Electronic Supplementary Information (ESI)
for

Rounded Cu2ZnSnS4 Nanosheet Networks as Cost-effective Counter Electrode for High-Efficiency Dye-Sensitized Solar Cells

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Experimental Section

Materials

Copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$), ethanol, and acetonitrile were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) in analytical purity. Tin (II) sulfate ($SnSO_4$), zinc (II) sulfate monohydrate ($ZnSO_4.H_2O$), sodium thiosulfate ($Na_2S_2O_3$), sodium citrate dihydrate ($Na_3C_6H_7O_6.2H_2O$), lithium perchlorate ($LiClO_4$), lithium iodide (LiI), and iodine were purchased from Aladdin Industrial Corporation (China) in analytical purity. FTO glass conductive substrate (sheet resistance 7-8 Ω sq^{-1}), N719 dye (0.3 mM $(Bu_4N)_2[Ru(dcbpyH)_2(NCS)_2]$), and electrolyte (DHS-Et23) were obtained from OPV Tech Co., Ltd (China), Dyesol (Australia), and HeptaChroma (China) respectively. All chemicals in the experiments were used as received. Distilled water was used throughout the work.

Fabrication of CZTS counter electrodes (CE)

A film of CZTS plate arrays was in-situ grown on a FTO conductive substrate, first by using electrodeposition followed by adopting a novel solvothermal treatment (as shown in Figure S1). In the electrodeposition process, metallic precursors of Cu, Sn, and Zn (CZT) films were electrodeposited on a FTO conductive substrate simultaneously. The CZT composite layer was deposited at -1.17 V (vs. SCE) for 150

s using an electroplating bath containing 3.5 mM copper sulfate pentahydrate ($CuSO_4.5H_2O$), 2.1 mM tin sulfate ($SnSO_4$), 20 mM zinc sulfate monohydrate ($ZnSO_4.H_2O$), and 50 mM sodium citrate dihydrate ($Na_3C_6H_7O_6.2H_2O$). The deposition temperature was kept at 24 ^oC and the exposed geometric area of FTO substrate (2×1.5 cm^2) was 1.5×1.5 cm^2. After electrodeposition, the CZT precursor film was soaked in distilled water and dried at 70 ^oC in air. The obtained CZT film on FTO was converted to the CZTS film via a novel solvothermal treatment. In a typical solvothermal treatment, the CZT film (with conductive area facing down), 35 ml ethanol and 2 mM (0.3162 g) excessive sodium thiosulfate powders were put into a 50 ml Teflon-lined autoclave successively. The autoclave was then maintained at 200 ^oC until the CZT precursor film had been reacted in adequate. After conversion process, the obtained dark grey film was washed with ethanol and dried at 70 ^oC. Finally, CZT particles film on FTO was converted to rounded CZTS nanosheet networks without any post heat treatment. Pt CE was purchased from Dyesol (Australia) for comparison. In details, Dyesol's PT1 platinum paste was oil-based and formulated for screen printing using a synthetic 100 T mesh screen (or similar). After drying, this paste was under annealing at or above 420 °C.

Assembly of the DSSCs

For a fair comparison, all the DSSCs were fabricated with TiO_2 photoanode materials relying on a standardized fabrication process. Firstly, the clean FTO substrate was subjected to $TiCl_4$ aqueous solution (0.05 M) treatment for the duration of 30 min at 70 ^oC. A commercial TiO_2 paste (P25, Degussa, Germany) was then coated on above pre-treated FTO substrate by doctor blading method. A portion of 0.20 cm^2 was selected as the active photo-anode area. The TiO_2-coated FTO glasses were gradually heated to 500 ^oC (rate=2 ^oC/min) in air and subsequently sintered at that temperature for 30 min to create TiO_2 film. The total thickness of the TiO_2 film was about 18 μm. After the heat treatment, the substrate was subjected to $TiCl_4$ aqueous solution treatment again to acquire more dye absorbing. Thereafter, the 80 ^oC baked electrode was immersed in solution, containing 0.3 mM N719 dye in anhydrous ethanol for 24 h at room temperature under dark condition. The TiO_2 electrode was coupled with one of the various CEs (CZTS and commercial Pt) to fabricate the DSSCs. The electrolyte was injected into the gap between the two electrodes by capillarity, and the hole was sealed with hot-melt glue after the electrolyte injection.

