

Supplementary Information

A low-cost, ligand exchange-free strategy to synthesize large-grained Cu₂ZnSnS₄ thin-films without a fine-grain underlayer from nanocrystals

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Experimental

Synthesis of CZTS nanocrystals in formamide (FA)

Preparation of precursor A

In our optimized synthesis protocol, 4.8 mmol of Cu(Ac)₂·H₂O (99.0%, Fluka) was first added to 20 mL of formamide (99.0+%, Sigma-Aldrich) and mixed under magnetic stirring at room temperature for 1 h to form a blue-green suspension. Next, 3.3 mmol of SnCl₂ (98%, Sigma-Aldrich) was added and mixed for 2 h 30 min to obtain a clear light green solution. Finally, 3.12 mmol of ZnCl₂ (98+%, Sigma-Aldrich) was added and mixed for 30 min to obtain precursor A. No colour change was observed after the addition of ZnCl₂.

Preparation of precursor B

Next, 13.2 mmol of thioacetamide (98%, Sigma-Aldrich) was added to 10 mL of formamide in a 50 mL three-neck flask and mixed under magnetic stirring to form a clear pale yellow solution (precursor B). The solution was then degassed under rapid N₂ flow for approximately 30 min. Next, precursor B was heated to and maintained at 110°C for 45 min under rapid N₂ flow. Finally, precursor B was heated to 170°C in 35 min under slow N₂ flow. During ramping to 170°C, precursor B was initially observed to change to a clear green black solution, then to a clear golden brown solution, and finally to a clear orange solution.

Hot injection

2.5 mL of precursor A was injected into the three-neck flask, causing the solution in the flask to turn black and cool to 158°C immediately. The solution was allowed to react for 2 min before the three-neck flask was removed from the heating mantle and quenched in water kept at room temperature. The black solution obtained was then mixed with 30 mL of ethanol and centrifuged at 10,000 rpm for 10 min to obtain a clear yellow supernatant and a black solid. The supernatant was discarded and the black solid was redispersed in formamide. The dispersion was then ultrasonicated for 15 min. The washing steps were repeated twice using an ethanol:formamide ratio of 4:1. This removed unreacted precursors and impurities from the nanocrystals.¹

Synthesis of CZTS nanocrystals in oleylamine (OLA)

Preparation of precursor A

40 mmol of sulfur (99.999%, Alfa Aesar) was dissolved in 20 mL of OLA (80-90%, Acros Organics) by mixing both reactants under magnetic stirring in a water bath set at 80°C for 4 h.

Preparation of precursor B

1.0 mmol of CuCl₂ (97%, Aldrich), 1.2 mmol of ZnCl₂ (98+%, Sigma-Aldrich), and 0.75 mmol of SnCl₄.5H₂O (98%, Sigma-Aldrich) were mixed in 10 mL of OLA in a 50 mL three-neck flask under magnetic stirring. The solution was then degassed under rapid N₂ flow for approximately 30 min. Next, the solution was heated to and maintained at 110°C for 45 min under rapid N₂ flow. Finally, precursor B was heated to 225°C in 45 min under slow N₂ flow.

Hot injection

2.5 mL of precursor A was injected into the three-neck flask, causing the solution in the flask to turn black and cool to 210°C immediately. The solution was allowed to react for 30 min before the three-neck flask was removed from the heating mantle and quenched in water kept at room temperature. The black solution obtained was precipitated by adding 30 mL of ethanol and centrifuged at 10,000 rpm for 10 min to obtain a clear red supernatant and a black solid. The supernatant was discarded and the black solid was redispersed in 10 mL of hexane (95%, Sigma-Aldrich). The washing steps were repeated twice to remove unreacted precursors and impurities.

Fabrication of annealed CZTS thin-films

Preparation of Mo discs

A piece of Mo foil 0.025 mm thick (99.95%, Alfa Aesar) was first cut into discs 12.7 mm in diameter. The Mo discs were then immersed in a Micro-90[®] cleaning solution (diluted to a concentration of 2% in deionized water) and ultrasonicated for 30 min. The solution was discarded and the process was repeated for acetone followed by isopropyl alcohol. After the final wash, the solution was discarded and the Mo discs were rinsed in deionized water. Finally, the cleaned Mo discs were blown dry using N₂ gas.

