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Cite this: DOI: 10.1039/c0xx00000x

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PAPER

Size and shape controlled hydrothermal synthesis of kesterite

Cu₂ZnSnS₄ nanocrystals

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Quaternary kesterite Cu₂ZnSnS₄ (CZTS) nanocrystals (NCs) have been synthesized using a simple, size and shape tunable, and low-cost hydrothermal technique without using the 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 (Na₃-citrate), and tetra-acetate disodium salt (Na₂EDTA). 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 Cu₂ZnSnS₄ (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)^{1,2}. They have several merits such as direct band gap energy of 1.5 eV, high absorption coefficient > 10⁴ cm⁻¹ in the visible wavelength region, less toxic material S instead of Se, high chemical stability, and p-type conductivity³⁻⁵. A previous literature survey reported a theoretical power conversion efficiency (PCE) limitation of 32.2 % for CZTS TFSCs by calculating the photon balance⁶. 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 achieved¹. 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 atmospheres⁷. Recently, CZTS nanocrystals (NCs) have been synthesized using various solution-based techniques such as solvothermal⁸, colloid⁹, and hot injection^{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 process²⁻⁴. 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 Cu₂ZnSn(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 solvents¹²⁻¹⁴. In addition, C. Steinhagen et al. reported the synthesis of CZTS NCs by a solvothermal method at 280 °C using oleylamine and hexadecylamine as stabilizers¹⁵. More recently, Y. Cao and co-workers reported the synthesis of CZTSSe-based TFSCs with 8.5 % PCE by selenization of binary (ZnS or SnS) and ternary (Cu₂SnS₃) NCs prepared using the hot injection technique¹⁶. 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, Na₃-citrate, 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^{3,4}.

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 compound³. 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 Cu_{2-x}S (475 cm⁻¹), ZnS (275 cm⁻¹ and 352 cm⁻¹), SnS (219 cm⁻¹), and Cu₂SnS₃ (CTS, 318 cm⁻¹, 294 cm⁻¹, 303 cm⁻¹, and 356 cm⁻¹) were not observed⁴.

Figure 3 shows bright-field (BF) TEM images of the synthesized CZTS NCs prepared without complexing agent (a), with hydrazine (b), Na₃-citrate (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 Na₃-citrate showed smaller in 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 Na₃-citrate 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 temperature¹⁸. 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 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 temperature¹⁹. 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 Na₃-citrate. 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 energy¹⁹. 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 without a complexing agent (a), with hydrazine (b), Na₃-citrate (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 d spacing of 0.314 nm, corresponding to the (112) planes of the kesterite CZTS structure⁴.

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 without any apparent elemental separation or aggregation. Figure S1 shows the STEM images for the synthesized CZTS NCs prepared without a complexing agent and with hydrazine and Na₃-citrate. 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 $(\alpha hv)^2$ on the x-axis vs the photon energy (hv). The optical band gap energies of CZTS NCs prepared without a complexing agent, with hydrazine, Na₃-citrate and Na₂EDTA were 1.67, 1.51, 1.44, and 1.5 eV, respectively, which are in good agreement with reported values^{2,3}. The optical results indicated good absorption 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.

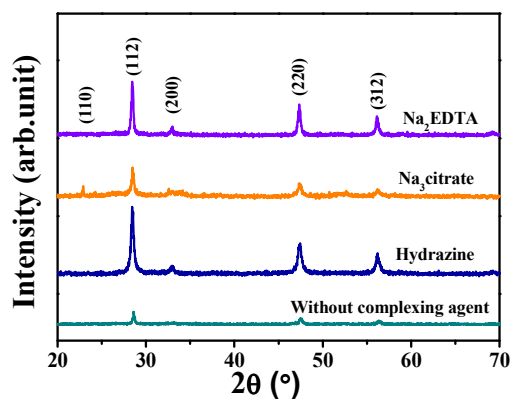


Figure 1. PXRD patterns of the synthesized CZTS NCs prepared with different complexing agents [Cu K α radiation ($\lambda = 1.54 \text{ \AA}$)]

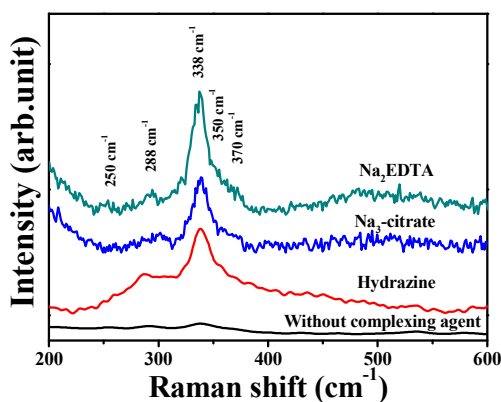


Figure 2. Raman spectra of synthesized CZTS NCs prepared with different complexing agents.

