

Supplementary Information (SI)

Cuprous Sulfide on Ni Foam as Counter Electrode for Flexible Quantum Dot Sensitized Solar Cells

Zhonglin Du, Jing Tong, Wenxia Guo, Hua Zhang* and Xinhua Zhong*

Shanghai Key Laboratory of Functional Materials Chemistry, Institute of Applied Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

*Corresponding author

Email: zhanghjy@ecust.edu.cn (H. Zhang); zhongxh@ecust.edu.cn (X. Zhong)

Phone/Fax: +86 21 6425 0281

Chemicals

Sulfur powder and copper sulfate anhydrate (CuSO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd. Oleic acid (90%) and thioglycolic acid (TGA, 97%) were obtained from Alfa Aesar. Oleylamine (OAm, 95%), 1-octadecene (ODE, 90%), triethylphosphine (TOP, 90%), cadmium oxide (CdO , 99.99%), selenium powder (200 mesh, 99.99%), tellurium powder (200 mesh, 99.99%) and polyvinylidene Fluoride (PVDF) were purchased from Aldrich. The Ni foam was purchased from Kunshan Yierda Trade Co., Ltd and the pore size, thickness, and purity of Ni foam were 0.5 mm, 1.0 mm, and 99%, respectively. P25 powder (20% rutile and 80% anatase) was purchased from Degussa. All the used reagents were analytical grade, without further purification.

Synthesis of Oil-Soluble CdSe and CdSeTeQDs

Oil-soluble OAm capped CdSe QDs with average size of 5.1 nm were synthesized as follows. Briefly, A Se stock solution (2.1 M) was obtained by dissolving Se powder in TOP. A Cd stock solution (0.4 M) was prepared by dissolving CdO in oleic acid and ODE (v/v, 1:1) at 250 °C. 0.5 mL of Se stock solution, 0.3 ml of TOP and 4.5 ml of OAm were heated to 275 °C under nitrogen atmosphere with stirring. 0.5 mL of Cd stock solution was injected into the reaction flask. The temperature was then set at 280 °C for the growth and annealing of nanocrystals. After that, the obtained CdSe QDs were precipitated by adding methanol into the hexane solution and further isolated and purified by centrifugation.

Meanwhile, around 5.2 nm sized CdSeTe QDs with an absorption onset at ~ 800 nm were synthesized by directly heating the mixed solution containing Cd, Se, and Te precursors. Typically, the Te precursor (0.1 M), Se precursor (0.1 M) and Cd stock solution (0.1 M) were loaded in a three-neck flask with a Cd:Te:Se volume ratio of 10:1:1. Then the temperature was then set at 320 °C and kept for 10 min under nitrogen atmosphere. Finally, the oil-soluble CdSeTe QDs were purified following the same procedure of CdSe QDs as described above.

Preparation of Water-Soluble CdSe and CdSeTe QDs.

Generally, 1.0 ml of MPA-methanol solution (0.4 mM, adjusted to pH 12 with 30% NaOH aqueous solution) was added into 30 mL CdSe QDs dichloromethane solution

and stirred for 2 h to obtain the precipitation of the QDs. Then 20.0 mL deionized water was added into the above mixture and stirred for another 20 min. The aqueous phase CdSe QDs capped with MPA was collected and purified for the next step use. The preparation of water-soluble CdSeTe QDs capped with TGA were similar to that of water-soluble CdSe QDs by replacing MPA with TGA.

Synthesis of TiO₂-sol and Binder Solution for Preparing TiO₂ Paste

Briefly, 25.0 mL acetic acid and 50 mL deionized water were mixed in the round bottom flask and stored in a 4 °C for 5 h. Then 9.0 mL titanium isopropoxide was diluted by 9.0 ml isopropanol and dripped into the cold solution as slowly as possible followed by stirring overnight in an ice-water bath. After that, the light blue TiO₂-sol was yielded by evaporating the solvents of mixture in an 80 °C oil bath. Binder solution was prepared by mixing 8.0 mL of terpineol, 0.01 g of PVDF and 50 µL of titanium isopropoxide.