Coating of CZTS FA nanocrystals

The washed CZTS FA nanocrystals were redispersed in 10 mL of ethanol and ultrasonicated in a water bath for 10 min. The dispersion was then centrifuged at 10,000 rpm for 10 min. The supernatant was discarded and the nanocrystals were redispersed in ethanol via ultrasonication in a water bath for 30 min to form an ink with a concentration of 125 mg/mL. The ink was then spin-coated onto the cleaned Mo discs at a spin speed of 5000 rpm. After each coating, the discs were placed on a hotplate kept at 200°C for 2 min and then cooled to room temperature before the next coating was applied. A total of 10 coatings were performed to obtain a CZTS FA nanocrystal film with the desired mass.

Compaction of the CZTS FA nanocrystal films

The CZTS FA nanocrystal film was first placed in a pellet die and overlaid with a disc of a chosen material, such as Mo. The nanocrystal was then subjected to a pressure of around 60 MPa using a hydraulic press for 5 min.

Annealing of CZTS FA nanocrystals

The compacted CZTS FA nanocrystal film on Mo and 30 mg of sulfur were placed in a graphite crucible and annealed in a tube furnace in an Ar atmosphere at 1 atm. In our optimized procedure, the CZTS FA nanocrystal film was heated to a temperature of 600°C at a ramping rate of 20°C per minute and maintained at 600°C for 30 min. The sample was then cooled to room temperature naturally.

Characterization

Energy-dispersive X-ray spectroscopy (EDX) was performed using an Oxford X-Max Silicon Drift Detector (50 mm²) attached to a Zeiss SupraTM 40 FESEM. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) were performed using a JEOL JEM-2010F TEM using an accelerating voltage of 200 kV. X-ray diffraction (XRD) was performed using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm). Raman spectroscopy was performed using a Horiba Scientific LabRAM HR Evolution system using an Ar laser with a wavelength of 514 nm. High resolution X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra DLD XPS spectrometer and all peaks were calibrated using C 1s as a reference (284.8 eV). UV-vis measurements were performed using a Shimadzu UV-1800 UV-Vis spectrophotometer. FTIR measurements were performed using a Cary 600 Series FTIR Spectrometer. Zeta potential measurements were obtained using a Malvern Instruments Zetasizer Nano Z with a 633 nm laser. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 under N₂ gas flow and at a heating rate of 5°C/min. Approximately 10 - 20 mg of sample was added to an alumina cup (TA Instruments, Part number 960070.901, 90 μ L) with an internal diameter of approximately 5.5 mm. The N₂ gas flow rate was set at 100 mL/min. Scanning Electron Microscope (SEM) images were obtained using a Zeiss SupraTM 40 FESEM. Weight measurements of the spin-coated CZTS FA nanocrystal films were performed using a Shimadzu electronic analytical balance AEM-5200 with a precision of 0.001 mg and an uncertainty of 0.002 mg.

Supplementary Information Figures

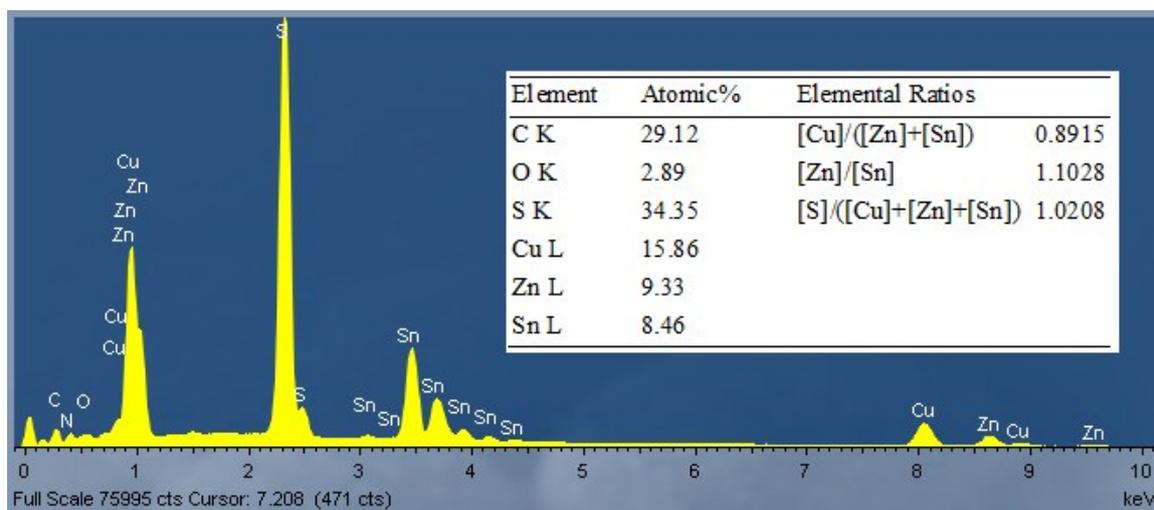


Figure S1 EDX of a film of CZTS nanocrystals that were synthesized in formamide. Insert: The atomic composition of the nanocrystal film and the elemental ratios between the constituents of CZTS.

