

## Electronic Supplementary Information

### Synthesis and Phase Transition of Wurtzite $\text{Cu}_3\text{ZnInSnS}_6$ Nanodisks

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#### Experimental Section:

##### I. Chemicals

$\text{CuCl}$  (99%),  $\text{InCl}_3$  (99.99%), and thiourea (99.9%) were purchased from Aladdin. Anhydrous  $\text{SnCl}_2$ ,  $\text{ZnCl}_2$  and n-dodecanethiol (DDT, 98%) were purchased from Alfa Aesar. oleylamine (OLA, 70%) was purchased from Sigma-Aldrich. Toluene (AR) and ethanol (AR) were purchased from Beijing Chemical Reagent Ltd, China. All chemicals were used as received without further purification.

##### II. Preparation of the thiourea/oleylamine solution

Thiourea stock solution (0.5 M) was obtained by dissolving thiourea powder (0.7612 g, 10 mmol) in 20 ml of OLA at 160 °C for 2 hours.

##### III. Synthesis of wurtzite $\text{Cu}_3\text{ZnInSnS}_6$ nanodisks

0.3 mmol of  $\text{CuCl}$ , 0.1 mmol of  $\text{ZnCl}_2$ , 0.1 mmol of  $\text{InCl}_3$ , 0.1 mmol of  $\text{SnCl}_2$ , 20 mL of OLA, and 1 mL of DDT were added to a 50 mL three-neck flask. The contents in the flask were heated to 130 °C and purged with nitrogen three times by repeating cycles of vacuuming and back filling with nitrogen gas, and then degassed at ~ 130 °C for 30 minutes. Subsequently, the temperature was increased to 220 °C, and 3.6 mL of the thiourea / OLA solution was swiftly injected into the solution under magnetic stirring. Then, the reaction was kept at 240 °C for 0.5h. After the reaction, the crude solution was cooled to room temperature and then precipitated with 30 mL of ethanol and further isolated by centrifugation and decantation. The purified nanocrystals were re-dispersed in toluene for various characterizations. The as-prepared nanocrystals are soluble in typical nonpolar solvents, such as hexane and toluene, which allows their processing through the simple casting or printing process.

##### IV. Annealing experiment

For ex-situ annealing experiments, CZITS nanodisks are annealed on a hot plate at

different temperatures of 300, 350, 400, 450 and 500 °C in a nitrogen glove box for 5 min. After annealing, the samples of CZITS are allowed to cool down to room temperature for SEM and XRD analysis.

## V. Device Fabrication

CZITS nanodisks films were fabricated onto a soda lime glass substrate by the spin-casting method using a dense toluene solution of CZITS nanocrystals. After coating, the CZITS nanocrystals film was then dried in the open air. When the solvents evaporated, a post annealing process was conducted in an N<sub>2</sub> atmosphere at 400 °C for 5 minute to remove ligands and solvents. Repeat the sequence three times. At last, the photoresponse device was completed by evaporating two Al electrodes onto the surface of the thin film. The photoresponse device is illustrated in Figure S1.

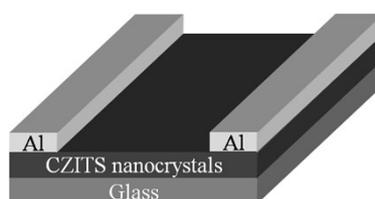


Fig. S1. Schematic illustration of the CZITS nanodisks-based photoresponse device.

