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Supporting Information for

Photoelectrochemistry of Colloidal Cu_2O Nanocrystal Layers: The Role of Interfacial Chemistry

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Chemicals: copper(II) acetylacetonate (≥99.9%), 1-octadecene (ODE, 90%), octadecylamine (ODA, ≥99%),1,2-Ethanedithiol (98%), Benzene-1,4-dithiol (99%), Benzenethiol (98%), 4-Methylbenzenethiol (98%), 4-Chlorothiophenol (97%), 4-Fluorothiophenol (98%) and 4-nitrobenzenethiol (80%), $CuSO_4$ (99%), lactic acid (85%), were purchased from Sigma Aldrich.

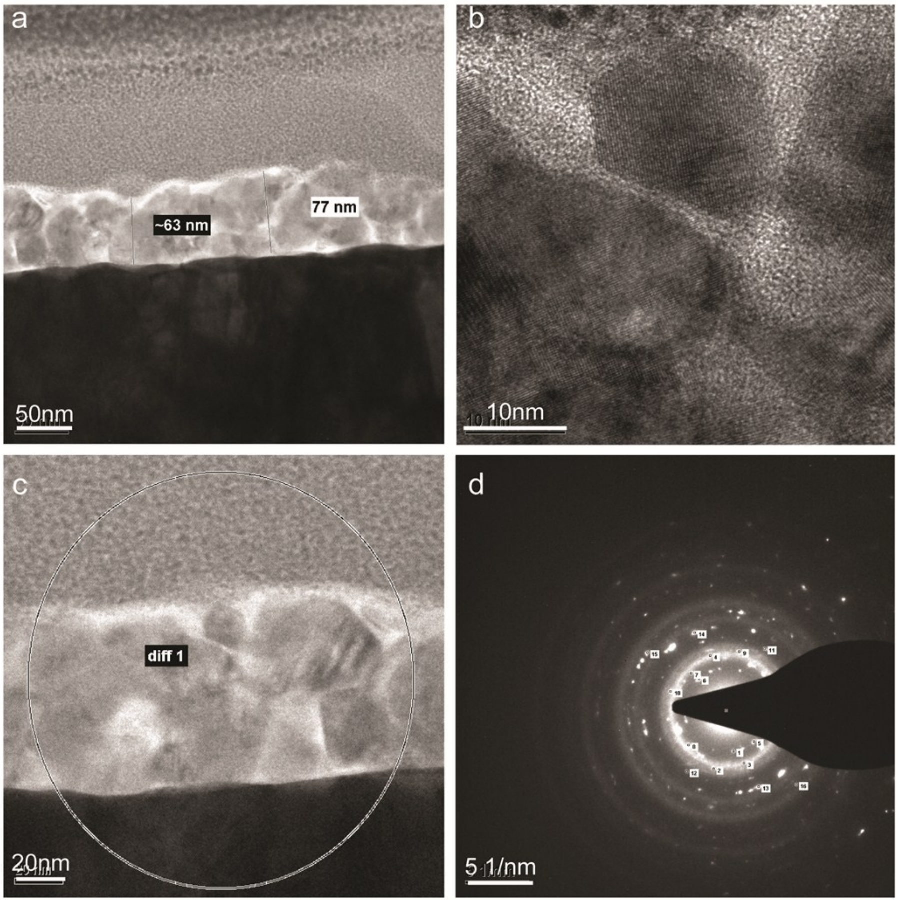

Figure S1. High resolution transmission electron (HR-TEM) cross section micrographs and electron diffraction of Cu_2O NCs film deposited on Au substrate.

Table S1. Diffraction values re. Figure S1

Spot#	d-Spacing (nm)	Rec. Pos.(1/nm)	Degrees to Spot 1	Degrees to x-axis	Amplitude
1	0.3049	3.28	0	-79.97	1487
2	0.2113	4.734	22.16	-102.13	799
3	0.2261	4.423	8.46	-71.51	234
4	0.2222	4.501	173.7	106.33	248
Cu_2O					
5	0.303	3.3	31.2	-48.77	1462
6	0.3042	3.287	149.16	130.87	3596
7	0.2485	4.025	146.67	133.36	634
8	0.2468	4.053	57.12	-137.09	556
9	0.2111	4.737	157.54	77.57	641
10	0.2148	4.655	118.63	161.4	366
11	0.174	5.746	137.91	57.94	423
12	0.1738	5.752	42.78	-122.75	142
13	0.1523	6.566	12.96	-67.01	824
14	0.1508	6.632	167.91	112.12	695
15	0.1293	7.732	136.19	143.84	799
16	0.124	8.066	33.39	-46.58	402
Au					
17	0.2279	4.388	162.14	117.89	261
18	0.199	5.024	141.54	138.49	145
19	0.1411	7.089	124.93	155.1	83
20	0.119	8.407	118.63	161.4	86

