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Short communication

Mild solvothermal synthesis of $Cu_2ZnSn(S_xSe_{1-x})_4$ nanocrystals with tunable phase structure and composition

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HIGHLIGHTS

- $Cu_2ZnSn(S_xSe_{1-x})_4$ alloy nanocrystals are synthesized by solvothermal method.
- The CZTSSe nanocrystals have tunable composition and band gaps.
- The phase structure of nanocrystals could be changed by varying the S/Se ratio.

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ABSTRACT

$Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) nanocrystals (NCs) are synthesized via a one-pot solvothermal method under the mild reaction condition. By varying the S/Se ratio in the solution, the chalcogen composition of CZTSSe NCs can be well controlled over the whole range, leading to a tunable bandgap from 1.11 to 1.49 eV. Furthermore, it reveals that the S/Se ratio of anionic precursors has a dramatic effect on the phase structure of CZTSSe NCs. When the S/(S + Se) ratio (x) is higher than 0.5, wurtzite (WZ)-derived structure is the dominant phase; on the contrary, the zinc blende (ZB)-derived structure overwhelms the former as x gradually reduces from 0.5 to 0. Our findings thus suggest a novel and facile method to obtain CZTSSe NCs with metastable WZ phase, which is distinguished from previously reported routes based on carefully choosing organic solvents and/or capping ligands. In addition, the obtained CZTSSe NCs are readily dispersed in low boiling point and low toxicity solvent to form homogeneous and stable NCs ink. The photocurrent response measurement on the CZTSSe NCs films demonstrates its potential as a low-cost, high-reproducibility and high-yield NC preparing approach towards efficient CZTSSe solar cells.

1. Introduction

$Cu_2ZnSn(S_xSe_{1-x})_4$(CZTSSe), emerged as a promising absorber material in photovoltaic devices, has recently received considerable research attention due to its ideal bandgap, earth abundance and low toxicity of elemental components [1]. Although the main processing technology is inherited from that of Cu(In,Ga) $(S,Se)_2$ counterpart, the highest conversion efficiency for CZTSSe solar cell is based on the solution method so far [2]. Such non-vacuum approaches are attractive in offering large-scale production without involving complex equipment, controlling the film composition over large area, and low wastage of raw materials [3]. Several solution deposition processes have been shown effective to achieve the conversion efficiency over 8%, including electrodeposition [4], direct solution coating [5] and nanocrystal (NC) ink spray [6] etc. Among them, NC ink spray is of particular interest due to its perfect compatibility with the roll-to-roll manufacturing technique [3]. Hot injection approach is generally adopted for the synthesis of monodisperse colloidal CZTS NCs [7,8]. Conversion efficiency up to 9% has been recently reported based on this method, where the selenization treatment was proved critical to both enter the preferred bandgap domain and promote the grain growth in the CZTSSe film [9]. However, post selenization at high temperature allows limited control over Se content in the absorber. Direct

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synthesis of multicomponent CZTSSe NCs with controllable and accurate Se composition is thus the promising step to obtain efficient CZTSSe absorber for NC ink-based methods. Limited studies have illustrated that CZTSSe NCs could be prepared via hot injection [10–12]. But most of them involve the relatively high reaction temperature, the environmental-unfriendly solvent and long-chain capping ligands, which hinder the scaling up of the process. On the other hand, several mild solvothermal approaches have been successfully developed for synthesizing high-quality CZTS and CZTSe NCs [13,14]. However, attempts towards the facile preparation of composition-tunable CZTSSe NCs have seldom been implemented. Challenge lies in the control of stoichiometry of NCs simultaneously involving five elements in the reaction. Furthermore, wurtzite (WZ)-derived CZTS and CZTSe have been predicted to exist theoretically [15,16] and also demonstrated experimentally as forms of NCs and nanorods [17,18]. Proper control on the kinetic processing through carefully choosing organic solvents and capping ligands during reaction has been illustrated crucial to obtain such a metastable structure. More importantly, a recent study revealed that large CZTS grains, which are particularly preferred for solar cell absorbers, can be obtained by sintering metastable WZ-derived CZTS NCs at low temperature [19]. The free energy released during the phase transition from the metastable WZ to ZB kesterite phase was believed to promote the grain growth.

Herein, we developed a facile solvothermal approach for synthesizing well-dispersed CZTSSe NCs and realized the adjustment of S/Se ratio over the full range. More interestingly, our work clearly shows that the crystallographic structure of NC products can be transformed between zinc blende (ZB)-derived and WZ-derived phases with solvents and capping ligands unchanged. To the best of knowledge, this is the first report that CZTSSe NCs can be converted from ZB-derived structure to metastable WZ-derived phase by solely varying the S/Se ratio. We also noted that similar phase transformation caused by Se/S ratio have not been disclosed on binary and ternary chalcogenides such as $Cu_2(Se,S)$ [20] and $Cu_2Ge(S,Se)_3$ [21] etc.

