## **Supporting Information (SI)**

## Phase transformations of novel Cu<sub>x</sub>S nanostructures as highly efficient counter electrodes for stable and reproducible quantum dot-sensitized solar cells

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Thin films	Cu (at%)	S (at%)	Ratio (Cu/S)	Average Ratio
Cu <sub>2</sub> S (Thin film1)	66.05	33.5	1.98	
Cu <sub>2</sub> S (Thin film2)	67.1	32.9	2.03	2.01±0.02
Cu <sub>2</sub> S (Thin film3)	66.9	33.1	2.02	
Cu <sub>1.75</sub> S (Thin film1)	64.2	35.8	1.79	
Cu <sub>1.75</sub> S (Thin film2)	63.8	36.2	1.76	1.76±0.03
Cu <sub>1.75</sub> 8 (Thin film3)	63.4	36.6	1.73	
Cu <sub>1.12</sub> S (Thin film1)	53.6	46.4	1.15	
Cu <sub>1.12</sub> S (Thin film2)	53.2	46.8	1.13	1.13±0.02
Cu <sub>1.12</sub> S (Thin film3)	52.9	47.1	1.12	
CuS (Thin film1)	51.9	49.1	1.07	
CuS (Thin film2)	51.4	48.6	1.05	1.03±0.04
CuS (Thin film3)	49.3	50.7	0.97	

Table S1. Atomic ratios of copper sulfides determined by SEM-EDX quantitative analysis



**Fig. S1** Cross-sectional SEM images of (a)  $Cu_2S$ , (b)  $Cu_{1.75}S$ , (c)  $Cu_{1.12}S$ , and (d) CuS thin film on the surface of FTO.



Fig. S2 3-Dimensional (3D) AFM images of (a) 0.005 mM, (b) 0.01 mM, (c) 0.02 mM, and (d) 0.03 mM L-cysteine based  $Cu_xS$  thin films on FTO substrate ( $Cu_2S$ ,  $Cu_{1.75}S$ ,  $Cu_{1.12}S$ , and CuS).

Counter Electrode	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF	η (%)
Cu <sub>2</sub> S (Cell1)	0.642	17.31	0.528	5.88
Cu <sub>2</sub> S (Cell 2)	0.645	17.32	0.527	5.89
Cu <sub>2</sub> S (Cell 3)	0.640	17.33	0.531	5.90
Cu <sub>1.75</sub> S (Cell 1)	0.640	15.86	0.523	5.32
Cu <sub>1.75</sub> S (Cell 2)	0.642	15.85	0.522	5.33
Cu <sub>1.75</sub> S (Cell 3)	0.644	15.84	0.521	5.32
Cu <sub>1.12</sub> S (Cell 1)	0.640	15.29	0.521	5.10
Cu <sub>1.12</sub> S (Cell 2)	0.646	15.26	0.518	5.11
Cu <sub>1.12</sub> S (Cell 3)	0.637	15.23	0.524	5.09
Cu8 (Cell 1)	0.643	14.46	0.525	4.89
CuS (Cell 2)	0.642	14.44	0.527	4.90
CuS (Cell 3)	0.642	14.45	0.527	4.90
Pt (Cell 1)	0.514	9.71	0.265	1.32
Pt (Cell 2)	0.517	9.98	0.263	1.36
Pt (Cell 3)	0.511	10.03	0.264	1.35

Table S2. Solar cell parameters of QDSSC (multiple cells) with various  $Cu_xS$  and Pt CEs



**Fig. S3** XRD spectra of the as-prepared  $Cu_{1,12}S$  CE, the  $Cu_{1,12}S$  CE after 5 days of immersion in the polysulfide electrolyte.