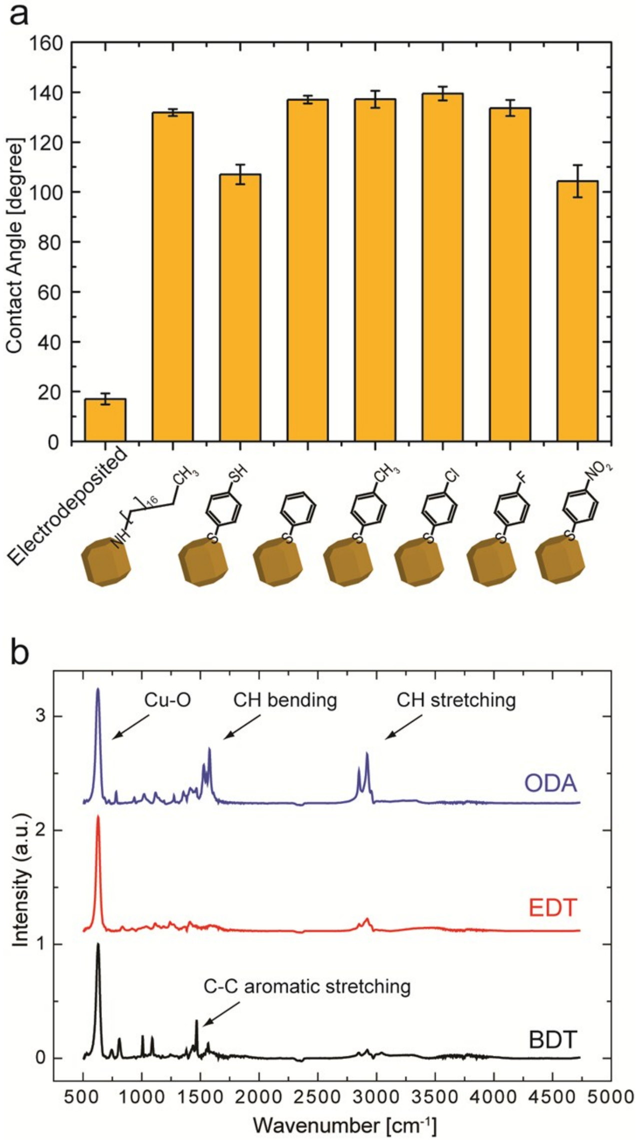

Figure S2. (a) Contact angle values of an electrodeposited Cu_2O film and of slow evaporated layers of ODA-Cu_2O NCs, before and after ligand exchange. The ligands that were in use: Benzene-1,4-dithiol, Benzenethiol, 4-Methylbenzenethiol, 4-Chlorothiophenol, 4-Fluorothiophenol and 4-nitrobenzenethiol. (b) FTIR absorption spectra of Cu_2O NCs in KBr pellets. 24 h Ligand-exchanged NCs with Ethanedithiol (EDT, red spectrum) and Benzene-1,4-dithiol (BDT, black spectrum) are compared to the original ODA coated Cu_2O NCs ((in blue). The strong peak at 628 cm^{-1} is assigned to the Cu(I)-O vibration and confirms the appearance of Cu_2O structure.[1–3] All spectra are baseline corrected and normalized according to the peak at 628 cm^{-1}. The absorption peaks at 2800-2900 cm^{-1} and 1580 cm^{-1} are assigned to linear alkyl chain C-H stretching and bending modes, respectively, and reduced upon ligand exchange with BDT. In parallel, a peak at around 1470 cm^{-1} that is attributed to C-C aromatic stretching mode is clearly identified.[4,5] Disappearance of alkyl chain vibration modes and appearance of C-C aromatic stretching modes are clear signs for successful ligand exchange from ODA to BDT. For EDT, CH stretching and bending are still present, though, at lower intensity, in agreement with the replacement of long octadecyl by shorter ethyl chains on top of the NCs.