2. Experiment

2.1. Materials

Copper(II) acetate ($Cu(CH_3COO)_2•H_2O$), zinc(II) acetate ($Zn(CH_3COO)_2•2H_2O$), and tin(II) chloride ($SnCl_2$) were purchased from Bohr Shanghai Chemical Reagent Co. Ltd. Polyvinylpyrrolidone (PVP), monoethanolamine (C_2H_7NO, MEA) and thioacetamide (C_2H_5NS, TAA) were obtained from Sinopharm Chemical Reagent Co. Ltd. Se powders were purchased from Shanghai Meixing Chemical Co. Ltd. All chemicals are analytical grade and were used without further purification.

2.2. Synthesis of CZTSSe NCs

CZTSSe NCs were prepared via a solvothermal route. For a typical synthesis, 0.36 mmol $Cu(CH_3COO)_2•H_2O$, 0.25 mmol $Zn(CH_3COO)_2•2H_2O$, and 0.205 mmol $SnCl_2$ were added into 15 mL MEA together with 1g PVP. All metal salts were completely dissolved under magnetic stirring and labeled as solution A. The metal salt composition in solution A was designed as $Cu/(Zn + Sn) = 0.8$ and $Zn/Sn = 1.2$, which slightly deviates from stoichiometry and is close to the reported component region with high solar cell efficiencies [22]. TAA and Se powders were also dissolved in 15 mL MEA to form solution B. The relative amount of TAA and Se was found to influence the solubility of Se powder in MEA. When the molar ratio of TAA and Se exceeds ~1, Se powder can completely dissolve in MEA. Solution B appears to be a clear solution, otherwise a suspension forms. Then solutions A and B were mixed and loaded into a Teflon-lined stainless steel autoclave of 100 mL capacity. The sealed autoclave was maintained at 180 °C for 48 h to complete the reaction, and allowed to cool to room temperature. The products were centrifuged and washed with acetone several times. The final precipitates were redispersed in ethanol for further usage. To vary S content in the final CZTSSe NCs, only the TAA and Se molar ratio in solution B was changed while maintaining the total molar amount of Se and S constant at 1 mmol.

2.3. Preparation of the CZTSSe thin films

The as-prepared CZTSSe NCs were dissolved in ethanol to get the NCs ink, which was spin-coated onto the ITO-coated glass with a spinning speed of 2000 rpm for 20 s. To form CZTSSe NC films with proper thickness, six deposition cycles were applied. Soft-baking on a hot plate at 300 °C for 2 min is required to improve the film quality between each deposition circle.

2.4. Characterization

X-ray diffraction (XRD) was performed to investigate the crystal structure of the sample on a Philips X′ pert MPD instrument with the Cu Kα radiation. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) measurements were acquired by a JEOLJEM-1210 instrument. UV–Vis spectrum was recorded on a Shimadzu UV-2600 spectrophotometer. Energy dispersive X-ray spectroscopy (EDX) data was collected by JSM-6701F field-emission scanning electron microscope (FE-SEM). An IE 300 X energy dispersive X-ray spectroscopy detector was used to analyze the element composition. Raman spectrum was obtained by using Renishaw inVia Raman microscope with the 514.5 nm line of an Ar ion laser as an excitation source.

The photoelectrochemical property of the CZTSSe electrode was characterized in a three-electrode cell with electrochemical station (CHI–633C, Shanghai Chenhua, China). Pt foil was used as the counter electrode, and Ag/AgCl (sat.KCl) the reference electrode. The electrolyte was an aqueous solution of 0.1 M KCl/0.1 M $Eu(NO_3)_3$. A 300W Xe lamp with an AM 1.5G filter (Beijing Perfect light Technology Co. Lt, PLS-SXE300UV) was used as the light source to generate the photocurrent. Current-voltage (I–V) plot was recorded by cathodically scanning the potential at a rate of 10 mV/s from 0 V to −0.6 V. Stability testing was done under an applied potential of −0.5 V vs Ag/AgCl.

3. Results and discussion

For the multicomponent semiconductor NCs, the accurate control of their stoichiometric composition is challenging. The formation of the homogeneous CZTSSe NCs depends on balancing the reactivity of the cationic precursors [23]. The existence of TAA enhances the solubility of elemental selenium in MEA. Meanwhile, the adequate temperature and pressure environment in solvothermal methods facilitate the further dissolution of Se powders. Those two factors guarantee Se and S sources to distribute uniformly in the reaction solution. MEA is also expected to act as the chelating and surface-passivating agent for the metal cation to suppress the byproducts, which in turn favors the homogeneous growth of CZTSSe nucleus. As a result, the Cu/Zn/Sn/S/Se atomic ratios of CZTSSe NCs are in close agreement with the ratios of the precursors (see Table 1). This indicates that the reactivity of the precursors could be well balanced through the proper solvent selection, and the CZTSSe NCs with tunable composition were formed successfully.

The XRD patterns of as-synthesized CZTSSe NCs are presented in