Synthesis and characterizations of quaternary Cu$_2$FeSnS$_4$ nanocrystals

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Electronic Supplementary Information
Experimental Details
Synthesis of Cu₂FeSnS₄ nanocrystal

1.5 mmol copper(II) acetylacetonate (97%, Aladdin), 0.5 mmol iron(II) acetylacetonate (98%, Aladdin), 0.75 mmol of tin(II) chloride (99%, Aladdin), and 10 ml oleylamine (C-18 content 80%-90%, Aladdin) were added into three neck flask (100 ml) connected to a Schlenk line. The temperature raised up to approximately 130 °C under vacuum and stirring, for degassing about 30 minutes and purged with Ar 3 times. The mixture then turned into brown-red colored solution. Then it was heated to 280 °C, where 4 ml of 1 M solution of sulfur in oleylamine is injected. After injection, the solution immediately turned dark, and eventually black when the temperature was holding at 280 °C for 1.5 hour. During the reaction aliquots were taken out at various time for monitoring the nanocrystals growth by TEM and XRD. The mixture was then cool to approximately 70 °C by air quenching. Then, 5 ml of toluene and 40 ml of isopropanol were added into the reaction mixture and the nanocrystals were collected using centrifuge (separated into eight 15 ml centrifuge tubes) at 8000 rpm for 15 minutes. The supernatant of the centrifuged mixture was decanted. And similar step of adding 5 ml of toluene and 40 ml of isopropanol and centrifuge was repeated. The supernatant was decanted again, the final precipitant was dispersed in approximately 40 ml toluene to form a stable ink solution.

S1 Spectrum of the Energy Dispersive Spectroscopy of Cu₂FeSnS₄ nanocrystals (reaction time 60min) and its quantitative analysis.

The sample used for determining the quantitative composition of tetragonal Cu₂FeSnS₄ films by EDS was prepared by dropping the concentrated dispersion of Cu₂FeSnS₄ nanocrystals onto the soda-lime glass substrate. In order to get average composition of as-synthesized nanocrystals, 7 different area nanocrystal films was examined. The results suggested that the elements distributed homogeneously and the average Cu/Fe/Sn/S composition of the nanocrystals is 2:1.05:1.04:4.69, which is close to 2:1:1:4.

Fig. S1 Spectrum of the Energy Dispersive Spectroscopy of Cu₂FeSnS₄ nanocrystals and its quantitative analysis
S2 Raman spectrum for the synthesized nanocrystals

![Raman spectrum graph](image)

Fig. S2 Raman spectrum of Cu$_2$FeSnS$_4$ nanocrystals

S3 TEM images for each aliquots taken out at different time.

![TEM images](image)

Fig. S3 TEM images for each aliquots taken out at different time (a) 1min, (b) 4min, (c) 15min, (d) 30min, (e) 60min, (f) 90min.
S4 XRD spectra of each aliquots taken out at different time.

Fig. S4 XRD spectra of each aliquots taken out at different time.

Additionally, although the peaks in the Raman spectra for the samples taken out at 15min, 30min, 1h and 1.5h can be assigned to tetragonal Cu₂FeSnS₄, no clear peaks can be found in the Raman spectra for the samples extracted before 15min. Therefore, it is very difficult to investigate the growth mechanisms by Raman characterization.