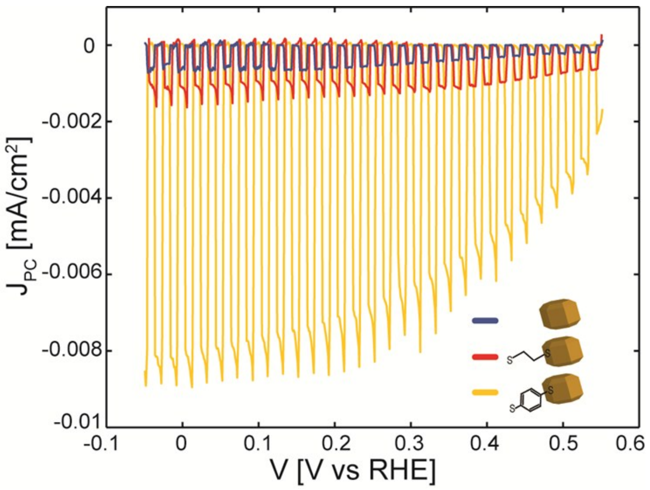

Figure S3. Linear sweep voltammetry measurements of slow evaporated ODA-Cu_2O NCs on Au substrate (blue) and on activated Au substrate with 1,2-Ethanedithiol (red) and Benzene-1,4-dithiol (yellow). 2nd backward sweeps, scan rate 10 mV/sec.

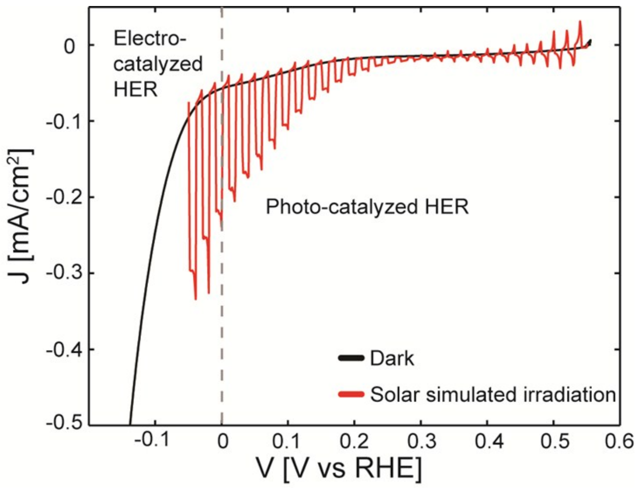

Figure S4. Linear sweep voltammograms (backward sweep #1, scan rate 10 mV/sec) of electrodeposited Cu_2O thin films (~1 µm) on Au substrates without prior chemical activation. The electrodeposition was conducted at pH > 10. The electrochemical measurements have been conducted at dark (black) and under solar simulated AM 1.5G chopped illumination (red).

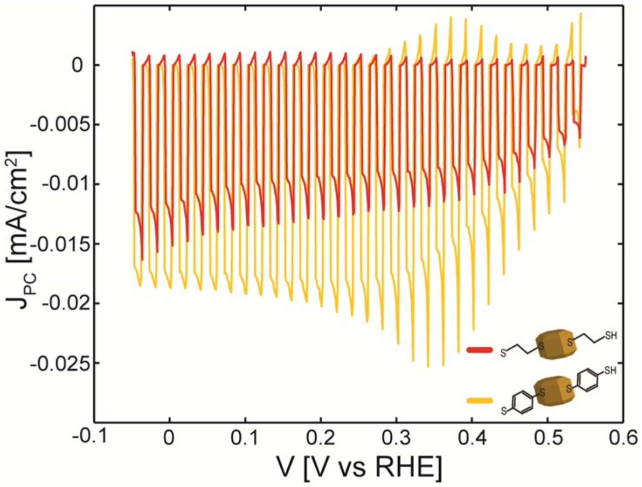

Figure S5. Linear sweep voltammetry of ODA-Cu_2O NCs, slow evaporated on Au substrates that were chemically-activated and consecutively exchanged NCs surface coating with 1,2-Ethanedithiol (red) and with Benzene-1,4-dithiol (yellow). The Au surface activation and ligand exchange were done for 60 min in chloroform 0.5 M solution. The measurements have been conducted under solar simulated AM 1.5G chopped illumination. 2nd backward sweeps are presented, scan rate 10 mV/sec.

