

## Facile synthesis of $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals

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### Experimental

**Materials.** Copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ , 99.9%), zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ , 99.9%), tin chloride ( $\text{SnCl}_4$ , 99.9%), technical grade octadecene (90%), n-dodecanethiol (98%) and sodium diethyldithiocarbamate ( $\text{S}_2\text{CNET}_2$ ) (99%) were purchased from Aladdin. Oleylamine (97%) and oleic acid (90%) were purchased from TCI, Shanghai and Sigma-Aldrich, respectively.

**Synthesis of  $\text{Cu}_2\text{ZnSn}(\text{S}_2\text{CNET}_2)_{10}$  precursor.**  $\text{Cu}_2\text{ZnSn}(\text{S}_2\text{CNET}_2)_{10}$  precursor was prepared by mixing 50 ml  $\text{Na}_2\text{S}_2\text{CNET}_2$  aqueous solution (10 mmol) with 100 ml aqueous solution containing  $\text{Cu}(\text{NO}_3)_2$  (2 mmol),  $\text{Zn}(\text{NO}_3)_2$  (1 mmol) and  $\text{SnCl}_4$  (1 mmol), washed 3 times at least with ionized water and ethanol followed by drying<sup>1</sup>.

**Synthesis of  $\text{Cu}_2\text{ZnSnS}_4$  nanocrystals.** In a typical synthesis of  $\text{Cu}_2\text{ZnSnS}_4$  nanocrystals, 100 mg  $\text{Cu}_2\text{ZnSn}(\text{S}_2\text{CNET}_2)_{10}$  precursor, 5 ml octadecene and 3 ml oleic acid were loaded into a three-neck flask equipped with  $\text{N}_2$  atmosphere. In control experiment, dodecanethiol was used as capping agent in nanocrystal synthesis instead of oleic acid. When the reaction mixture was heated to 220 °C, 2 ml Oleylamine was swiftly injected into the flask under gentle magnetic stirring. The color of the reaction changed from colorless to yellow, finally dark brown. After keeping the mixture at the reaction temperature for 60 minutes, the resulting solution was cooled to room temperature and precipitated with 5 ml ethanol followed by further centrifugation and decantation. The product could be washed and isolated by adding 10 ml hexane/ethanol (1:1 volume ratio) mixed solution. The dispersion/precipitation cycle was repeated several times in order to eliminate byproducts, unreacted precursors and octadecene. The purified nanocrystals were re-dispersed in hexane for X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurement. The control experiment for synthesis of ZnS was performed as the same, except that only  $\text{Zn}(\text{S}_2\text{CNET}_2)_2$  precursor was used.

**Characterizations.** The obtained crystalline phases were identified using powder X-ray diffraction (XRD) (Bruker, D8 advance, Cu Ka radiation using a curved graphite receiving monochromate), with a step of  $0.02^\circ$  at a scan rate of 1.0 sec/step. Morphologies and structural analysis were undertaken using transmission electron microscopy (TEM, JEOL 2100, accelerating voltage 200 kV). The samples for TEM were collected by placing a drop of dilute solution of sample in hexane onto carbon-film-supported molybdenum grids. Energy disperse spectroscopy (EDS) spectrum was obtained by using a scanning electron microscopy (SEM, FEI Nova NanoSEM 200). STEM-EDS were measured on Tecnai G2 F30 S-Twin microscopy at accelerating voltage of 300kV. UV-vis absorption spectra were recorded on a Unioco 482H spectrometer with a resolution of 1.0 nm. The binding energy of CZTS nanocrystals was examined by X-ray photoelectron spectroscopy (XPS, ESCALAB MKII), and all the peaks were calibrated by using C1s at 284.60 eV as the reference. Raman spectra of CZTS nanocrystals on quartz plate were collected from JY-T64000 Raman spectrometer under ambient conditions by using a laser excitation of 514.5 nm (2.41 eV, 20 mW) from an air-cooled  $\text{Ar}^+$  laser. The beam size is 2  $\mu\text{m}$ .

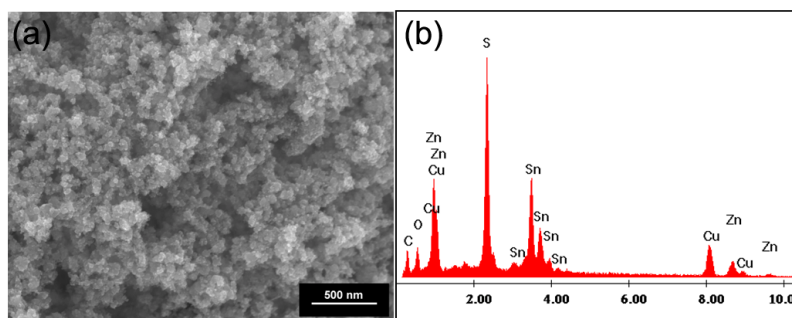


Figure S1. (a) SEM image of as-synthesized CZTS nanocrystals; (b) EDS profile of the CZTS nanocrystals.

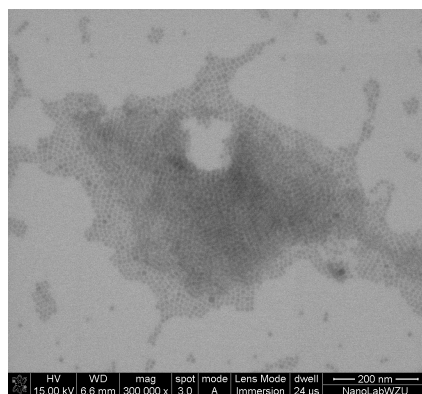


Figure S2. STEM image of as-synthesized CZTS nanocrystals with low magnification.

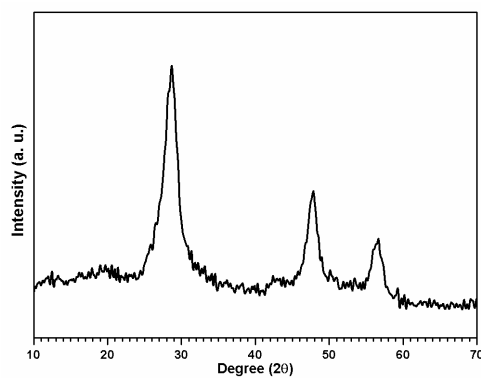


Figure S3. XRD pattern of ZnS nanocrystals derived from control experiment that only  $\text{Cu}(\text{dedc})_2$  precursor was used.

## References

1. (a) D. C. Pan, L. J. An, Z. M. Sun, W. Hou, Y. Yang, Z. Z. Yang and Y. F. Lu, *Journal of the American Chemical Society*, 2008, 130, 5620-5621; (b) D. C. Pan, D. Weng, X. L. Wang, Q. F. Xiao, W. Chen, C. L. Xu, Z. Z. Yang and Y. F. Lu, *Chemical Communications*, 2009, 4221-4223.