Tuning Interfacial Electron Transfer in Nanostructured Cuprous Oxide Photoelectrochemical Cells with Charge-Selective Molecular Coatings

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Supporting Information (14 pp.)

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Experimental Section:

Sensitizers. The syntheses of **NcQ-A**, **C60M-A**, and **ZnP-A** have been reported elsewhere.[1-4] C343 and 1-adamantanecarboxylic acid were obtained commercially (Aldrich), as was the N3 dye (Solaronix) and all were used as received.

Preparation of Cu_2O Nanorod arrays. Cu_2O nanorod films were prepared as previously described,[5] with changes that included passivation of bare F-SnO_2 areas of the conductive glass substrate, as well as slightly elevated temperature and pH for Cu_2O deposition. The elevation of pH and temperature was observed to improve the reproducibility of Cu_2O nanorod growth. ZnO nanorods that were hydrothermally grown on F-SnO_2/glass substrates pre-seeded with MnOOH nanoparticles in an aqueous bath of $ZnSO_4$, ethanolamine and NH_4OH at 90°C were then subjected to anodic passivation of bare F-SnO2 via graft polymerization of poly(phenylene oxide).[6,7] Retail fingernail polish, diluted to 15% solution (v/v) in 1,2-dichloroethane/acetone (1:1) was spincoated over the ZnO nanorod films at 2000 rpm for 2 min. Fingernail polish is typically 13-22 wt% nitrocellulose, so the final nitrocellulose solution for spin-casting is estimated at 1-2 wt% nitrocellulose. Polymer-coated slides were then immersed in an aqueous solution of phosphoric acid (0.5 M) or boric acid (0.5 M) and left for 5 min or overnight, respectively. Nanopore membrane-coated substrates were subjected to electrodeposition using the F-SnO_2/glass substrate as a working electrode, and fitting a glass joint with an o-ring over the substrate with a clamp to make a seal. The glass vessel was filled with an aqueous solution containing lactic acid and $CuSO_4$, adjusted to pH 10 with 1 M NaOH (aq). A platinum counterelectrode and Ag/AgCl quasi reference electrode were each fitted into the vessel and wired through a septum used to seal the vessel. The electrolyte was purged with argon through the septum. The vessel was immersed in a water bath at 40°C and electrodeposition was performed cathodically at constant potential (400–600 mV).[8]

Sensitization of the Cu_2O films. Sensitizers were dissolved in anhydrous CH_3CN (N3, C343) or anhydrous DMF (**C60M-A**, **ZnP-A**, **NcQ-A**) to 1-3 mM concentration, and allowed to soak for 24 h. SEM images were collected before and after soaking (*vide infra*). Upon observation of etching by the N3 dye, an additional film was soaked for just 6 h to assess the etching at shorter time.

Preparation and testing of photoelectrochemical cells. Cells were assembled by melt-adhesion of a thin film of Surlyn® polymer between the Cu_2O/F-SnO_2 electrode and a platinized F-SnO_2 counterelectrode.[9] The cells were filled by capillary action with an electrolyte composed of 0.1 M $LiClO_4$, 50 mM methyl viologen tetrafluoroborate, and 25 mM decamethylcobaltocene. After filling the cells with electrolyte, the entry/exit ports were sealed with Hysol 1C epoxy. Current-voltage measurements were done with a Keithley 2400 sourcemeter and solar simulator (SolarLight, Inc.). IPCE spectra were measured against a calibrated silicon photodiode using monochromatic light from a Xenon lamp (PV Measurements QEX7).

