# **Electronic Supplementary Information**

## A self-doping strategy to improve photoelectrochemical performance

## of Cu<sub>2</sub>ZnSnS<sub>4</sub> nanocrystal films for water splitting

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### **Experimental section**

## Synthesis of Cu<sub>2</sub>ZnSnS<sub>4</sub> nanocrystals (NCs)

The quaternary Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) NCs with varying compositions were prepared by a hot-injection method as described in the following procedures. Herein, the Sn element was partially replaced by Zn element, depending on the doping ratios, they are denoted as CZTS-x NCs. First, 1.6 mmol of total metal salts (Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, SnCl<sub>4</sub>·5H<sub>2</sub>O, and  $Zn(OAc)_2 \cdot 2H_2O$  in a stoichiometric molar ratio) and 20.0 mL of oleylamine (OLE) were loaded in a 50 mL of three-necked round bottom flask. The present work mainly explored the effect of self-doping on the performance of CZTS, so different x values need to be chosen to determine the amount of each metal salt. In this reaction, OLE acts as both the solvent and ligand for synthesis of NCs. The reaction flask was heated up to 135 °C and kept under vacuum for 120 minutes in order to remove oxygen and water. After evacuation, the flask was filled with Ar (g) and heated to 245 °C. The S-OLE solution (1.6 mmol of S dissolved in 2 mL of OLE) was rapidly injected into the flask with vigorous stirring at 245 °C. With a growth of 60 minutes, the reaction was terminated by removing the heating mantle. Once the temperature of the mixture reached room temperature, isopropanol was added and the solution was centrifuged for 10 minutes to precipitate the NCs. The quaternary NCs were finally dispersed in 30 mL of hexane for the following measurements and characterization.

### Preparation of Cu<sub>2</sub>ZnSnS<sub>4</sub> films

CZTS-x films were prepared by electrophoretic deposition (EPD) of CZTS-x NCs on

fluorine-doped tin oxide (FTO) coated glass substrates (Hartford Glass TEC 8 with sheet resistance of 8  $\Omega$ /square). First, the obtained CZTS-x NCs should be centrifuged for 4 min under 4000 rpm, and isopropyl alcohol was added to remove the excess oleylamine. The washed CZTS-x NCs were dispersed in hexane for EPD. In a typical EPD process, a Keithley digital sourcemeter was used with a DC voltage of 210 V and a separation distance of approximately 1 cm between the two pieces of FTO glass. An EPD process should not be stopped until the current of the sourcemeter is stable, which usually takes about 6 minutes.

It should be noted that after each EPD cycle was completed, the FTO was taken out and rinsed with ethanol to remove residual organic substances. After the ethanol was completely evaporated, the FTO was soaked in the solution (50 mL of acetonitrile and  $30 \ \mu$ L of ethylenediamine) for 10 seconds so that the ethylenediamine molecule replaced the oleylamine molecule as a new ligand on the surface of the CZTS-x NCs, and then the film was washed again with ethanol to avoid excessive residual acetonitrile on the surface. When the EPD process was completed, the film was washed with ethanol and dried.

## Characterization

The crystal structure of the CZTS NCs was examined by an X'Pert PRO X-ray diffractometer (Cu target, 40 eV, 40 mA, PANalytical company). Raman spectra were recorded on a Jobin Yvon LabRAM HR spectrometer using 514.5 nm radiation from an argon ion laser at 20 mW. The light absorption properties of the CZTS NCs were

determined by a U-4100 UV-Vis spectrophotometer from HITACHI. The morphology of the CZTS NCs was characterized with a Tecnai G2F30 transmission electron microscope (TEM). The morphology and film thickness were analyzed with a JEOL JSM-6700F field emission scanning electron microscopy (FESEM). X-ray photoelectron spectroscopy (XPS) data could be measured by a Kratos Axis-Ultra DLD instrument with a monochromatized Al K $\alpha$  line source (150 W). The binding energies of all spectra were calibrated to the adventitious C 1s peak at 284.8 eV. The chemical compositions were analyzed by X-ray fluorescence spectrometer (XRF, Bruker S4 Pioneer).

### **Photoelectrochemical measurements**

All PEC measurements were conducted on a CHI 760D workstation (CH Instruments). The photoelectrochemical performances of CZTS photoelectrodes were examined in a three-electrode cell with an Ag/AgCl electrode as a reference electrode and a platinum wire as a counter electrode. 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH adjusted to 3 by using  $H_2SO_4$ ) was used as the electrolyte. The simulated light source was a 500 W xenon lamp equipped with an AM 1.5G filter. The light intensity was calibrated to 100 mW·cm<sup>-2</sup>. The potential vs reversible hydrogen electrode (RHE) could be obtained from the measured potential vs Ag/AgCl, according to the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.197$$
(1)

where  $E_{RHE}$  denotes the converted potential vs RHE, and  $E_{Ag/AgCl}$  denotes the measured potential vs Ag/AgCl.

The incident photon-to-current conversion efficiency (IPCE) test was carried out by measuring the photocurrent produced under chopped monochromatic light irradiation at a fixed potential of 0 V vs RHE, according to the following equation:

$$IPCE = \frac{1240 \times j(\lambda)}{P(\lambda) \times \lambda}$$
(2)

where  $\lambda$  corresponds to the wavelength of incident monochromatic light (nm), j ( $\lambda$ ) is the photocurrent density (mA·cm<sup>-2</sup>) under illumination at wavelength  $\lambda$ , and P( $\lambda$ ) is the incident light intensity (mW·cm<sup>-2</sup>) at wavelength  $\lambda$ .

### **Theoretical calculation**

The DFT calculation of density of state (DOS) was performed using the projector augmented wave (PAW) basis set, together with the HSE06 hybrid exchange-correlation functional, implemented by VASP code. K-points mesh in Brillouin-zone (BZ) was set to 5\*5\*2 by the Monkhorst-Pack scheme with Gamma point in the center in reciprocal space for pristine CZTS cell, and 2\*2\*2 for the self-doped super cell. The energy cut off was set to 300 eV. For the calculation of self-doped CZTS, the doping ratio is 12.5%.



Fig. S1 Schematic of preparation process of CZTS nanocrystal films.



Fig. S2 Particle size distribution of CZTS-x NCs with increasing x values: (a) x = 0, (b) x = 20%, and (c) x = 40%.



Fig. S3 UV-vis absorption spectra of CZTS and self-doped CZTS.



**Fig. S4** Plots of  $(\alpha hv)^2$  vs photon energy (hv) of (a) CZTS and (b-f) self-doped CZTS, where  $\alpha$  is the optical absorption coefficient and hv is the photon energy.



**Fig. S5** XPS spectra of CZTS and self-doped CZTS: (a) S 2p; (b) Sn 3d; (c) Zn 2p; (d) Cu 2p.



**Fig. S6** Measured (solid line) and theoretical (dashed line) element concentrations of CZTS and self-doped CZTS determined by XRF analysis.