

## **Complete assembly of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) Nanorods at Substrate Interfaces Using a Combination of Self and Directed Organisation**

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**Chemicals.** Copper(II) acetylacetonate ( $\text{Cu}(\text{acac})_2$ , > 99.99%), Tin(IV) acetate ( $\text{Sn}(\text{OAc})_4$ , > 99.99%), Zinc acetate ( $\text{Zn}(\text{OAc})_2$ , > 99.99%), trioctylphosphine oxide (TOPO, > 99%), 1-octadecene (ODE, > 90% tech), 1-dodecanethiol (1-DDT, 98%), tert-dodecylmercaptan (t-DDT) were purchased from Aldrich. Tetradecylphosphonic acid (TDPA, >99%) was purchased from PCI Synthesis. All chemicals were used as received without any further purification.

**Synthesis of copper-poor CZTS nanorods.** CZTS nanorods were synthesized by using a modification of our previously published procedure.  $\text{Cu}(\text{acac})_2$  (0.1525 g), Zinc acetate (0.0735), Tin(IV) acetate (0.1165 g) and TOPO (0.6766 g) were mixed with 5 ml of ODE in a 25ml three-neck flask and evacuated at room temperature for 45 min. The solution was then heated to 250 °C in 10 min under an argon atmosphere, and at 156 °C, 1ml mixture of 1-DDT and 1.75 ml t-DDT in a ratio of 1:7 was injected into the flask. This resulted in an immediate color change from dark green to yellow and then finally to brown. After injection, the reaction was allowed to proceed for 30 min with continuous stirring. Subsequently, the heating mantle was removed, the reaction vessel was allowed to cool to 160 °C and the product was transferred to a sample vial without treatment.

**Formation of CZTS-DDTs assembled sheets.** 1 ml anhydrous toluene was added to 1 ml as-synthesized product solution, and vortexed for 1 min. 5 ml isopropanol was then added and this mixture was centrifuged at 4000 rpm for 5 min. The dark brown centrifuged product was collected and redispersed in 1 ml anhydrous toluene. The above procedure was repeated twice to yield CZTS close packed sheets in micrometer size.

**Electrophoretic deposition of CZTS-DDTs sheets.** As-synthesized CZTS nanorods were dispersed in anhydrous toluene with addition of isopropanol, forming floating sheets suspension. A field strength of 925 V/cm was applied (Using a high voltage power supply unit (TECHNIX SR-5-F-300, S/N: BU08/04971)) between two pieces of Si electrodes (25 mm × 10 mm, n-type, 2-4 ohm-cm) for 5 min, then the electrodes were slowly lifted from solution and allowed to dry slowly under toluene atmosphere. The dark brown colored CZTS film was formed on the positive side. The voltage was monitored using a Black star 3225 MP millimeter.

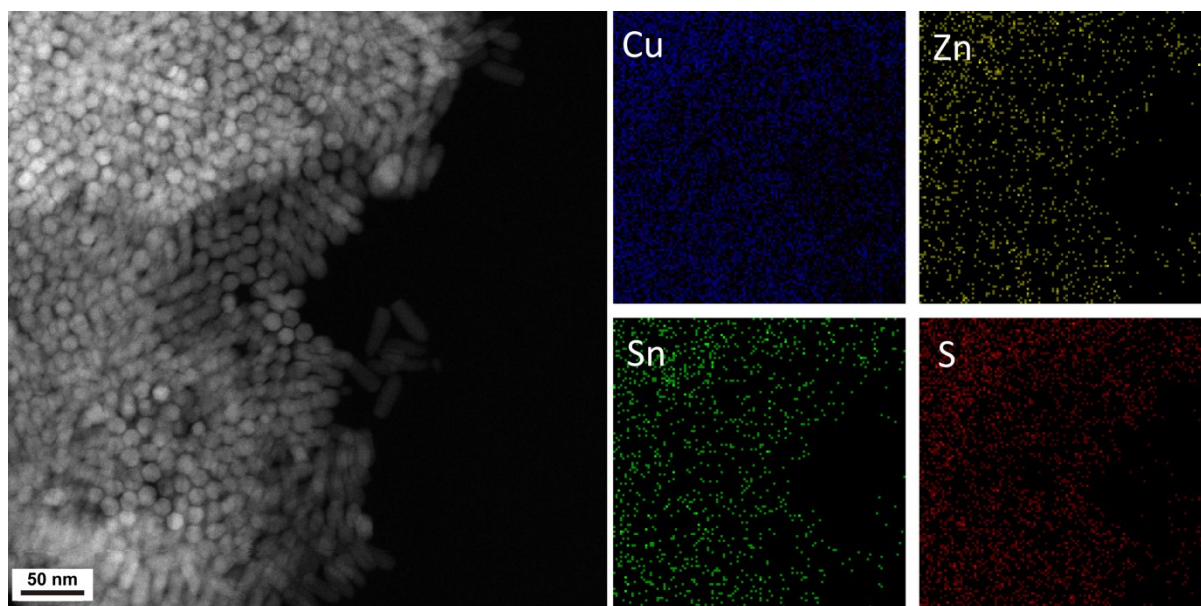
**Ligands exchange of CZTS-TDPA Nanorods.** 0.05 g TDPA was added into 1 ml as-synthesized product and this was sonicated in a water bath for 1 or 5 min. 1 ml isopropanol was added afterwards and centrifuged at 4000 rpm for 5 min. The centrifuge product was collected and redispersed in 1 ml n-hexane.

