Electronic Supporting Information

Nanostructured flower-shaped $CuCo_2S_4$ as a Pt-free counter electrode for dye-sensitized solar cells

Methods

Materials

All chemicals, reagents and solvents were purchased from commercial sources and unless otherwise stated were used without purification. Fluorine-doped tin oxide (FTO) coated glass substrates with 2.2 mm thickness and surface resistivity ~ 7 Ω/sq, TiO_2 paste (Dyesol(R) 18NR-AO Titania Paste) and N719 dye (Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)) were purchased from Sigma-Aldrich. Redox electrolyte (MPN-based triiodide / iodide electrolyte Dyenamo DN-OD05) and Pt paste (Dyenamo DN-EP01) were purchased from Dyenamo.

Preparation of nanostructured flower shaped $CuCo_2S_4$ grown TCO substrate

FTO substrates were cleaned by 20 min sonication in soap, water, acetone, 0.1 M HCl and kept in ethanol.

The synthesis of ternary $CuCo_2S_4$ on FTO substrate was done following a solvothermal method. $CoCl_2 \times 6H_2O$, $CuCl_2 \times 2H_2O$ and Thiourea with 1:2:8 ratios were dissolved in ethanol (60 mL) to obtain a deep blue colored solution and stirred for 1 h at room temperature. Then the solution was transferred to 100 mL Teflon liner, a cleaned FTO substrate was placed against the wall of Teflon liner and it was sealed in a stainless steel reactor. The reactor was heated at 200^{o}C for 4 h before naturally cooling. The FTO substrates were removed from Teflon liner, washed with ethanol, distilled water and dried at 70^{o}C for 5 h.

Fabrication of dye-sensitized solar cells

The photoanode was prepared by doctor blading TiO_2 paste over the FTO glass substrate which was pre-treated with 50 mM $TiCl_4$ solution at 70^{o}C for 30 min. The applied paste was air dried for 2 h and sintered at 125^{o}C, 325^{o}C, 425^{o}C and 500^{o}C for 5, 10, 15, 30 min, respectively. When the electrodes were cooled to 80^{o}C they were placed in a 0.285 mM solution of N719 dye in ethanol and kept at ambient temperature in the dark for 22 h before rinsing with ethanol and drying with N_2.

The reference Pt counter electrode was prepared by doctor blading Pt paste on clean and dry FTO glass substrate and sintering at 500^{o}C for 30 min.

The photoanodes and counter electrodes were assembled in a sandwich type configuration via double side tape, placing triiodide / iodide based electrolyte in between.

Characterization

The prepared nanostructured flower shaped ternary $CuCo_2S_4$ electrode was characterized with Scanning Electron Microscope (Auriga Crossbeam 540 Carl Zeiss) equipped with Energy Dispersive X-Ray Spectroscopy (EDX). X-Ray Diffraction and Raman spectrums were obtained from Rigaku SmartLab® X-ray diffraction (XRD) and Horiba LabRam Evolution Raman Spectroscopy with 532 nm laser beam. The XRD and Raman spectrums of the nanostructured flower shaped $CuCo_2S_4$ are shown in Figure S4 and Figure S5. Isothermal adsorption / desorption curves and pores size distribution were obtained using N_2 porosimeter at 77.35 K with prior degassing the samples at 110^oC for 8.5 h. The adsorption / desorption isotherms and pore size distribution curves are shown in Figures S6 and S7, respectively.

Photovoltaic measurements were carried out on Dyenamo Toolbox (DN-AE01). At least five devices (replicates) were measured for each sample and the reported value is the average of all devices (replicates). The deviation from the mean value is calculated using the formula of standard deviation. The electrochemical analysis were done using IM6 Zahner Elektrik electrochemical station under dark condition with -0.72 V bias, 0.1 – 100000 Hz frequency range and 10 mV amplitude. The working electrode of the EIS was connected to the photoanode of the DSSCs and the counter / reference electrodes of the instrument were connected to the CE of the analyzed solar cells. The obtained data were fitted using EIS Spectrum Analyzer [1] and an equivalent electrical circuit presented at Figure S5. Symmetrical dummy cells were constructed by face-to-face alignment of two identical counter electrodes with electrolyte in between. Their electrochemical impedance and Tafel polarization analysis were obtained on IM6 Zahner Elektrik electrochemical station. For the dummy cell EIS analysis, the dummy cells were analyzed under dark condition with 0 V bias, 0.1 – 100000 Hz frequency range and 10 mV amplitude, whereas for Tafel plot the scan rate was 5 mV/s. The IPCE analysis was carried out on IPCE toolbox from Dyenamo (DN-AE02).