## VI. Characterizations

X-ray diffractions (XRD) of drop-cast films of CZITS nanocrystals on a glass substrate were recorded using a Bruker D8 X-ray diffractometer. The simulated CZITS XRD pattern was obtained using the Diamond 3.0 program. Rietveld refinement was carried out using GSAS.<sup>1</sup> Lattice parameters, zero point error, scale factor and the background are refined. Profile parameters (i.e. U, V, W) were refined next. Raman spectra were taken on a Horiba-Jobin Yvon LabRAM ARAMIS system with 532 nm radiation. The samples were obtained through dropping the ink of CZITS nanodisks on a glass substrate and drying in the air. The content of Cu<sup>+</sup>, Zn<sup>2+</sup>, In<sup>3+</sup>, Sn<sup>4+</sup> and S<sup>2-</sup> ions in the products were determined by inductively coupled plasma mass spectroscopy (ICP-OES-MS, Thermo Jarrell-Ash Corporation, Franklin, MA, USA). X-ray photoelectron spectroscopy (XPS) was measured with VG ESCALAB MKII spectrometer (VK Company, UK). The UV-Vis-NIR absorption spectrum was measured by a Shimadazu UV-3600. Transmission Electron Microscopy (TEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS) and elemental mapping images were obtained using a JEOL JEM-2010 instrument operating at a FEI Tecnai G2 F20 transmission electron microscope with an acceleration voltage of 200 kV. The EDS analyses were performed using carbon-coated nickel grids. The *I-V* curve was measured with a Keithley 2400 source meter in the dark and under AM 1.5 G solar simulation (Abet Inc. Sun 2000). The light intensity was calibrated to 100 mW/cm<sup>2</sup> using a Newport optical power meter (model 842-PE). Scanning electron

microscopy (SEM) images were taken using Philips XL 30 and a JEOL JSM-6700F microscope.

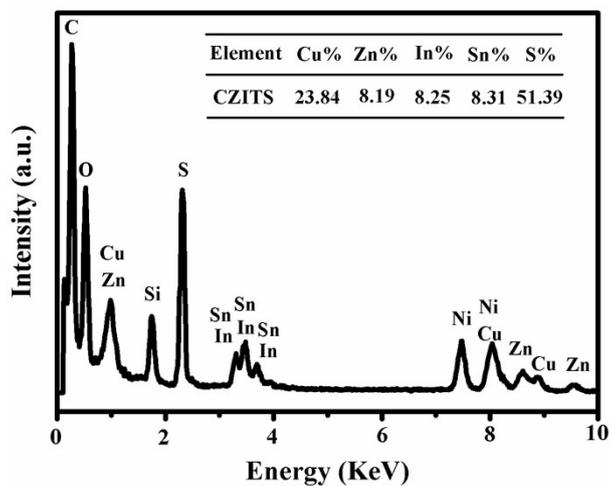


Fig. S2. EDS of a single CZITS nanodisk. The relative elemental ratios for Cu:Zn:In:Sn:S are 2.91:1:1.01:1.01:6.27. The C, O and Ni signals result from the carbon substrate. The observed Si signal is from the Si detector.

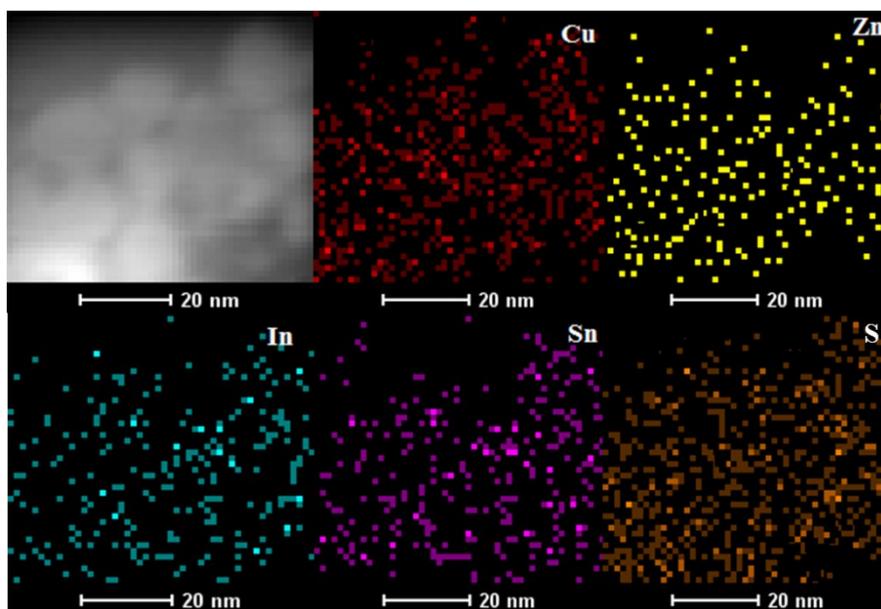


Fig. S3. HAADF STEM image of CZITS nanodisks, and corresponding elemental mapping images.

