Synthesis and characterizations of quaternary Cu_2FeSnS_4 nanocrystals

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Electronic Supplementary Information

Experimental Details

Synthesis of Cu_2FeSnS_4 nanocrystal

1.5mmol copper(Ⅱ) acetylacetonate (97%, Aladdin), 0.5mmol iron(Ⅱ) acetylacetonate (98%, Aladdin), 0.75mmol of tin(Ⅱ) chloride (99%, Aladdin), and 10ml oleylamine (C-18 content 80%-90%, Aladdin) were added into three neck flask (100ml) 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 4ml of 1M 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 of time for monitoring the nanocrystals growth by TEM and XRD. The mixture was then cool to approximately 70 °C by air quenching. Then, 5ml 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 5ml of toluene and 40 ml of isopropanol and centrifuge was repeated. The supernatant was decanted again, the final precipitant was dispersed in approximately 40ml toluene to form a stable ink solution.

S1 Spectrum of the Energy Dispersive Spectroscopy of Cu_2FeSnS_4 nanocrystals (reaction time 60min) and its quantitative analysis.

The sample used for determining the quantitative composition of tetragonal Cu_2FeSnS_4 films by EDS was prepared by dropping the concentrated dispersion of Cu_2FeSnS_4 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.

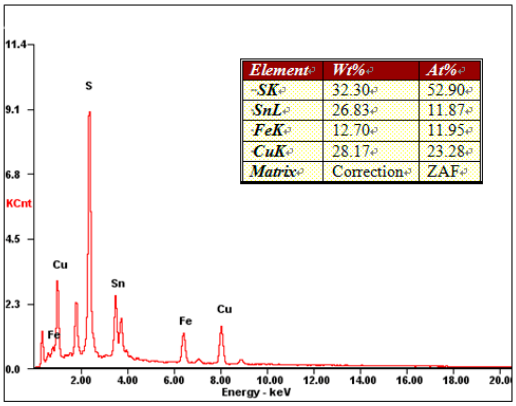

Fig. S1 Spectrum of the Energy Dispersive Spectroscopy of Cu_2FeSnS_4 nanocrystals and its quantitative analysis