**Electrophoretic deposition of CZTS-TDPA nanorods.** CZTS-TDPA nanorods obtained from the above procedure dispersed in 1 ml hexane were used as electrolyte solution. The silicon substrates or molybdenum coated glass substrates (25 mm × 10 mm) were attached onto the electrodes which were 2.15 mm apart. The electrodes were immersed in a nanorod solution, and a potential of 300 V was applied to the substrate for 5 min, then dried in toluene atmosphere slowly.

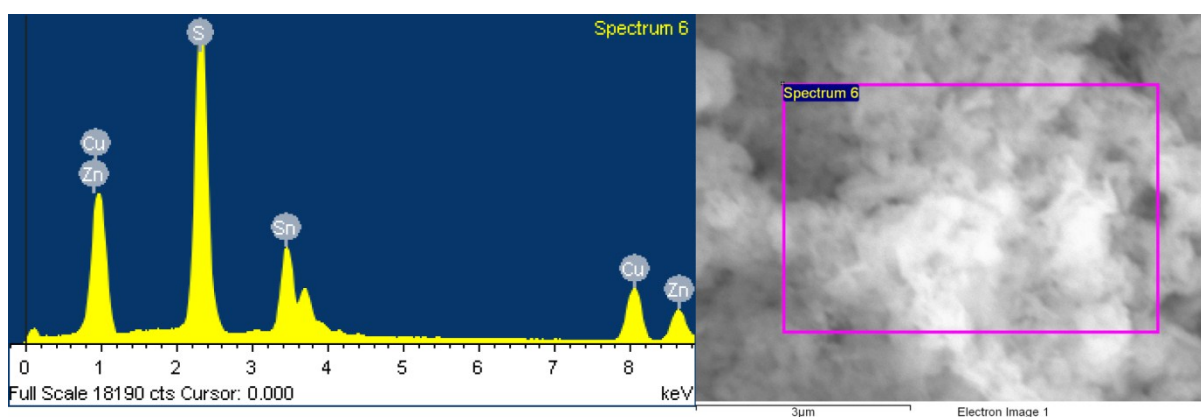
**Dynamic Light Scattering (DLS) measurements.** DLS measurements were performed by using Zetasizer Nano-ZS (Malvern Instruments, UK). Toluene solutions of rods were placed into a glass 1 x 1 cm rectangular cuvette and a specific amount of isopropanol was added prior to beginning.

**X-ray photoelectron spectroscopy (XPS).** XPS measurement of CZTS nanorods were carried out using a Kratos Axis 165 spectrometer. High resolution spectra were taken using

monochromated Al K $\alpha$  radiation of energy of 1486.6 eV at fixed pass energy of 20 eV. For peak synthesis, a mixed Gaussian-Lorentzian function with a Shirley type background subtraction was used. Samples were flooded with low energy electrons for efficient charge neutralization. Binding energies (BE) were determined using C 1s at 284.8 eV as the charge reference.



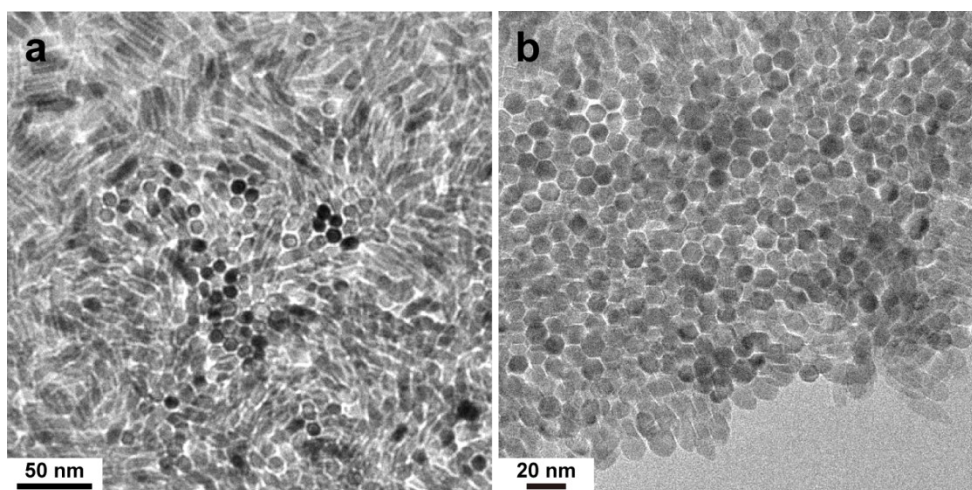
**Figure S1.** Dark field TEM image of aligned CZTS-DDTs sheets in three layers and the corresponding EDX mapping.