### Simulated crystal structures of wurtzite and tetragonal $\text{Cu}_3\text{ZnInSnS}_6$

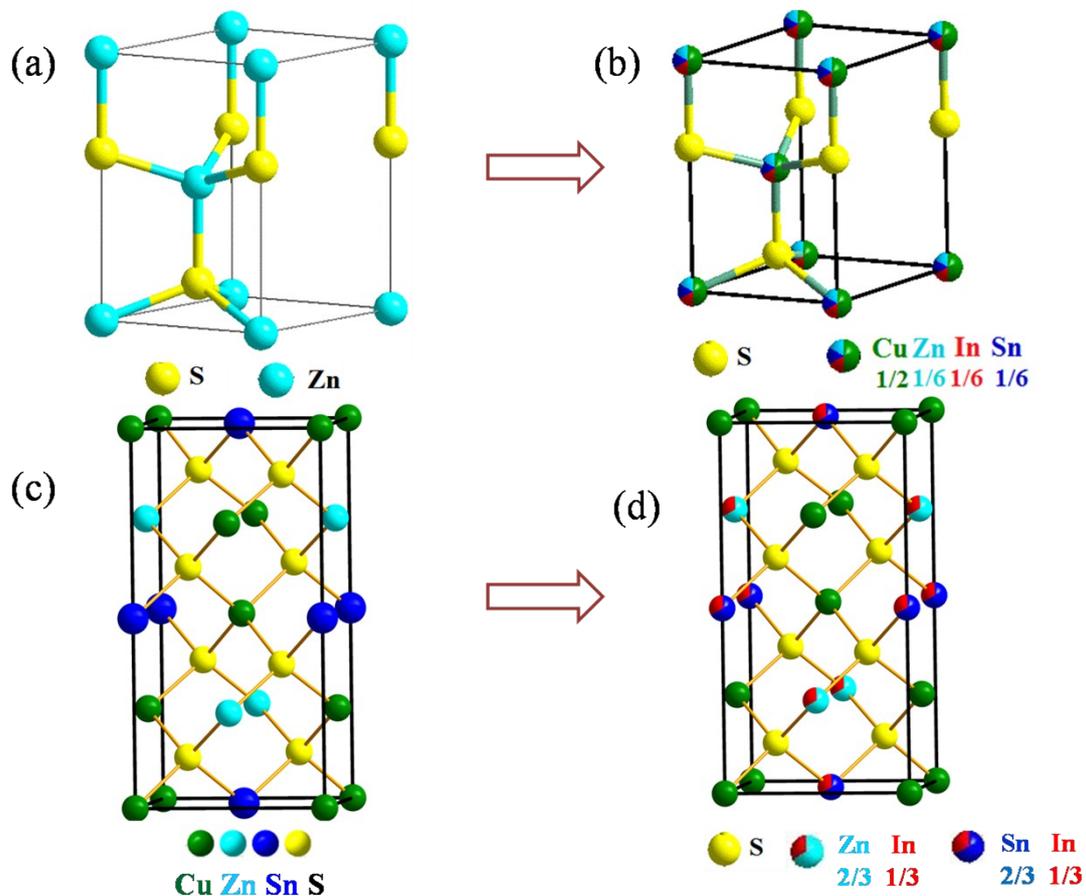


Fig. S4. Crystal structures of (a) Wurtzite ZnS; (b) Wurtzite CZITS; (c) Tetragonal  $\text{Cu}_2\text{ZnSnS}_4$  and (d) Tetragonal CZITS.

### Crystal data

Formula	$\text{Cu}_3\text{ZnInSnS}_6$	
Crystal system	Wurtzite	Tetragonal
Space group	$P6_3mc$ (No. 186)	$I-4$ (No. 82)
Unit cell dimensions	$a = b = 3.8674 \text{ \AA}, c = 6.3552 \text{ \AA}$	$a = b = 5.4566 \text{ \AA}, c = 10.9430 \text{ \AA}$

### Atomic coordinates

Atom	Wyck.	x/a	y/b	z/c
Wurtzite				
S	2b	1/3	2/3	0
Cu	2b	1/3	2/3	0.3752
Zn	2b	1/3	2/3	0.3752
In	2b	1/3	2/3	0.3752
Sn	2b	1/3	2/3	0.3752

