

Electrocatalytic Sulfur Electrodes for CdS/CdSe Quantum Dot–Sensitized Solar Cells

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Experimental

Chemicals and Instrumentation: Commercially available P-25 TiO₂ powders (Degussa), cadmium nitrate, cobalt nitrate, selenium power, zinc sulfate, sodium sulfide, hydrogen hexachloroplatinate(IV), thioacetamide, ethylene glycol, 3-mercaptopropionic acid (3-MPA), potassium chloride, sodium hydroxide, poly(vinylpyrrolidone) (PVP, M_w 55,000), polyethylene glycol (M_w 5,000), methyl cellulose, sulfur, and methanol were purchased from Sigma–Aldrich (Milwaukee, WI).

Preparation of TiO₂-CdS/CdSe/ZnS Electrodes: TiO₂ electrodes having an effective area of 0.2 cm² were immersed into a solution of Cd(NO₃)₂ (0.5 M) for 5 min, rinsed with dd H₂O, and dried with an air gun. They were then dipped for 5 min into 0.5 M aqueous Na₂S, rinsed with dd H₂O, and dried with an air gun. The process was repeated up to three cycles. These as-prepared electrodes are represented herein as “TiO₂-(CdS)₃” electrodes. The TiO₂-(CdS)₃ electrodes were dipped into a solution of Cd²⁺ (0.5 M) for 5 min at room temperature and then immersed into 0.08 M aqueous Na₂SeSO₃ for 1 h at 50 °C, followed by rinsing with dd H₂O and drying with an air gun. The process was repeated up to two cycles. These as-prepared electrodes are represented herein as “TiO₂-(CdS)₃-(CdSe)₂” electrodes. The TiO₂-(CdS)₃-(CdSe)₂ electrodes were immersed into a solution of Zn(NO₃)₂ (0.5 M) for 5 min, rinsed with

dd H₂O, and dried with air gun. They were then dipped for 5 min into 0.5 M aqueous Na₂S, followed by rinsing with dd H₂O and drying with an air gun, to obtain TiO₂-(CdS)₃-(CdSe)₂-ZnS electrodes.

Preparation of MS (M = Co, Cu, Ni) Electrodes: A cleaned FTO glass was dipped into 0.5 M Co²⁺ (or Cu²⁺ or Ni²⁺) for 30 s, rinsed with ethanol, and dried with an air gun. The sample was then dipped for 30 s into 0.5 M aqueous Na₂S, followed by rinsing with ethanol and drying with an air gun. The process was repeated up to three cycles to obtain the CoS (or CuS or NiS) electrode.

Preparation of Pt Electrodes: A mixture of PVP (0.14 g), 0.01 M H₂PtCl₆·H₂O, and ethylene glycol (50 ml) was heated at 160 °C for 2 h, during which time the color of the solution turned black, indicating the formation of Pt NPs. The as-prepared Pt NPs were subjected to three centrifugation/wash cycles (15,000 rpm, 10 min) and then they were stored in ethanol. Pt electrodes were prepared by placing a drop of the ethanol solution of these Pt NPs (5 nm) onto FTO glass substrates, drying them at 100 °C for 30 min, and then sintering them at 450 °C for 30 min prior to use.

Fabrication of QDSSCs: The QDSSC devices were obtained after assembling one of the as-prepared electrodes with a counter electrode and a U-like spacer in a sandwich configuration and then annealing at 100 °C for 30 min. The electrolyte was a

polysulfide solution: 2.0 M Na₂S, 2.0 M S, and 0.2 M KCl in methanol/water (7:3, v/v).

