Syntheses of Cu₂SnS₃ and Cu₂ZnSnS₄ nanoparticles through simple sonochemical method under multibubble sonoluminescence conditions

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Supplementary Information

1. Results

Figure S1 shows large area image of CZTS nanoparticles. In the TEM-elemental mapping image, each four atoms homogenously spread in the particles.



Figure S1. TEM-elemental mapping of CZTS nanoparticles



Figure S2. The Zn/Sn atomic ratio of CZTS nanoparticles

Figure S2 shows Zn/Sn atomic ratio of CZTS nanoparticles on the base of EDS analysis results that have different ratio between Zn and Sn. Each data result from five different nanoparticles that were synthesized in the same condition.



Figure. S3 (a) Band gap of CZTS1; (b) CZTS2; (c) CZTS3; (d) CZTS4; (e) CZTS5; (f) Cu₂SnS₃ nanoparticles



Figure S4. X-ray photoelectron spectroscopy (XPS) of the CZTS4 nanoparticles.

The XPS spectrum of Cu 2p have two narrow peaks at 932.9 and 952.7 eV, with a peak separation of 19.8 eV, that indicate Cu(I). The XPS spectrum of Zn 2p shows peaks located at 1022.5 and 1045.5 eV with a peak separation of 23 eV are consistent with zinc(II). And then, the XPS spectrum of Sn 3d proves Sn(IV) with two peaks located at 486.3 and 494.7 eV that show a peak separation of 8.4 eV. Finally, sulfur XPS spectrum shows peaks located at 162.3 and 163.5 eV are consistent with S in sulfide phases.



Figure S5. XRD patterns of CZTS 1-5 obtained after annealing the ZnS-coated CTS at 450 $^{\rm o}{\rm C}$

2. Hot injection method.

This experiment was performed to show it is not easy to synthesize high quality CZTS in the large scale synthesis. When we followed a literature that researched by *Korgel et al.*¹, we easily got CZTS nanoparticles. However, after 2 times scale-up, we found impurities such as SnS, and ZnS. We think this type experiment should be studied to control the specific stoichiometric ratios between the four elements for large scale synthesis.



Figure S6. XRD patterns of CZTS nanoparticles synthesized by hot injection

Reference

1. C. Steinhagen, M. G. Panthani, V. Akhavan, B. Goodfellow, B. Koo, B. A. Korgel, J. Am. Chem. Soc., 2009, 131, 12554