

## Supplementary Information

### Facile single-component precursor for $\text{Cu}_2\text{ZnSnS}_4$ with enhanced phase and composition controllability

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#### AUTHOR INFORMATION

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Supporting Information

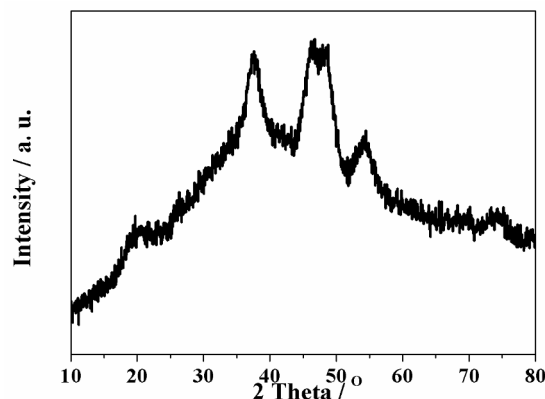
#### Experimental

**Preparation of Zn-Sn ligand solution:** The Zn-Sn hydrazine solution was prepared according to the previous work of our group.<sup>24</sup> Firstly, hydrazinocarboxylic acid ( $\text{H}_2\text{NNHCOOH}$ )-saturated hydrazine solution was prepared through adding hydrazine to a vial containing excess solid-state carbon dioxide:  $\text{CO}_2 + \text{N}_2\text{H}_4 \rightarrow \text{NH}_2\text{NHCOOH}$ ; Secondly, for the formation of the Zn-hydrazinocarboxylic acid (Zn-hyc), zinc nanopowder (2 mmol) was mixed and stirred with  $\text{H}_2\text{NNHCOOH}$  saturated hydrazine solution; Thirdly, for the  $\text{SnS}_2$  precursor solution,  $\text{SnS}_2$  (1 mmol) and excess sulfur (2 mmol) was mixed in a separate vial in  $\text{N}_2\text{H}_4$  (1 mL) with stirring; Fourthly, the Zn-Sn hydrazine precursor solution was obtained by mixing the above Zn-hyc paste (1 mmol) and  $\text{SnS}_2$  hydrazine solution (1 mmol) with excess sulfur (0.5 mmol) with adjusted molar ratio of  $\text{Zn/Sn} = 1.2$ . Note: Hydrazine is highly toxic, and appropriate protective equipment should be used to prevent direct contact with the liquid or vapor. The reaction between carbon dioxide and hydrazine is highly exothermic. The hydrazine-based solutions were prepared in a nitrogen-filled glove box where the oxygen and moisture levels were both below 1 ppm. The Zn-Sn dried precursor was prepared by pumping Zn-Sn hydrazine solution overnight.

This dried precursor was further dissolved in appropriate amount of benign solvents, such as formamide (FA), ethanolamine (EA) with continuous stirring at 100 °C for 1–2 h. The as-prepared Zn-Sn species in EA or FA are adjusted with desired concentration for the construction of CZTS precursor solution in the next step.

**Synthesis of  $\text{Cu}_2\text{ZnSnS}_4$  nanocrystals:** The synthesis of  $\text{Cu}_2\text{ZnSnS}_4$  nanocrystals follows the literature method<sup>18</sup>. In a typical synthesis, 1.332 mmol of copper acetylacetonate, 0.932 mmol copper acetylacetonate, and 0.75 mmol tin acetylacetonate dichloride were mixed with 10 mL of oleylamine in a three-neck flask. Then, the solution was heated up to 130 °C under Argon (Ar) flow and maintained at 130 °C for 30 minutes, followed by a quick injection of a solution composed of 2 mmol of sulfur in 2 mL of oleylamine. After that, the solution was quickly heated up to 225 °C and kept at this temperature for 30 min. The solution containing  $\text{Cu}_2\text{ZnSnS}_4$  nanocrystals was then cooled down naturally to room temperature and was centrifuged at 7500 rpm for 8 min with adding 50 mL ethanol. The supernatant was discarded and the precipitation was first fully dissolved in 5 mL of toluene and then precipitated out by adding 30 mL of ethanol followed by centrifuging at 7500 rpm for 8 min. The as-obtained precipitation was fully dissolved in toluene with mass concentration of 100 mg/mL for CZTS nanocrystals. The CZTS film was made by coating the as-prepared CZTS nanocrystals for multiple times, and annealed at 500 °C for 10 minutes.