Characterization

The crystalline phase and purity of CZTS samples were examined by a X-ray diffractometer (RIGAKU, Smartlab TM9 KW, Cu Kα radiation at λ=1.541 Å,) operated at 40 kV/200 mA, and a confocal Raman microscope (Renishaw, inVia) using the 488 nm laser line of an air cooled Ar-ion laser. The optical images were taken by digital camera. The morphologies of synthesized nanostructures were observed by using field-emission-scanning electron microscopy (FE-SEM, HITACHI, SU-4800). Energy-dispersive spectroscopy (EDS) from FE-SEM was used for the elemental analysis of the CZTS films. The detailed nanostructures and crystal

structure were further investigated by a transmission electron microscopy (TEM, FEI Tecnai G2), coupled with selected area electron diffraction (SAED). The thin films were scraped from their substrates and dispersed in ethanol to form the suspensions for TEM observation. The assembled DSSCs were illuminated by a solar simulator (94042A, AM1.5 G, Newport, America), and the incident light intensity (100 mW/cm^2) was calibrated with a standard Si cell (91150V, Newport, America), so as to measure the J-V curves of the solar cells devices. The Cyclic voltammetric (CV) measurements were performed at a scan rate of 100 mV s^{-1} in acetonitrile solution consisting of 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$ in a three-electrode system, by using CHI 660E potentiostat, in which the as-fabricated CEs acted as the working electrode, in addition to a Pt sheet (6 cm^2) counter electrode and a Ag/Ag^+ (CHI 112) couple served as a reference electrode. Tafel polarization curves were obtained using symmetrical cells, at 10 mV s^{-1}, using a CHI 660E potentiostat with a two-electrode system. The symmetrical cell contained two identical electrodes and the film area was confined to be 0.25 cm^2. The two electrodes were separated by a 60 μm thick Teflon tape. The EIS tests of the symmetric thin layer CEs were carried out in the frequency ranging from 0.05 to 10^6 Hz at 0 V bias with perturbation amplitude of 5 mV, under dark condition, using a system of Solartron Sl 1260 and 1287 (Electrochemical interface, the United Kingdom). The impedance spectra were analyzed using equivalent circuit models by Zview fitting software.

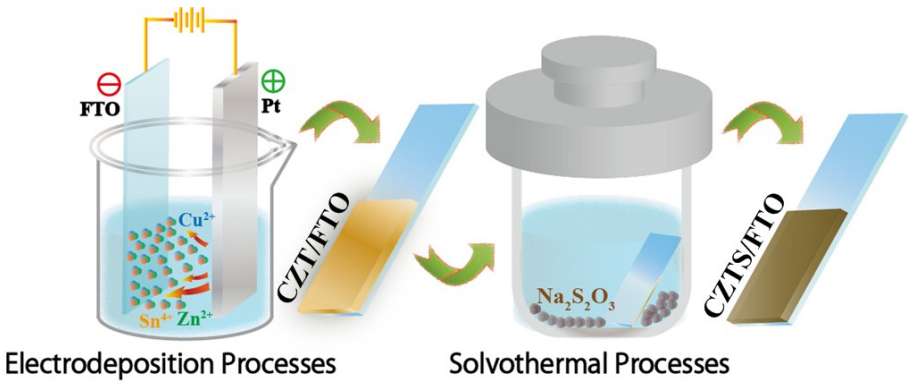

Figure S1. Schematic illustration of the fabrication processes of CZTS CE using $Na_2S_2O_3$ as sulfur resource.

