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ARTICLE TYPE

Facile hot-injection synthesis of stoichiometric $\text{Cu}_2\text{ZnSnSe}_4$ nanocrystals using bis(triethylsilyl) selenide†

Chunyu Jin, Parthiban Ramasamy and Jinkwon Kim*

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$\text{Cu}_2\text{ZnSnSe}_4$ is a prospective material as absorber in thin film solar cells due to its many advantages including direct band gap, high absorption coefficient, low toxicity, and relative abundance (indium-free) of its elements. In this report, CZTSe nanoparticles have been synthesized by hot-injection method using bis-(triethylsilyl) selenide $[(\text{Et}_3\text{Si})_2\text{Se}]$ as selenium source for the first time. The energy dispersive X-ray spectroscopy (EDS) confirmed the stoichiometry of CZTSe nanoparticles. X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies showed that the nanocrystals were single phase polycrystalline and size within the range of 25-30 nm. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy measurement ruled out the existence of any secondary phases such as Cu_2SnSe_3 and ZnSe . The effect of reaction time and precursor injection order on the formation of stoichiometric CZTSe nanoparticles has been studied using Raman spectroscopy. UV-vis-NIR data indicates that the CZTSe nanocrystals have an optical band gap of 1.59 eV, which is optimal for photovoltaic applications.

1. Introduction

Photovoltaic (PV) devices based on thin films of light absorbing materials such as amorphous silicon, CdTe, and $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) technologies have been successfully developed over recent years and are being commercialized.^{1,2} Among these, CIGS-based devices, which have now demonstrated ~ 20% at the laboratory level, are the most efficient of all thin film solar cells.³ However, increasing prices of the rare metals such as Indium and Gallium have highly affected the cost/efficiency ratio of PV devices based on CIGS. As an alternative material for CIGS, the application of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) in thin film solar cells has been explored over the years.^{4,5}

$\text{Cu}_2\text{ZnSnSe}_4$ is a prospective material as absorber in thin film solar cells due to its many advantages including direct band gap, high absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$), low toxicity, and relative abundance (indium-free) of its elements.^{6,7} In addition, CZTSe films have promising thermoelectric properties (ZT value of 0.91 at 860 K), making these materials suitable for high temperature applications.⁸ Several vacuum based expensive and low-throughput techniques such as co-evaporation, sputtering, and pulsed laser deposition have been reported for the fabrication of CZTSe thin films.^{4,9,10} On the other hand, solution-based methods offer low-cost and high throughput techniques which are being explored as alternatives to the expensive vacuum-based processing techniques.^{5,11} A new solution method for the fabrication of CZTSe thin films is based on the synthesis of nanocrystals and disperses them in an “ink”.

It is well known that the optical and electrical properties of nanoparticles are highly dependent on the structure and

composition of nanoparticles, which in turn can be readily controlled by source materials, capping ligands, as well as reaction temperature.¹²⁻¹⁴ Wet chemical methods such as hot-injection and solvothermal methods have been reported for the synthesis of colloidal CZTSe nanoparticles.^{15,16} The choice of selenium precursor is very important in the synthesis of metal selenide nanoparticles. By controlling the precursor reactivity we can control the composition and size of the metal selenide nanoparticles.¹⁷ Selenium precursors, such as TOP-Se and selenium powder has been widely used in the synthesis of CZTSe nanoparticles. For example, Shavel et al. synthesized CZTSe nanoparticles using TOP-Se as selenium source.⁷ Wei et al. used selenium powder as selenium source to obtain CZTSe nanoparticles.¹⁸ However, both the precursors have some drawbacks such as TOP-Se resulted in non-stoichiometric CZTSe nanoparticles.⁷ On the other hand, selenium powder has poor solubility in organic solvents and makes it less reactive.^{19,20} Consequently, the synthesis of high quality and stoichiometric CZTSe nanoparticles remains a big challenge.