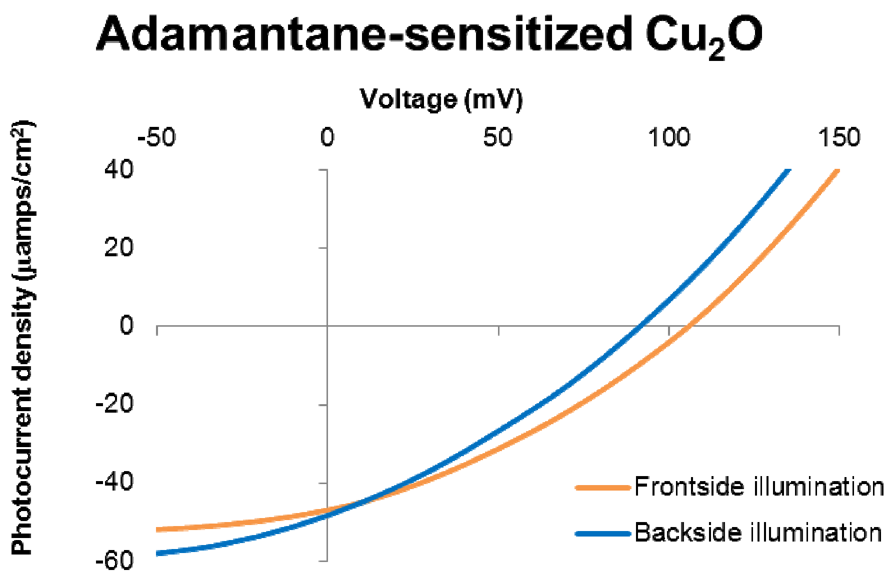

Figure S1. Current-voltage behavior of a photoelectrochemical cell wherein the Cu_2O nanorod film was sensitized with 1-adamantanecarboxylic acid (from EtOH soln, for 24 h) prior to cell assembly. The decreased photocurrent relative to bare Cu_2O nanorods suggest that forward electron transport to the methyl viologen has been inhibited by the adamantyl sensitization.

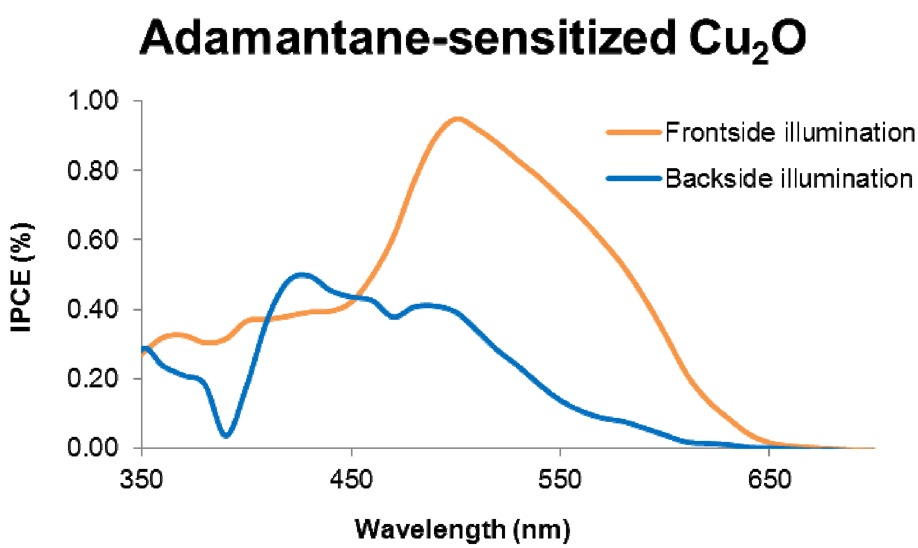

Figure S2. External quantum efficiency behavior of a photoelectrochemical cell wherein the Cu_2O nanorod film was sensitized with 1-adamantanecarboxylic acid (from EtOH soln, for 24 h) prior to cell assembly.