High resolution X-ray photoelectron spectroscopy (XPS) measurements of the CZTS FA nanocrystals are shown in Figure S2. The spectra shows that the $2p_{1/2}$ and $2p_{3/2}$ peaks of Cu are positioned at 951.8 eV and 931.9 eV respectively, with a peak splitting of 19.9 eV. The $2p_{1/2}$ and $2p_{3/2}$ of Zn are positioned at 1044.6 eV and 1021.6 eV respectively, with a peak splitting of 23.0 eV. The $3d_{3/2}$ and $3d_{5/2}$ of Sn are positioned at 494.6 eV and 486.2 eV respectively, with a peak splitting of 8.4 eV. The $2p_{1/2}$ and $2p_{3/2}$ of S are positioned at 162.4 eV and 161.3 eV, which lies between 160 eV and 164 eV. These values correspond to the valence states of Cu^+ , Zn^{2+} , Sn^{4+} , and S^{2-} , and closely match those reported for CZTS in the literature.^{2,3}

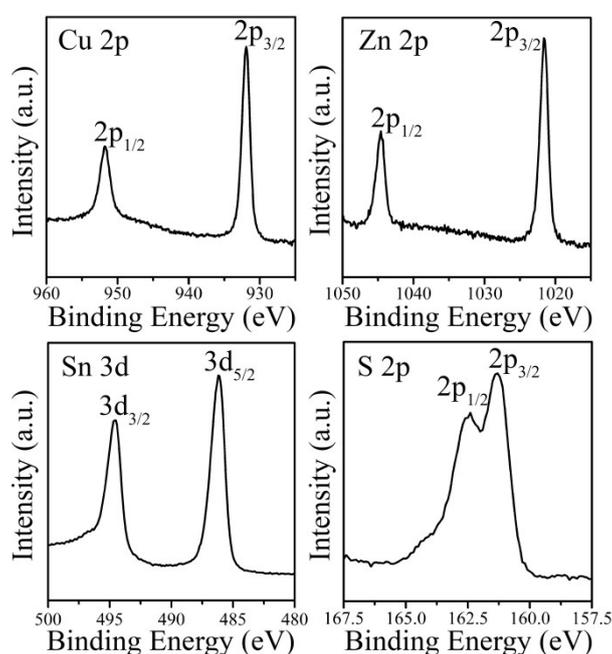


Figure S2 High resolution XPS spectra of the as-synthesized kesterite CZTS FA nanocrystals (JCPDS 026-0575).

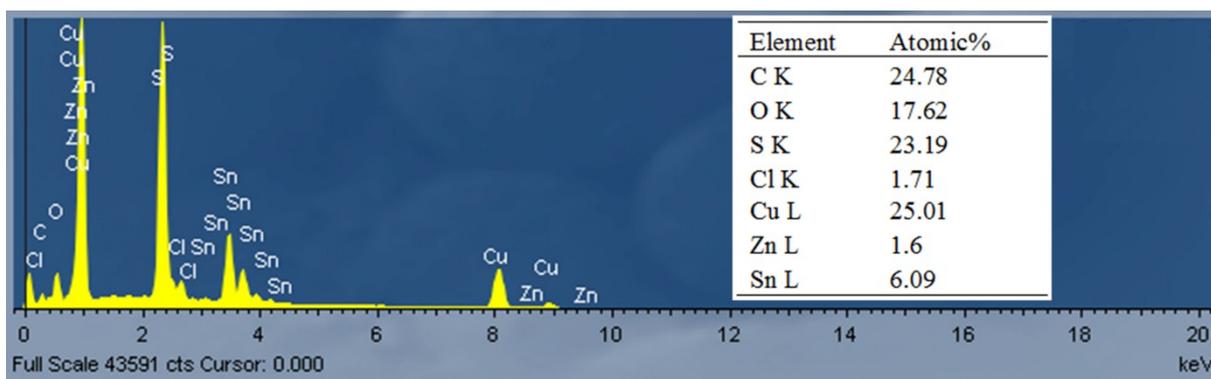


Figure S3 EDX of the precipitate formed from the reaction between the metal precursor and the clear yellow supernatant from the first wash. Insert: The atomic composition of the precipitate.