Herein, we report the synthesis of stoichiometric CZTSe nanoparticles using highly reactive bis-(triethylsilyl) selenide $[(\text{Et}_3\text{Si})_2\text{Se}]$ as selenium source. The structure, composition, morphology and optical properties of the as-prepared CZTSe nanoparticles have been investigated by using XRD, EDS, XPS, TEM, Raman and UV-NIR spectroscopy. Our synthetic method offers many advantages over the reported synthetic methods such as monodispersity, pure crystal phase and stoichiometry of CZTSe nanoparticles. For example, when SeO_2 and selenium

powder were used as Se^{2-} source, only non-stoichiometric (rich in Sn and poor in Zn) CZTSe nanocrystals were produced.^{8,21} On the other hand, diphenyldiselenide precursor resulted in non-stoichiometric mixed phase CZTSe (kesterite and wurtzite) nanoparticles. In addition the size of the nanocrystals varied from 15 nm to 80 nm.²² The products obtained by our method were nearly uniform in size (25 - 30 nm), single tetragonal phase and more importantly stoichiometric. Precursor injection order and reaction time plays an important role in the formation of stoichiometric CZTSe nanoparticles.

2. Experimental

2.1. Materials

Copper(II) chloride (CuCl_2 , 97%), Zinc acetate (Zn(OAc)_2 , 99.99% trace metals basis), Tin(IV) chloride (SnCl_4 , 1.0M solution in heptanes), Selenium powder (Se), Sodium (Na, 99.9%), Chlorotriethylsilane ($(\text{C}_2\text{H}_5)_3\text{SiCl}$, 99%), Oleic acid (OA, 90%), 1-Octadecene (ODE, 90%) were purchased from Sigma-Aldrich. All chemicals were used as delivered without further purification. All the reactions were carried out using standard Schlenk line techniques under an atmosphere of pure nitrogen. $(\text{Et}_3\text{Si})_2\text{Se}$ was prepared by reacting Na_2Se with Et_3SiCl following literature methods.²³

2.2 Synthesis of CZTSe nanoparticles

In a typical synthesis, 12 mL of 1-Octadecene (ODE) and 8 mL of oleic acid (OA) were taken in a 100 mL flask and heated to 150 °C under vacuum for 1 h. Subsequently, the flask was cooled down to room temperature and 0.5 mmol copper(II) chloride (CuCl_2) and 0.25 mmol zinc acetate (Zn(OAc)_2) were added. Then the temperature was raised to 280 °C, followed by the addition of 1 mmol $(\text{Et}_3\text{Si})_2\text{Se}$. After 5 min, 0.25 mmol SnCl_4 solution was added and the reaction mixture was kept at 280 °C for 2 h under stirring. The flask was then cooled to room temperature and the nanoparticles were precipitated by adding ethanol (20 mL) and centrifuged. The nanoparticles were dispersed in 10 mL toluene and precipitated out by adding ethanol. The process was repeated one more time to purify the NPs.

2.3 Characterization

The products were characterized by X-ray diffraction (XRD, Rigaku Miniflex II), transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDS, Teina G2F30), X-ray photoelectron spectroscopy (XPS, Multilab ESCA 2000). Raman spectrum was recorded on a Horiba Jobin Yvon spectrometer using He-Ar laser ($\lambda_{\text{ex}}=521$ nm) laser as excitation source. Optical absorption spectrum was recorded on a UV-3600 SHIMADZU UV-vis-NIR spectrophotometer.