Fabrication of the Rigid Photoanode and Assembly of Solar Cells

The rigid TiO₂/FTO photoanodes were prepared by successively screen-printing several layers composed of a transparent layer (thickness of 9.0 µm) and a scattering layer (thickness of 6.0 µm). The pre-prepared CdSeTe QDs were firstly deposited onto the TiO₂ films via capping ligand-induced self-assembly approach and then the sensitized electrodes were overcoated with thin layer of amorphous TiO₂, ZnS, and SiO₂. Briefly, 45.0 µL of TGA-capped water-soluble CdSeTe QDs were dropped onto the TiO₂ film and kept for 10 h. Then the above photoanodes were immersed in the TiCl₄ aqueous solution (containing 0.01 M TiCl₄ and 0.01 M TGA) for 30 min at 35 °C. After that the photoanodes were soaked alternately into Zn(OAc)₂ methanol solution (0.1 M) and Na₂S aqueous solution (0.1 M) for 1 min/dip followed by rinsing with water and ethanol sequentially. The SiO₂-coated photoanodes were prepared by soaking the electrode in 0.01 M tetraethyl orthosilicate ethanol solution for 2 h. The gel electrolyte was prepared by adding 0.4 g of sodium polyacrylate into 10 mL polysulfide electrolyte (2.0 M Na₂S and S aqueous solution) under stirring at room temperature for 10 min. The sandwich-type cells were assembled by sealing the sensitized photoanode and the investigated CEs using a Surlyn thermoplastic spacer (60 µm) and the gel electrolyte was then filled.

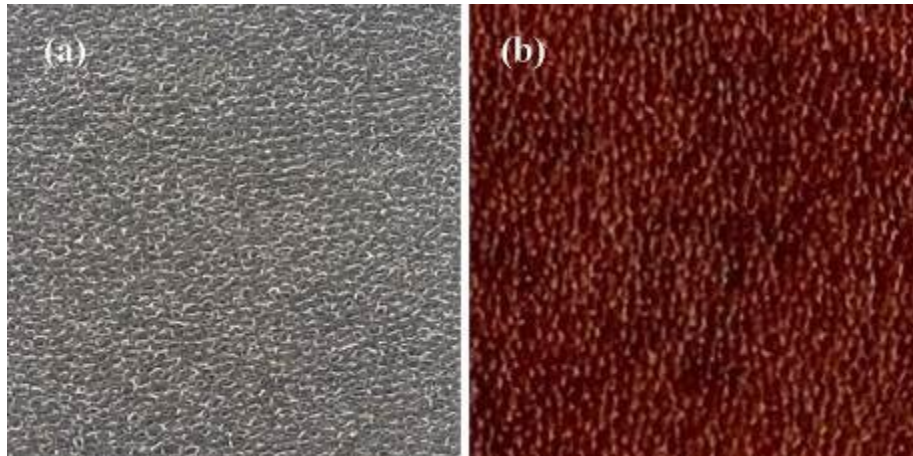


Figure S1. Digital photos of the original Ni foam (a) and the prepared Cu/Ni film (b).

