Materials Letters 150 (2015) 12–15

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

A facile and low-cost synthesis of $Cu_2ZnSn(S_xSe_{1-x})_4$ nanocrystals with tunable composition and optical band gap

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ARTICLE INFO

Article history:
Received 4 February 2015
Accepted 4 March 2015
Available online 11 March 2015

Keywords:
$Cu_2ZnSn(S_xSe_{1-x})_4$
Nanocrystals
Tunable band gap

ABSTRACT

$Cu_2ZnSn(S_xSe_{1-x})_4$ nanocrystals have been successfully synthesized by a novel two-step route involving a solvothermal reaction of $Cu_2ZnSnSe_4$ and a sulfurization post-annealing. The Se^{2-} is gradually replaced by the S^{2-} to form the CZTSSe solid solutions with a tetragonal structure when increasing the sulfurization time. The A_1 Raman modes of CZTSSe display a typical two-mode behavior, revealing that S composition plays an important role on tuning the vibrating modes. The optical band gap becomes large gradually from 0.91 to 1.30 eV with increasing S content from 0 to 0.76. CZTSSe nanocrystals derived from this method can be used as low-cost absorber layer for photovoltaic applications.

1. Introduction

Due to the high absorption coefficients ($>10^4\,cm^{-1}$) and a proper direct band gap, Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) have been considered as an ideal candidate of absorber materials [1–3]. More importantly, the band gap of $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) can be tuned from about 0.96 eV of CZTSe to 1.5 eV of CZTS by changing the molar ratio of S/Se [4]. Shin et al. and Qu et al. [5,6] have explored a solution-based approach in order to solve some drawbacks, such as vacuum requirement, high cost and temperature dependence. Guo et al. [7] has fabricated CZTSSe solar cells by selenization of CZTS nanocrystallines with the efficiency up to 7.2%. These exciting results show great prospects of CZTSSe low-cost solar cells with enhanced power conversion efficiency. Nanocrystals 'ink' can be 'printed' on nearly any type of surface to fabricate large-scale and low-cost solar cells. Moreover, semiconductor nanocrystals, also known as quantum dots (QDs), promise new opportunities for solar cell devices due to their tunable band gap and multiple exciton generation capability. Herein, we present a novel synthetic strategy to prepare CZTSSe nanocrystals. The effect of sulfurization time on the structural, compositional, and optical band gap of CZTSSe has been investigated by means of a series of analytical methods.

2. Experimental

In a typical synthesis procedure, copper (I) chloride, zinc (II) chloride, and tin (IV) chloride pentahydrate were dissolved in a solvent of ethylenediamine (EN). The selenium EN solution was also obtained by dissolving the elemental selenium in EN. Then the selenium EN solution was added into the metal chloride EN solution. The final concentration of the precursor solution was fixed to 0.02 M. The mixture was then transferred to a 50 ml Teflon-lined stainless autoclave, sealed and maintained at 200 °C for 24 h. After the solvothermal process, the autoclave was cooled to room temperature naturally. The precipitate was centrifuged, washed with deionized water and ethanol repeatedly, and baked at 60 °C overnight. Finally the powders were subjected to post-annealing at 500 °C for different times of 0, 30, 60, and 90 min under a flow of 5% H_2S and 95% N_2. We also synthesized pure Cu_2ZnSnS_4 nanocrystals by a similar solvothermal method as control samples. The details have been described elsewhere [8,9].

X-ray diffraction (XRD) and Raman scattering were explored to characterize the structures of samples. X-ray diffraction (D/max 2000, Rigaku) was operated at 40 kV and 40 mA using Cu Kα radiation ($\lambda=1.5418$ Å). Data was collected with 3°/min and 0.02°/step. Raman spectrum (Horiba Jobin Yvon HR800) was excited by a 633 nm laser with the spectral resolution of 0.4 nm. A microscope was used to focus the incident laser beam to a spot of around 8 μm in diameter. Raman spectra were collected with a 100× lens system in back scattering geometry with a charge-coupled device detector. The composition of samples was determined by energy dispersive spectroscopy (EDS) attached to a field-emission

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http://dx.doi.org/10.1016/j.matlet.2015.03.012
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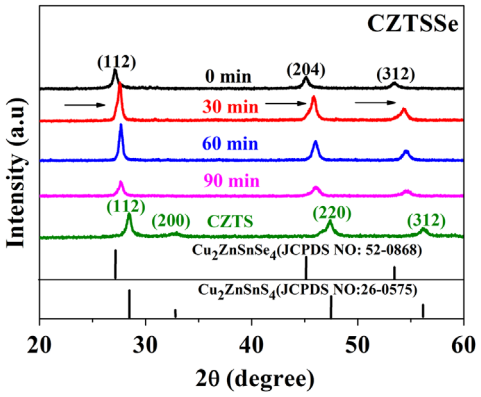

Fig. 1. XRD patterns of CZTSSe nanocrystals with different sulfurization times and CZTS's.

scanning electron microscopy (FESEM, Zeiss) system. The chemical valence state of CZTSSe was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo fisher K-alpha), with a monochromatic Al Kα source ($h\upsilon = 1486.6$ eV) and all of the spectra were calibrated by assigning the adventitious carbon peak to 284.6 eV. The optical properties of samples were measured by ultraviolet–visible–near infared spectrophotometer (UV-3600, Shimadzu).