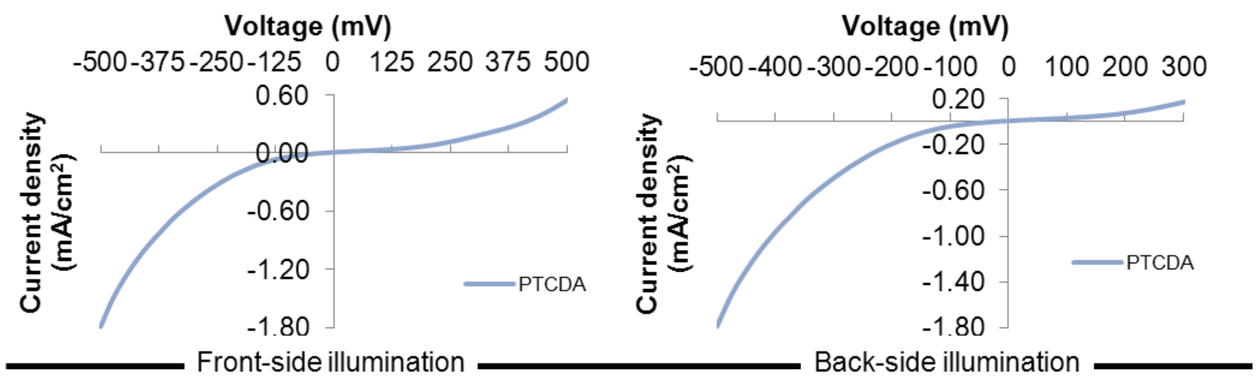

Figure S3. Device data for PTCDA-coated cuprous oxide nanorods (full voltage range).

Table S1. Device Performance Metrics for Photoelectrochemical Cells using Bare and Molecule-Coated Cu_2O Nanorod films.

Surface coating	Illumination	Active area (cm^2)	J_{SC} ($\mu Amp/cm^2$)	V_{OC} (mV)	FF	η (%)
ZnP-A	Front	0.60	1760	197	0.28	0.096
ZnP-A	Back	0.60	836	183	0.28	0.043
C60M-A	Front	0.52	1480	175	0.29	0.076
C60M-A	Back	0.52	575	140	0.30	0.024
NcQ-A	Front	0.53	688	140	0.24	0.023
NcQ-A	Back	0.53	299	103	0.26	7.9×10^{-3}
C343	Front	0.42	717	102	0.27	0.020
C343	Back	0.42	271	102	0.27	7.4×10^{-3}
bare Cu_2O	Front	0.60	207	81	0.27	4.6×10^{-3}
bare Cu_2O	Back	0.60	140	90	0.28	3.5×10^{-3}
N3	Front	0.63	56	124	0.22	1.5×10^{-3}
N3	Back	0.63	32	94	0.26	7.7×10^{-4}
Adamantane-A	Front	0.61	47	104	0.33	1.6×10^{-3}
Adamantane-A	Back	0.61	48	92	0.29	1.3×10^{-3}
PTCDA	Front	0.46	-32*	-27*	n/a	n/a
PTCDA	Back	0.46	10	5	0.26	1.3×10^{-5}

Front side illumination (through Cu_2O) is shown in shaded rows. Surface coatings (and bare Cu_2O) are vertically arranged in descending order of highest to lowest overall efficiency across each given illumination direction. Adamantane-A = adamantane-1-carboxylic acid. *Device photocurrent broke down before reaching short-circuit conditions.

