photocatalysts mainly act as photoelectrodes and absorb sunlight to generate electrons for water reduction, thereby producing clean hydrogen energy [1,2]. Multinary metal chalcogenide solar absorbers have sufficient conversion efficiency, ranging from 16.0 to 20.5% [3,4]. Ternary chalcogenides AgInTe, AgSnTe and their analogues, compared to metal oxide photoelectrodes such as WO_3, TiO_2 and ZnO, exhibit better stability and higher photoelectrochemical performance as a result of their higher light absorption capacity [5]. However, due to the scarcity and cost of Te and In, they are rarely used. In recent times, quaternary chalcogenides Ag_2ZnSnS_4 (AZTS) and Cu_2ZnSnS_4 derived from non-toxic and cheaper Zn and Sn sources were used as substitutes to afford excellent optical, energy band structures and electrical properties to these compounds [6]. Several investigations on ternary metal sulfides of Ag origin, such as $AgInS_2$ [7], $AgBiS_2$ [8], $AgSbS_2$ [9], and Ag_3SbS_3 [10], have been conducted to establish their applications in photovoltaic and photocatalytic cells. Among this class of ternary chalcogenides, Ag_8SnS_6 has many essential properties, such as high absorption coefficients of $\alpha \sim 10^4$ cm^{-1} in the visible range and an ideal energy bandgap (E_g) of 1.3–1.5 eV, near the optimal E_g of 1.4 eV for a solar cell [11]. In addition, Ag, Sn and S, the three elements in Ag_8SnS_6, are non-toxic, cost-effective, and eco-friendly. Nanocrystalline Ag_8SnS_6 has been synthesized for several applications, including photoelectrochemical salt-water splitting [12,13], as counter electrodes in dye-sensitized solar cells (DSSC) [14], thermoelectric and photocatalytic degradation of dyes [15,16]. Recently Ag_8SnS_6 solar cells were reported to have an efficiency of 0.25% [17].
STS can provide broad absorption in the visible region as a direct bandgap semiconductor with an E_g equivalent range of 1.4–2.1 eV [18]. The electronic band edge made it a suitable catalyst for reducing/oxidizing water and an ideal for photocatalytic water splitting [19,20]. Wang and Wang used density functional theory (DFT) calculations, photoelectron spectroscopy and diffuse reflectance studies to establish the energy band structure of the STS materials and also to show the efficient hydrogen generation capacity [9,21,22].
Different synthetic routes were reported to prepare STS nanoparticles with good light absorption and quantum yield properties, these include electrodeposition [19], improved

chemical bath deposition CBD [23] and spin/dip-coating with anticipated enhanced performance of STS photoanode [5,24]. However, their PEC performance is unstable with low photon-to-electron conversion efficiency [5]. To improve the efficiency of their photon-electron conversion, Cheng and Hong studied the effect of Zn and Ag contents on the PEC performance of stannite Ag_2ZnSnS_4. The silver-zinc-tin precursors produced the stannite Ag_2ZnSnS_4 phase by a two-step sulphurization process at 160 °C for 60 min and 450 °C for 30 min under nitrogen purge. The reaction produced the Ag_2ZnSnS_4 (N-type) stannite phase with carrier concentrations of 5.54×10^{12}–9.11×10^{12} cm^{-3}. A higher silver content resulted in an improved PEC performance and low resistivity [20].
Likewise, Jing et al. produced mixed chalcogenide solid solution alloys, that is, $Ag_2ZnSn(S_{1-x}Se_x)_4$ (x = 0–1), and investigated them for photocatalytic water splitting [25]. Hybrid functional methods, a class of approximation to the exchange-correlation energy, were used to investigate the electrochemical structures and photocatalytic properties of $Ag_2ZnSn(S_{1-x}Se_x)_4$ (x = 0–1). The results indicated that $Ag_2ZnSnSe_4$ (x = 1) and Ag_2ZnSnS_4 (x = 0) had small electron effective masses and a dispersive conduction band, which aided the separation of photogenerated carriers. Moreover, the effective hole masses aligned along the (100) and (010) planes, direction-dependent and sensitive to strain, indicating easy modulation of photocatalytic properties. However, by controlling the x component, the band gaps (E_g) of the $Ag_2ZnSn(S_{1-x}Se_x)_4$ solid solution could be tuned continuously, indicating the easy modulation of the visible light wavelength [25,26].
Similarly, Ag_8SnS_6 nanocrystals were synthesized by Boo-on et al. (2018) using a spin coating technique with a bandgap E_g range of 1.24–1.41 eV [27]. A power conversion efficiency (PCE) of 0.64% was obtained under maximum incident light irradiation using polysulphide electrolyte and Au counter electrode. When the light intensity was reduced by 10%, the efficiency improved to 1.43%. Moreover, an outstanding efficiency for new solar material resulted when a cobalt electrolyte replaced polysulphide with a lower redox level because PCE increased to 2.29% under 0.1 sun. Experimentally, the EQE spectrum ranges from 300 to 1000 nm with a 600 nm wavelength maximum of 77%. The excellent photovoltaic performance and near-optimal E_g indicate Ag_8SnS_6 as a suitable material for IR solar absorbers [[27], [28], [29]].
Herein, we introduce a new dimension to the facile synthesis of predominantly orthorhombic Ag_8SnS_6 nanoparticles with high light absorption coefficients and quantum yields. Different mole ratios of single-source precursors bearing the component atoms in the metal-ligand bond of the corresponding complexes of mono and dithiocarbamate were thermalized in coordinating solvents. These complexes were used as a mixed solid solution and thermalized in high molecular weight coordinating solvents such as oleylamine and dodecanethiol to produce phase pure orthorhombic Ag-Sn-S nanocrystals.