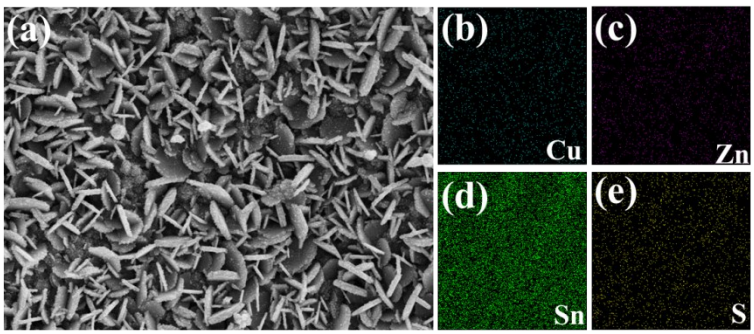

Figure S2. (a) FE-SEM images of rounded CZTS nanosheet networks on FTO substrate. (b-e) EDS mapping of Cu, Zn, Sn and S showing the homogeneous element

distribution. The Sn signal is larger than the other element signal for (d) due to the contribution from the SnO/TCO layer, and is not completely representative of the CZTS nanosheet distribution.

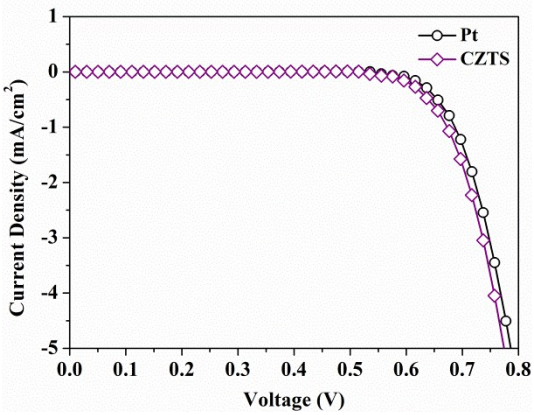

Figure S3. Photovoltaic performances of DSSCs with Pt and CZTS CE, measured under dark condition.

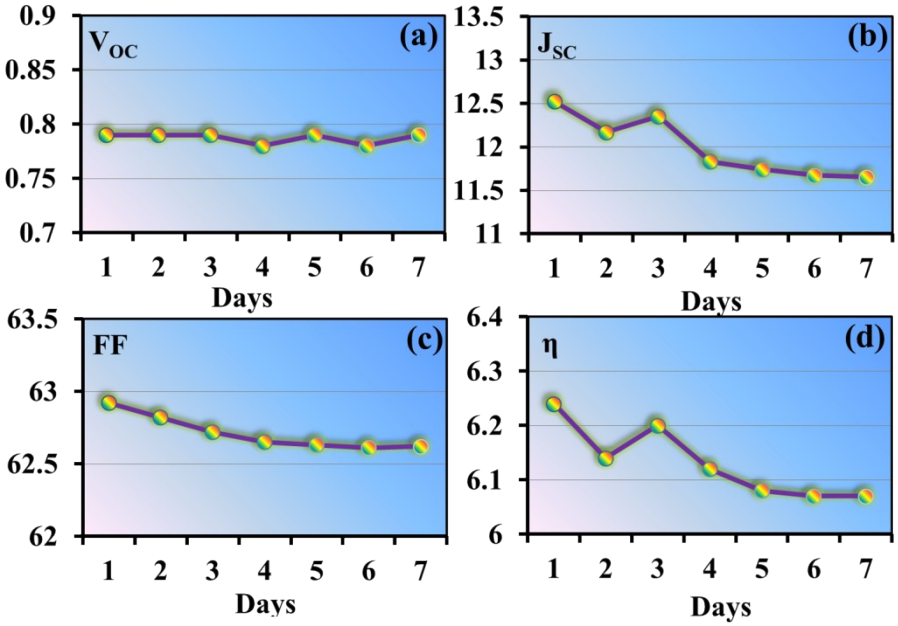

Figure S4. Long-term stability test for DSSCs based on CZTS CE.