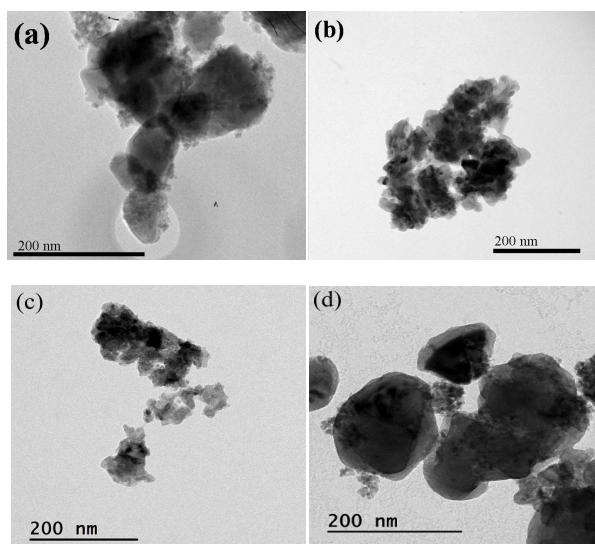


Figure 3. Bright-field TEM images of the synthesized CZTS

NCs prepared without complexing agent (a), with hydrazine (b), Na₃-citrate (c) and Na₂EDTA (d).

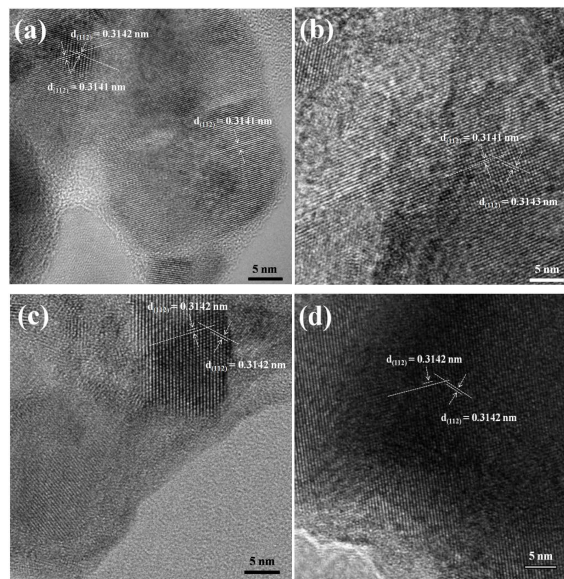


Figure 4. High resolution TEM images of the synthesized CZTS NCs prepared without complexing agent (a), with hydrazine (b), Na₃-citrate (c) and Na₂EDTA (d).

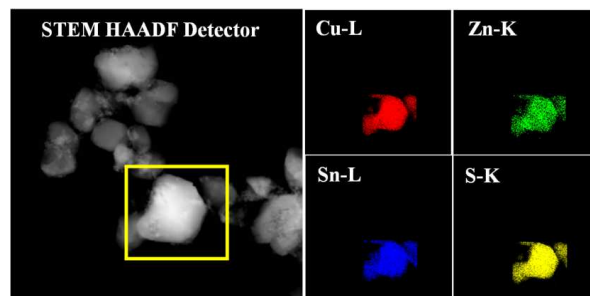


Figure 5. HAADF-STEM image and elemental mapping images of synthesized CZTS NCs prepared with Na₂EDTA.

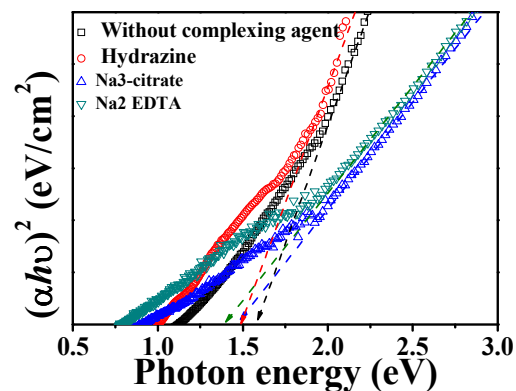


Figure 6. Optical band gap energy of synthesized CZTS NCs prepared with different complexing agents.