3. Results and Discussions

The crystalline structure of the as synthesized product was characterized by powder XRD analysis. Fig. 1 shows the XRD patterns of the as synthesized nanoparticles. XRD patterns confirmed it to be compatible with that of tetragonal CZTSe and all the diffraction peaks can be attributed to (112), (204), (312),

(400)/(008), (316), and (424/228) planes, respectively (JCPDS Card, No. 52-0868). No impurity peaks were detected in the XRD pattern indicating the high purity of final synthesized product. The average crystallite size of the nanoparticles can be calculated from XRD data using Scherrer's equation.²⁴

$$d = K\lambda/\beta\cos\theta$$

where d represents the crystallite size, $\lambda = 1.54$ Å is the X-ray wavelength (for Cu $K\alpha$ line), β (in rad) is the peak width at half-maximum, θ is the angle of reflection, and $K = 0.9$ is the shape factor. The calculated sizes of the CZTSe nanoparticles were 24 nm. The chemical stoichiometry of the obtained CZTSe nanocrystals was investigated using EDS analysis (Fig 1b). EDS data obtained from three locations suggests that the composition of CZTSe nanoparticle is close to the stoichiometry $\text{Cu}_2\text{ZnSnSe}_4$ (Table 1). The ratio of the compositional elements is estimated as $\text{Cu/Zn/Sn/Se} \sim 2.2/0.9/1.2/4$.

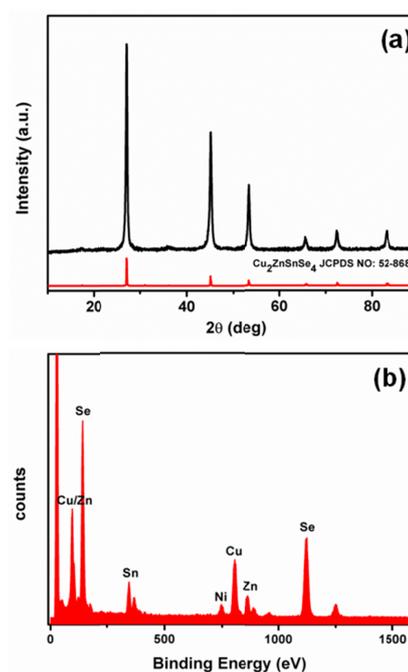


Fig. 1 (a) XRD pattern and (b) EDS spectrum of CZTSe nanoparticles.

Table 1 Three representative EDS data taken from CZTSe nanoparticles.

	Cu (at%)	Zn (at%)	Sn (at%)	Se (at%)
1	29.2	9.1	14.8	46.9
2	24.6	13.4	13.9	48.1
3	25.1	9.7	16.2	49.1
Average	26.3	10.7	14.9	48.0
ratio	2.2	0.9	1.2	4.0

The oxidation state of all four elements in the CZTSe nanoparticles was obtained from XPS analysis. Fig. 2 shows the High-resolution XPS spectrum of Cu 2p, Zn 2p, Sn 3d, and Se 3d. The copper 2p_{3/2} and 2p_{1/2} peaks appeared at 933.1 and 952.8 eV with a peak splitting of 19.7 eV, characteristic of monovalent copper (Fig 2a). The zinc 2p peaks (Fig. 2b) located at 1022.6 and 1045.6 eV have a peak separation of 23.0 eV, consistent with the standard splitting of 22.97 eV, suggesting Zn(II). The Sn 3d_{5/2} and 3d_{3/2} peaks were located at 486.62 and 495.22 eV, respectively (Fig. 2c). The peak separation of 8.6 eV indicates the +4 oxidation state for Sn. The Se 3d_{5/2} peak (Fig. 2d) located at 54.6 eV, indicating Se²⁻.

