

Syntheses of Cu_2SnSe_3 and Their Transformation into $\text{Cu}_2\text{ZnSnSe}_4$ Nanoparticles with Tunable Band Gap under Multibubble Sonoluminescence Conditions

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Cu_2SnSe_3 (CTSe) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) nanoparticles were synthesized by sonochemical reactions under multibubble sonoluminescence (MBSL) conditions. First, Cu_2SnSe_3 nanoparticles were synthesized by the sonochemical method with an 85% yield, using CuCl , SnCl_2 , and Se. Second, ZnSe was coated on the CTSe nanoparticles by the same method. Then, they were transformed into CZTSe nanoparticles of 5–7 nm diameters by heating them at 500 °C for 1 h. The ratios between Zn and Sn could be controlled from 1 to 3.75 by adjusting the relative concentrations of CTSe and ZnSe. With relatively lower Zn:Sn ratios (0.75–1.26), there are mostly CZTSe nanoparticles but they are believed to include very small amount of CTS and ZnSe particles. The prepared nanoparticles show different band gaps from 1.36 to 1.47 eV depending on the Zn/Sn ratios. In this sonochemical method without using any toxic or high temperature solvents, the specific stoichiometric element Zn/Sn ratios in CZTSe were controllable on demand and their experimental results were always reproducible in separate syntheses. The CZTSe nanoparticles were investigated by using X-ray diffractometer, a UV-Vis spectrophotometer, scanning electron microscope, Raman spectroscopy, and a high resolution-transmission electron microscope.

Key Words : Cu_2SnSe_3 nanoparticles, $\text{Cu}_2\text{ZnSnSe}_4$ nanoparticles, Sonochemistry, Solar cell materials

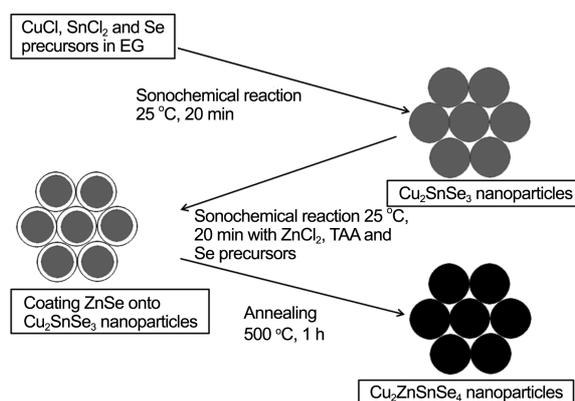
Introduction

Recently, solar cell materials such as CdTe, CuInSe_2 , and CuInGaSe_2 have been extensively developed for the last few decades. These materials seemed to be very fascinating in solving future energy problems. However, the solar materials have drawbacks like heavy costs and environmental pollutions.^{1,2} For these reasons, many researchers tried to adopt new solar cell absorber materials such as SnS, Cu_2S , Cu_2O , Cu_2SnS_3 , $\text{Cu}_2\text{ZnSnS}_4$, and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe).³⁻⁷ Among them, CZTSe is very important semiconductor for high efficiency light absorber material because it contains relatively cheap and earth-abundant elements and has a direct band gap energy of ~1.5 eV with absorption coefficient $\sim 10^4 \text{ cm}^{-1}$.^{8,9}

The ordinary syntheses of metal selenide nanoparticles were usually carried out with Se precursors using alkylphosphines, such as trioctylphosphine (TOP) and tributylphosphine (TBP).¹⁰ However, TOP and TBP are unstable in air and hazardous and these chemicals must be used under argon gas. To synthesize $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) nanoparticles without toxic chemicals, we adopted a sonochemical method through sonoluminescence, which is a light emission phenomenon associated with the collapse of gas bubbles oscillating under an ultrasonic field. The estimated highest temperature and pressure in the liquid layer adjacent to the bubble were reported to be about 1000 °C and 500 bar.¹¹⁻¹³ Especially, this study used multibubble sonoluminescence (MBSL) conditions which are relatively very powerful and efficient

in comparison to other typical sonochemical reactions. Under the MBSL conditions, all the sonochemical reactions were operated at 20 KHz and a power of 220 W. By this method, various homogeneously coated nanoparticles such as CdTe/PbS, CZTS with a core-shell structure were reported in our previous researches.^{6,14} It is noteworthy that not only coating process but the nucleation of nanocrystals also occurred in the ultrasonic field.¹⁵

