

Supplementary Information

Highly Electrocatalytic Carbon Black/Copper Sulfide Composite Counter Electrodes Fabricated by a Facile Method for Quantum-Dot-Sensitized Solar Cells

I-Ping Liu,^a Hsisheng Teng^{abc} and Yuh-Lang Lee^{*ab}

^aDepartment of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan (R. O. C.)

^bResearch Center for Energy Technology and Strategy (RCETS), National Cheng Kung University, Tainan 70101, Taiwan (R. O. C.)

^cCenter for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 70101, Taiwan (R. O. C.)

*Corresponding author. *E-mail address*: ylllee@mail.ncku.edu.tw (Y.-L. Lee)

EXPERIMENTAL SECTION

Materials

Carbon black powder (PRINTEX®L, furnace black, 99%) was acquired from Orion Engineered Carbons; according to the manufacturer's specifications, this powder's properties include: BET surface area of $150 \text{ m}^2 \text{ g}^{-1}$, particle diameter of $\sim 23 \text{ nm}$, pH value of 9.0, sieve residue less than 25 ppm (45 μm residue), toluene extraction less than 0.1% (8 h) and DBP absorption of 120 ml per 100 g powder.

Titanium dioxide pastes of 30 NR-D and PST-400C were procured from Dyesol and JGC C&C (JGC Catalysts and Chemicals Ltd., Japan), respectively. Copper(II) nitrate trihydrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99+%) and cadmium nitrate tetrahydrate [$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99%] were obtained from Sigma-Aldrich. Ethyl cellulose (EC, 10 cps, 48% in ethoxyl content), selenium dioxide (SeO_2 , 99.9%) and sodium borohydride (NaBH_4 , 99.99%) were acquired from Aldrich Chemistry. Copper(II) sulfate pentahydrate [$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 100.8%], sodium acetate anhydrous (CH_3COONa , 99.9%) and ethanol (99.9%) were purchased from J. T. Baker. Zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99+%) and sulfur powder (S, 99.5+%) were obtained from Riedel-de Haën. Sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 98+%), thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, >98%), acetic acid (CH_3COOH , 99.5%), methanol (99.9%) and titanium(IV) chloride (TiCl_4 , 98%) were acquired from Acros Organics, Tokyo Chemical Industry, Kanto Chemical, Merck and Fluka, respectively. All chemicals and solvents were used as received without further purification.

Preparation of Quantum-Dot-Sensitized Photoelectrodes

In this study, mesoporous titanium dioxide (TiO_2) films were utilized to accumulate semiconductor QD sensitizers. Prior to printing the TiO_2 films, a compact layer was coated on cleaned FTO substrates by the TiCl_4 pre-treatment (a reaction in a 40 mM aqueous TiCl_4 solution at 70°C for 30 min). A transparent layer was first screen-printed onto the TiCl_4 -treated FTO substrate using the 30 NR-D TiO_2 paste, and a light-scattering layer was further printed directly on top of the transparent film with the PST-400C paste. After sintering at 500°C , the mesoporous TiO_2 film showed a double-layered architecture and a total thickness of $\sim 12.5 \mu\text{m}$ (7.5 ± 0.4 and $5.0 \pm 0.2 \mu\text{m}$ for the transparent and scattering regions, respectively).

Semiconductor QD sensitizers were synthesized by successive ionic layer adsorption and reaction (SILAR). SILAR is a conventional solution-processing method, in which the TiO_2 films are dipped in cationic and anionic precursors alternately. Upon finishing each dipping, rinsing and drying were executed. For the CdS QD, the cationic precursor was a methanol solution containing 0.03 M $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.05 M CH_3COONa , and the anionic precursor was a methanol/deionized water mixture (7/3 by volume) containing 0.06 M Na_2S . For the CdSe sensitizer, the cationic precursor was 0.03 M $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in ethanol, and the anionic precursor was prepared by vigorously stirring a mixture of 0.03 M SeO_2 and 0.06 M NaBH_4 in ethanol until becoming clear under a nitrogen atmosphere. A complete SILAR cycle involved dipping the TiO_2 films once in both cationic and anionic precursors; in this work, CdS and CdS/CdSe photoelectrodes were prepared by 5 and 2/6 SILAR cycles, respectively, and the reaction time was fixed to 1 min for each dipping. After the QD deposition, all the photoelectrodes were further coated with ZnS passivation layers by the SILAR method. The as-prepared QD electrodes were dipped sequentially into a 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ methanol

solution for 1 min, and then into a methanol/deionized water mixture (7/3 by volume) containing 0.1 M Na₂S for 1 min. Two SILAR cycles were performed for the ZnS deposition; after that, the preparation of QD-sensitized photoelectrode was accomplished.