S2 Raman spectrum for the synthesized nanocrystals

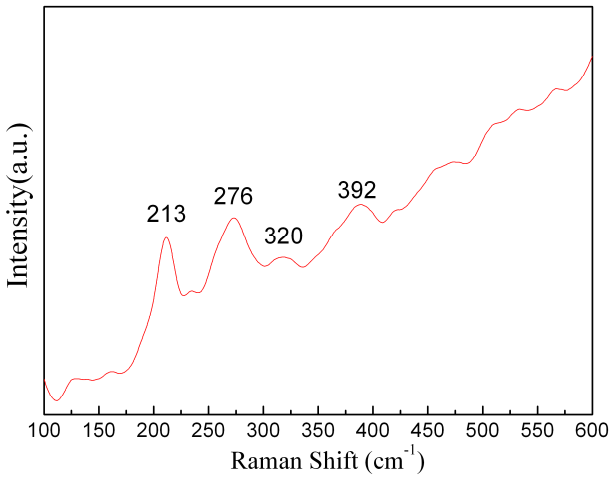

Fig. S2 Raman spectrum of Cu_2FeSnS_4 nanocrystals

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

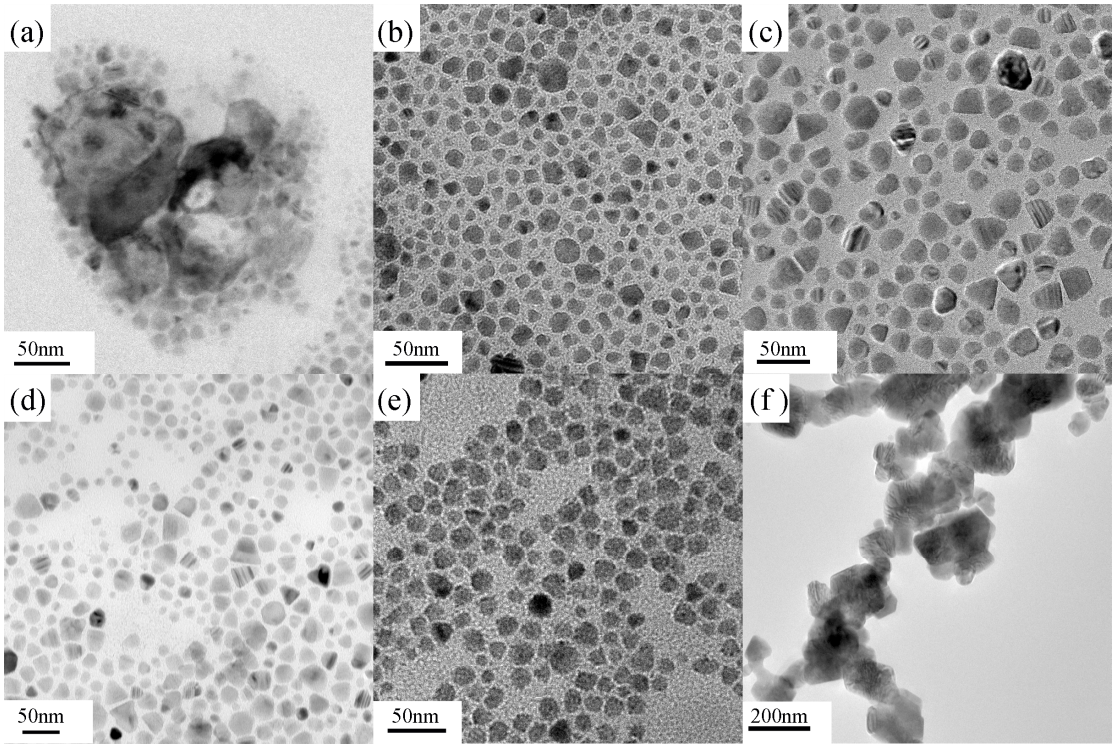

Fig. S3 TEM images for each aliquots taken out at different time (a) 1min, (b) 4min, (c) 15min, (d) 30min, (e) 60min, (f) 90min.

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

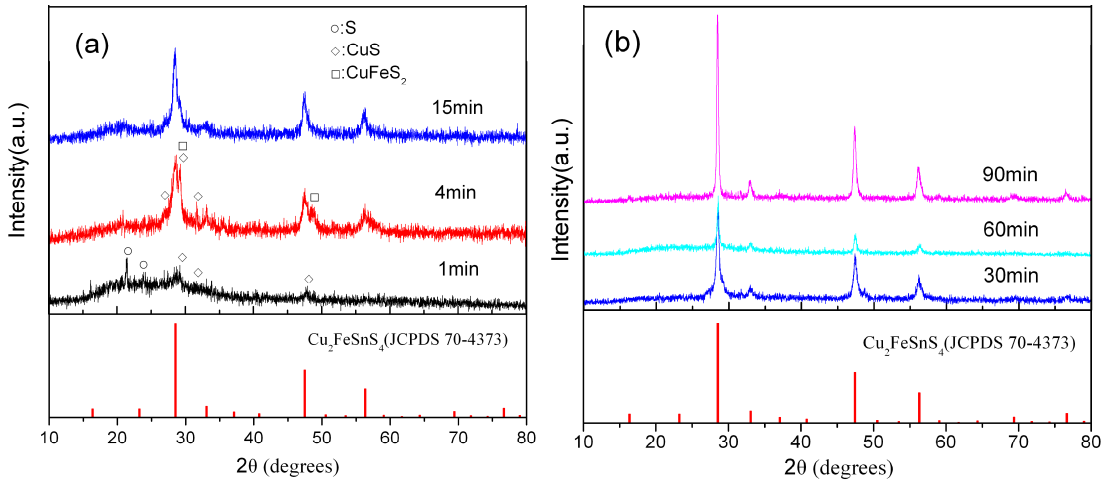

Fig. S4 XRD spectra of each aliquots taken out at different time.

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 Cu_2FeSnS_4, 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.