## Supporting information for

# Hydrophilic Cu<sub>2</sub>ZnSnS<sub>4</sub> nanocrystals for printing flexible, low-cost and environmentally friendly solar cells

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# 1. Experimental details

## **1.1 Materials**

All of the chemicals used are commercially available and were used as received without further purification. Polyvinylpyrrolidone (PVP) K-30, tri-sodium citrate, SnCl<sub>2</sub>·2H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, NH<sub>4</sub>OH, CS(NH<sub>2</sub>)<sub>2</sub>, ethylene glycol, Na<sub>2</sub>S·9H<sub>2</sub>O, and ethanol were purchased from Sinopharm Chemical Reagent Co. (China).

## 1.2 Preparation of hydrophilic Cu<sub>2</sub>ZnSnS<sub>4</sub>(CZTS) nanocrystals

In a typical synthesis of hydrophilic CZTS nanocrystals, 0.25 mmol  $SnCl_2 \cdot 2H_2O$ , 0.45 mmol  $CuCl_2 \cdot 2H_2O$ , and 0.3 mmol  $ZnSO_4 \cdot 7H_2O$  were dissolved in 10 mL ethylene glycol solution containing 4 g PVP, and the solution was magnetically stirring until a homogeneous pale-blue solution formed. Then, 10 mL ethylene glycol solution containing 1.2 mmol  $Na_2S \cdot 9H_2O$  was added into the above solution. Subsequently, the resulting solution was transferred to a 30 mL autoclave, sealed, and treated at 180 °C for 12 hrs. The black precipitate was collected by centrifugation and washed with ethanol. The black precipitate was collected and washed with distilled water several times and then redispersed in ethanol for later use.

#### 1.3 Construction of the flexible CZTS/ZnS solar cell

**Printing of the dense CZTS nanocrystal film:** Molybdenum (Mo) film with a thickness of ~ 1.5  $\mu$ m was deposited on a commercial aluminum foil substrate (thickness: ~ 0.1 mm) by radio-frequency (RF) magnetron sputtering (Magnetron Sputtering Equipment JPGF-400B-G, CAS Shenyang Scientific Instruments Development Center Co., LTD, China). The CZTS nanocrystal absorber layer with a thickness of ~ 1.2  $\mu$ m was printed on the flexible Mo-coated aluminum foil substrate by a so-called roll-to-roll printing technique using the ethanol dispersion (ink) of CZTS nanocrystals. Then CZTS nanocrystal film was subjected to annealing at 500 °C for 20 min under Ar and S vapors.

*Chemical bath deposition of a ZnS buffer layer:* A ~ 50 nm ZnS layer was deposited by a chemical bath deposition (CBD) technique. First, 10 mL ZnSO<sub>4</sub> aqueous solution (0.2 M) and 10 mL tri-sodium citrate aqueous solution (0.1 M) were placed in a 100 mL beaker. After being stirred for several minutes, the deionized water was added to make the volume up to 50 mL. When the solution became clear and homogenous, the pH value of the result solution was adjusted to ~ 10 by a NH<sub>3</sub>•H<sub>2</sub>O solution. Subsequently, the flexible CZTS film mounted near-vertically on a glass slide was immersed in the solution, and the solution was then heated up to 80 °C. At last, 10 mL CS(NH<sub>2</sub>)<sub>2</sub> aqueous solution (0.375 M) was added to the above solution, and the slide was deposited for 8 min.

*DC magnetron sputtering of i-ZnO/ITO/Ni-Al:* A ~ 50 nm high resistivity *i*-ZnO film and a ~ 100 nm high conductivity ITO layer were deposited in turn by DC magnetron sputtering. Prior to the deposition, the chamber was evacuated to a base pressure of  $3 \times 10^{-3}$  Pa. Then the *i*-ZnO film was deposited with a working pressure of 0.4 Pa by applying pure Ar gas and 60 W discharge power at temperature for 20 min. The ITO layer was then deposited as the same condition as that of the *i*-ZnO film except that the sputtering time was 1 h. After deposition of the oxide layers, the final device was scribed into a small area on a side (~ 0.24 cm<sup>2</sup>) for sputtering Ni-Al as top contact under a working pressure of 2.2 Pa for 5 min.

## 1.4 Characterization and photoelectrical measurement

X-ray diffraction (XRD) measurement was performed on a Bruker D4 X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). Size and morphology of CZTS NCs samples were

examined by using a high-resolution transmission electron microscope (JEOL, JEM-2010F). The elemental composition and distribution of the CZTS NCs and the structure of the CZTS NCs films were analyzed and demonstrated using a scanning electron microscopy (Hitachi S-4800) equipped with an energy-dispersive X-ray spectroscopy (EDX). Fourier transform infrared (FTIR) spectra were recorded using an IRPRESTIGE-21 spectrometer (Shimadzu) using the KBr pressed pellets. UV-visible absorption spectra were taken on a Shimadzu UV-2550 ultraviolet-visible-near-infrared spectrophotometer using quartz cuvettes with an optical path of 1 cm.

Photocurrent density–voltage curves of the cell were recorded under standard AM 1.5 solar illumination with an intensity of 100 mW cm<sup>-2</sup> using a computerized Keithley Model 2400 SourceMeter unit. A 300 W xenon lamp (Newport Oriel) served as the light source. The active electrode area was typically 0.24 cm<sup>2</sup>.

## 2. Supplementary Figures



**Figure S1** Histogram shows the particle size distribution of CZTS NCs. The size distribution is obtained from the TEM image covering 200 particles, and their average diameter is ~ 10 nm.



**Figure S2** Elemental mappings of the as-prepared CZTS NCs reveal the uniform distribution of elemental Cu, Zn, Sn and S within this observed area of this sample.



Figure S3 An EDX spectrum of the as-prepared CZTS NCs shows that the elemental composition of the CNs is  $Cu_{1.72}Zn_{1.11}Sn_{1.01}S_{4.17}$  which was investigated by averaging over 10 random spots of 100 nanocrystals.



**Figure S4** TGA of the as prepared CZTS NCs indicates that the content of the PVP ligands on the CZTS NCs' surfaces is about 10.04 wt %.



**Figure S5** (a) The low- and (b) high-magnification SEM images of the as-printed CZTS film before annealing show that the film consists of small sized particles.