Electronic Supporting Information

for

Heat-up and gram-scale synthesis of Cu-poor CZTS nanocrystals with controllable compositions and shapes

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1. Characterization of the Cu-rich CZTS nanocrystals



Fig. S1 XRD pattern (a), TEM (b) and HRTEM image (c), particle size distribution (d), optical spectrum (e) and its band gap (f) of synthesized Cu-rich CZTS NCs with atomic composition of $Cu_{2.1}Zn_{0.7}Sn_{1.2}S_4$ (found by ICP analysis). The precursor ratio Cu:Zn:Sn:S designed for the synthesis is 2:1:1:4.

The XRD pattern (Fig. S1a) shows that the resulting Cu-rich CZTS nanocrystals (NCs) are in kesterite phase (PDF: 00-026-0575). The NCs are pseudospherical in shape with an average particle size of 16.0 ± 2.3 nm (Fig. S1b,d). The lattice fringes of the single nanocrystal exhibit interplanar distance of 3.01Å and 3.24 Å, which are attributed to the (103) and (112) planes of kesterite phase, respectively. The optical properties of the as-synthesized CZTS NCs have been studied by UV-Vis-NIR absorption spectroscopy (Fig. S1e), from which the direct band gap is estimated to be 1.6 eV (Fig. S1f).

2. Morphology, phase and optical spectra of Cu-poor CZTS NCs with different compositions.



Fig. S2 (a-d) TEM images of the Cu-poor CZTS NCs with different average compositions (as found by ICP analyses): $Cu_{1.9}Zn_{0.4}Sn_{1.6}S_4$ (a), $Cu_{1.5}Zn_{0.7}Sn_{1.7}S_4$ (b), $Cu_{1.4}Zn_{0.9}Sn_{1.6}S_4$ (c), and $Cu_{0.8}Zn_{0.9}Sn_{2.3}S_4$ (d). XRD patterns (e) of the samples shown in a-d. XRD pattern of the sample $Cu_{0.8}Zn_{0.9}Sn_{2.3}S_4$ (f). Peaks from both kesterite Cu_2ZnSnS_4 (JCPDS No. 00-026-0575) and herzenbergite orthorhombic SnS (JCPDS No. 00-014-0620) are observed. Absorption spectra (g) and calculated optical band gap of the samples shown in a-d. The band gap values are 1.53 eV for $Cu_{1.9}Zn_{0.4}Sn_{1.6}S_4$ (black), 1.5 eV for $Cu_{1.5}Zn_{0.7}Sn_{1.7}S_4$ (green), 1.42 eV for $Cu_{1.4}Zn_{0.9}Sn_{1.6}S_4$ (red) and and 1.4 eV for $Cu_{0.8}Zn_{0.9}Sn_{2.3}S_4$ (blue), respectively. The precursor ratio Cu:Zn:Sn:S for the



four samples are 2.0:1.6:1:5.2, 1.6:1.6:1:5.2, 1.2:1.6:1:5.2, and 0.8:1.6:1:5.2, respectively.

Fig. S3 Size distribution histogram of the Cu-poor CZTS NCs with composition of $Cu_{1.9}Zn_{0.4}Sn_{1.6}S_4$ (a), $Cu_{1.5}Zn_{0.7}Sn_{1.7}S_4$ (b), $Cu_{1.4}Zn_{0.9}Sn_{1.6}S_4$ (c), and $Cu_{0.8}Zn_{0.9}Sn_{2.3}S_4$ (d).



Fig. S4 HRTEM images of the representative single pyramid-like nanocrystal shown in Fig. S2d. The lattice fringes of the NC exhibits interplanar distance of 3.24 Å, which is attributed to the (021) plane of SnS (JCPDS No. 00-014-0620).

XRD characterization in Fig. S2f confirms that the resulting NCs with average composition of $Cu_{0.8}Zn_{0.9}Sn_{2.3}S_4$ are composed of both kesterite CZTS and orthorhombic SnS. The XRD peaks at two theta 28.6°, 47.2°, and 56.1° are indexed to (112) (220) and (312) of kesterite phase (JCPDS No. 00-026-575), while the strong peaks at around 32.1°, 45.5° and 66.8° could be assigned to the (040), (150) and (080) planes of SnS (JCPDS No. 00-014-0620).



