

## Electronic supplementary information

### Low-cost, Mo(S,Se)<sub>2</sub>-free superstrate-type solar cells fabricated with tunable band gap Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> nanocrystal-based inks and the effect of sulfurization

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## Experimental Details

### 1. Synthesis of Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> nanocrystals

The Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> nanocrystals were prepared by a hot-injection method. The Cu, Zn, and Sn ionic precursors were chosen as copper(II) acetylacetonate [Cu(acac)<sub>2</sub>], zinc acetate [Zn(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>], and tin(II) chloride dihydrate [SnCl<sub>2</sub>·2H<sub>2</sub>O], respectively. The Cu-poor and Zn-rich compositions were kept during the synthesis of these Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> nanocrystals. In a typical synthesis, 1.68 mmol of copper(II) acetylacetonate, 1.4 mmol of zinc acetate, and 1.0 mmol of tin(II) chloride dehydrate were added into a 500 mL 3-neck flask with 30 mL of oleylamine. A (S+Se) anion precursors to Cu ratio of higher than 2.5times was prepared for the hot-injection process. As that oleylamine solution of Cu, Zn, and Sn ionic precursors was heated at 200 °C, a 10 mL of oleylamine solution with various ratios of elemental S and Se (x = 0, 0.25, 0.5, 0.75, and 1) was injected, followed by heating at 250 °C for 1 h under argon atmosphere. After the reaction, the solution was precipitated by methanol and washed by isopropyl alcohol /hexane three times to remove the residual oleylamine.

### 2. Fabrication of devices

A 30 nm thick anatase TiO<sub>2</sub> layer was fabricated by a sol-gel synthesis, followed by heat treatment at 450 °C for 2 h on ITO-coated glass slides purchased from Nanocs (New York, NY). The CdS buffer layer using the mixed aqueous solutions of CdSO<sub>4</sub>, NH<sub>2</sub>CSNH<sub>2</sub>, NH<sub>4</sub>OH, and

deionized water was deposited on the top of the TiO<sub>2</sub> layer by chemical bath deposition (CBD). Dense CdS thin-film layers were obtained during CBD inside a water bath maintained at 65 °C for 15 min. An ink consisting of Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> nanocrystals and ethanol was prepared and spincoated onto the top of the CdS buffer layer. The Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> film was formed by sulfurization of the spincoated Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> layer. The sulfurization process was carried out by placing the sample of as-synthesized Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> nanocrystals/CdS/TiO<sub>2</sub>/ITO/soda-lime glass inside a graphite box with sulfur powders at 570 °C in a tubular furnace for 45 minutes under Argon flow. A mild hydrogen chloride (HCl) etching process was applied for the whole devices after the sulfurization. Finally, a thermally evaporated gold electrode was used to define an active device area of 0.1 cm<sup>2</sup>.

### 3. Characterization of Materials

The Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> crystals were characterized with a Philips X-ray diffractometer (XRD) using Cu K $\alpha$  radiation. The cross-sectional SEM images were collected with a FEI Quanta 650. The compositional analyses were carried out by an energy-dispersive X-ray spectroscopy (EDS) equipped in a JOEL5610 SEM. The current density-voltage (J - V) characteristics using a solar simulator with a 100 mWcm<sup>-2</sup> light illumination under AM 1.5 G conditions were measured by a Keithley 2400 source measurement unit. All samples for the solar device performances were tested with the light illuminating through the ITO side of the substrate.