Measurements. Reflection absorption spectra of the as-prepared electrodes were recorded using a Cary 100 UV–Vis spectrophotometer from Varian (Palo Alto, CA). Scanning electron microscopy (SEM) images were recorded using an S-2400 SEM system from Hitachi (Tokyo, Japan). Potentiostatic current–voltage (I – V) curves were recorded using a CHI 660A electrochemical analyzer (CH Instruments, Austin, TX). A CHI 614D electrochemical impedance spectrometer (CH Instruments, Austin, TX) was employed to determine the charge-transfer resistance between the electrode and the electrolyte at zero bias potential over the frequency range of 0.1–100 KHz. The irradiation source for determining the photocurrent density–voltage (J – V) characteristics was a 450-W xenon arc lamp (Oriel, Stratford, CT) equipped with an AM 1.5 filter. A Keithley 2400 digital source meter (Test Equipment Connection, Lake Mary, FL) was used to record the J – V curves of the as-prepared QDSSCs. A metal mask with an area of 0.16 cm² covering the QDSSCs was used to ensure the effective area of the QDSSCs. A commercial available silicon based reference cell (Oriel, Stratford, CT) was employed to check the light intensity (100 mA/cm²). All of the J – V measurements were recorded after at least 10 reproducible cycles to ensure

no change in $J-V$ curves. The IPCE spectra were recorded using a PEC-S20 instrument (Peccell Technologies, Inc., Kanagawa, Japan).

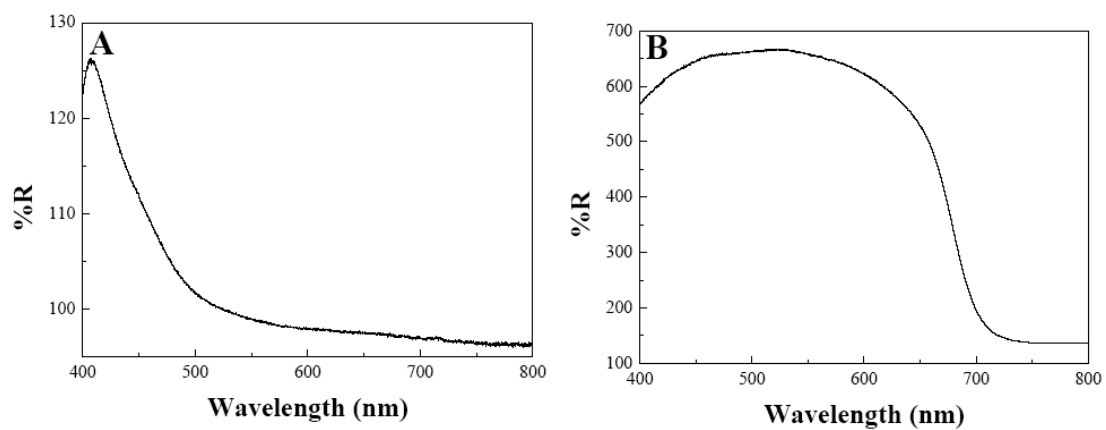


Figure S1. Reflection spectra of (A) TiO₂/CdS and (B) TiO₂/CdSe electrodes.

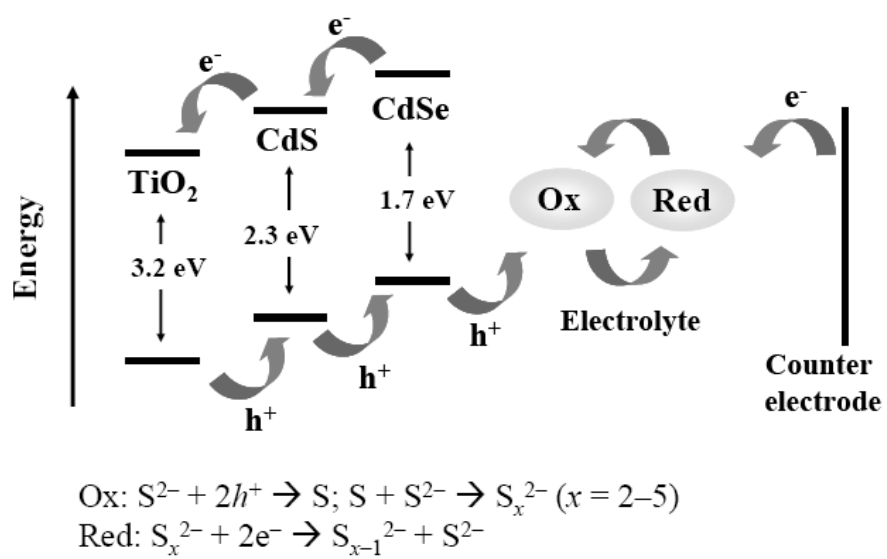


Figure S2. The energy level diagram of the components in QDSSCs devices.