**Materials Characterization:** Both the films and powder samples were annealed at the desired temperature on a hot plate with the temperature verified by an IR thermometer.

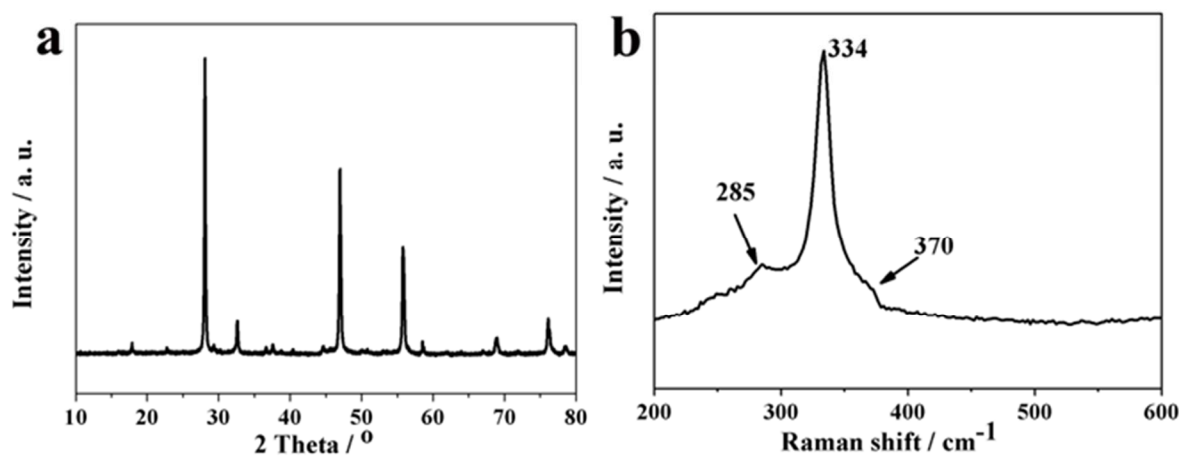


**Figure S1:** XRD pattern of as-prepared  $\text{Cu}_{2-x}\text{S}$  nanocrystals

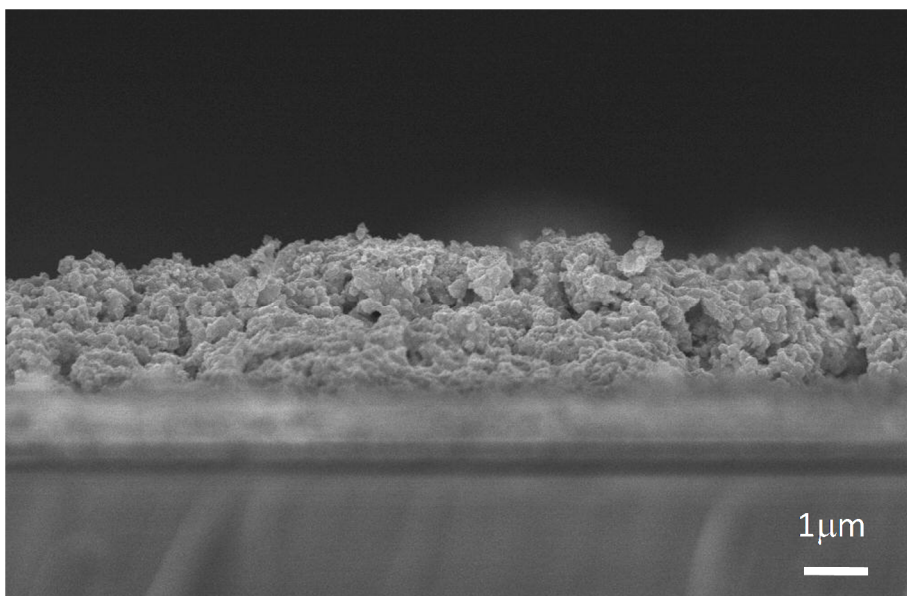
Figure S1 shows the X-ray diffraction pattern of as-prepared  $\text{Cu}_{2-x}\text{S}$  nanocrystals. It is clear that the sample displays four main peaks at  $37^\circ$ ,  $46.3^\circ$ ,  $48.5^\circ$  and  $54.3^\circ$ , indicating  $\text{Cu}_{2-x}\text{S}$  prepared in this way are hexagonal chalcocite (JCPDS 012-0176). This is in consistent with the TEM imaging.