In this study, CZTSe nanoparticles were prepared through a sonochemical reaction for high efficiency solar cell application. We used ethylene glycol (EG) and ethanolamine to synthesize CZTSe nanoparticle instead of other long chain molecule solution and alkylphosphines.¹⁰ As shown in Scheme 1, Cu_2SnSe_3 nanoparticles were firstly synthesized using CuCl , SnCl_2 , and Se source solution by the sonochemical method under MBSL conditions. Second, ZnSe



Scheme 1

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was coated onto the Cu_2SnSe_3 nanoparticles using ZnCl_2 , Se, and ethanolamine (EA) under the same conditions as above. Finally, they were transformed into CZTSe nanoparticles by heating them at 500 °C for 1 h under Ar conditions. The band gaps of the nanoparticles could be controlled by adjusting the ZnSe coating depth in comparison to the core Cu_2SnSe_3 , leading to a variation of the Zn and Sn ratios.¹⁶

Experimental

Reactants and Apparatus. Copper chloride (CuCl), zinc chloride (ZnCl_2), tin chloride (SnCl_2), selenium (Se), ethanolamine (EA), and ethylene glycol (EG) were purchased from Sigma-Aldrich Corporation and used to synthesize CZTSe. EG was heated at 120 °C in vacuum condition for 24 h and it was stored under inert atmosphere. Other chemicals were used without further purification. Ethanol was used for purification of final product. The MBSL apparatus consists of a cylindrical quartz cell in which a 5 mm diameter titanium horn (Misonix XL2020, USA) was inserted. Circulation of water was adopted to keep the temperature of the solution and the cell around 25 °C. All the conditions of MBSL system such as ultrasound intensity, solvent temperature, and distance between the horn tip and the bottom of the cell were fixed.

Preparation of Cu_2SnSe_3 Nanoparticles. Se (0.8 mmol) was put into EA (1 mL) and this solution was heated to 150 °C for 3 h. When this step was completed, all Se was dissolved and colour of solution was red-brown. SnCl_2 (1.33 mmol) and prepared Se solution were mixed with EG (10 mL) and then placed in quartz cell without any treatment. The condition of solution in cell was kept at 25 °C and 1.4 atm under argon surrounding. This solution was sonicated under the MBSL conditions for 20 min. CuCl (0.66 mmol) was dissolved in EG (2 mL) with heating. Prepared Cu solution was introduced to quartz cell which contained Sn-Se solution. This solution was sonicated for 30 min. Prepared Cu_2SnSe_3 nanoparticles were purified by triple centrifugations at 8000 rpm for 5 min in ethanol. Precipitated particles were collected each time and the final products were dried under vacuum for 12 h (yield: 78%).

Preparation of ZnSe-coated Cu_2SnSe_3 Nanoparticles and $\text{Cu}_2\text{ZnSnSe}_4$ Nanoparticles. The prepared Cu_2SnSe_3 nanoparticles were coated with ZnSe. This process was performed with EG (11 mL), Cu_2SnSe_3 , ZnCl_2 , and Se solution at 25 °C for 30 min under the above sonochemical conditions. Se solution was prepared with same methods as above. In order to synthesize $\text{Cu}_2\text{ZnSnSe}_4$ nanoparticles with different Zn/Sn ratios, 0.2 mmol Cu_2SnSe_3 nanoparticles were reacted with different amounts of ZnCl_2 and Se solution for Zn/Se precursors: 0.2 mmol (CZTSe 1), 0.4 mmol (CZTSe 2), 0.6 mmol (CZTSe 3), 0.7 mmol (CZTSe 4), and 0.75 mmol (CZTSe 5). The resulting ZnSe-coated particles were washed with 3 times centrifugation in ethanol and dried under vacuum for 12 h. Purified particle was heated to 500 °C under Ar condition. After this thermal treatment,

ZnSe-coated Cu_2SnSe_3 particles were transformed into $\text{Cu}_2\text{ZnSnSe}_4$.