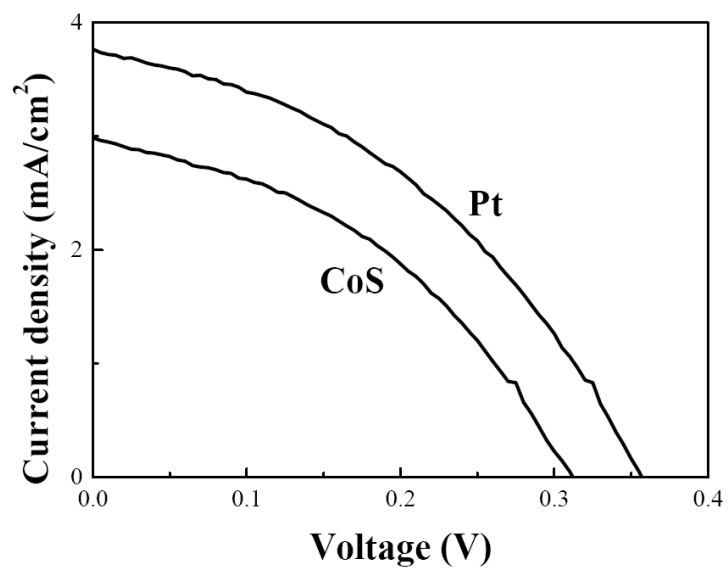


Figure S3. J - V curves of QDSSCs featuring CoS and Pt as electrodes. Polysulfide electrolyte: 0.5 M Na₂S, 2.0 M S, and 0.2 M KCl in methanol/water (7:3, v/v).

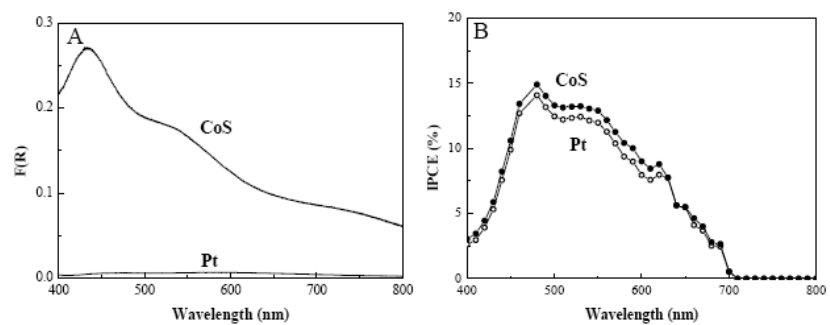


Figure S4. (A) Reflection spectra of Pt and CoS electrodes. (B) IPCE spectra of QDSSCs featuring CoS or Pt as the counter electrode.

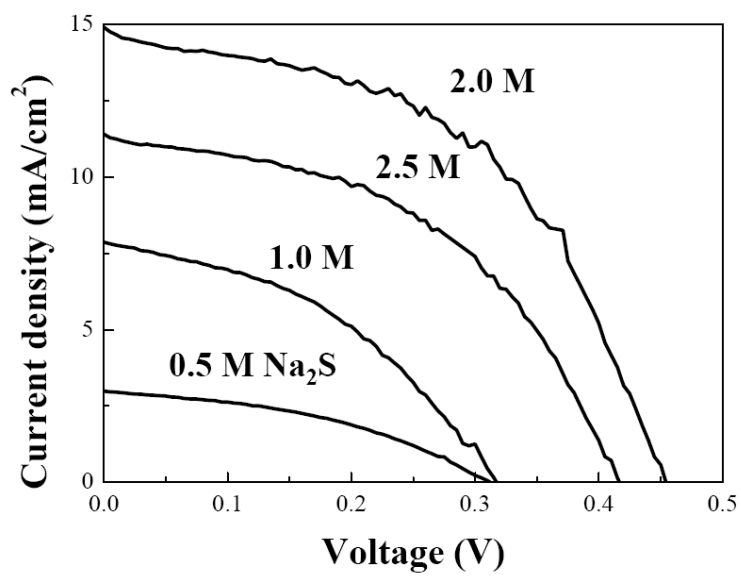


Figure S5. J - V curves of QDSSCs featuring electrolytes comprising Na₂S (0.5–2.5 M), 2.0 M S, and 0.2 M KCl in methanol/water (7:3, v/v).