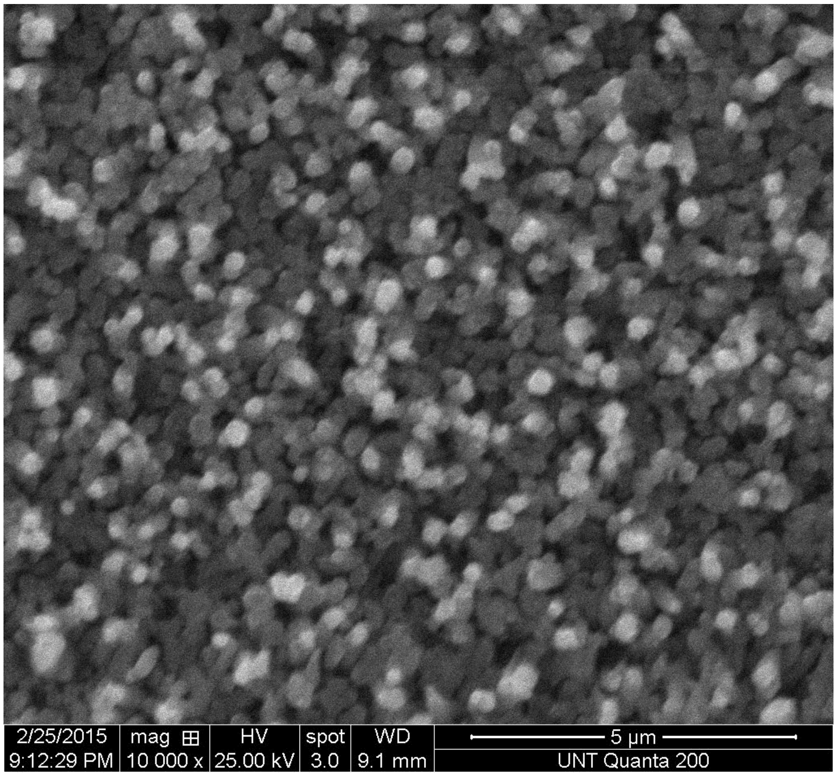

Figure S4. SEM image of Cu_2O nanorod film before sensitization with **ZnP-A**.

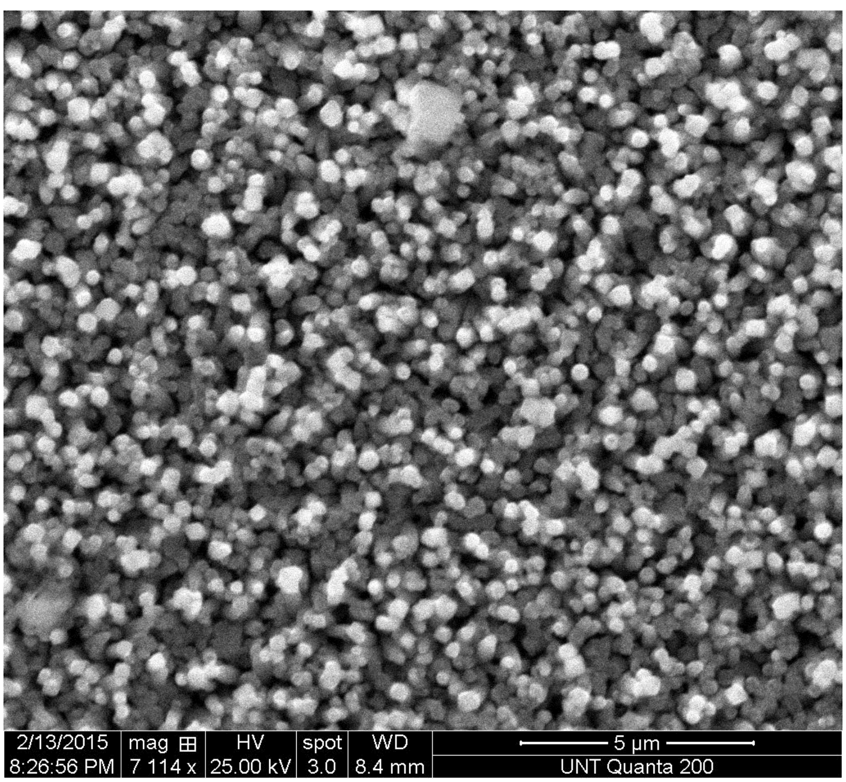

Figure S5. SEM image of Cu_2O nanorod film after 24 h sensitization with **ZnP-A**.