Atom	Wyck.	x/a	y/b	z/c
Tetragonal				
S	8g	0.75622	0.24342	0.12821
Cu1	2a	0	0	0
Cu2	2c	0	0.5	0.25
Zn/In1	2d	0	0.5	0.75
Sn/In2	2b	0	0	0.5

The structure of Wurtzite and tetragonal  $\text{Cu}_3\text{ZnInSnS}_6$  (Fig. S4b, d) can be obtained by replacing  $\text{Zn}^{2+}$  sites with  $\text{Cu}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{In}^{3+}$  and  $\text{Sn}^{4+}$  in wurtzite  $\text{ZnS}$  (Fig. S4a) and substituting  $\text{Zn}^{2+}$ ,  $\text{In}^{3+}$  for  $\text{Zn}^{2+}$ , and  $\text{In}^{3+}$ ,  $\text{Sn}^{4+}$  for  $\text{Sn}^{4+}$  in tetragonal  $\text{Cu}_2\text{ZnSnS}_4$  (Fig. S4c), respectively, while the  $\text{S}^{2-}$  sites are remained. Note that all of Cu, Zn, In and Sn atoms occupy the same position in the wurtzite CZITS, and their occupation is 50%, 16.67%, 16.67% and 16.67%, respectively. While in tetragonal CZITS,  $\text{Zn}^{2+}$  and  $\text{In}^{3+}$  occupy the  $\text{Zn}^{2+}$  sites in tetragonal  $\text{Cu}_2\text{ZnSnS}_4$ , and  $\text{In}^{3+}$  and  $\text{Sn}^{4+}$  occupy the  $\text{Sn}^{4+}$  sites in tetragonal  $\text{Cu}_2\text{ZnSnS}_4$ . However, the whole symmetry in the crystal remains the same as tetragonal  $\text{Cu}_2\text{ZnSnS}_4$ . Since the standard XRD pattern for wurtzite and tetragonal  $\text{Cu}_3\text{ZnInSnS}_6$  is not available in the database, we have simulated the diffraction pattern based on the structure shown in Fig. S4b and d.

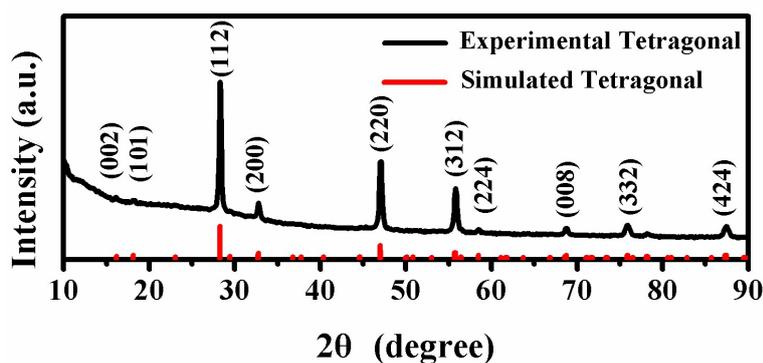


Fig.S5 Experimental and simulated XRD patterns of CZITS annealed at 450°C with a tetragonal structure.

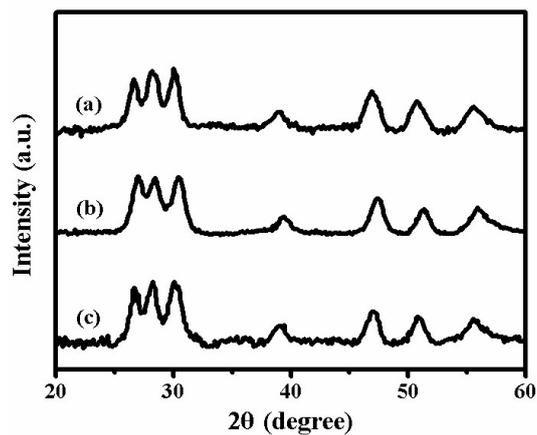


Fig. S6. XRD patterns of the wurtzite CZITS nanocrystals with different [Cu]/[Zn]/[In]/[Sn]/[S] ratios. (a)  $\text{Cu}_{4.76}\text{Zn}_{1.09}\text{In}_{2.34}\text{Sn}_{1.21}\text{S}_{9.72}$  (b)  $\text{Cu}_{2.88}\text{Zn}_{1.13}\text{In}_1\text{Sn}_{1.01}\text{S}_{6.37}$  (c)  $\text{Cu}_{1.78}\text{Zn}_{1.43}\text{In}_{1.16}\text{Sn}_{1.37}\text{S}_{7.24}$ .