Figures S4a-c and S5a-b shows the TEM, HRTEM, SAED, XRD, and Raman spectrum of the CZTS nanocrystals that were synthesized in OLA. Similar to the CZTS nanocrystals synthesized in formamide, these characterizations show that our CZTS OLA nanocrystals are crystalline, nano-sized, and of the kesterite phase. The FTIR of CZTS OLA nanocrystals shown in Figure S5c features sharp bands near 2852 and 2922 cm^{-1} , attributed to the C-H vibration modes originating from OLA.⁴⁻⁶ This shows that our CZTS OLA nanocrystals are capped by OLA, an organic molecule with a long hydrocarbon chain. These properties of our CZTS OLA nanocrystals are similar to those reported elsewhere.⁷ Thus, a comparison between our CZTS FA nanocrystals and our CZTS OLA nanocrystals is representative of how our CZTS FA nanocrystals compare to the state of the art.

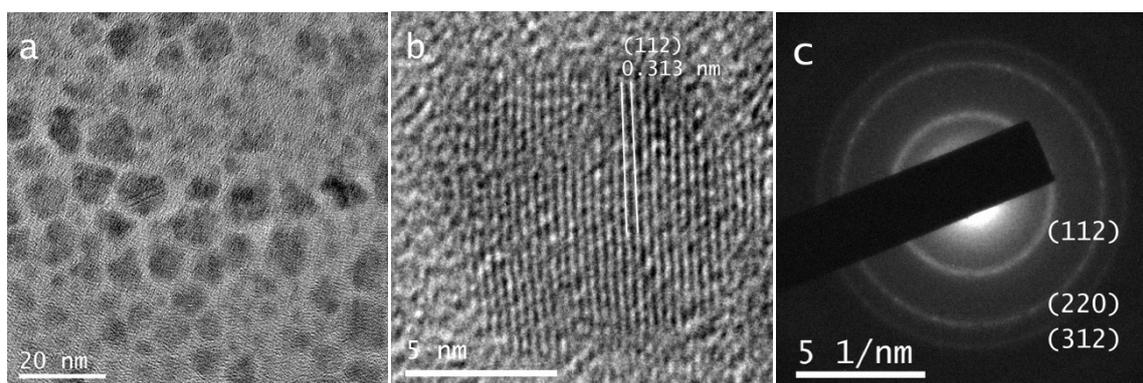


Figure S4 (a) TEM, (b) HRTEM, and (c) SAED images of the kesterite CZTS nanocrystals synthesized in OLA (JCPDS 026-0575).

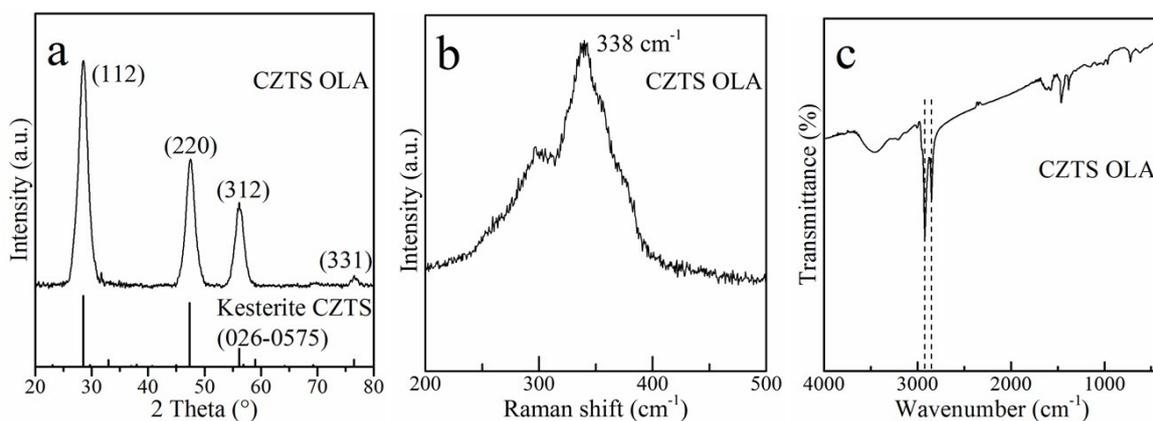


Figure S5 (a) XRD pattern, (b) Raman spectrum, and (c) FTIR of the kesterite CZTS nanocrystals synthesized in OLA (JCPDS 026-0575).