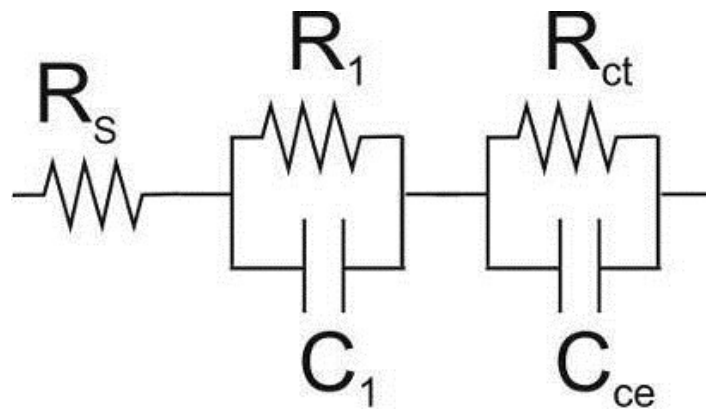


Figure S2. Simulation circuit used for fitting EIS. R_s accounts for series resistance, R_1 and C_1 represent the charge transfer resistance and capacitance at $\text{Cu}_2\text{S-Ni}$ interface, R_{ct} and C_{ce} represent the charge transfer resistance and capacitance at CE/electrolyte interface.

Table S1. Individual and average photovoltaic parameters of CdSeTe QDSCs based on different CEs at AM 1.5 G irradiation.

CEs	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF	PCE (%)
Cu ₂ S/Ni	20.22	0.651	0.679	8.94
	20.67	0.655	0.647	8.76
	20.36	0.648	0.667	8.80
Average	20.42	0.651	0.664	8.83
Cu ₂ S/FTO	20.44	0.653	0.618	8.25
	20.37	0.665	0.606	8.21
	20.35	0.654	0.623	8.29
	20.46	0.667	0.615	8.39
	20.51	0.655	0.623	8.37
Average	20.43	0.659	0.617	8.31
NiS/Ni	17.82	0.633	0.557	6.28
	17.79	0.641	0.548	6.25
	17.45	0.629	0.555	6.09
	17.66	0.637	0.552	6.21
	17.67	0.635	0.557	6.25
Average	17.68	0.635	0.554	6.22

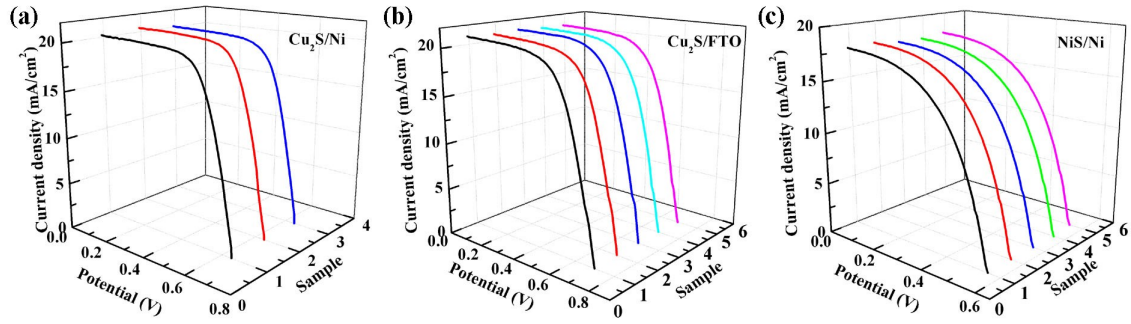


Figure S3. J - V curves of CdSeTe QDSCs based on different CEs at AM 1.5 G irradiation.

Table S2. Current densities (J_{sc}) from IPCE and J - V for different CEs, in which $\text{Cu}_2\text{S}/\text{Ni}$ -0.02 M is corresponding to the sample of $\text{Cu}_2\text{S}/\text{Ni}$ in Table 1.

CEs	J_{sc} from IPCE (mA/cm^2)	J_{sc} in J - V curves (mA/cm^2)
$\text{Cu}_2\text{S}/\text{Ni}$ -0.01 M	17.49	18.01
$\text{Cu}_2\text{S}/\text{Ni}$ -0.02 M	19.71	20.22
$\text{Cu}_2\text{S}/\text{Ni}$ -0.03 M	18.80	19.84
$\text{Cu}_2\text{S}/\text{FTO}$	20.08	20.46
NiS/Ni	17.46	17.82