Table S1 Elemental composition of nanostructured flower shaped $CuCo_2S_4$

Elements	Wt % calculated from EDX	Wt % of actual $CuCo_2S_4$
Cu	20.30±0.19	20.52
Co	38.61±0.19	38.06
S	41.09±0.12	41.41

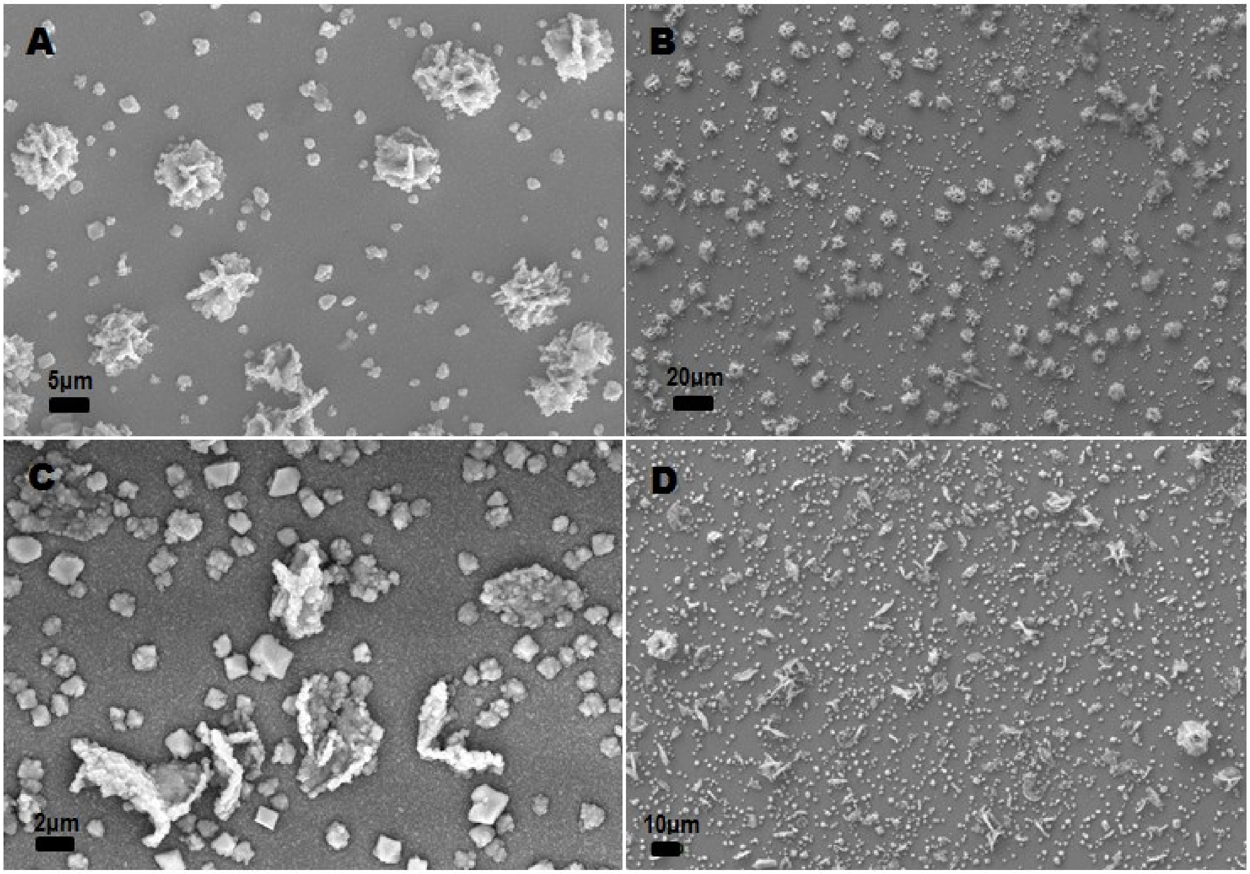

Figure S1 SEM images of the products formed at 8 h (A-B) and 12 h (C-D)

