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Size and shape controlled hydrothermal synthesis of kesterite 

$\text{Cu}_2\text{ZnSnS}_4$ nanocrystals

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Quaternary kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanocrystals (NCs) have been synthesized using a simple, size and shape tunable, and low-cost hydrothermal technique without using toxic chemicals. The size and shape of the kesterite CZTS NCs could be controlled by using different complexing agents including non-complexing agent, hydrazine hydrate, tri-sodium citrate ($\text{Na}_3$-citrate), and tetra-acetate disodium salt ($\text{Na}_2$-EDTA). The hydrothermally synthesized CZTS nanocrystals showed a kesterite structure, high optical absorption, and suitable band gap energy characteristics, indicating potential for application to thin film solar cells.

Quaternary kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a promising candidate absorber material that contains earth abundant elements. CZTS-based semiconductors have attracted considerable interest for use in thin film solar cells (TFSCs)\textsuperscript{1-2}. They have several merits such as direct band gap energy of 1.5 eV, high absorption coefficient $> 10^5 \text{cm}^{-1}$ in the visible wavelength region, less toxic material S instead of Se, high chemical stability, and p-type conductivity\textsuperscript{3-5}. A previous literature survey reported a theoretical power conversion efficiency (PCE) limitation of 32.2 % for CZTS TFSCs by calculating the photon balance\textsuperscript{3}. These reports and the characteristics of CZTS indicate that CZTS-based materials can be easily fabricated and commercialized for low-cost and high PCE TFSCs, if a PCE of over 20 % can be achieved\textsuperscript{1}. The highest PCE of CZTS-based TFSCs of 12.6 % was obtained by annealing the precursor prepared using the hybrid solution-particle approach of the hydrazine-based solution method in the sulfo/selenization atmospheres\textsuperscript{7}. Recently, CZTS nanocrystals (NCs) have been synthesized using various solution-based techniques such as solvothermal\textsuperscript{8}, colloidal\textsuperscript{9}, and hot injection\textsuperscript{10,11}. These methods for yielding high-quality NCs seem very attractive due to the possibility of fabricating low-cost CZTS solar cells with high PCE. They are also easily scalable. Moreover, inks consisting of NCs and various organic solvents are beneficial for ultra-low-cost TFSCs obtained using a roll-to-roll process\textsuperscript{12,13}. Previous literature surveys reported the synthesis and characterizations of kesterite or wurtzite CZTS-based NCs with good size distribution and shape control that were prepared using hot-injection method. A 7.2 % PCE for $\text{Cu}_2\text{ZnSn(S,Se)}_4$ (CZTSSe) obtained by a robust thin film coating technique was obtained using NCs in organic solvent under light soaking conditions. S. C. Riha, A. Shavel and Q. Guo et al. reported the synthesis of CZTS or CZTSSe NCs by a hot injection solution method over 225 °C, using oleylamine or hexadecylamine, which stabilize the NCs in organic solvents\textsuperscript{12-14}. In addition, C. Steinhagen et al. reported the synthesis of CZTS NCs by a solvothermal method at 280 °C using oleylamine and hexadecylamine as stabilizers\textsuperscript{15}. More recently, Y. Cao and coworkers reported the synthesis of CZTSSe-based TFSCs with 8.5 % PCE by selenization of binary (ZnS or SnS) and ternary ($\text{Cu}_2\text{ZnSn}_3$) NCs prepared using the hot injection technique\textsuperscript{16}. Although previous research has indicated that sharply controlled, distributed and high-quality CZTS-based NCs can be synthesized using organic solvent chemicals such as hydrazine, oleylamine, and hexadecylamine to fabricate CZTS-based TFSCs with high PCEs, the synthesis process requires vacuum equipment, high temperature, and toxic organic solvents and chemicals. In particular, hydrazine is a highly toxic and hazardous chemical. These drawbacks have led to serious environmental problems and have limited the possibility of commercialization. Therefore, it is necessary to develop a simple and non-toxic synthesis route for CZTS NCs without using toxic organic solvent chemicals in order to fabricate and commercialize the high-PCE TFSCs. W. Liu et al. have recently reported the synthesis of ultrafine CZTS NCs prepared by a simple hydrothermal process, which...
ethylenediamine (EN) was used as the chelating agent and stabilizer. However, EN is toxic chemical and their indicated the necessity for the development of a synthesis process using the hydrothermal method without using toxic chemicals. In this paper, we report the synthesis and characterization of CZTS NCs with size and shape controlled characteristics synthesized using the hydrothermal technique without the use of hazardous chemicals.

