

Electronic Supplementary Information (ESI)

Cu_xS nanoparticle@carbon nanorod composites prepared from metal-organic framework as efficient electrode catalysts in quantum dot sensitized solar cells

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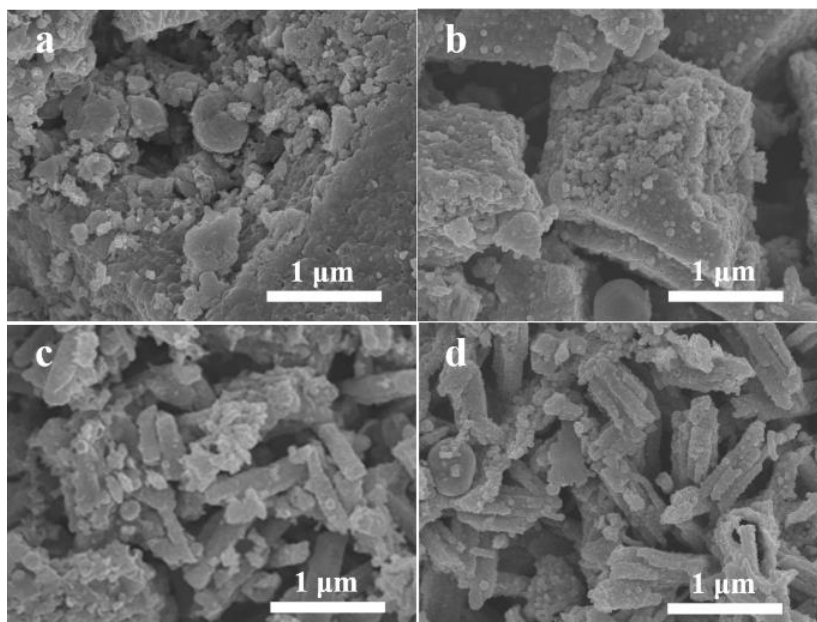


Fig. S1 SEM images of internal of (a) Cu@C-800, (b) Cu@C-900, (c) Cu@C-1000, (d) Cu@C-1100.

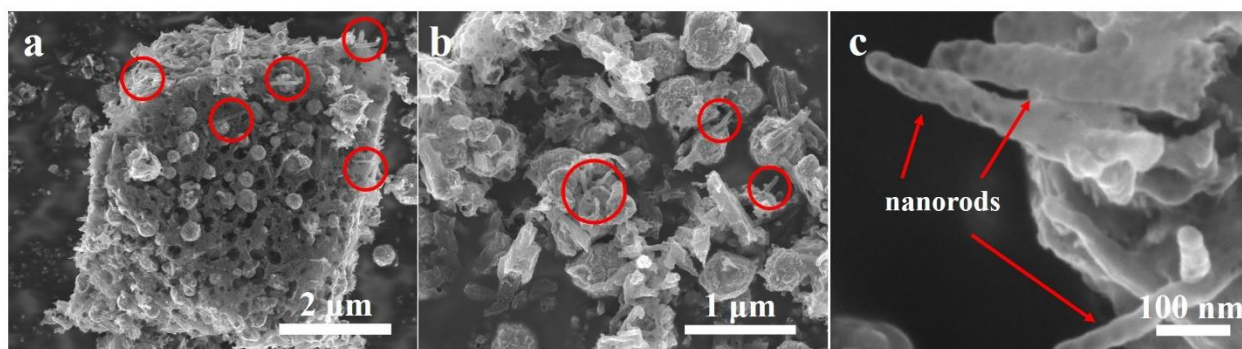


Fig. S2 SEM images of (a) octahedral geometry and (b) internal of Cu@C-950 (inside red circles are half-baked carbon nanorods). (c) Enlarged view of nanorods on the surface of Cu@C-950.