Characterization. The resulting Cu_2SnSe_3 , ZnSe-coated Cu_2SnSe_3 , and $\text{Cu}_2\text{ZnSnSe}_4$ nanoparticles were characterized by various instruments: X-ray diffractometer (XRD) data was investigated using New D8-Advance operated under ($\text{Cu K}\alpha = 1.54056 \text{ \AA}$) scanning for 15 min with a step size of 0.02° at scan rate of $0.04^\circ \text{ sec}^{-1}$. High resolution transmission electronic microscopy (HR-TEM) images and atomic ratio were obtained using the JEOL JEM-2100F with an energy dispersive X-ray spectroscopy (Oxford, INCA Energy) operated at accelerating voltage of 200 kV. The samples for HR-TEM analysis were prepared on carbon-coated 200 mesh nickel grids. Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra of which range was from 200 nm^{-1} to 2700 nm^{-1} were collected using UV-VIS-NIR spectrophotometer (Jasco, V-670 spectrophotometer). Raman spectra were recorded by Raman spectrometer (HORIABA, T64000) with 514 nm Ar Laser. The field emission scanning electron microscopy (FE-SEM) images were prepared using SIGMA (Carl Zeiss). The atomic ratios were analyzed by energy dispersive X-ray spectroscopy (EDS, Thermo NORAN System 7).

Results and Discussion

As shown in Figure 1 and 2, Cu_2SnSe_3 nanoparticles were

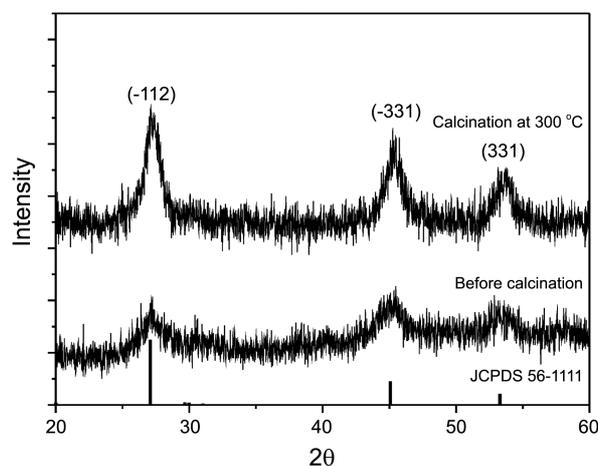


Figure 1. XRD patterns of CTSe nanoparticles before and after annealing.

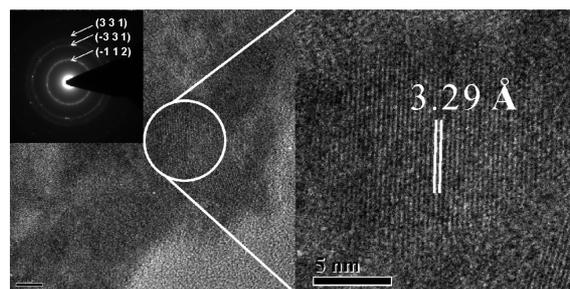


Figure 2. HR-TEM image of annealed CTSe nanoparticles at 300 °C.

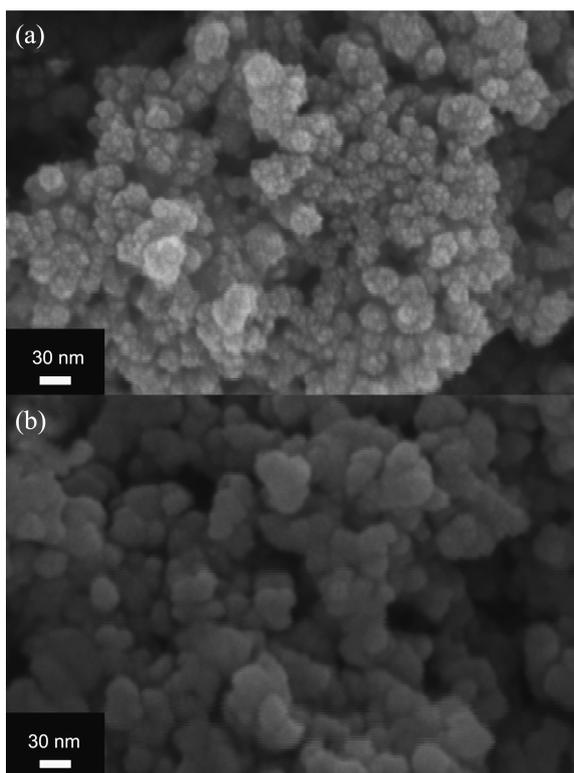


Figure 3. (a) FE-SEM image of CTSe nanoparticles before annealing, (b) FE-SEM images of ZnSe-coated CTSe for CZTSe 4.