Kesterite CZTS NCs were prepared using a simple and low-cost hydrothermal route without using toxic chemicals. Precursor solutions were obtained from aqueous solutions containing 40 mL of 0.2M Cu acetate, 40 mL of 0.1M Zn acetate, 40 mL of 0.1M Sn chloride and 40 mL of 0.2M thioacetamide in deionized water complexing agents including hydrazine, Na₃citrate, and Na₂EDTA were further added. The pH of the precursor solutions was controlled to 7 by adding a solution containing 28 % ~ 30 % ammonium hydroxide. The precursor solutions were placed in a Teflon-liner stainless steel autoclave and heated at 200 °C for 24 h.

Figure 1 shows the powder X-ray diffraction (PXRD) patterns of synthesized powders prepared with different complexing agents. The PXRD patterns of all the synthesized powders showed several peaks corresponding to the (110), (112), (200), (220) and (312) planes of a single kesterite-type CZTS structure (JCPDS No.: 26-0575). The peak intensities of the (112) planes for the synthesized CZTS NCs prepared with complexing agents were enhanced compared to those prepared without a complexing agent. The synthesized CZTS NCs prepared with hydrazine showed the highest peak intensity value from the (112) plane. It was also observed that the shoulder peaks from the left of the (112) plane could be caused by stacking faults related to cation disordering similar to the faulting in CuInSe₂ and CIGS.

Figure 2 shows the Raman spectra at room temperature of the CZTS NCs prepared with different complexing agents. The CZTS NCs prepared without a complexing agent showed weak peaks located at 250 cm⁻¹, 288 cm⁻¹, and 338 cm⁻¹ resulting from a kesterite CZTS compound. However, a strong peak located at 338 cm⁻¹ was observed corresponding to the kesterite CZTS compound in the synthesized CZTS NCs prepared with complexing agents. The CZTS NCs prepared with Na₂EDTA showed the highest intensity value. Secondary phases such as Cu₂S (475 cm⁻¹), ZnS (275 cm⁻¹ and 352 cm⁻¹), SnS (219 cm⁻¹), Cu₃SnS₄ (CTS, 318 cm⁻¹, 294 cm⁻¹, 303 cm⁻¹, and 356 cm⁻¹) were not observed.

Figure 3 shows bright-field (BF) TEM images of the synthesized CZTS NCs prepared without complexing agent (a), with hydrazine (b), Na₃citrate (c) and Na₂EDTA (d). The BF TEM images of the synthesized CZTS NCs show irregular and faceted shapes. The NC prepared without a complexing agent was poly-dispersed sizes ranging from 10 nm to 70 nm. However, the NCs prepared with hydrazine and Na₃citrate showed smaller size, ranging from 10 nm to 70 nm with narrower distribution than those prepared without a complexing agent. The NCs prepared with Na₂EDTA show the largest size of 160 nm with smaller sizes ranging from 10 nm to 60 nm (Fig. 2S).