3. Characterization of CZTS NCs obtained in the presence of different amounts of DT

Fig. S5 TEM (a-d) and HRTEM (e-h) images of CZTS NCs obtained in the presence of different amounts of DT: 0 mL (a,e), 0.5 mL (b,f), 2 mL (c,g) and 4 mL (d,h). XRD patterns (i) and optical spectra (j) of the corresponding CZTS NCs. The synthesis reactions were performed at 220 °C for 30 min.

Fig. S5 displays the evolution of morphologies, phase and optical spectra of the CZTS NCs obtained in the presence of different amounts of DT. It is noteworthy that bullet-like CZTS NCs are achieved with increasing DT amount in the reaction (Fig. S5c-d). New diffraction peaks were observed compared with kesterite as the DT amount increased to 2 mL (red curve in Fig. S5i). These XRD peaks are similar with those previously reported by Coughlan et al.,¹ and could be indexed to wurtzite (WZ) phase of CZTS. We also simulated the wurtzite pattern since no database of this phase could be available (Fig. S5i).

4. Characterization of aliquots collected at different stages during heating up



Fig. S6. TEM images (a-d) of aliquots collected at different stages of the reaction during the heating up. XRD patterns (e) and optical spectra of the corresponding aliquots shown in a-d, respectively.



Fig. S7. Particle size distribution of the aliquots collected at RT (a), 150 °C (b) and 220 °C (c) during the heating and at 220 °C for 1 h, respectively.

Fig. S6-S7 provide the evolution of morphologies and size, XRD patterns and optical spectra of various aliquots of NCs obtained at different stages of the reaction during the heating up. The diffraction peaks of the samples collected at RT and 150 °C could be indexed to covellite phase (PDF: 00-006-0464), however, kesterite phase of CZTS are formed with increasing temperature up to 220 °C (Fig. S6e). The phase attributions were confirmed by HRTEM analyses, as shown in the manuscript. The particle size increases from 4.0±0.5 nm at RT to 17.0±1.4 nm at 220 °C for 1 h (Fig. S7).

It is noteworthy that the samples collected at RT and 150 °C exhibit well-defined NIR absorption band (Fig. S6f), which is a feature of the localized surface plasmon resonance of binary copper chalcogenides. This is in agreement with the phase analysis discussed above. With increasing temperature, the cations of Zn²⁺ and Sn²⁺ in the solution diffuse into the asformed CuS NCs, which leads to the formation of quaternary CZTS NCs and the complete damping NIR plasmon absorbance.



5. The effect of the reaction temperature on the morphology, phase and optical spectra

Fig. S8. TEM (a-c) and HRTEM images (d-f) of various CZTS NCs achieved at different temperatures for 30 min: 150 °C (a,d), 220 °C (b,e) and 250 °C (c,f), respectively. XRD patterns (g) and optical spectra (h) of the corresponding samples shown in a-c, respectively.





Fig. S9. (a) Survey XPS spectrum of the scale-up synthesis of CZTS NCs obtained at 220 °C. Representative binding energy regions for S 2p, Sn 3d, Zn 2p and Cu 2p are indicated in the boxes. (b) High resolution XPS of S 2p from the Cu-poor CZTS NCs, which is split into two main peaks located at 162.4 eV (2 $p_{1/2}$) and 161.3 eV (2 $p_{3/2}$), respectively.

7. Results of the Cu-poor CZTS NCs achieved by gram-scale synthesis



Fig. S10. TEM image (a), optical spectrum (b), band gap (c), particle size distribution (d) weighing measurement (e) and TGA analysis (f) of the Cu-poor CZTS NCs obtained by large-scale synthesis. The composition of the as-synthesized sample is Cu_{1.8}Zn_{0.7}Sn_{1.5}S₄ (found by ICP analysis). The ligand oleylamine was completely removed at around 470 °C. The synthesis yields of Cu-poor CZTS NCs (48.47%) are estimated based on the comparison of the total weight of the final compound and that of the starting precursors, where the ligand weight calculated from TGA analysis was subtracted.

References:

1 C. Coughlan and K. M. Ryan, *Cryst. Eng. Comm.*, 2015, **17**, 6914-6922.