ASSOCIATED CONTENT

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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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ACKNOWLEDGMENT :

This work is supported by the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy (No.: 20124010203180) and supported partially by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST No. 2011-0016564)

REFERENCES

1. D. B. Mitzi, O. Gunawan, T. K. Todorov, K. Wang, S. Guha, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 1421-1236.
2. S. W. Shin, J. H. Han, Y. C. Park, G. L. Agawane, C. H. Jeong, J. H. Yun, A. V. Moholkar, J. Y. Lee, J. H. Kim, *J. Mater. Chem.*, 2012, **22**, 21727-21732.
3. S. W. Shin, J. H. Han, C. Y. Park, S.R. Kim, Y. C. Park, G. L. Agawane, A. V. Moholkar, J. H. Yun, C. H. Jung, J. Y. Lee, J. H. Kim, *J. Alloys Compds.*, 2012, **541**, 192-197.
4. S. W. Shin, J. H. Han, C. Y. Park, A. V. Moholkar, J. Y. Lee, J. H. Kim, *J. Alloys Compds.*, 2012, **516**, 96-101.
5. H. Katagiri, K. Jimbo, W. S. Maw, K. Oishi, M. Yamazaki, H. Araki, A. Takeuchi, *Thin Solid Films* 2009, **517**, 2455-2460.
6. W. Shockley, H. J. Queisser, *J. Appl. Phys.* 1961, **32**, 510-519.
7. W. Wang, M.T. Winkler, O. Gunawan, T.K. Todorov, Y. Zhu, D. B. Mitzi, *Adv. Energy Mater.*, 2013, **27**, 2-5.
8. M. Cao, Y. Shen, *J. Cryst. Growth* 2011, **318**, 1117.
9. M.D. Regulacio, C. Ye, S. H. Lim, M. E. Bosman, S. Chen, Q.H. Xu, M.Y. Han, *Chem. A Eur. J.* 2012, **18**, 3127-3131.
10. W.S. Ki, H. W. Hillhouse, *Adv. Energy Mater.* 2011, **1**, 732-735.
11. H. Wei, W. Guo, Y. Sun, Z. Yang, Y. Zhang, *Mater. Lett.* 2010, **64**, 1424-1426.
12. S. C. Riha, B. A. Parkinson, A. L. Prieto, *J. Am. Chem. Soc.* 2009, **131**, 12054-12055.
13. Q. Guo, G. M. Ford, W. C. Yang, B. C. Walker, E. A. Stach, H. W. Hillhouse, R. Agrawal, *J. Am. Chem. Soc.* 2010, **132**, 17384-17386.
14. Q. Guo, M. G. Ford, W.C. Yang, C. J. Hages, H. W. Hillhouse, R. Agrawal, *Sol. Energy Mater. Sol. Cells* 2012, **105**, 132-136.
15. C. Steinhagen, M. Panthani, G. V. Akhavan, B. Goodfellow, B. Koo, B. A. Korgel, *J. Am. Chem. Soc.* 2009, **131**, 12554-12555.
16. Y.Y. Cao, M. S. Denny, J. V. Caspar, W. E. Farneth, Q. Guo, A. S. Ionkin, Johnson, L. K. Lu, M. Malajovich, I. Radu, D.H.

- D. Rosenfeld, K. R. Choudhury, W. Wu, *J. Am. Chem. Soc.* 2012, **134**, 15644-15645.
17. W. Liu, B. Guo, C. Mak, A. Li, X. Wu, F. Zhang, *Thin Solid Films* 535 (2013) 39-43
18. M. Suryawanshi, S.W. Shin, W.R. Bae, K.V. Gurav, M.G. Kang, G.L. Agawane, P.S. Patil, J.H. Yun, J.Y. Lee, A.V. Moholkar, J. H. Kim, *Phys. Sta. Sol.* 211 (2014) 1-4.
19. S.W. Shin, G.L. Agawane, M.G. Gang, A.V. Moholkar, J.H. Moon, J.H. Kim, J.Y. Lee, *J. Alloys Compd.* 526 (2012) 25-30