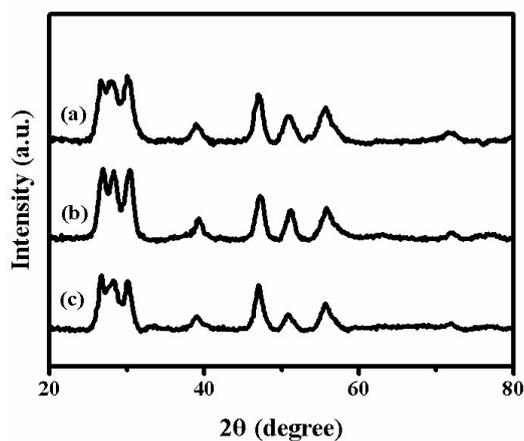


Fig. S7. XRD patterns of the as-synthesized CZITS nanocrystals at different reaction temperatures under otherwise identical conditions. (a) 220°C (b) 240°C (c) 260°C.

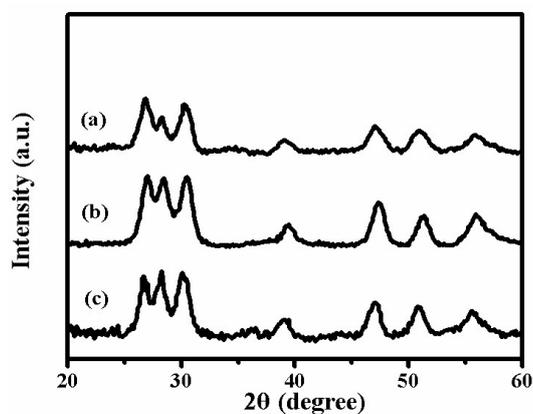


Fig. S8. XRD patterns of the as-synthesized CZITS nanocrystals at different injection temperatures under otherwise identical conditions. (a) 200°C (b) 220°C (c) 240°C.

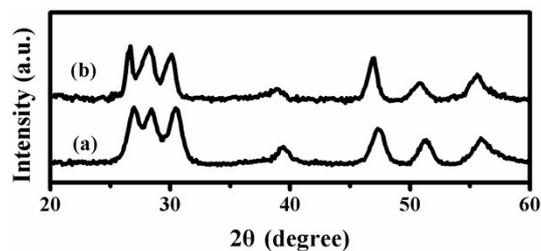


Fig. S9. XRD patterns of as-synthesized CZITS nanocrystal prepared by different solvent under otherwise identical conditions (a) DDT+ OLA (b) OLA.

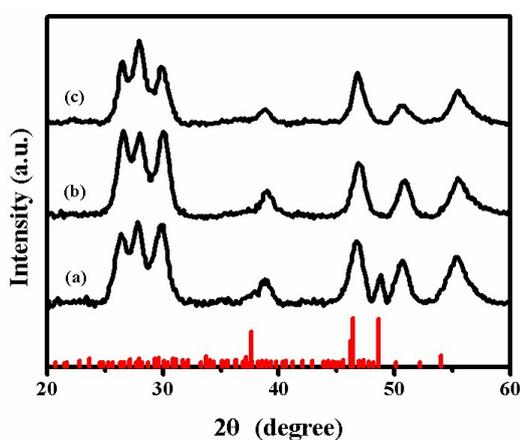


Fig. S10 XRD patterns of the nanocrystals obtained at 240°C at varying reaction times: t = 1 (a), 30 (b) and 60 min (c). Red lines are from standard JCPDS file [34-0660] for monoclinic Cu<sub>1.94</sub>S (djurleite).