The formation of stable CZTS precursor solution is mainly attributed by selecting the appropriate solvents and mixing the adequate amount of the ligands. In order to develop an environmentally benign and air-stable preparation, a large number of solvents have been tested to redissolve the dried Zn-Sn precursor, derived from the hydrazine precursor solution. It is found that only FA or ethanolamine (EA) provides accepted solubility, while dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) which are commonly used for dissolving water insoluble inorganic compound, hardly redissolve the Zn-Sn precursor. Interestingly, the combination of EA and DMSO, which showed great solubility for the Cu and In hydrazinium precursor,<sup>28</sup> are not effective when it applies on the Zn-Sn precursor, but EA alone is capable to dissolve Zn-Sn precursor. This could be ascribed to the polarity, the reducing and the coordination ability of EA. An alternative solvent FA, shares some similar structure features as EA, which both possess an  $\text{NH}_2$  group in their molecular structures. The prepared

solutions, either Zn-Sn in FA, or Zn-Sn in EA are further used to conduct the ligand exchange for the  $\text{Cu}_{2-x}\text{S}$  nanocrystals. Experimental results indicate that FA can give a more stable CZTS precursor solution, while EA cannot stabilize the nanocrystals after ligand exchange, since  $\text{Cu}_{2-x}\text{S}$  nanocrystals tend to precipitate after the phase transfer. This can be resulted from the different dielectric constants of EA and FA,<sup>35</sup> where FA ( $\epsilon = 106$ ) has a much higher dielectric constant value than that of EA ( $\epsilon = 37.7$ ). Different solution stability comparisons between EA and FA suggest that the higher dielectric constant solvent likely assists to stabilize nanocrystals. In addition to the choice of solvent, the amount of Zn-Sn in the final precursor solution also plays an important role to facilitate the process of ligand exchange, since inadequate Zn-Sn amount versus Cu species would lead to the precipitation of  $\text{Cu}_{2-x}\text{S}$  nanocrystals.



**Figure S2:** XRD patterns (a) and Raman spectra (b) of  $\text{Cu}_{2-x}\text{S}$  nanocrystal and Zn/Sn ligand precursor annealed at 500 °C.



**Figure S3:** SEM image of the cross section of an as-deposited CZTS film.

	Cu atom%	Zn atom%	Sn atom%	Cu/(Zn+Sn)	Zn/Sn
spot 1	9.59	6.62	6.3	0.74	1.05
spot 2	10.47	7.54	6.83	0.73	1.10
spot 3	7.73	5.6	5.29	0.71	1.06
spot 4	9.01	6.64	6.04	0.71	1.10
spot 5	8.57	6.16	5.65	0.73	1.09

**Table S1:** Energy dispersive x-ray spectroscopy data from five different spots along a CZTSSe film after selenization. The spots were separated by approximately 1 μm from one another. The composition ratio of [Cu]/([Zn]+[Sn]) and [Zn]/[Sn] remain nearly constant at around 0.73 and 1.06, respectively, thus confirming the film homogeneity. Cu, Zn and Sn atomic percentages were extracted from Cu K line, Zn K line and Sn L line, respectively.