Table S2 EDX derived elemental composition of the products obtained at 8 and 12 h

Elements	Wt % for 8 h	Wt % for 12 h
Cu	14.16±0.23	12.19±0.22
Co	47.54±0.32	44.47±0.30
S	38.30±0.18	43.33±0.18

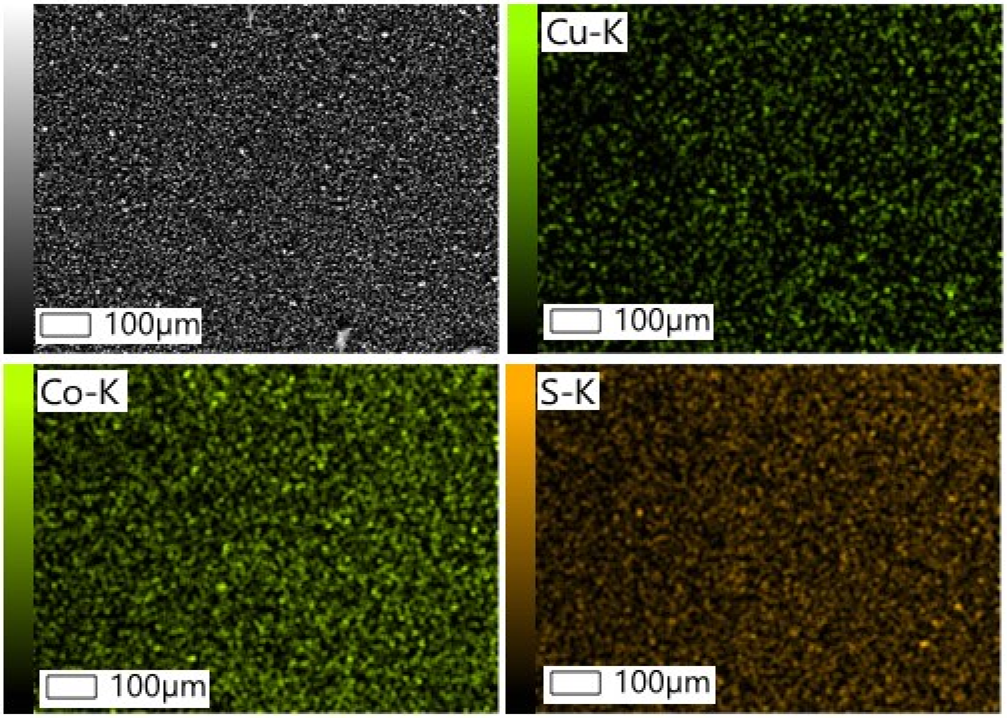