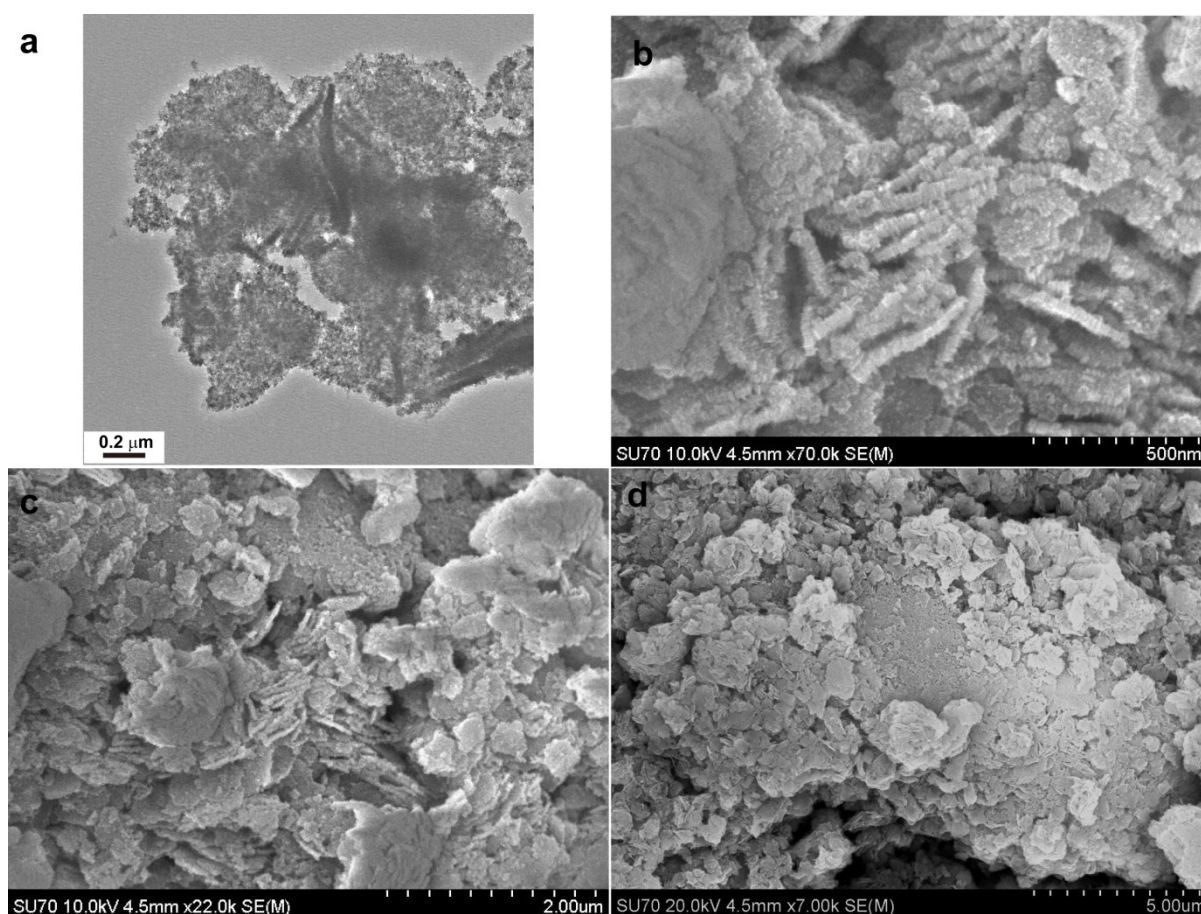
**Figure S2.** EDX spectrum and SEM image of pristine CZTS nanorods.

**Table S1.** The composition of copper-poor CZTS nanorods from SEM-EDX analysis.

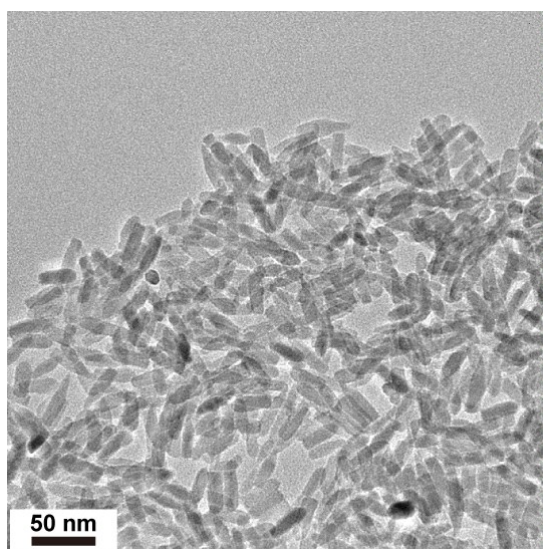
Atomic (%)	1	2	3	4	5	6	7	Average
Cu	21.5	19.90	19.56	20.94	20.24	20.60	20.06	20.4
Zn	14.8	13.9	13.72	14.51	14.15	14.86	14.27	14.32
Sn	12.95	13.04	12.94	12.94	13.02	12.78	12.82	12.93
S	51.2	53.16	53.79	51.61	52.59	51.76	52.85	52.45