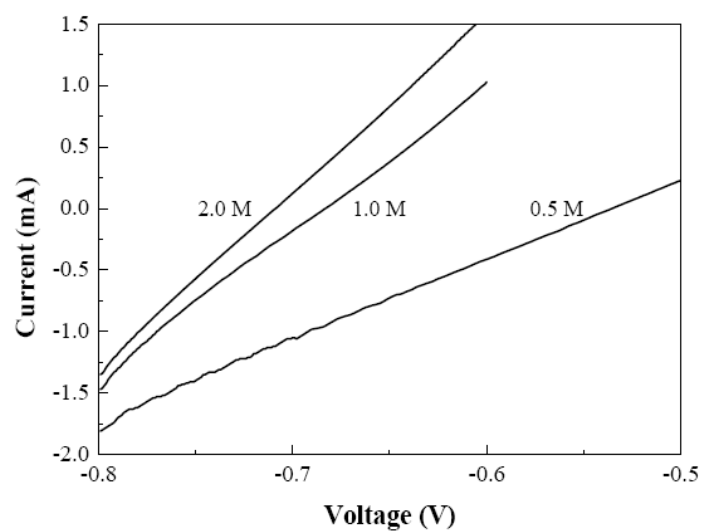


Figure S6. Potentiostatic I - V plots of a CoS electrode in the presence of electrolytes comprising Na_2S (0.5–2.0 M), 2.0 M S, and 0.2 M KCl in methanol/water (7:3, v/v).

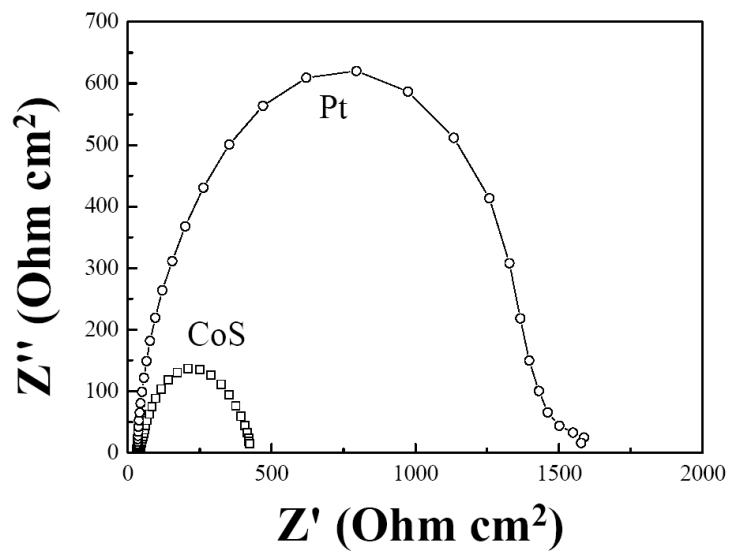


Figure S7. Impedance spectra of CoS and Pt electrodes.