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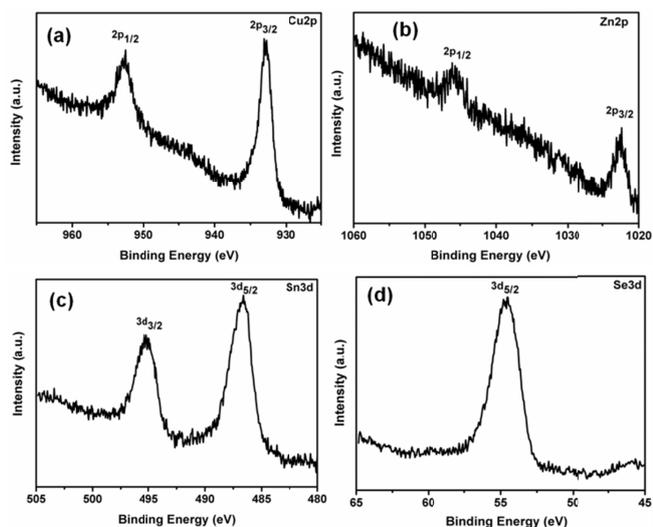


Fig. 2 XPS (a) Cu 2p (b) Zn 2p (c) Sn 3d and (d) Se 3d spectra of CZTSe NPs.

The morphology of the nanoparticles was characterized by TEM. Fig. 3a,b show the TEM images of the obtained CZTSe nanoparticles. The average size of the nanoparticles was found to be 25-30 nm. This is consistent with the average size of the crystallographic domains calculated from XRD spectra using the Scherrer's equation (24 nm). A high-resolution TEM image (Fig. 3c) confirms that the nanocrystals displays well-defined lattices with a spacing of 0.328 nm, which corresponds to the lattice spacing of the (112) plane of the tetragonal CZTSe. The SAED pattern (Fig. 3d) confirms the polycrystalline nature of the nanoparticles, and the most distinct three diffraction rings can be assigned to (112), (204), and (312) planes.

Raman spectroscopy measurements were carried out to further confirm the composition of the nanoparticles. The absence of the characteristic ZnSe peaks at 252 and 205 cm⁻¹ in Raman spectrum; confirms the purity of the final synthesized CZTSe nanoparticles (Fig. 4).²⁶ The three major peaks observed at 173, 191, and 235 cm⁻¹ can be attributed to CZTSe, according to the literature reports.²² The effect of reaction time and precursor injection order on the formation of stoichiometric CZTSe nanoparticles was investigated using Raman spectroscopy.

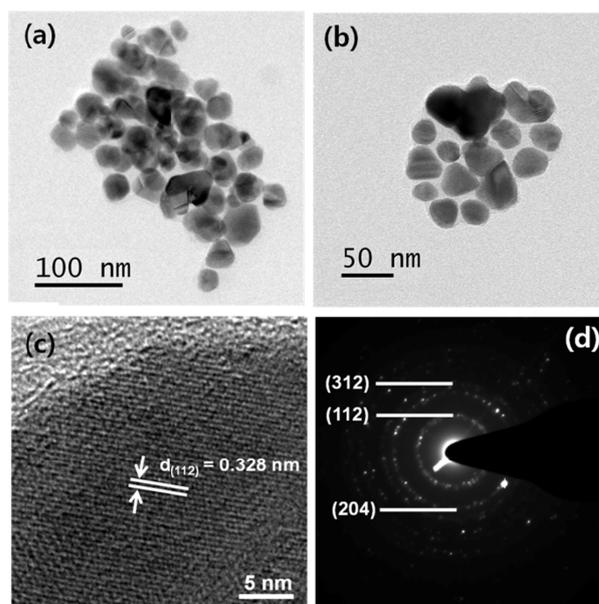


Fig. 3 (a,b) TEM images, (c) HRTEM image and (d) SAED pattern of CZTSe NPs.

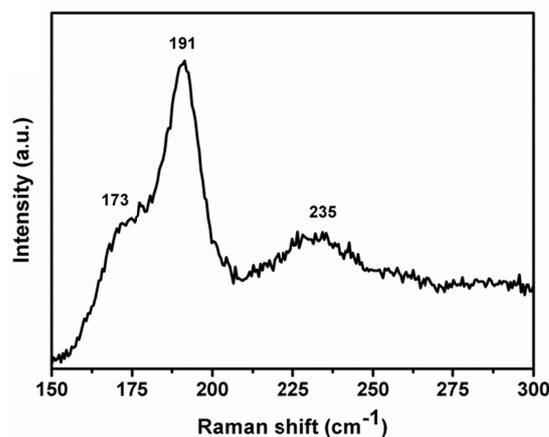


Fig. 4 Raman spectrum of CZTSe nanoparticles.