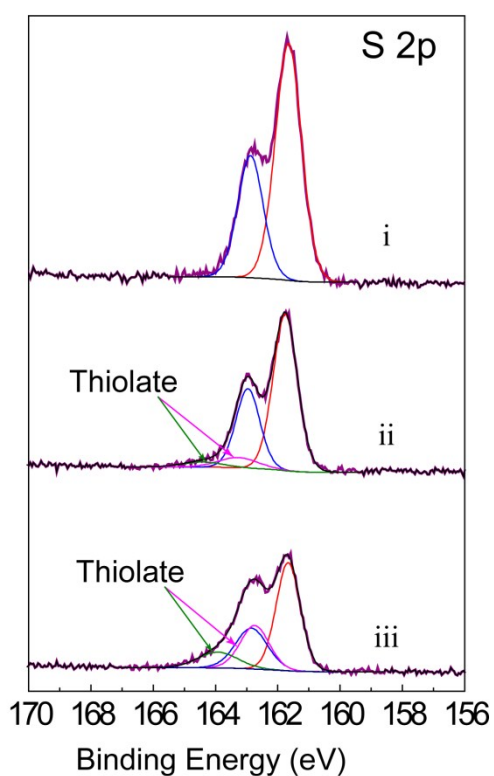
**Figure S3.** TEM image of (a) as-synthesized nanorods washed with 1:1 anhydrous toluene and isopropanol and (b) 1:2 ratio.



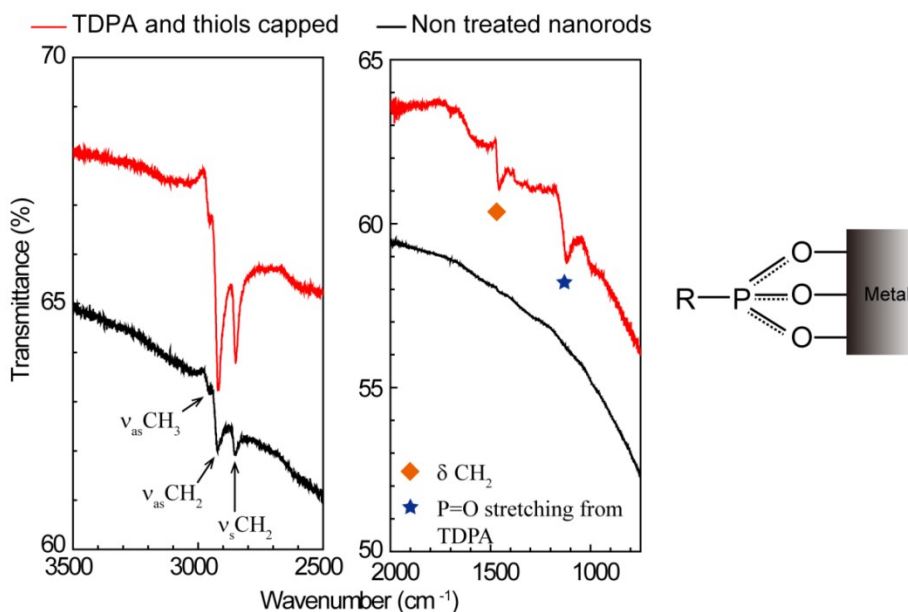
**Figure S4.** (a) TEM and (b-d) SEM images of CZTS assembled sheets. The sample was prepared by dropcasting supercrystals suspension directly on substrate.



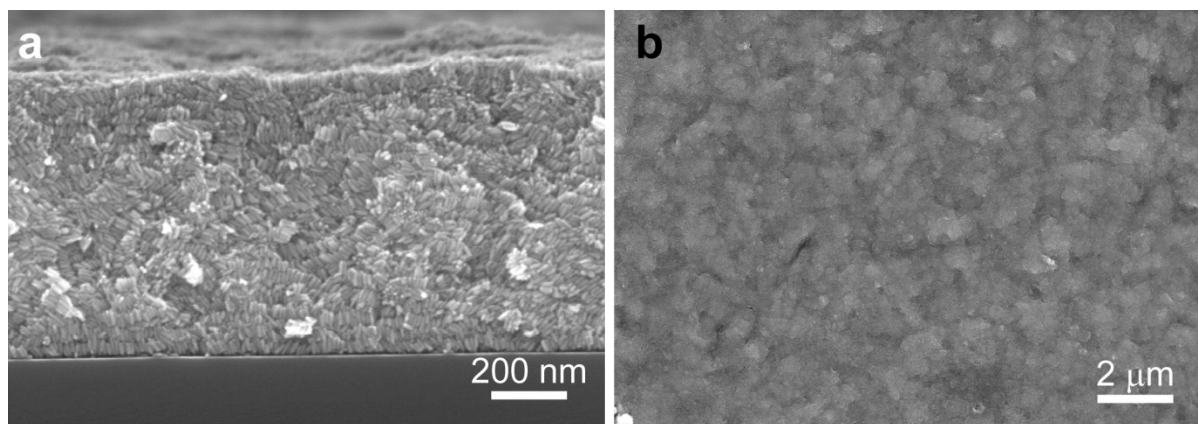
**Figure S5.** Dispersed nanorods obtained by breaking supercrystals with TDPA ligands.