Figure S2 EDX mapping of the product formed at 8 h

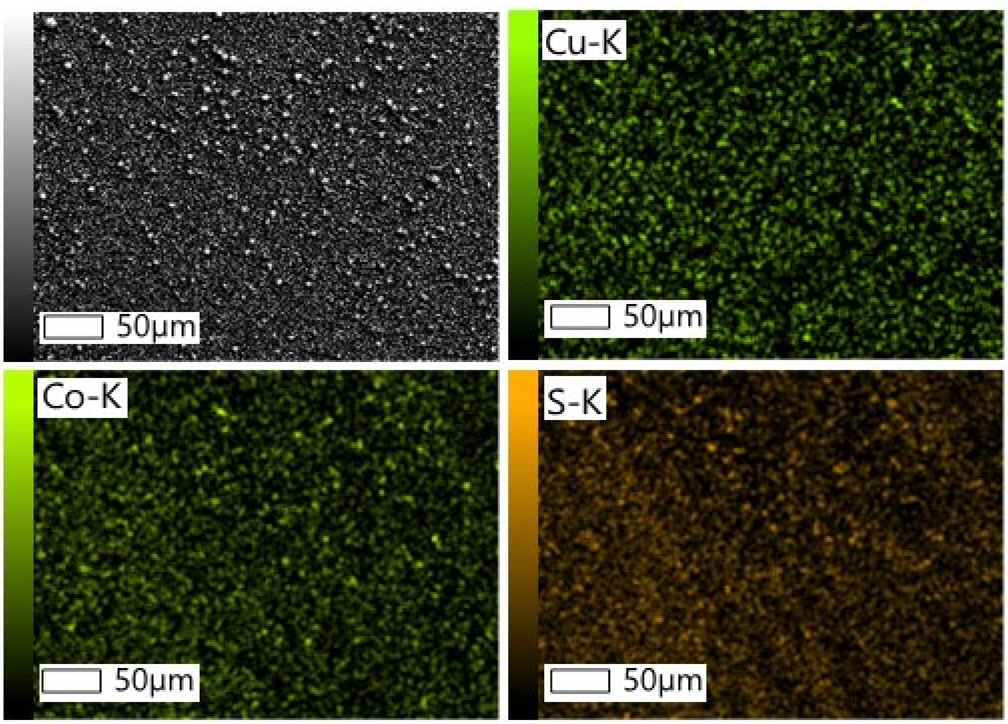

Figure S3 EDX mapping of the product formed at 12 h

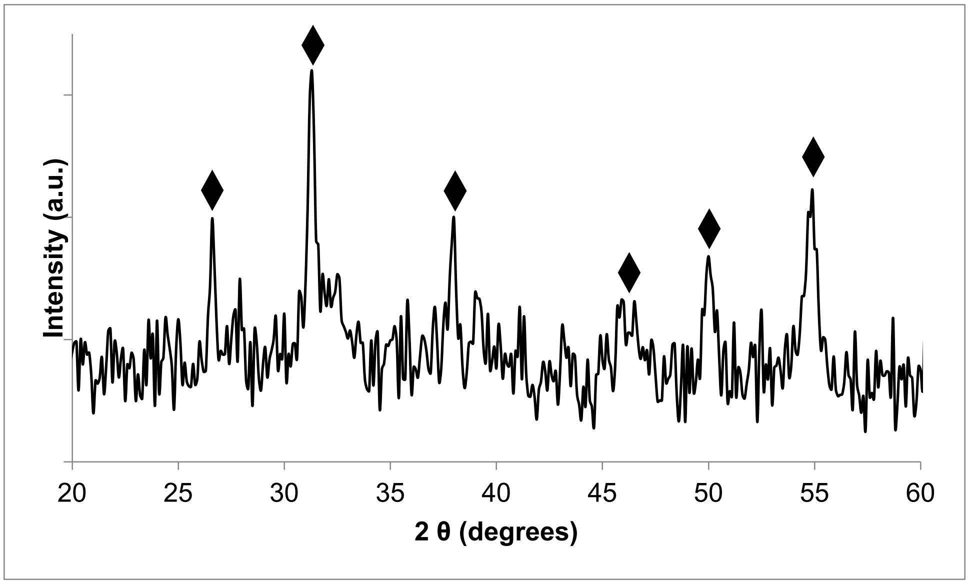

Figure S4 XRD spectrum of nanostructured flower shaped $CuCo_2S_4$