Characterization and Measurements

The Raman spectrum of the CB/Cu_xS composite film was accumulated using a confocal DXR Raman microscopy system (Thermo Scientific, USA) with a 532 nm laser source at 7 mW. A transmission electron microscope (TEM, H-7500, Hitachi, Japan) was employed to investigate the microstructure of the composite sample. The morphology of composite electrodes was examined using a scanning electron microscope (SEM, SU8010, Hitachi, Japan). The chemical states of elements in composite films were studied using an X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, ULVAC-PHI, Inc., Japan) with Al K α as the X-ray source (1486.7 eV for excitation energy); elemental binding energies were determined by calibration and fixing the C(1s) peak to 284.8 eV, and peak deconvolution was carried out using XPSPEAK 4.1 software with the Shirley-type baseline, as well as Gaussian–Lorentzian functions. Electrochemical impedance spectroscopy (EIS) and Tafel polarization were measured using a potentiostat (PGSTAT30, Metrohm Autolab, Netherlands) equipped with an FRA module; the EIS measurements were conducted at 0 V with 10 mV AC sinusoidal amplitudes applied over a frequency range of 100 kHz to 100 mHz, and the Tafel polarization analysis was performed at a scan rate of 10 mV sec⁻¹. A CH Instruments potentiostat (CHI627D, USA) was utilized to carry out cyclic voltammetry with a three-electrode system at a scan rate of 50 mV sec⁻¹; a platinum foil and a saturated calomel electrode (SCE) were adopted as the counter and reference electrodes, respectively, and the electrolyte was an aqueous polysulfide solution containing 1.0 M S and 1.0 M Na₂S. The photovoltaic properties (*J–V* curves) of the assembled solar cells were

recorded under simulated sunlight irradiation using a computer-controlled digital source meter (6240A, ADCMT, Japan) scanning from 0 V to the open-circuit voltage at a scan rate of 50 mV sec⁻¹. Calibration of the solar simulator (XES-301S, AM 1.5G, class AAA, San-Ei Electric, Japan) was implemented with a reference silicon cell (BK7, PV Measurements, USA) which was certified by the National Renewable Energy Laboratory in the USA. Incident photon-to-current efficiency spectra were analyzed using a quantum efficiency measurement system equipped with a xenon lamp (QE-R3011, DC mode, Enlitech, Taiwan).

Table S1. Comparison of photovoltaic performance based on CdS/CdSe sensitizers and carbon-related composite counter electrodes.

Carbon-related composite counter electrode	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η (%)	Reference
RGO-Cu ₂ S	18.4	520	0.46	4.40	36
RGO-Cu ₂ S	15.85	556	0.44	3.85	37
PbS/CB	13.32	509.58	0.58	3.91	38
CuInS ₂ /carbon	14.16	512	0.60	4.32	39
Cu ₂ S/carbon	13.69	593.0	0.48	3.87	40
CB/Cu _x S-3	16.96	584	0.567	5.62	present work

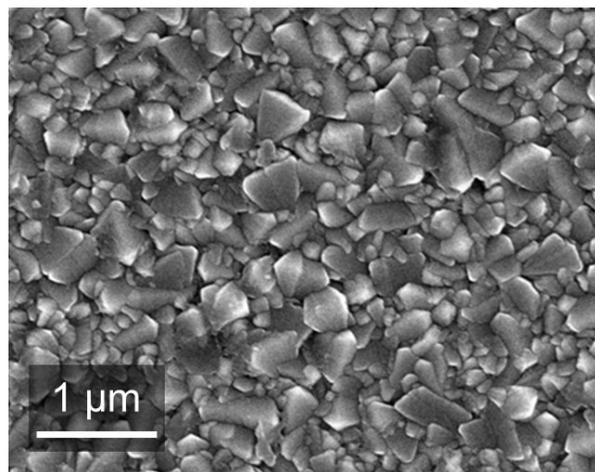


Fig. S1 Top-view SEM image of a pristine FTO surface.

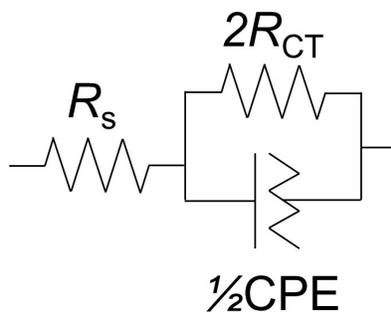


Fig. S2 Equivalent circuit utilized in the EIS measurements.