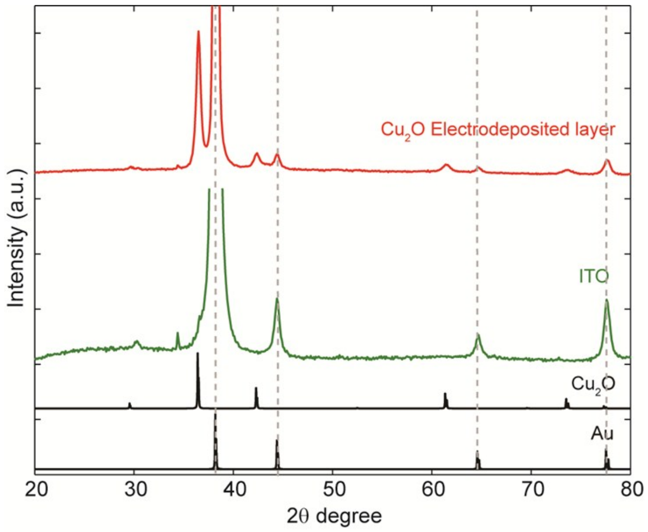

Figure S6. XRD patterns for electrodeposited Cu_2O thin film (red), compared with Cu_2O database card 01-078-2076 (black). Au database card 00-004-0784 data (blak) and ITO measured XRD pattern (green) are added, as well. The peaks of Au and ITO are marked with dashed lines.

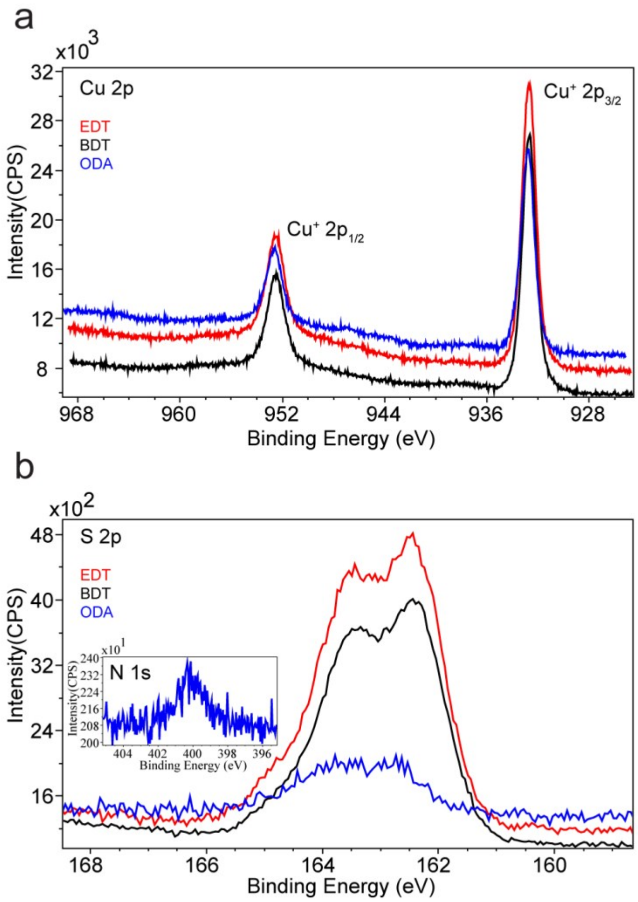

Figure S7. X-ray photoelectron spectroscopy (XPS) measurements on deposited layers of the nanocrystals before and after ligand exchange. (a) Distinct peaks centered at 932.7 and 952.5 eV are observed and correspond to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ in Cu_2O, respectively.[6,7] Moreover, satellite Cu2p peaks (at 942.9 and 954.2 eV) which associated with CuO and indicating Cu^{2+} having a partially filled d^9 shell configuration in the ground state, are absent in the XPS spectra for our NCs, indicating the existence of Cu_2O phase solely and rationalized due to a full d^{10} shell that inhibits screening via charge transfer involving d states.[3] (b) In addition, ligand exchange is confirmed by the XPS measurements, with strong sulfide peak for EDT and BDT (S2p at 162 eV), and a small, but discernible N peak for ODA (N1s at 400 eV) (inset).

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