Section snippets

Materials and methods

All chemicals, *i.e.* methanol, ethanol, acetone, ethyl acetoacetate, salicylaldehyde, thiosemicarbazide, N, N′-dicyclohexyldithiooxamide, tin(II) chloride, silver nitrate, oleylamine (OLA), dodecanethiol (DT), were purchased from Sigma Aldrich.

Synthesis of $[Ag(H_3L^1)NO_3(OH_2)_2]$, $[Sn(H_3L^1)Cl_2OH_2]$, $[Ag(H_3L^1)(H_2L^1)NO_3]$, and $[Sn(H_3L^1)(H_2L^1)Cl]$ precursors

The precursor $[Ag(H_3L^1)(H_2L^1)NO_3]$ was prepared by using the ligand, (E)-2-(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide (H_3L^1) previously reported in our earlier work [6], and N, N′-dicyclohexyldithiooxamide (H_2L^1). An amount of 1.00 g

Characterization

Carlo Erba EA 1108 CHN elemental analyzer was calibrated with standard reference materials and used for the micro elemental analysis of the complexes. FTIR analysis was performed on Bruker FTIR tensor 27 spectrophotometer in the range of 200–4000 cm^{-1}. The thermal stability of the precursor was determined from 30 to 600 °C at 10 °C min^{-1} using a PerkinElmer Pyris 6 TGA under a constant flow of N_2 gas. The JEOL 1400 TEM and JEOL 2100 HRTEM models gave the Transmission electron microscopy (TEM)

Results and discussion

The synthesis of (E)-2-(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide (H_3L^1), a tridentate ligand, which was used as one of the starting materials for the precursors, was reported previously [6]. A second chelating ligand, N, N′-dicyclohexyldithiooxamide with H_2L^1 denticity, was incorporated to enrich the anticipated sulfur-containing ternary nanoparticles. These Schiff base scaffolds were coupled with Ag^+ and Sn^{2+} sources to give the desired complexes. Visual screening of the

Conclusions

The outcome of this study showed that ternary nanocrystals, especially chalcogenides such as $Ag_8(SnS_4)S_2$, can be efficiently synthesized by the solvothermal method with the mixed solid solution of single precursors under varying reaction conditions. The *p*-XRD patterns and their Rietveld refinements confirmed the existence of a pure phase high indexed orthorhombic system supported by nanocubes with well-refined symmetry and a narrow size range of 12.00–50.90 nm from the TEM micrographs. The STS

CRediT authorship contribution statement

Joseph Adeyemi Adekoya: Conceptualization, Data curation, Formal analysis, Methodology, Writing - original draft. **Malik Dilshad Khan:** Writing – review & editing. **Sixberth Mlowe:** Investigation, Methodology. **Neerish Revaprasadu:** Project administration, Supervision, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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