Important information was obtained from the aforementioned XRD, Raman, and TEM analysis. The CZTS NCs with hydrazine and Na₃citrate showed an improved crystallinity and uniform size distribution compared to those without a complexing agent. The metal ions easily reacted with OH in the solution bath without the complexing agent as compared to that between metal ions and S²⁻, and the metal-OH compounds with poor size distribution were then formed in solution at room temperature. Finally, the metal-OH compounds were transferred to metal-sulfide compounds at high reaction temperature. This reaction behavior leads to poor size distribution due to the difficulty of reaction speed in the solution. When solutions are heated with complexing agents, the complexing agents react with the metal ions, which produce [metal-complexing agent] ions at relatively low reaction temperature.

Many [metal-complexing agent] ions exist compared to the number of ions without a complexing agent. This reaction leads to an easy formation of metal-sulfide compounds at relatively low temperature. Based on the general CZTS synthesis process, the quaternary CZTS compounds are easily formed at high reaction temperature. However, the size distribution of CZTS NC with Na₂EDTA is poor compared to that with hydrazine and Na₃citrate. It is well known that the Na₂EDTA is a strong complexing agent compared to other complexing agents indicating that it is difficult to react metal ions with S²⁻ ions due to the strong binding energy. This reaction behavior leads to poor size distribution similar to the solution without using the complexing agent.

Figure 4 shows the high-resolution (HR) TEM images of the CZTS NCs prepared with different complexing agents (a) with hydrazine (b), Na₃citrate (c), and Na₂EDTA (d), respectively. HR-TEM images of all the CZTS NCs prepared with different complexing agents exhibit clear lattice fringes with a measured spacing of 0.314 nm, corresponding to the (112) planes of the kesterite CZTS structure.

Figure 5 shows the images obtained from scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), and elemental mapping equipped with a high-angle annular dark field (HAADF) of the CZTS NCs prepared with Na₂EDTA. It can be seen that Cu, Zn, Sn and S are well-distributed in the NCs with an apparent elemental separation or aggregation. Figure S1 shows the STEM images for the synthesized CZTS NCs prepared without a complexing agent with hydrazine and Na₂citrate. These results are similar to those shown in Fig. 5.

Figure 6 shows the optical band gap energy of the CZTS NCs prepared with different complexing agents. The optical band gap energy of the CZTS NCs was measured by linear extrapolation of the plot of (∆hv)² on the x-axis vs the photon energy (hv). The optical band gap energies of CZTS NCs prepared without a complexing agent, with hydrazine, Na₃citrate and Na₂EDTA were 1.67, 1.51, 1.44, and 1.5 eV, respectively, which are in good agreement with reported values. The optical results indicated good adsorption characteristics of the synthesized CZTS NCs.

In conclusion, quaternary CZTS NCs were synthesized by a simple hydrothermal route without hazardous chemicals. The XRD, TEM, Raman, and UV-vis results confirmed the kesterite structured CZTS NCs with irregular and faceted shapes. Studies on optimizing the synthesis process through different synthesis conditions and additives are currently underway.
NCs prepared without complexing agent (a), with hydrazine (b), Na$_3$-citrate (c) and Na$_2$-EDTA (d).

Figure 1. PXRD patterns of the synthesized CZTS NCs prepared with different complexing agents [Cu Kα radiation (λ = 1.54 Å)]

Figure 2. Raman spectra of synthesized CZTS NCs prepared with different complexing agents.

Figure 3. Bright-field TEM images of the synthesized CZTS NCs prepared without complexing agent (a), with hydrazine (b), Na$_3$-citrate (c) and Na$_2$-EDTA (d).

Figure 4. High resolution TEM images of the synthesized CZTS NCs prepared without complexing agent (a), with hydrazine (b), Na$_3$-citrate (c) and Na$_2$-EDTA (d).

Figure 5. HAADF-STEM image and elemental mapping images of synthesized CZTS NCs prepared with Na$_2$-EDTA.

Figure 6. Optical band gap energy of synthesized CZTS NCs prepared with different complexing agents.

ASSOCIATED CONTENT
Supporting Information. Experimental methods and synthesis procedures, characterization, additional STEM images, and the size distribution of the CZTS NCs prepared with different complexing agent are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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