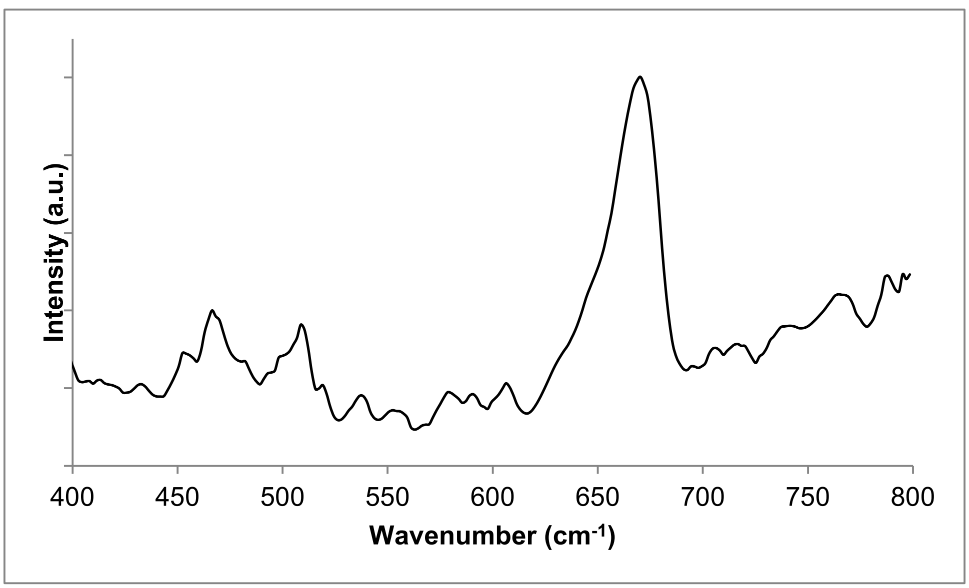

Figure S5 Raman spectrum of nanostructured flower shaped $CuCo_2S_4$

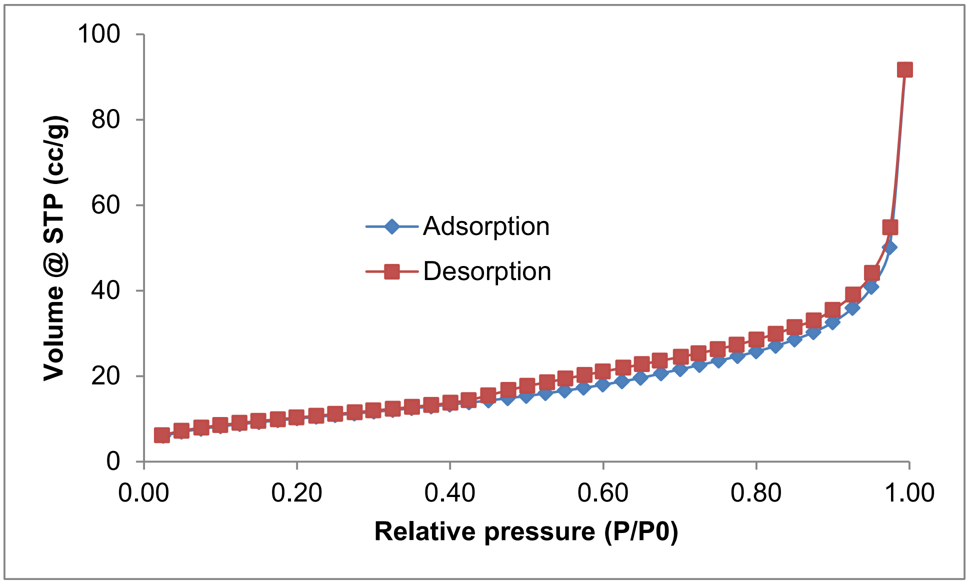

Figure S6 Isothermal N_2 adsorption / desorption curves of nanostructured flower shaped $CuCo_2S_4$