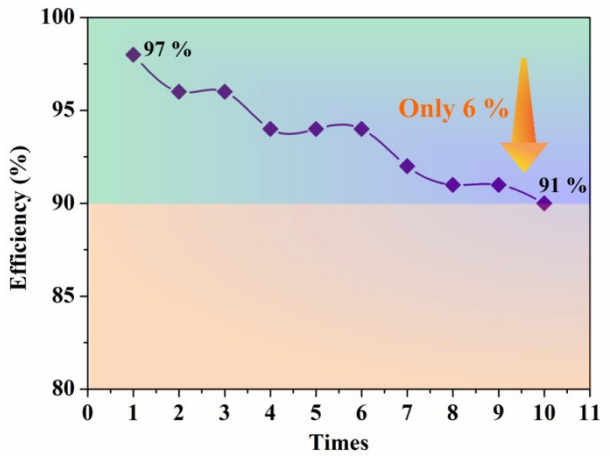

Figure S5. Mechanical stability measurements of DSSCs after repeated peel-off experiment.

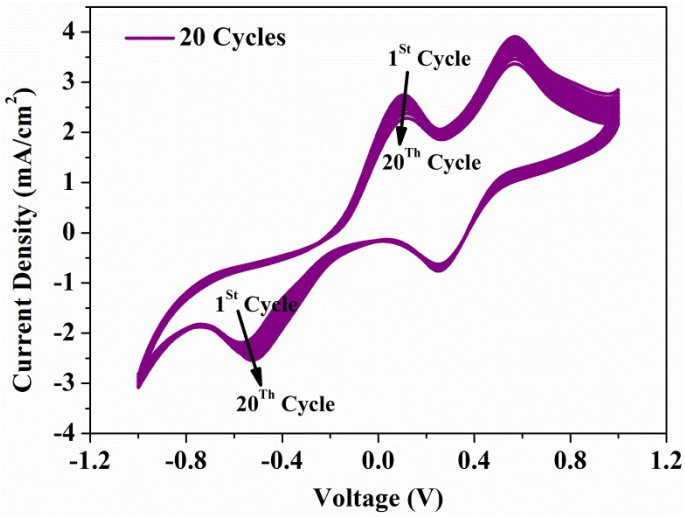

Figure S6. Cyclic voltammograms of CZTS electrodes measured in the condition of 20 cycles scanning.

Table S1. Comparison with the photoelectrochemical performance of DSSCs using various CE.

CE	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
Aligned CZTS nanoplates on FTO[1]	0.68	10.27	0.55	3.65
Pt[1]	0.69	8.72	0.54	3.33
CZTS nanofibers on FTO[2]	0.57	8.42	0.65	3.90
Pt[2]	0.62	4.66	0.57	1.72
CZTS graphene composite on FTO[3]	0.71	16.77	0.65	7.81
Pt[3]	0.70	16.79	0.56	6.66
CZTS ultrathin film on FTO[4]	0.65	14.54	0.59	5.63
Pt[4]	0.65	11.99	0.69	5.44
Porous CZTS thin film on FTO[5]	0.59	3.03	0.68	1.23

Pt[5]	0.69	2.47	0.67	1.15
200-300 nm $Cu_2ZnSnSe_4$ nanoparticles on FTO[6]	0.78	10.39	0.47	3.85
Pt[6]	0.70	12.23	0.47	4.03
CZTS film on FTO with big grain size[7]	0.74	17.20	0.62	7.94
Pt[7]	0.73	18.30	0.63	8.55
Hierarchical CZTS structures on FTO[8]	0.74	14.26	0.66	6.98
Pt[8]	0.71	14.30	0.68	6.91
CZTS nanoflakes on FTO substrate[9]	0.65	18.63	0.53	6.40
Pt[9]	0.62	18.18	0.74	8.30
Rounded CZTS nanosheet networks on FTO substrate	0.79	12.52	0.62	6.24
Pt	0.76	12.90	0.61	6.01

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Table S2. Electrochemical parameters of Pt and CZTS CE.

CE	R_S (Ω/cm^2)	R_{Ct} (Ω/cm^2)	C_μ (μF)	ΔE_P (V)
CZTS	12.44	4.82	11.94	0.60
Pt	4.67	7.17	13.92	0.71