synthesized by sonicating under MBSL conditions, which are environment-friendly compared to other reported methods.^{8-10,16} Figure 1 indicates that the CTSe nanoparticles are in monoclinic phase. The most intense peaks correspond to (-112), (-331), and (331) planes, which are well matched with the reported CTSe peaks (PDF 56-1111). To improve the crystallinity of CTSe nanoparticles, the product was heated at 300 °C in vacuum for 1 h. The calculated crystallite size of the nanoparticles by the Scherrer's formula¹⁷ on the base of XRD spectra was about 5-6 nm in diameter. As shown in Figure 2, the average size of prepared CTSe

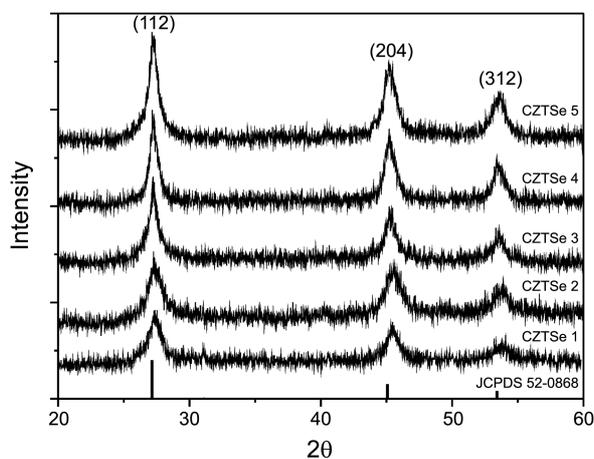


Figure 4. XRD patterns of CZTSe 1-5 obtained after annealing the ZnSe-coated CTS at 500 °C.

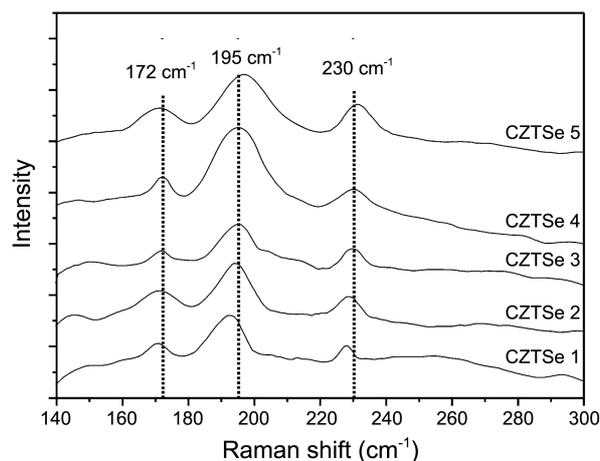


Figure 5. Raman spectra of CZTSe 1-5 nanoparticles.

nanoparticles was about 5-7 nm in diameter with a lattice spacing of 3.29 Å, corresponding to (-112), and the ED pattern of CTSe shows the (-112), (-331), and (331). But it should be noted that the size was not controllable to a substantial extent by adjusting concentrations of reactants and/or sonication power and time. The atomic ratio of CTSe nanoparticles from EDS experiments was Cu : Sn : Se = 2.00 : 1.24 : 3.04. Figure 3 shows FE-SEM images of ZnSe-coated CTSe nanoparticles for CZTSe 4. After treatment with Zn/Se on the CTSe particles, they became relatively larger and the rough surface of CTSe nanoparticles smoother due to corresponding ZnSe coating on the CTSe nanoparticles. Figure 4 shows the XRD patterns of CZTSe nanoparticles, which were synthesized by heating ZnSe-coated CTSe nanoparticles at 500 °C in Ar and displays the characteristic intense peaks at $2\theta = 27.1^\circ$, 45.1° , and 53.4° , corresponding to (112), (204), and (312) planes, revealing that they are in a tetragonal phase (PDF 52-0868). However, it should be mentioned that their XRD patterns do not provide a clear distinction between CZTSe and other materials such as CTSe and ZnSe since they have very close XRD patterns as shown in Figures 1 and 4. To clarify the CZTSe product and their composition, Raman spectroscopy and chemical analysis with nanoscale spatial resolution were performed. Figure 5 shows a Raman spectra of the CZTSe nanoparticles, in which three peaks around 172, 195, and 230 cm^{-1} were observed; this result is consistent with the reported values for the typical characteristic one for kesterite

