

Solution processed transition metal sulfides: application as counter electrodes in dye sensitized solar cell (DSC)

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Supporting Information:

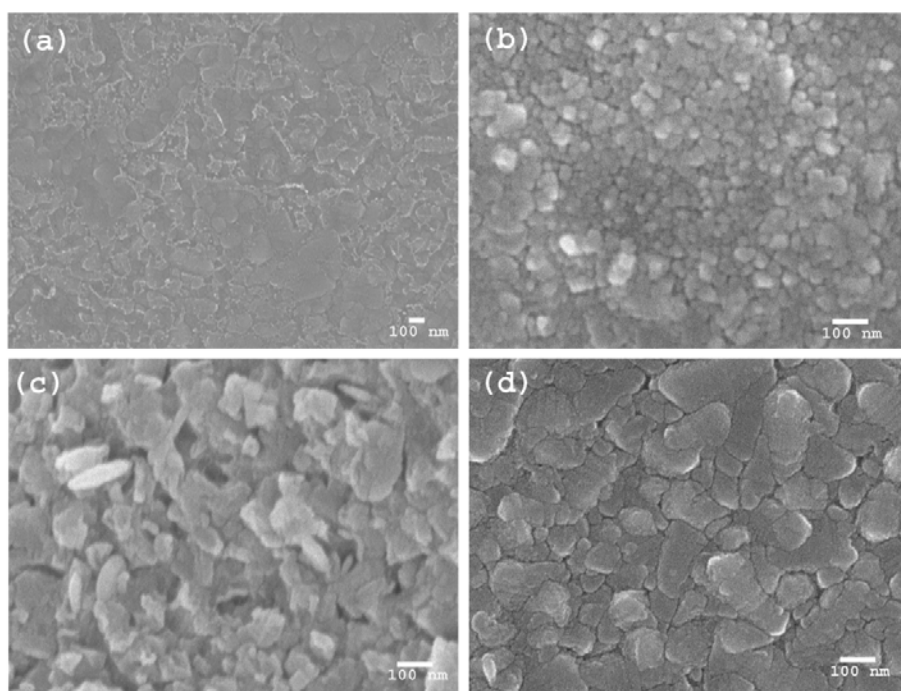


Fig S1. FESEM images of annealed samples on FTO (a) Pt, (b) Co_{8.4}S₈, (c) Cu_{1.8}S and (d) Ni₃S₂.

Cyclic voltammetry in polysulfide electrolyte:

To investigate the catalytic activities of the counter electrodes prepared, cyclic voltammetry (CV) (Solartron-analytical, 1470E) was performed in a three electrode system (Pt mesh, Ag/AgCl as counter and reference electrode respectively) with 1 M Na₂S, 1 M S, and 0.1 M NaOH, at a scan rate of 100 mVs⁻¹, Fig S2. The rest potentials of all the electrodes when immersed in the electrolyte were found to be ≈ -0.7 V which is equal to the values reported for E_{redox,PS}. (1) The value of E_{redox,PS} is in good agreement with

the predicted values using Nernst equation. (1, 2) All the sulfide counter electrodes show a better response than Pt in polysulfide electrolyte.

Preparation of Pt counter electrode

Preparation of platinum counter electrode on drilled FTO was done by thermal decomposition at 400 °C of hexachloroplatinic acid (8 mM, isopropanol solution).