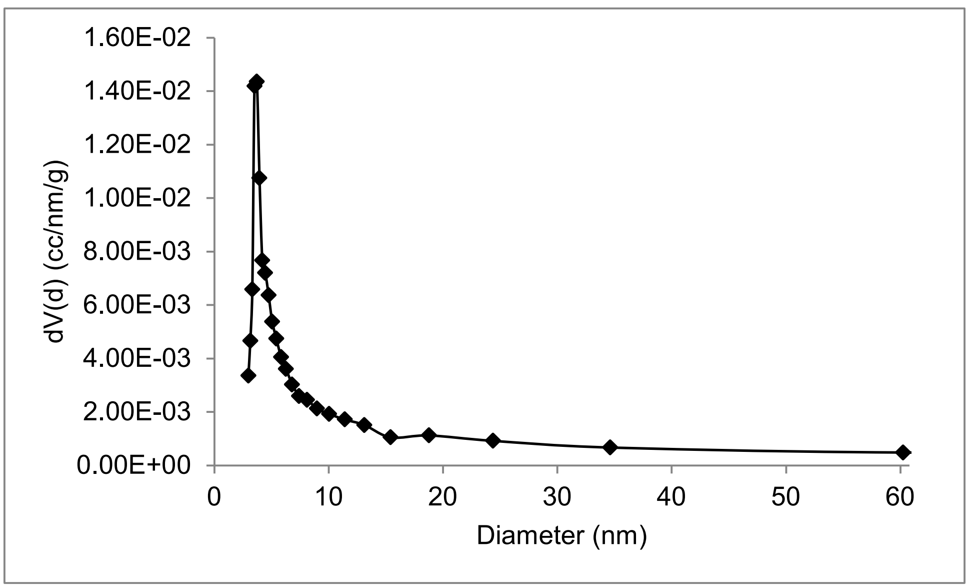

Figure S7 BJH pore size distribution of nanostructured flower shaped $CuCo_2S_4$

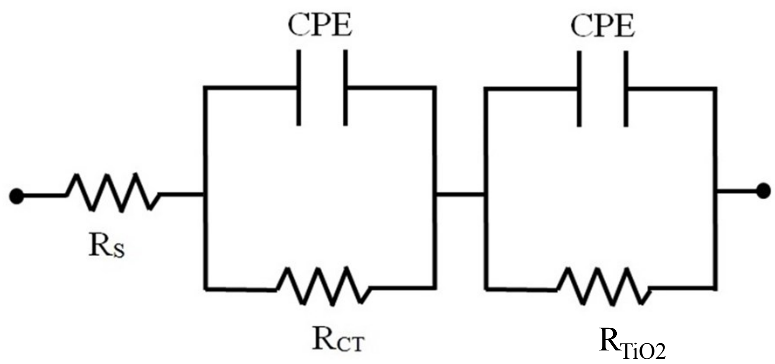

Figure S8 Equivalent electrical circuit used for fitting EIS data

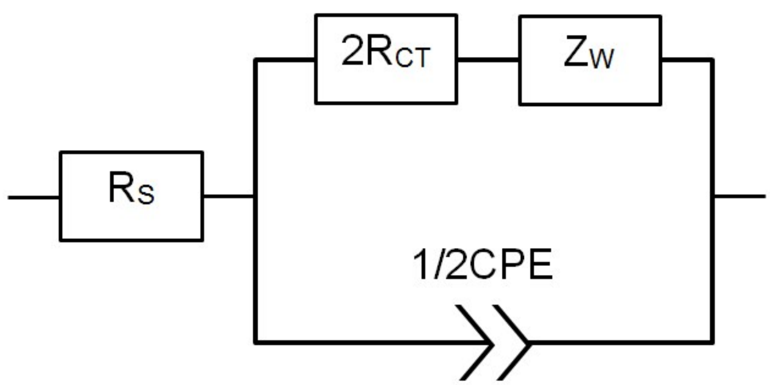

Figure S9 Equivalent electrical circuit used to fit electrochemical impedance spectroscopy data of symmetrical dummy cells

Table S3 Photovoltaic parameters of $CuCo_2S_4$ and Pt cells for rear side irradiation at 100 mW/cm^2

DSSCs	Eff (%)	Voc (V)	Jsc (mA cm^{-2})	FF
$CuCo_2S_4$	4.24±0.33	0.72±0.00	7.93±0.77	0.74±0.02
Pt	5.26±0.42	0.72±0.00	10.27±1.04	0.71±0.02