3. Results and discussions

Fig. 1 shows the XRD θ–2θ patterns of the as-synthesized CZTSe and the post-annealed powder samples with different sulfurization times. The as-synthesized CZTSe powder shows pure stannite structure with three diffraction peaks at 27.14°, 45.14° and 53.41°, corresponding to (112), (204) and (312) planes (JCPDS 052-0868).

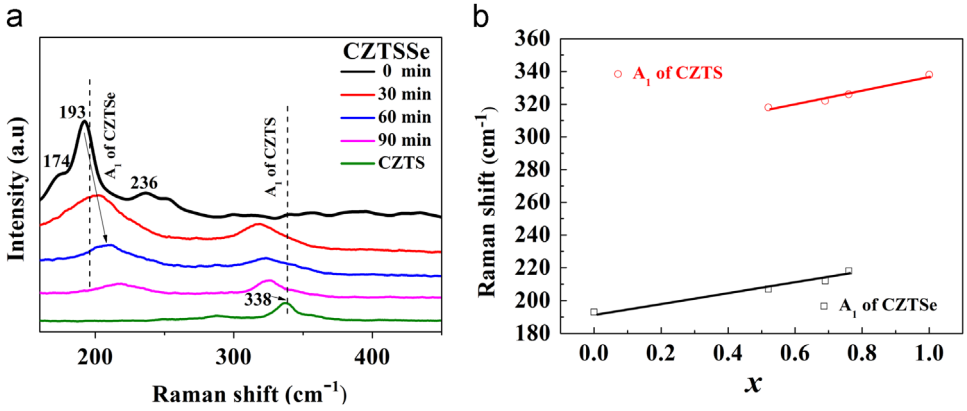

Fig. 2. (a) Raman spectra of CZTSSe nanocrystals with different sulfurization times. (b) Frequency dependence of CZTS and CZTSe A_1 Raman mode on x values.

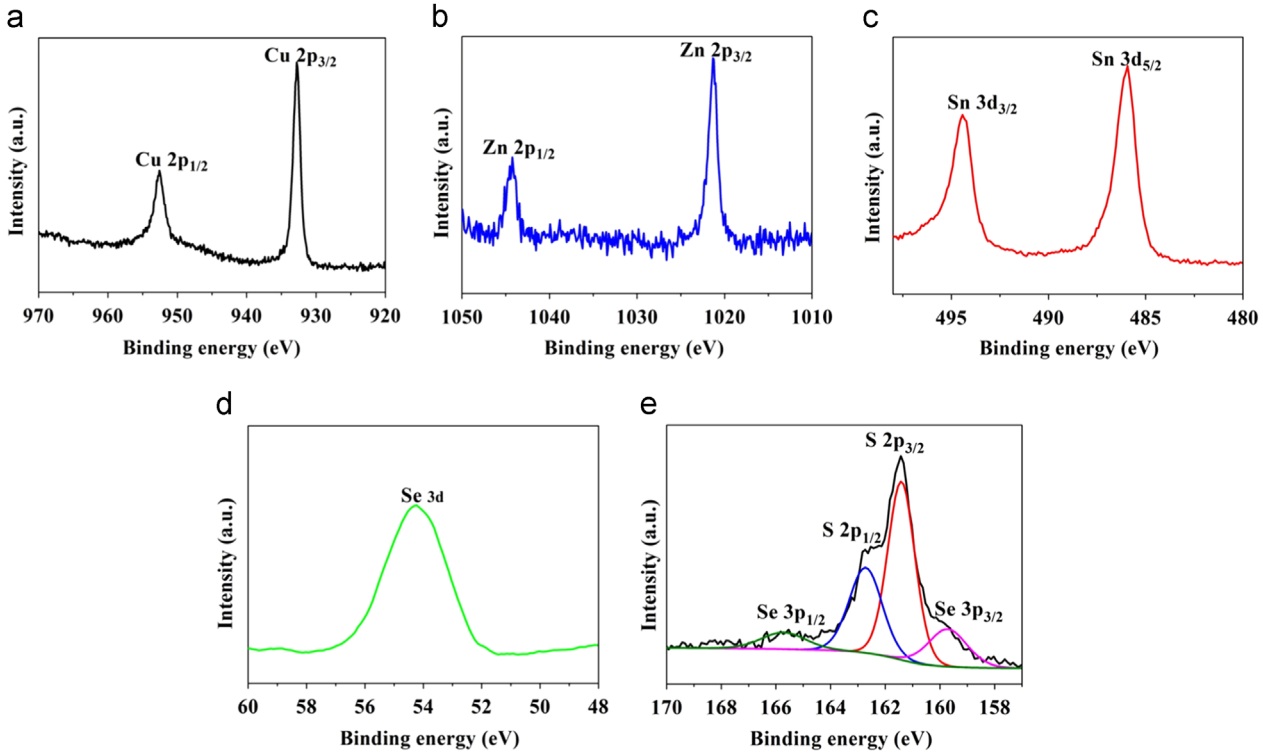

Fig. 3. XPS spectra of (a) Cu 2p, (b) Zn 2p, (c) Sn 3d, (d) Se 3d, (e) S 2p and Se 3p of CZTSSe nanocrystals sulfurized for 60 min.