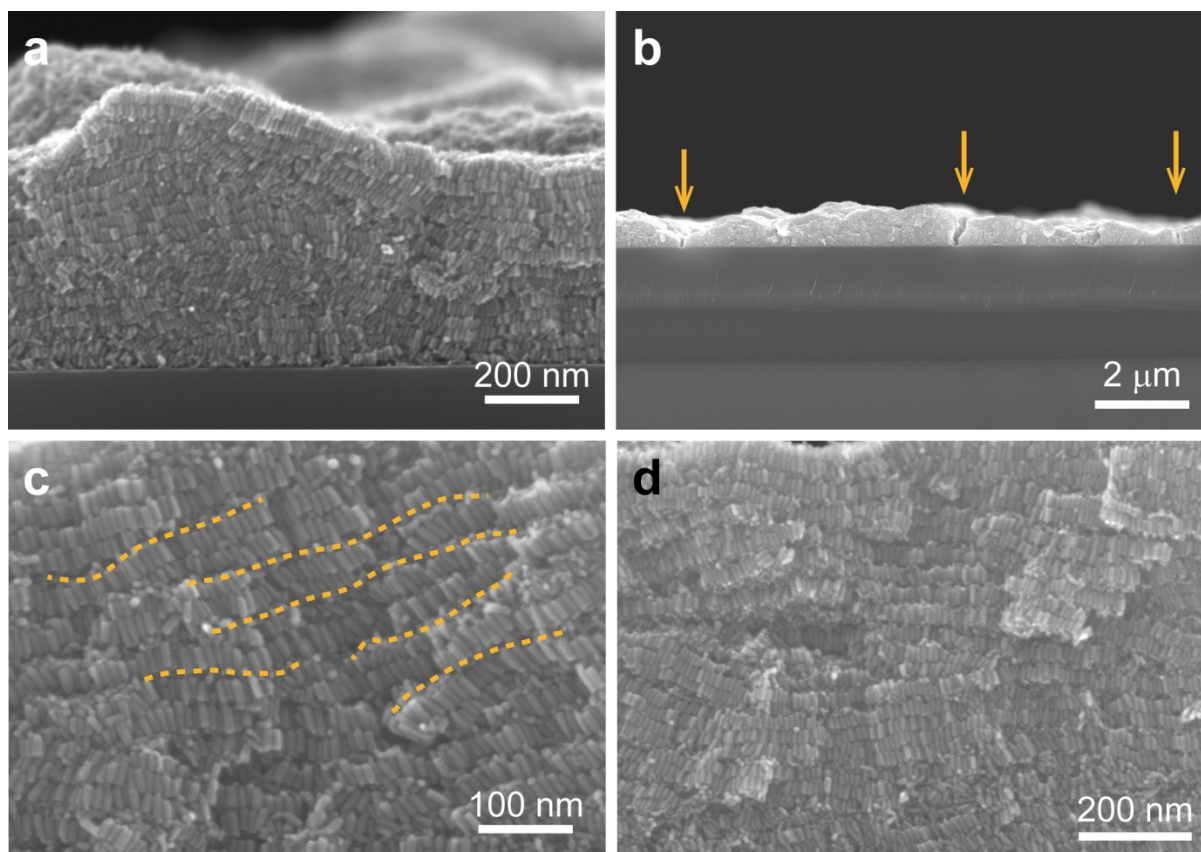
**Figure S6.** The high resolution XPS scan of the S 2p region. (i) non-treated nanorods with thiols and TOPO as capping ligands; (ii) and (iii) are same batch of sample treated with TDPA under sonication for 1 min and 5 min, respectively.



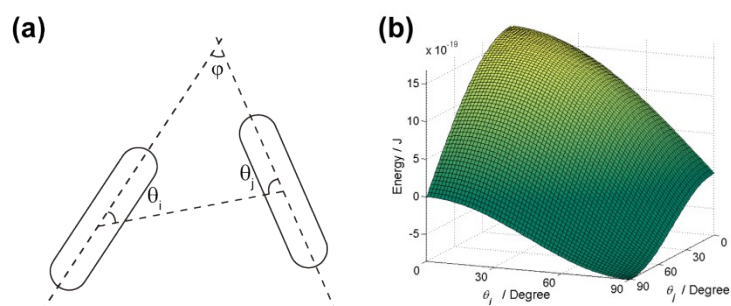
**Figure S7.** Fourier Transform Infrared Spectroscopy (FTIR) analysis of CZTS nanorods before and after ligand exchange with TDPA. Infrared absorption peaks characteristics of phosphine oxide (P=O) at  $1120 \text{ cm}^{-1}$  indicate that the surface of the nanorod is covered with TDPA as surfactant. This broad peak from  $1000 - 1200 \text{ cm}^{-1}$  contains P=O stretching peaks from P-OH and P-O-Metal. The drawing indicates the possible tri-dentate bonding formed by the phosphate group and metal.



