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

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Supporting Information:

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 mV s⁻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).

![Graph showing CVs of Pt, Co₈S₈, Ni₃S₂, and Cu₁.₈S](image)

**Fig S2.** CVs of Pt, Co₈S₈, Ni₃S₂, and Cu₁.₈S 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 (≥ 98%, Riedel-De-Haën), cobalt (II) chloride hexahydrate (reagent grade, Sigma Aldrich) and copper (II) chloride dehydrate (ACS reagent, ≥ 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 µl 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 V₀ and lift height of 10 nm at a scan rate of 0.2 Hz, on a typical scan area of 1 µm × 1 µm. The contact potential difference (CPD, ΔV_{sp}) measured in the KPFM can be translated to the work function of the sample, where in ΔV_{sp} = Φ_t - Φ_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 ± .05 eV was obtained for the platinum tip. The contact potential difference for the samples was used to estimate the work function (Fig S3).

**Cell fabrication:**

A 11 µm film consisting of transparent TiO2 nanocrystalline paste (DSL 18NR-T) was screen-printed onto FTO substrate which was pre-treated in 40 mM TiCl4 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 TiCl4 at 70°C for 30 min and sintered at 500 °C for 30 min. Once cooled, the TiO2 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 TiO2/FTO electrode and platinized FTO as a counter electrode with a 25 µm thick hot-melt spacer (Surlyn, 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 cm² 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 (Surlyn, 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. Rs is the series resistance, CPE is the constant phase element, Rct is the charge transfer resistance and ZN is the Nernst diffusion impedance.