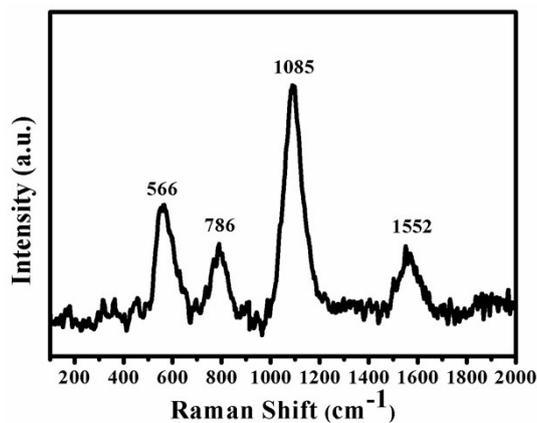
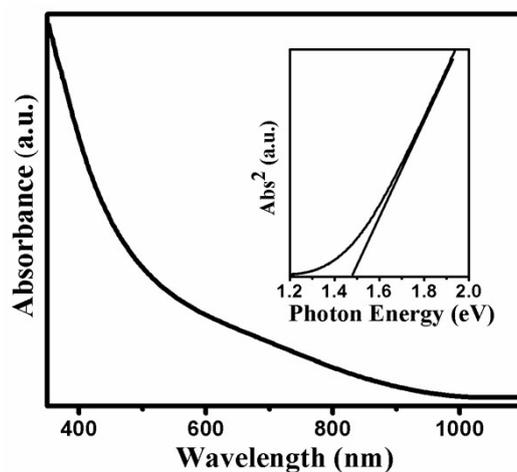
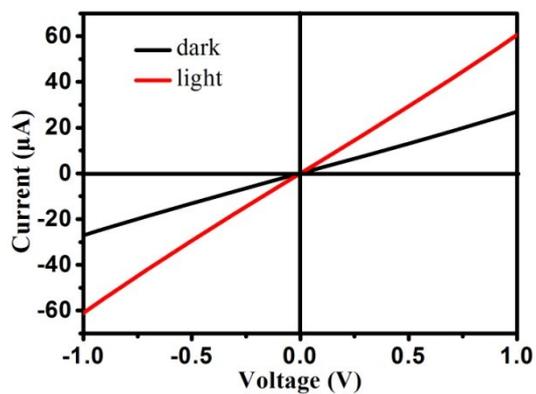


Fig. S11 Raman spectrum of the Cu<sub>3</sub>ZnInSnS<sub>6</sub> nanodisks.



**Fig. S12** UV-Vis-NIR absorption spectrum of wurtzite CZITS nanodisks. The inset displays a plot of the squared absorbance vs. photon energy.



**Fig. S13** The current–voltage ( $I-V$ ) curves of CZITS thin film: in the dark (black) and under simulated solar light illumination (red).