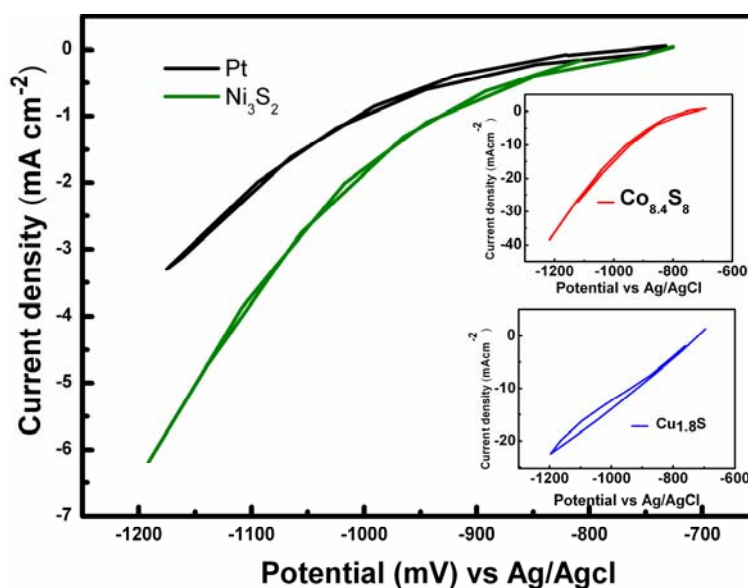


Fig S2. CVs of Pt, Co_{8.4}S₈, Ni₃S₂ and Cu_{1.8}S electrodes in polysulfide electrolyte (1 M Na₂S, 1 M S, and 0.1 M NaOH).

Preparation of transition metal sulfide counter electrode

The precursor solution was prepared using nickel(II) acetate tetrahydrate ($\geq 98\%$, Riedel-De-Haën), cobalt (II) chloride hexahydrate (reagent grade, Sigma Aldrich) and copper (II) chloride dehydrate (ACS reagent, $\geq 99.0\%$) and thioacetamide (reagent grade, Sigma Aldrich). Molarity of metal salts was 0.2 mM while that of thioacetamide was 0.8 mM. 10 μ l of each precursor solution was drop casted onto drilled FTO (2.5 x 1 cm²). These samples were later annealed at 500 °C for 30 mins under Argon flow (200 sscm) to get the corresponding sulfides.

Kelvin Probe measurements

Kelvin probe force microscopy (KPFM) was carried out on various sulfides to measure the contact potential difference of the films. The KPFM measurement was performed in a commercial Asylum Research MF3PD AFM system using commercially available platinum-coated Si cantilever. KPFM images of the sample were acquired with the tip biased as 3 V_{ac} and lift height of 10 nm at a scan rate of 0.2 Hz, on a typical scan area of 1 μ m x 1 μ m. The contact potential difference (CPD, ΔV_{sp}) measured in the KPFM can be translated to the work function of the sample, where in $\Delta V_{sp} = \Phi_t - \Phi_s$, with Φ_t and Φ_s

are the work functions of the tip and the sample respectively. Work functions of the samples have been calculated from the surface potential by calibrating the platinum tip cantilever on a sputtered platinum film on a glass substrate. Work function of $5.3 \pm .05$ eV was obtained for the platinum tip. The contact potential difference for the samples was used to estimate the work function (Fig S3).

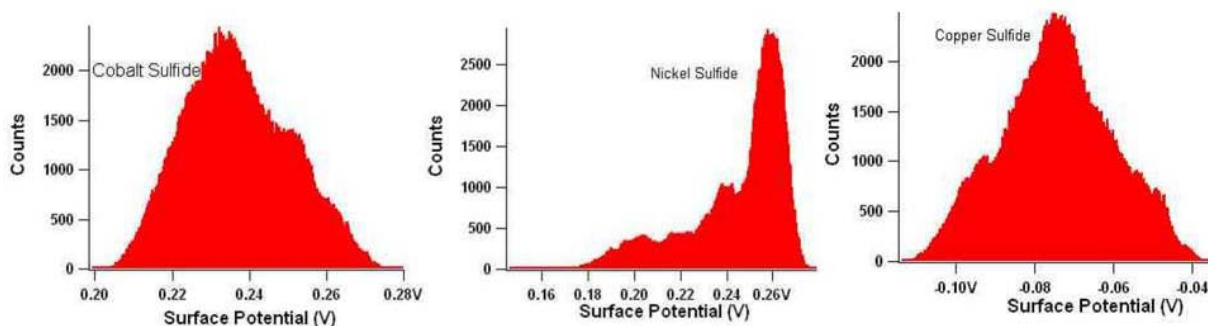


Fig S3. Surface potential histogram distribution for the various sulfide films deposited on glass substrate. Histogram extracted from the Kelvin images using the Igor software.