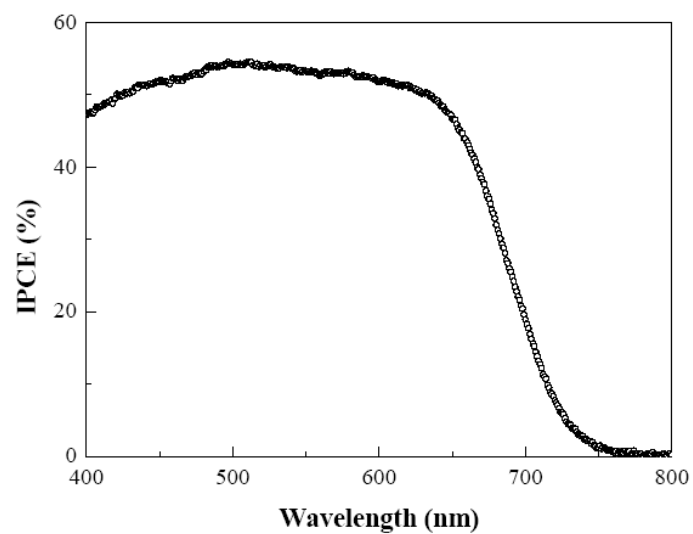


Figure S8. IPCE spectrum of a CdS/CdSe QDSSC featuring a CoS electrode. Polysulfide electrolyte: 2.0 M Na₂S, 2.0 M S, and 0.2 M KCl in methanol/water (7:3, v/v).

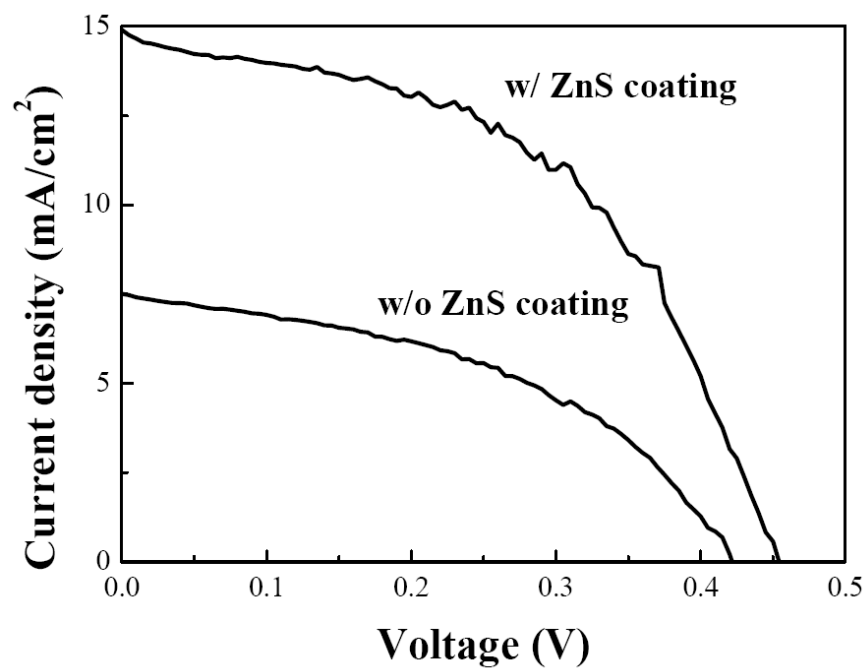


Figure S9. J - V curves of QDSSCs with and without ZnS coating.

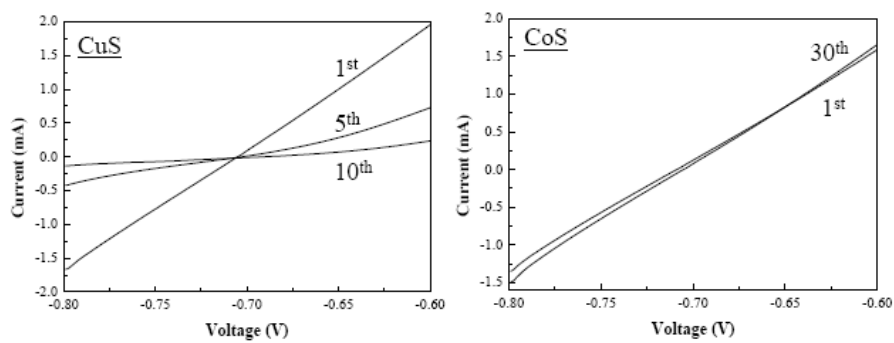


Figure S10. Potentiostatic $I-V$ curves of (A) CuS and (B) CoS electrodes after several scan cycles. Polysulfide electrolyte: 2.0 M Na_2S , 2.0 M S, and 0.2 M KCl in methanol/water (7:3, v/v).