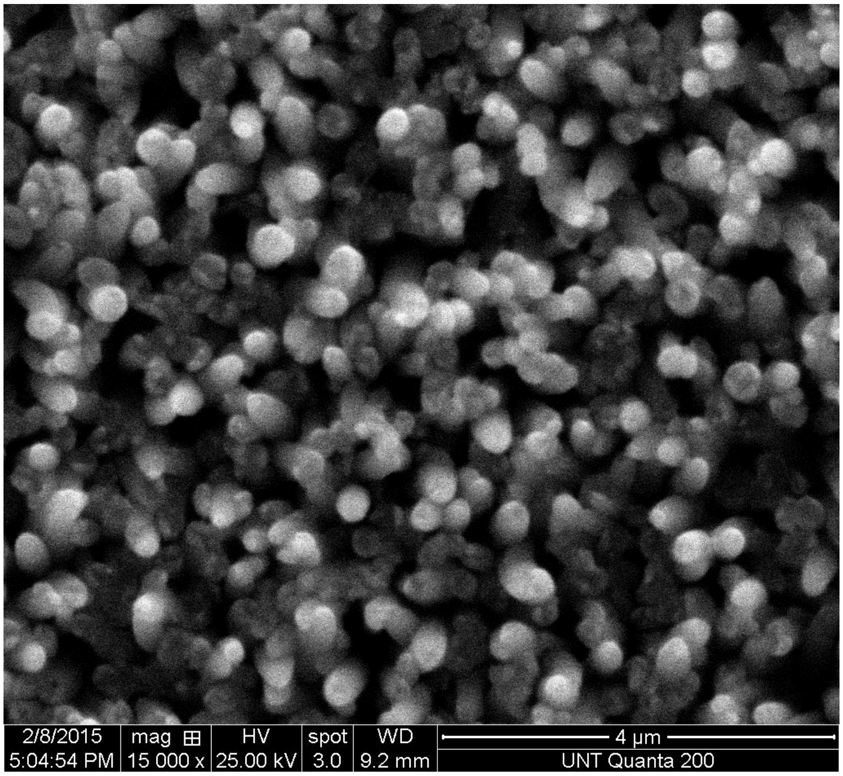

Figure S6. SEM image of Cu_2O nanorod film before sensitization with **C60M-A**.

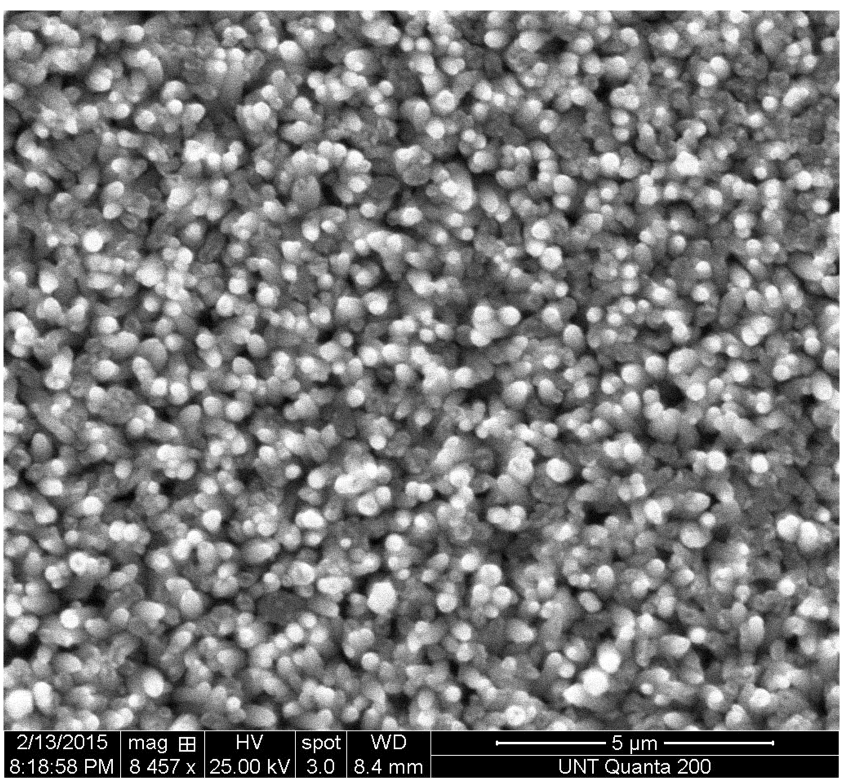

Figure S7. SEM image of Cu_2O nanorod film after 24 h sensitization with **C60M-A**.