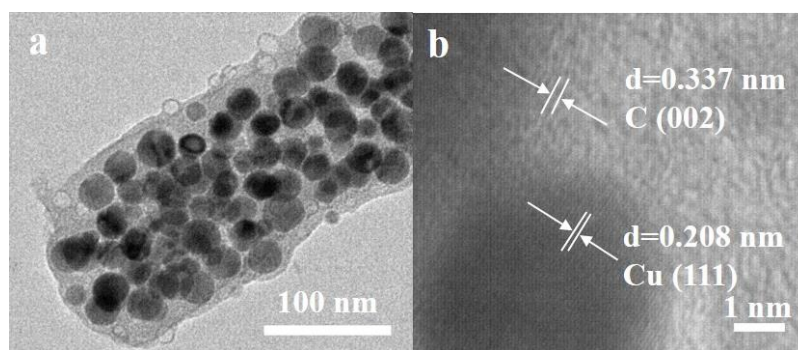


Fig. S3 TEM images of (a) Cu@C-1100, (b) High-resolution TEM of Cu@C-1100 with Cu nanoparticles encased in the graphitic carbon (insert: lattice fringes of the crystalline Cu NPs of Cu@C-1100).

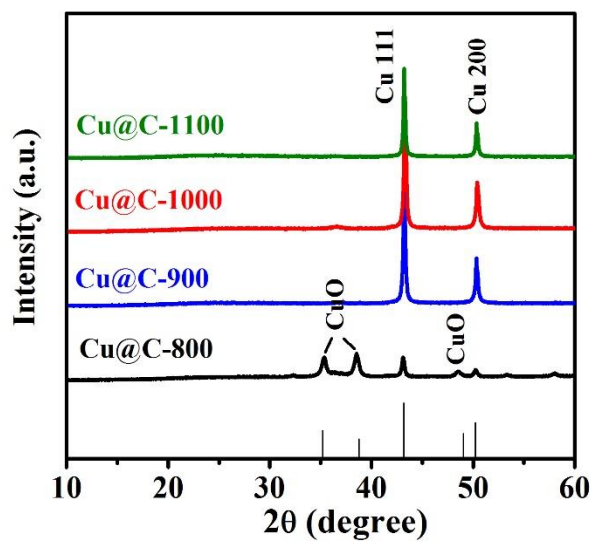


Fig. S4 Powder XRD patterns of Cu@C-x (Cubic Cu: 00-001-1241, Cubic CuO: 00-002-1041)

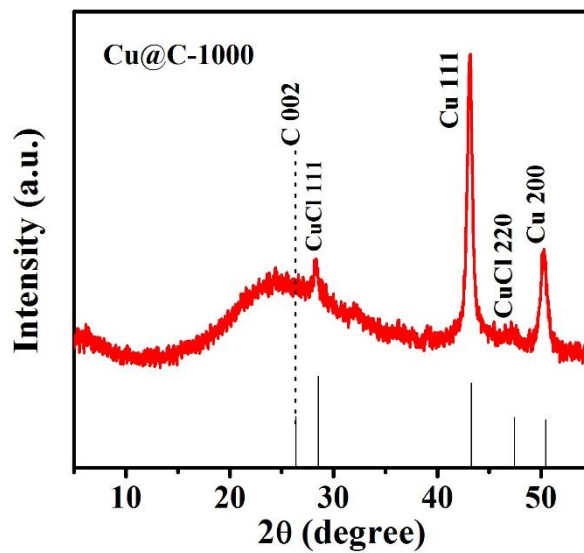


Fig. S5 Powder XRD patterns of the Cu@C-1000 sample treated by aqua regia (C: 41-1487, CuCl: 06-0344).

The presence of CuCl diffraction peaks at $2\theta = 28.5^\circ$ and 47.4° are attributed to the chemical reaction between aqua regia and Cu NPs.

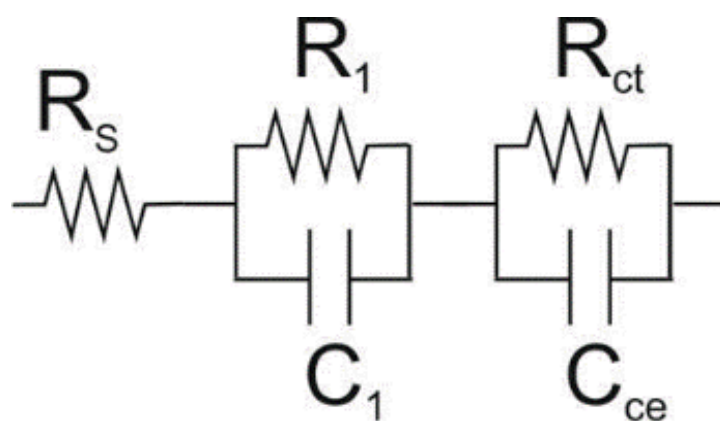


Fig. S6 Simulation circuit used for analysing the EIS data for symmetric dummy cells. R_s accounts for substrate resistance, R_1 and C_1 , associated to high frequency arc, for charge transfer resistance and contact capacitance at interface between substrate and carbon electrode, R_{ct} and C_{ce} , associated to low frequency arc, for charge transfer resistance and electrode capacitance at CE/electrolyte interface.