Fig. 5 shows the Raman spectra of products obtained at different reaction times. After 5 min the Raman spectrum contains two broad peaks around 180 and 270 cm⁻¹ correspond to Cu₂SnSe₃ and Cu₂Se.^{27,28} After 30 min the intensity of peak at 270 cm⁻¹ started to decrease and the peak intensity corresponding to Cu₂SnSe₃ (180 cm⁻¹) increased. This shows that the added Sn⁴⁺ is incorporated to Cu₂Se and became Cu₂SnSe₃. After 2 h the Raman spectrum shows only the characteristic peaks of CZTSe.

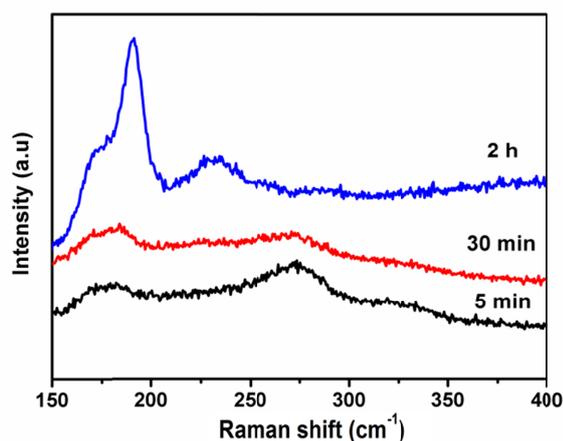


Fig. 5 Raman spectra of the products obtained at different reaction time.

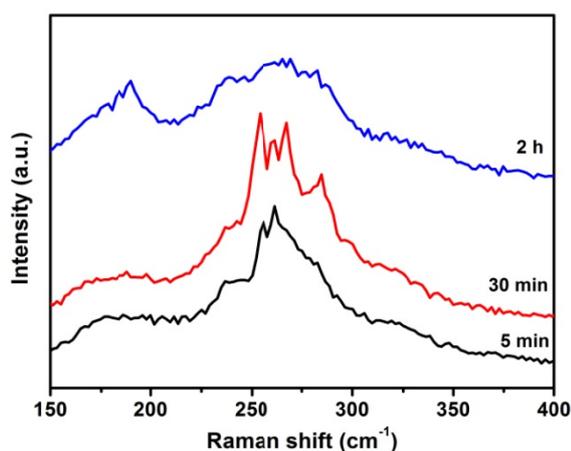
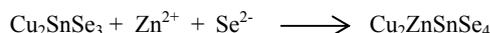
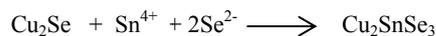


Fig. 6 Raman spectra of the products at different times obtained from the reaction in which Se precursor was added after SnCl₄ addition.

Fig. 6 shows the Raman spectra of the products at different times obtained from the reaction in which Se precursor was added after SnCl₄ addition. After 5 min the spectrum has peaks correspond to Cu₂Se (263-268 cm⁻¹) which became intense after 30 min. There were no peaks correspond to Cu₂SnSe₃ even after 30 min which is different from the results where Se precursor was added before SnCl₄ addition (Fig. 5). After 2 h Cu₂SnSe₃ and CZTSe peaks started to appear at 180, 191 cm⁻¹, respectively. The spectrum also has a broad peak from 260 to 270 cm⁻¹ which indicates that the as formed Cu₂Se has not completely converted into CZTSe and remains in the nanoparticles. When Se precursor was added in the presence of Sn⁴⁺ and other metal cations, the rate of formation of Cu₂SnSe₃ becomes very slow and the reaction is not completed even after 2h. These results clearly indicated that the reaction time and precursor injection order play an important role in the formation of stoichiometric CZTSe nanoparticles. Based on the above results the formation of CZTSe nanoparticles can be given by the following equation. Cu₂Se was first formed after adding Se precursor to the solution containing Cu⁺ and Zn²⁺ cations. Sn⁴⁺

cation is then reacting with Cu₂Se to form Cu₂SnSe₃ which later converted into CZTSe by the incorporation of Zn²⁺ ions.