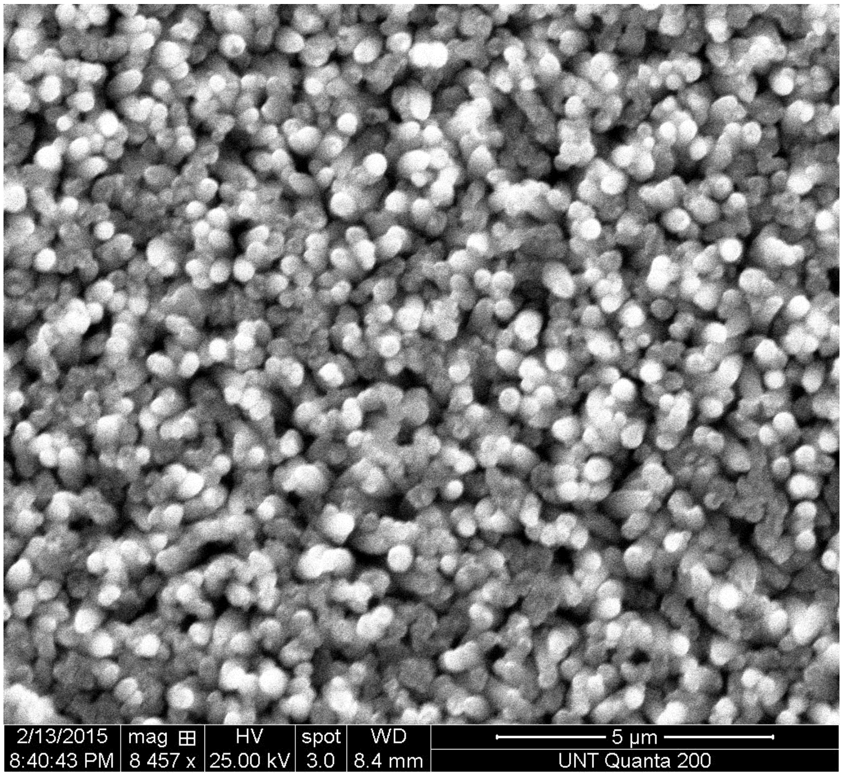

Figure S8. SEM image of Cu_2O nanorod film before sensitization with C343.

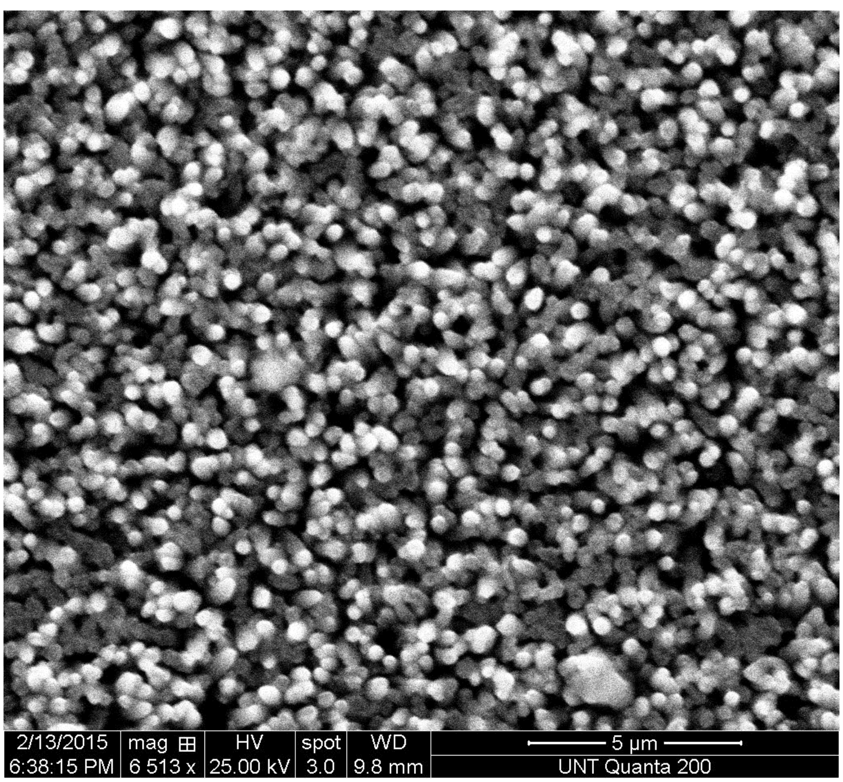

Figure S9. SEM image of Cu_2O nanorod film after 24 h sensitization with C343.