**Figure S8.** (a) SEM of electrophoresis deposited film contains aligned CZTS-TDPA nanorods; (b) top view SEM image of crack free film.



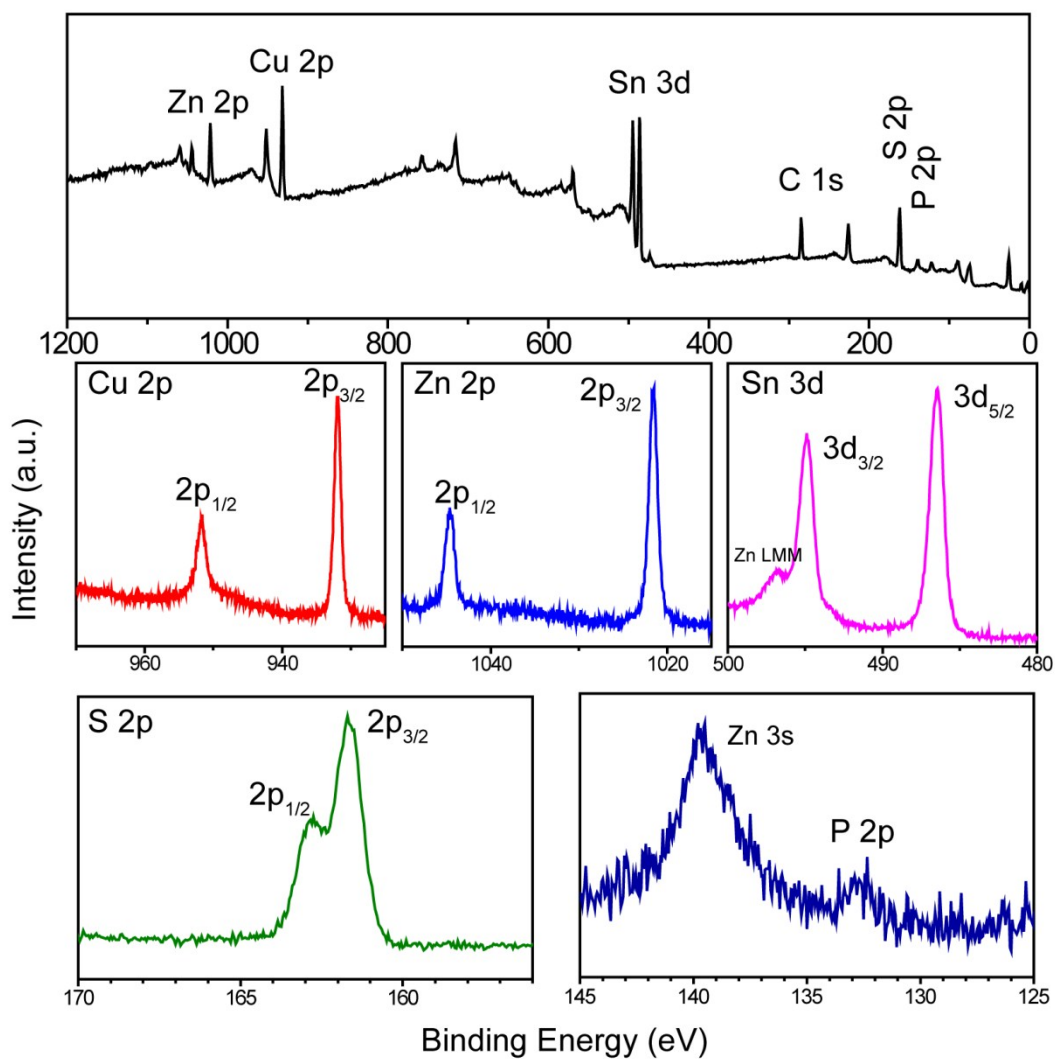
**Figure S9.** The SEM images demonstrate several defect issues occurred during electrophoretic deposition, such as rough surface (a), cracks (b) and separated layers (c-d).