UV-vis-NIR absorption spectroscopy was used to evaluate the optical properties of the nanoparticles and the results are shown in Fig. 7. The optical band gap of the nanoparticles was calculated by plotting $(\alpha h\nu)^2$, the square of the absorption coefficient (α) multiplied by the photon energy ($h\nu$), versus $h\nu$. The optical band gap was found to be 1.59 eV, consistent with the literature values (0.8-1.6 eV).

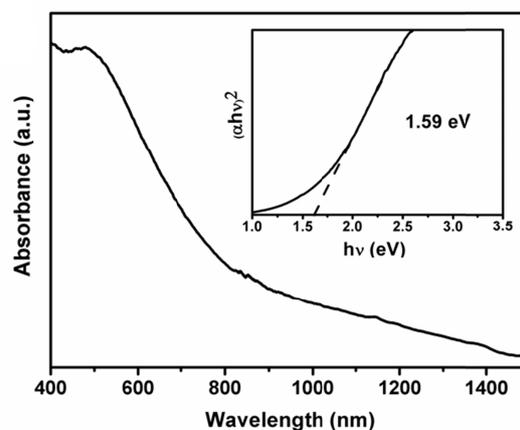


Fig. 7 Uv-vis-NIR absorption spectrum of CZTSe NPs. Inset is the plot of $(\alpha h\nu)^2$ versus $h\nu$ (eV) for the nanocrystals.

4. Conclusions

In summary, we have reported the hot-injection synthesis of CZTSe nanoparticles using bis-(triethylsilyl) selenide as selenium source for the first time. CZTSe nanoparticles were nearly monodisperse and size in the range of 25-30 nm. The stoichiometry of the CZTSe nanoparticles was confirmed by EDS analysis. The as-synthesized nanoparticles were single phase and polycrystalline, as confirmed from XRD and TEM studies. No impurity phases such as ZnSe or Cu₂SnSe₃ were observed in Raman studies. Precursor addition order plays an important role in determining the composition of the final product. It was found that stoichiometric CZTSe nanoparticles can be obtained only when the Sn⁴⁺ precursor was added after the addition of Se²⁻ precursor. The optical band gap of the CZTSe NCs in solution was estimated to be 1.59 eV, which is ideal for solar energy conversion.

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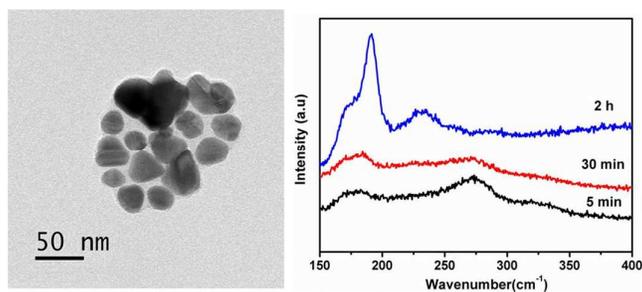
Notes and References

Department of Chemistry and GETRC, Kongju National University, 182,
5 Shinkwondong, Kongju, 314-701, Chungnam-do, Republic of Korea. Phone:
+82-41-850-8496; Fax: +82-41-850-8613; E-mail: jkim@kongju.ac.kr

†Electronic supplementary information (ESI) available: XRD pattern of the
70 samples obtained at different reaction time where Se precursor added
before and after SnCl₄ addition.

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Table of Contents



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