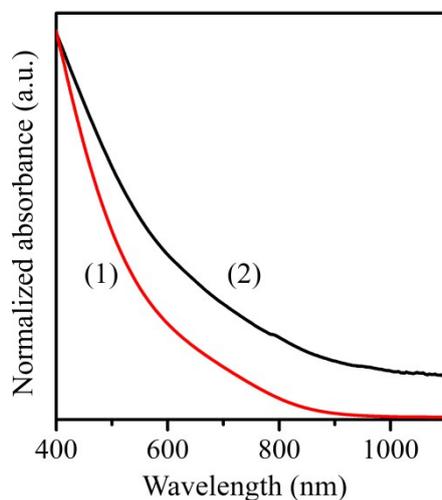


Figure S6 UV-vis spectra of CZTS nanocrystals dispersed in (1) formamide and (2) ethanol. The spectra were normalized to the absorbance at 400 nm.

Figure S6 shows a significant scattering background in the UV-vis spectrum for CZTS nanocrystals dispersed in ethanol, in contrast to CZTS nanocrystals dispersed in formamide. This shows that the dispersion of CZTS nanocrystals in ethanol is poorer than in formamide.

Table S1 Calculated theoretical thickness of the spin-coated CZTS nanocrystal films if they possess the same density as a single crystal CZTS thin-film.

Mass of Mo disc (mg)	Mo disc + CZTS nanocrystals (mg)	Mass of CZTS nanocrystals (mg)	Volume of CZTS deposited (cm ³)	Theoretical film thickness (μm)
32.053	33.032	0.979	2.128E-04	1.680
29.527	30.792	1.265	2.749E-04	2.170
32.448	33.431	0.982	2.135E-04	1.686
32.085	33.023	0.937	2.037E-04	1.608
33.223	34.185	0.963	2.093E-04	1.652
32.493	33.516	1.023	2.223E-04	1.755
30.732	31.810	1.077	2.342E-04	1.849
32.895	33.871	0.976	2.121E-04	1.675
32.000	33.106	1.106	2.405E-04	1.899
31.247	32.314	1.068	2.321E-04	1.832
Density of CZTS (mg/cm ³)		4600 ⁸		
Surface area of Mo disc (cm ²)		1.267		
Average theoretical film thickness (μm)		1.781 ± 0.167		

Detailed interpretation of TGA results of OLA and formamide

The TGA result in Figure 2 shows that OLA and formamide were totally gone at temperatures of 255°C and 165°C respectively. These temperatures are far below their boiling temperatures of 348-350°C for OLA and 210°C for formamide. This may be because the amount of sample typically used for TGA measurements was too little for solvents. Thus, they were totally evaporated far before reaching their boiling temperatures. To prove this interpretation, we increased solvent sample loading and shortened the heating period. After fully loading OLA and formamide in the TGA sample container and decreasing the heating period, the curves as shown in Figure S7 below were obtained. It is seen that the sharpest decrease did occur close to the boiling temperatures of OLA and formamide.

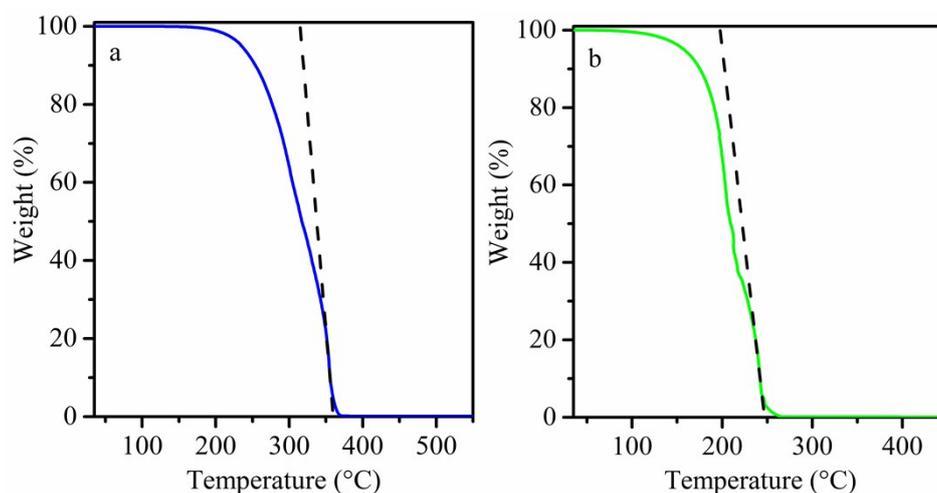


Figure S7 (a) TGA of oleylamine (OLA) and (b) formamide at a higher heating rate of 80°C/min.

References

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