Cell fabrication:

A 11 μm film consisting of transparent TiO_2 nanocrystalline paste (DSL 18NR-T) was screen-printed onto FTO substrate which was pre-treated in 40 mM TiCl_4 at 70°C for 30 min. Subsequently, a 5 μm layer of Ti-Nanoxide R/SP paste (Solaronix, scattering layer) was screen printed on the same film. These electrodes were then heated at 500 °C for 15 min under programmed ramping. After annealing, the electrodes were treated again with 40 mM TiCl_4 at 70°C for 30 min and sintered at 500 °C for 30 min. Once cooled, the TiO_2 films were immersed overnight in a 0.3 mM acetonitrile/tert-butyl alcohol (v:v=1:1) solution of N719 dye (Solaronix). Fabrication of DSC was done by sandwiching dye soaked TiO_2 /FTO electrode and platinized FTO as a counter electrode with a 25 μm thick hot-melt spacer (Surllyn, Dupont). The Iodine/Iodide (AN 50, Solaronix) based electrolyte was introduced between the sandwiched electrodes through a hole by capillary action using a vacuum pump. The photocurrent density-photovoltage (J-V) characteristics of the PECC with an active area of 0.2826 cm^2 were measured under an illumination of AM 1.5 (100 mW cm^{-2}) using a solar simulator (San-EI Electric, XEC-301S) which was coupled with an Agilent semiconductor parameter analyser (4155C) for recording the J-V plot.

EIS of symmetric cells

Symmetric cells were fabricated by sandwiching the respective counter electrodes with a 25 μm thick hot-melt spacer (Surllyn, Dupont). The Iodine/Iodide (AN 50, Solaronix) based electrolyte was introduced between the sandwiched electrodes through a hole by capillary action using a vacuum pump. The same cells were used to measure Tafel polarization curves using Agilent semiconductor parameter analyser (4155C) for recording the J-V plot with a step size of 10 mV.

Electrochemical impedance spectroscopic (EIS) measurements were carried out using an automated potentiostat (Solartron-analytical, 1470E) coupled with a frequency response analyzer (Solartron-analytical, 1255B). The superimposed ac signal was maintained at 10 mV while the frequency was scanned from 100 KHz to 0.1 Hz at potentials between 0.3 V under dark conditions.

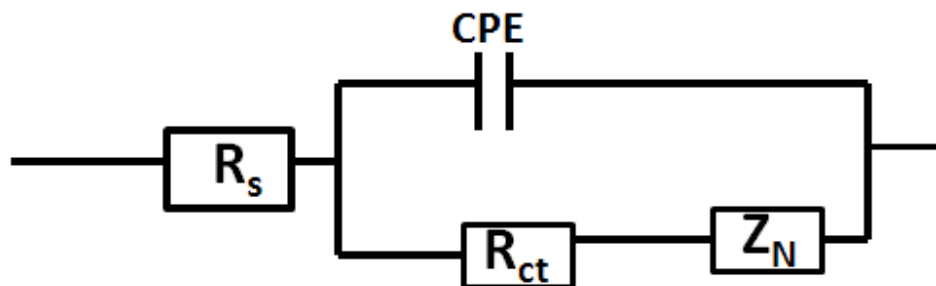


Fig S4. Equivalent circuit used for fitting the EIS data of the symmetric cells. R_s is the series resistance, CPE is the constant phase element, R_{ct} is the charge transfer resistance and Z_N is the Nernst diffusion impedance.

- (1) Hodes, G.; Manassen, J.; David, C. *Journal of The Electrochemical Society*. **1980**, *127*, 544.
- (2) Esposito, D. V.; Dobson, K. D.; McCandless, B. E.; Birkmire, R. W.; Chen, J. G. *Journal of The Electrochemical Society*. **2009**, *156*, B962.