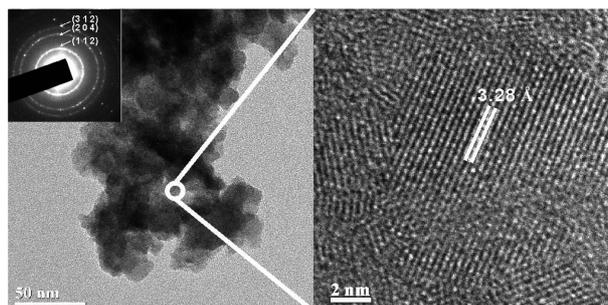


Figure 6. HR-TEM image of CZTSe nanoparticles.

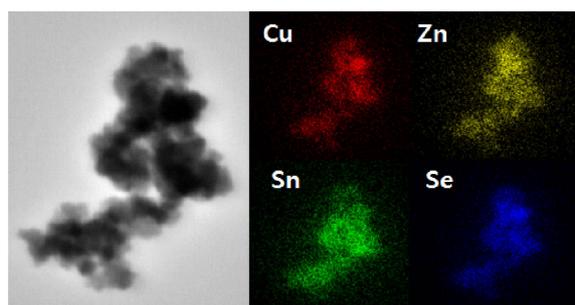


Figure 7. TEM-elemental mapping of CZTSe 4 nanoparticles.

Table 1. Band gap of CZTS nanoparticles depending on the Zn/Sn ratio on the base of EDS analysis results

Sample	Zn/Sn ratio	Cu/(Zn+Sn) ratio	Se/metal ratio	Band gap (eV)
CZTSe 1	0.52	1.45	0.87	1.36
CZTSe 2	0.75	1.07	0.9	1.39
CZTSe 3	0.80	1.02	1.10	1.42
CZTSe 4	0.92	1.12	0.97	1.44
CZTSe 5	1.26	0.70	0.92	1.47

CZTSe.¹⁸⁻²⁰ It is noteworthy that in the spectra for CZTSe 2-5 two other peaks at 180 cm⁻¹ or 250 cm⁻¹ arising from CTSe or ZnSe did not appear, suggesting there are mostly CZTSe nanoparticles in the product.²⁰ But it is believed that those samples include some small amount of CTS or ZnSe particles. In CZTSe 1 case, there seems to be some CTSe in the product. Also, the formation of CZTSe nanocrystals can be confirmed with the HR-TEM image and a corresponding ED pattern as shown in Figure 6. ED pattern shows (112), (204), and (312) planes and the expanded HR-TEM image of CZTSe also indicates a lattice spacing of 3.28 Å, corresponding to (112). As shown in Figure 7 for TEM-EDS elemental mapping, EDS data collected from all the points on the CZTSe surface verify that the Cu, Zn, Sn, and Se elements evenly spread all over the CZTSe particles. Table 1 shows the elemental ratios and band gaps of the CZTSe nanoparticles, which are from the UV-VIS-NIR spectra and the equation, $(\alpha h\nu)^2 = (E_g \times \alpha)^2$.²⁴ Figure S1 and S2 show UV-VIS spectra and band gap of CZTSe nanoparticles. As listed Table 1, the band gaps of CZTSe nanoparticles are in optimal range for the high efficiency photovoltaic solar cell and increase from 1.36 to 1.47 eV as the Zn/Sn ratios increase.^{8-10,18-20}

Conclusion

In summary, CTSe and CZTSe nanoparticles were easily synthesized through sonochemical method under multibubble sonoluminescence (MBSL) conditions, which are relatively

quite mild and facile compared to other typical high temperature solution-based methods. In this environmentally benign process, it was possible to make relatively larger quantity of CTSe and CZTSe nanoparticles in high yield and the Zn/Sn ratio of CZTSe was controllable on demand. Depending on the amount of coated ZnSe, Zn/Sn ratio in CZTSe nanoparticles varied from 0.52 to 1.26 in CZTSe and consequently, the band gap of CZTS nanoparticles changed from 1.36 to 1.47 eV.

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Supporting Information. Additional supporting information contains band gap and UV-VIS data of CZTSe nanoparticles.

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