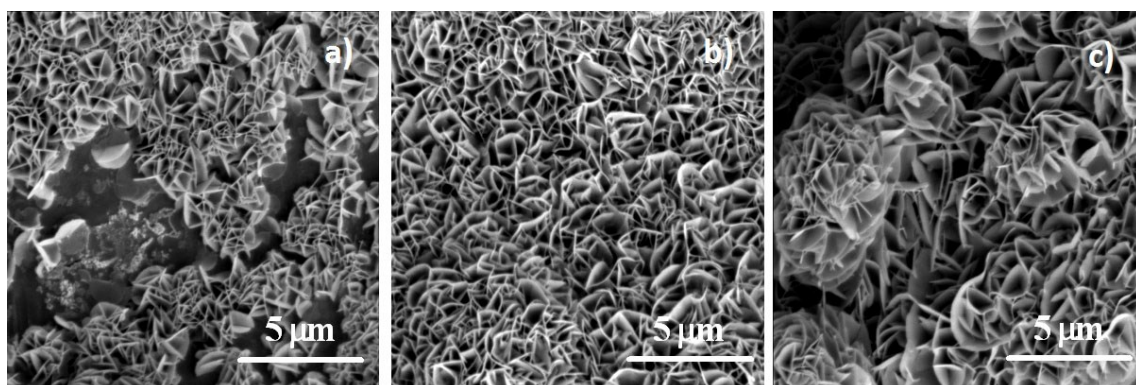


Figure S4. SEM images from $\text{Cu}_2\text{S}/\text{Ni}$ CEs prepared with 20 mL of CuSO_4 solution having different concentrations of 0.01, 0.02 and 0.03 M corresponding to a), d) and c) respectively.

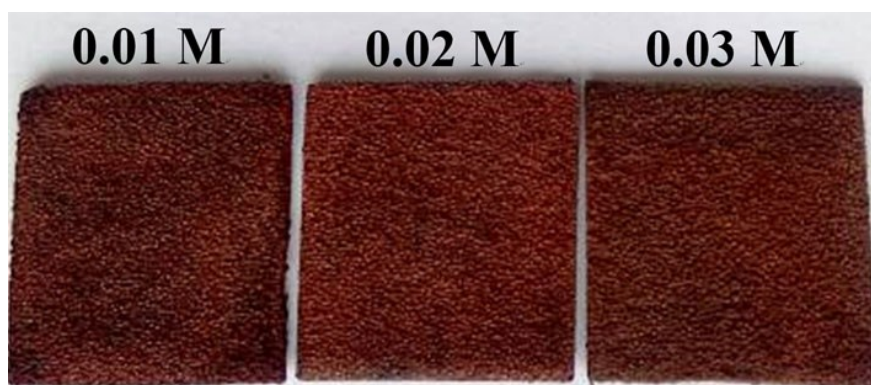


Figure S5. Digital photos of $\text{Cu}_2\text{S}/\text{Ni}$ CEs that shown in Figure S4.

Table S3. Photovoltaic parameters of individual CdSeTe QDSC based on the Cu₂S/Ni CEs prepared with 20 mL of CuSO₄ solution having different concentrations of 0.01, 0.02 and 0.03 M in one batch.

concentration	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF	PCE (%)
0.01 M	18.13	0.632	0.581	6.66
	18.01	0.640	0.579	6.67
	18.07	0.633	0.574	6.57
	18.11	0.623	0.588	6.63
	18.24	0.629	0.577	6.62
Average	18.11	0.631	0.580	6.63
0.02 M	20.22	0.651	0.679	8.94
	20.67	0.655	0.647	8.76
	20.36	0.648	0.667	8.80
Average	20.42	0.651	0.664	8.83
0.03 M	20.12	0.65	0.653	8.54
	19.84	0.655	0.658	8.55
	20.07	0.652	0.643	8.41
	20.08	0.641	0.649	8.35
	19.93	0.643	0.657	8.42
Average	20.01	0.648	0.652	8.46