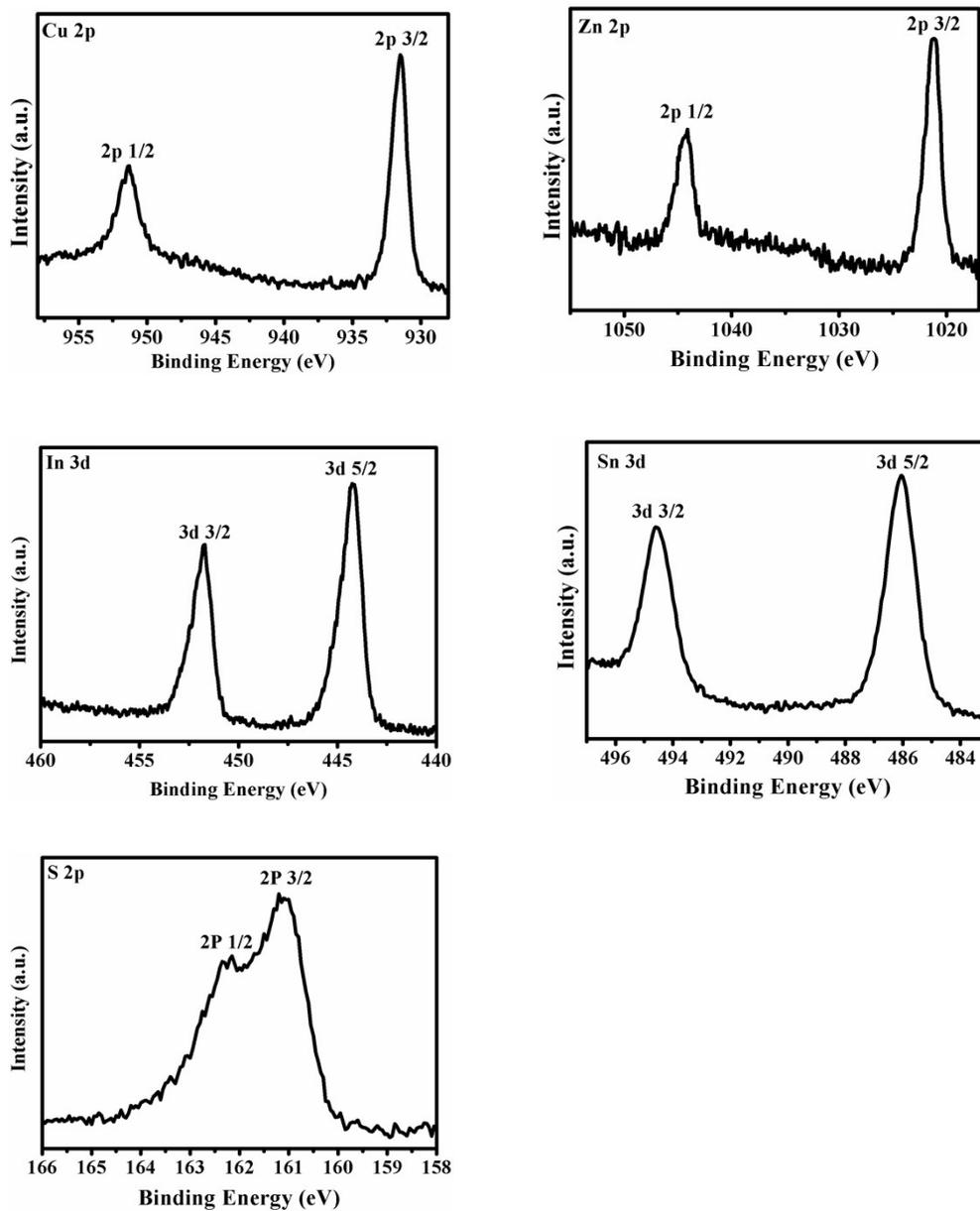


Fig. S14 XPS spectra of the CZITS nanodisks.

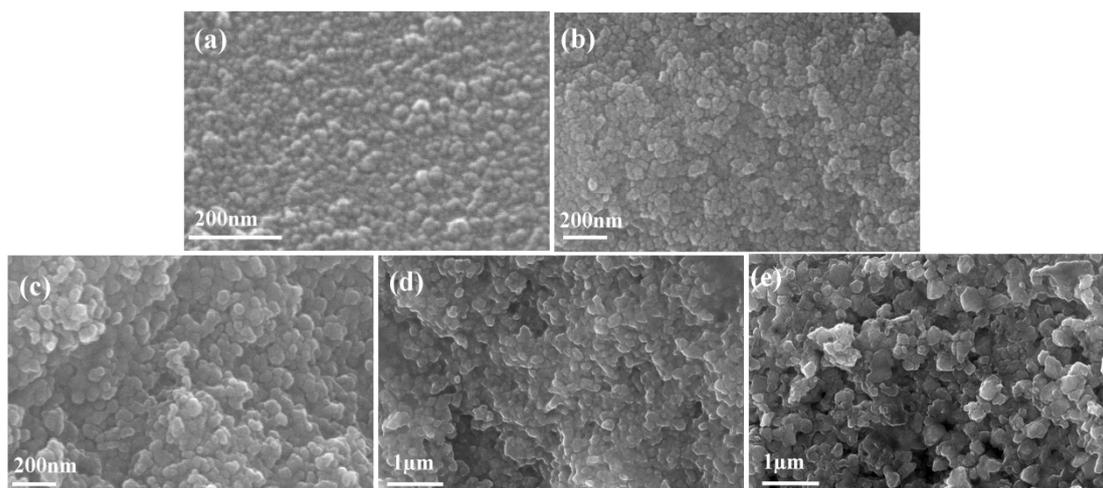


Fig. S15 SEM images of CZITS grains after annealing at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C for 5 min.

1. Larson, A.; Von Dreele, R. General Structure Analysis System (GSAS). Report LAUR 86-748; Los Alamos National Laboratory: Los Alamos, NM2004.