Table S1 Parameters from EIS measurements of different CEs.

Electrodes	R_s ($\Omega \text{ cm}^2$)	$2R_1$ ($\Omega \text{ cm}^2$)	$2C_1$ (mF/cm ²)	$2R_{ct}$ ($\Omega \text{ cm}^2$)	$2C_{ce}$ (F/cm ²)
Cu@C-800	8.257	0.864	24.358	1.478	0.264
Cu@C-900	8.325	0.660	14.362	1.382	0.373
Cu@C-1000	8.280	0.325	0.026	0.353	0.069
Cu@C-1100	8.295	0.244	0.503	0.702	0.058
Cu ₂ S	8.456	0.583	3.592	1.328	0.288

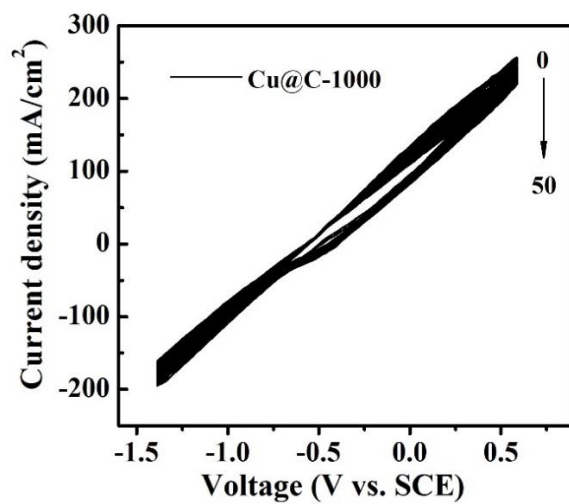


Fig. S7 Consecutive CV measurement for 50 cycles about Cu@C-1000/FTO CEs at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$ in the media of $\text{Sn}^{2-}/\text{S}^{2-}$ redox electrolyte.

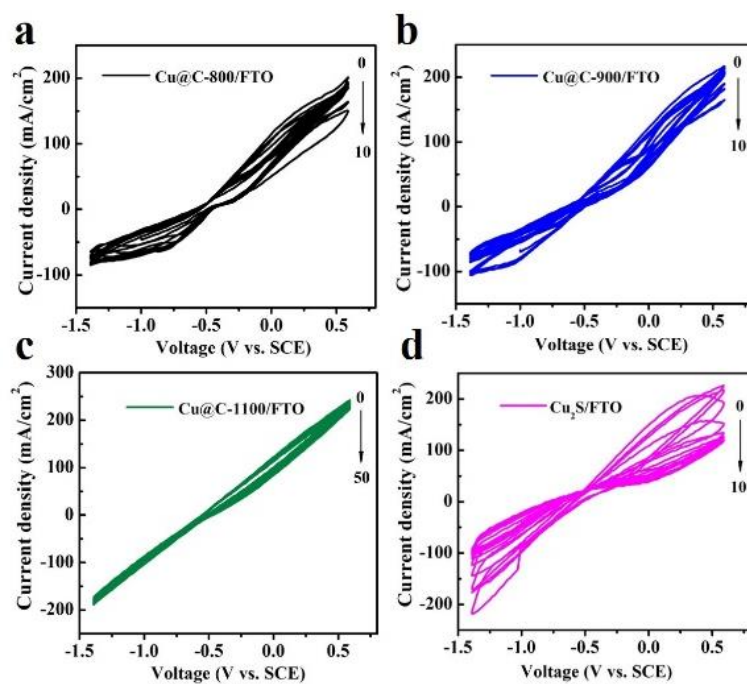


Fig. S8 Electrochemical stability of different CEs. Consecutive CV measurement for 10 cycles of (a) Cu@C-800/FTO, (b) Cu@C-900/FTO, 50 cycles of (c) Cu@C-1100/FTO, and 10 cycles of (d) Cu₂S/FTO, and at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ in the media of $\text{Sn}^{2+}/\text{S}^{2-}$ redox electrolyte, respectively.