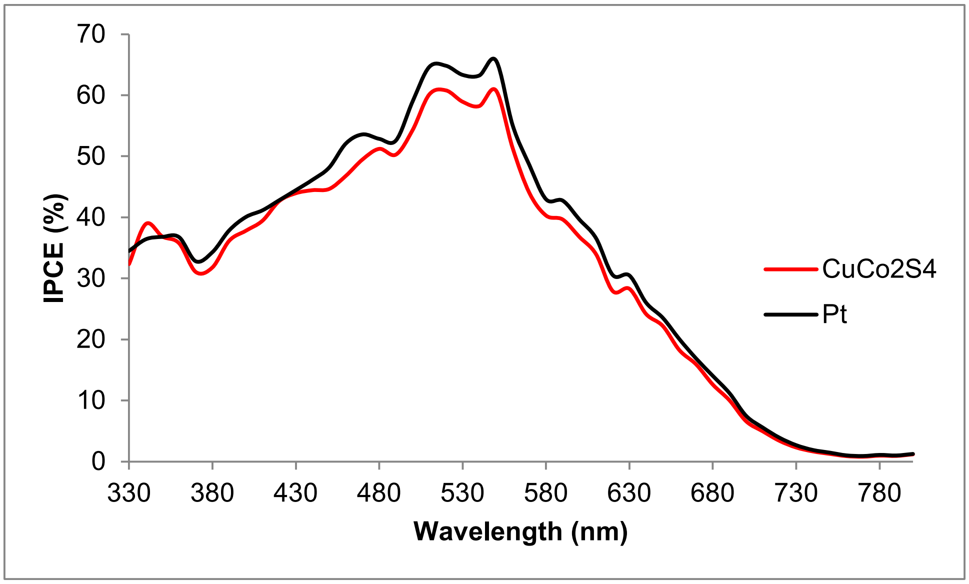

Figure S10 IPCE of DSSCs with $CuCo_2S_4$ and Pt counter electrodes

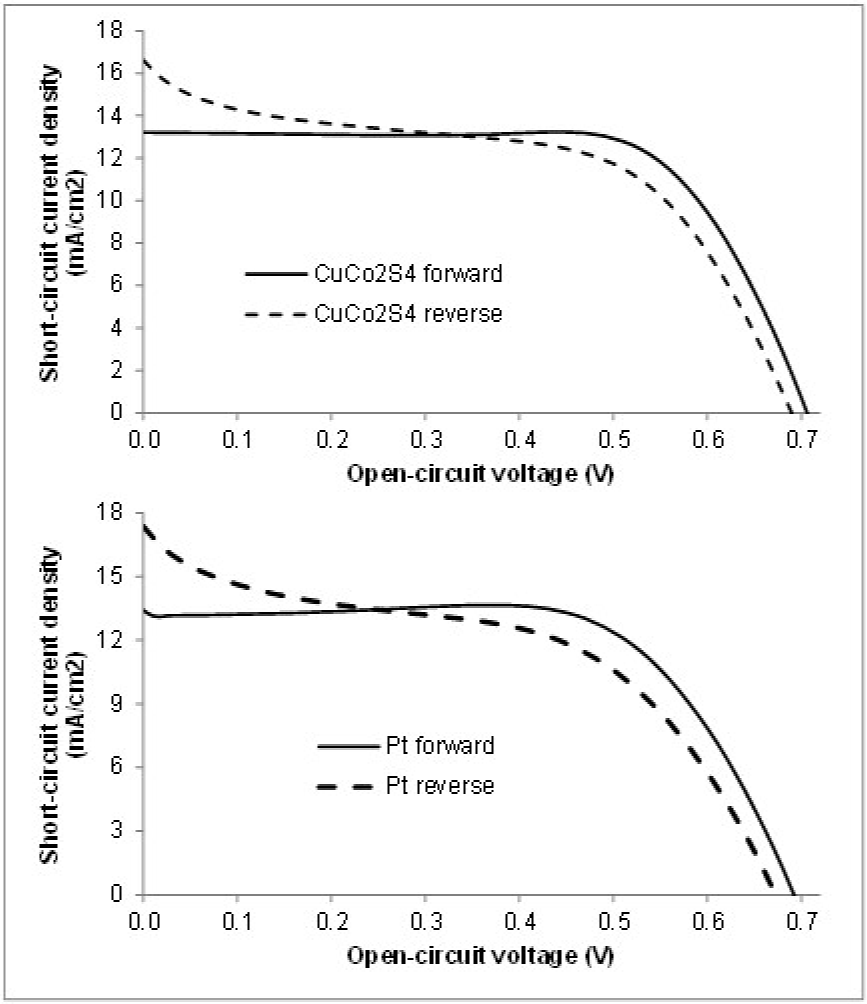

Figure S11 Forward and reverse measurements of I-V curves of $CuCo_2S_4$ and Pt cells

References

1. A. Bondarenko, G. Ragoisha, Inverse problem in potentiodynamic electrochemical impedance, in: A.L. Pomerantsev (Ed.), Progress in Chemometrics Research, Nova Science Publishers, New York, 2005, pp. 89–102. DOI: 10.1002/cem.939.