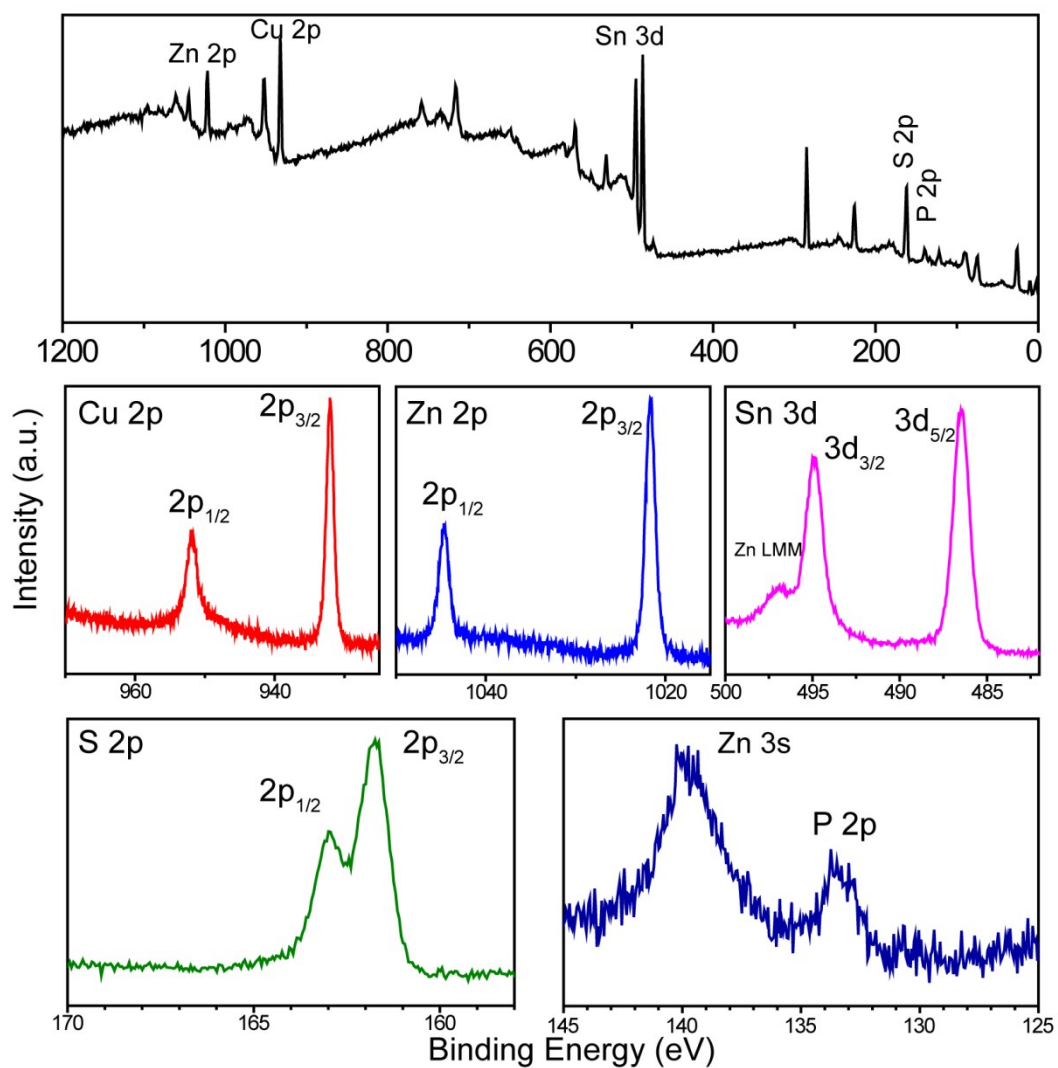
**Figure S10.** (a) The scheme of two randomly positioned rods; (b) The simulation plot of total energy as a function of  $\theta_i$  and  $\theta_j$  for self-assembled nanorods with  $0.2e$  net charge and distance of 4 nm. From the plot, the lowest state occurs when  $\theta_i = \theta_j = 90^\circ$ , which means two nanorods are parallel to each other.