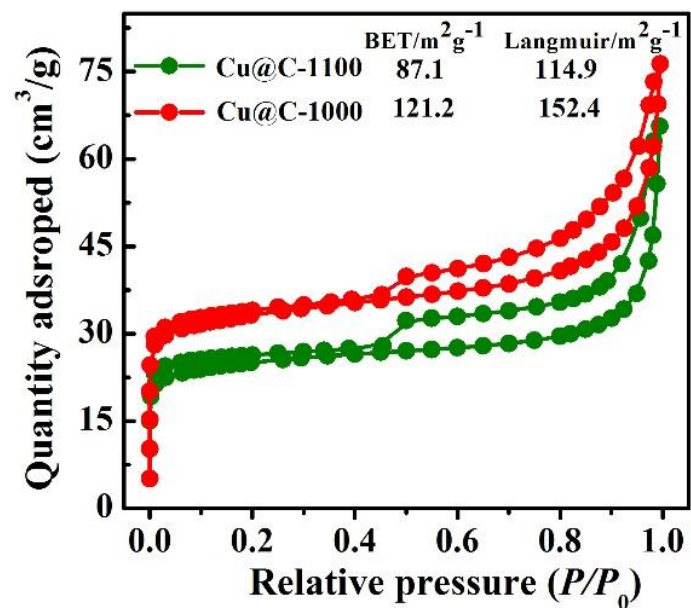


Fig. S9 Nitrogen adsorption isotherms measured at 77 K of Cu@C-1000 and Cu@C-1100 (insert: pore parameters of Cu@C-1000 and Cu@C-1100).

Table S2 Pore parameters of Cu@C-*x* samples.

Samples	S _{BET} (m ² /g)
Cu@C-800	130.88
Cu@C-800	114.85
Cu@C-800	99.59
Cu@C-800	121.69
Cu@C-800	87.13

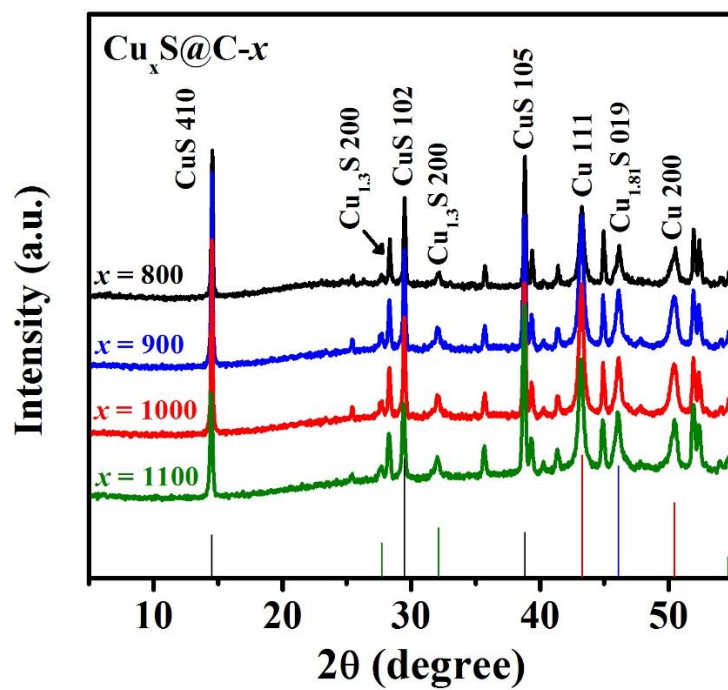


Fig. S10 Powder XRD patterns of obtained $\text{Cu}_x\text{S}@C-x$. (JCPDS information: red line is cubic Cu 04-0836, green line is Cubic $\text{Cu}_{1.3}\text{S}$ 24-0061, blue line is cubic $\text{Cu}_{1.81}\text{S}$ 41-0959, black line is cubic CuS 06-0464).

Table S3 Inductively coupled plasma atomic emission spectrometry (ICP-AES) results for Cu contents in the aqueous solution soaked by $\text{Cu}_x\text{S}@C-x$ samples.

Samples	Cu (mg/L)
$\text{Cu}_x\text{S}@C-800/\text{FTO}$	2.77
$\text{Cu}_x\text{S}@C-900/\text{FTO}$	2.58
$\text{Cu}_x\text{S}@C-1000/\text{FTO}$	0.74
$\text{Cu}_x\text{S}@C-1100/\text{FTO}$	0.72
$\text{Cu}_2\text{S}/\text{FTO}$	1.10