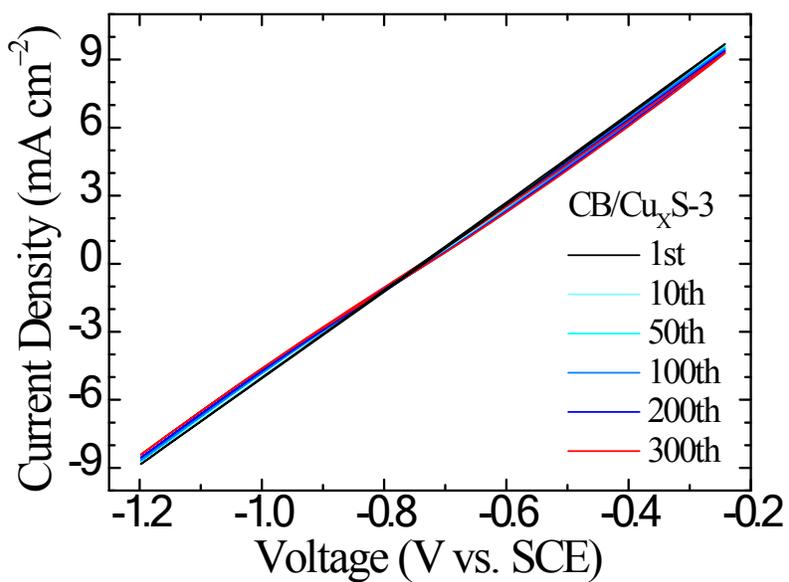


Fig. S3 Cyclic voltammograms of the CB/Cu_xS-3 thin film electrode at various specific cycles measured using a three-electrode system (a continuous measurement for 300 cycles at a scan rate of 50 mV sec⁻¹).

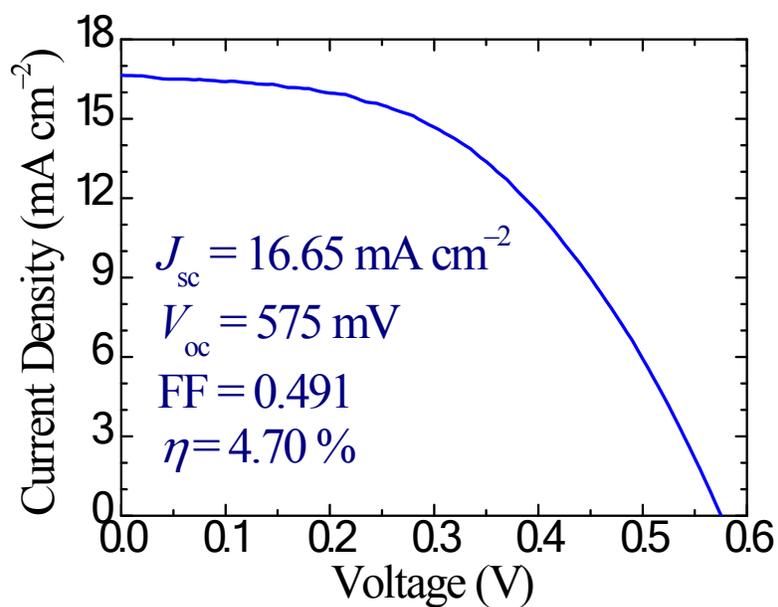


Fig. S4 Photovoltaic J - V curve of the CdS/CdSe QDSSC based on the CBD-CuS counter electrode measured under standard 1 sun irradiation.

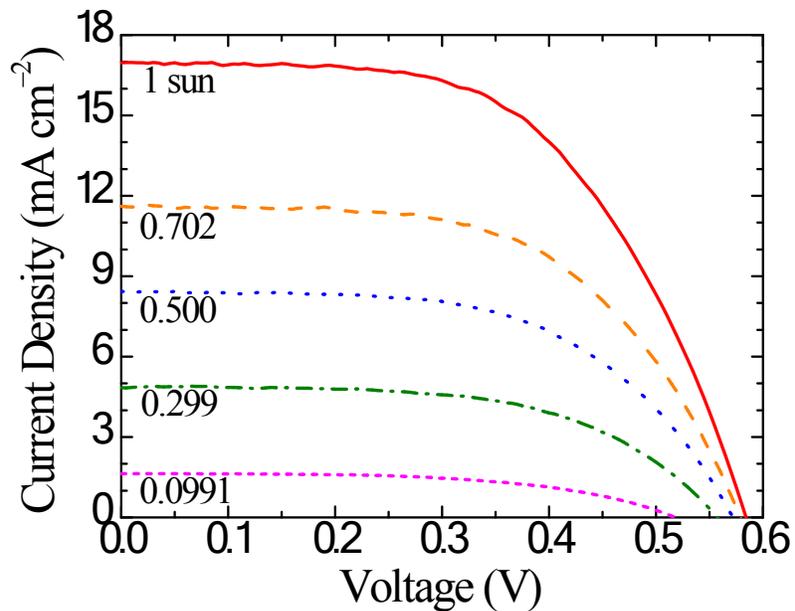


Fig. S5 Photovoltaic J - V curves of the CdS/CdSe QDSSC employing a CB/Cu_xS-3 composite thin film counter electrode measured under different irradiation conditions (in sun).