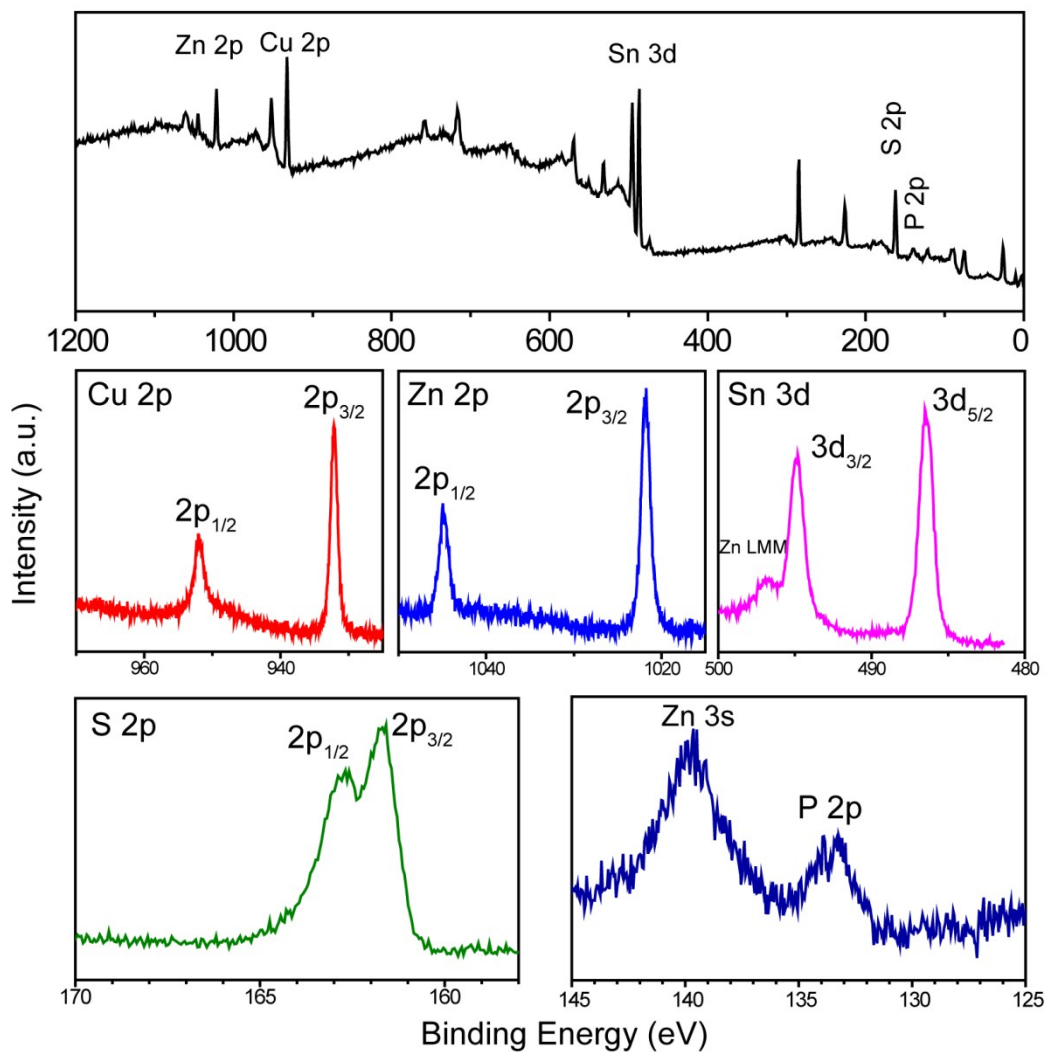
## X-Ray Photoelectron Spectroscopy (XPS) Characterization



**Figure S11.** XPS survey spectra of pristine CZTS nanorods (before ligand exchange).



**Figure S12.** XPS survey spectra of CZTS nanorods with TDPA treatment (sonication for 1min).



**Figure S13.** XPS survey spectra of CZTS nanorods with TDPA treatment (sonication for 5min).

## Orientation Distribution Function

A few assumptions need to be made: 1) the composition of rods is considered to be homogeneous, while the rods can only rotate around the body center point; 2) the rotation of the rod is not influenced by its neighbor or surface charge. However in the real system, the coupling from neighboring rods becomes apparent and cannot be negligible at high concentration. We consider a number of rods with aspect ratio  $\gamma$  and semi-long axis  $l$  are placed under external field  $E_\infty$  in toluene ( $\varepsilon = 2.38$ ). The Péclet number ( $Pe$ ) is denoted as a function of applied field: [1]

$$Pe = \frac{32\pi\varepsilon l^3 E_\infty^2}{kT \log(2\gamma)} \quad (S1)$$

Where  $\varepsilon$  is the permittivity of the fluid,  $k$  is Boltzmann's constant and  $T$  is room temperature. The orientation distribution function (ODF) of rods under different values of  $Pe$  is given by the following normalization:

$$\Psi(\phi) = A \exp\left(\frac{Pe}{96} G_{\parallel} G_{\perp} \cos 2\phi\right) \quad (S2)$$

$$\int_0^{\pi} \Psi(\phi) \sin \phi d\phi = 1 \quad (S3)$$

Where  $A$  is a constant derived from normalized condition Eq. 3,  $G_{\parallel}$  and  $G_{\perp}$  are the geometric tensor relative to the surface of rods determined by  $\gamma$  for elongated particle, and  $\phi$  is the angle between the orientation of the rods and the field direction.

$$G_{\parallel} = \frac{e^3}{2e - (1 - e^2) \log\left(\frac{1+e}{1-e}\right)} \quad (S4)$$

$$G_{\perp} = \frac{2e^3}{e + (1 - e^2) \left( \log\left(\frac{1+e}{1-e}\right) - 2e \right)} \quad (S5)$$

$$e = \sqrt{1 - \frac{1}{\gamma^2}} \quad (S6)$$

Because the permanent dipole is a function of  $\gamma$  and of the dielectric constant of nanorods and solvents, the orientation distribution function can also be derived as a function of dipole moment. The rods are assumed to be randomly orientated and positioned within suspension when no field is applied ( $Pe = 0$ ), and as  $Pe$  increases the alignment of rods along field direction becomes stronger.

## References

[1] D. Saintillan, E. Darve, and E. S. G. Shaqfeh, *J. Fluid Mech.*, 2006, **563**, 223.