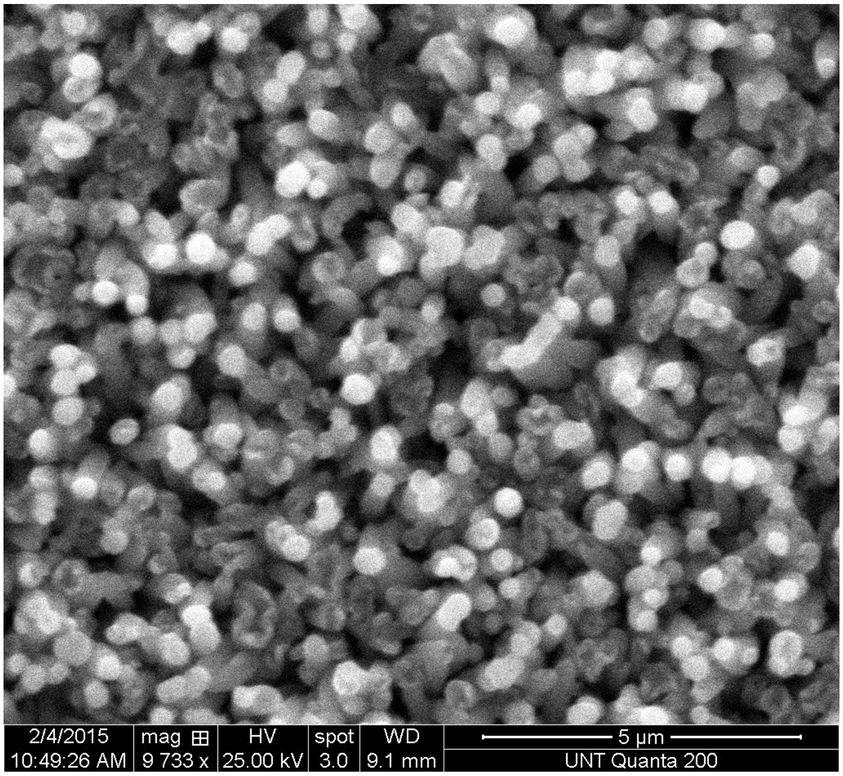

Figure S10. SEM image of Cu_2O nanorod film before sensitization with **NcQ-A**.

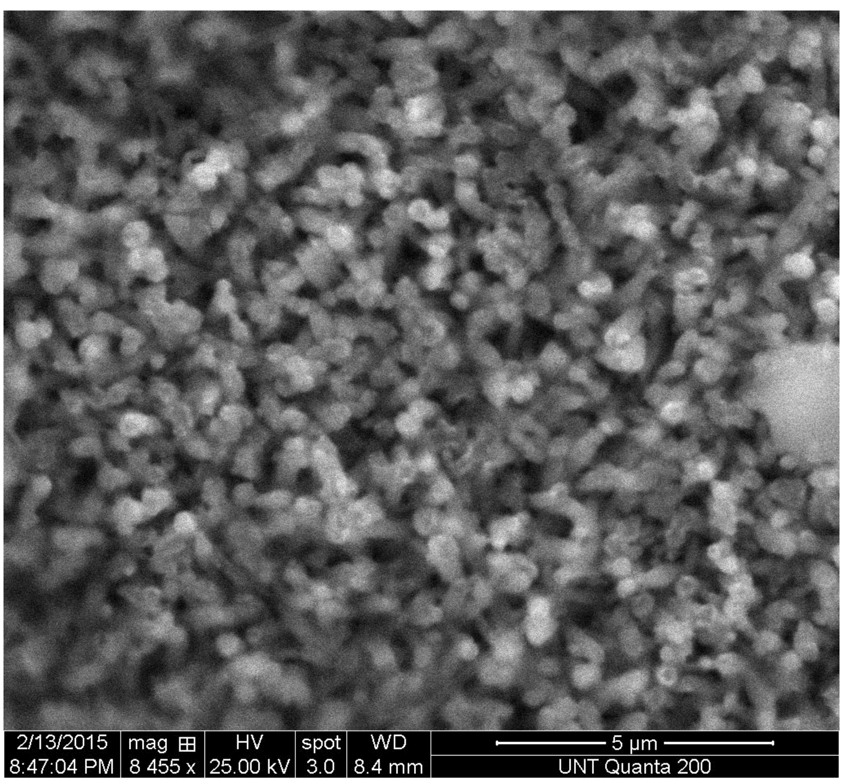

Figure S11. SEM image of Cu_2O nanorod film after 24 h sensitization with **NcQ-A**.

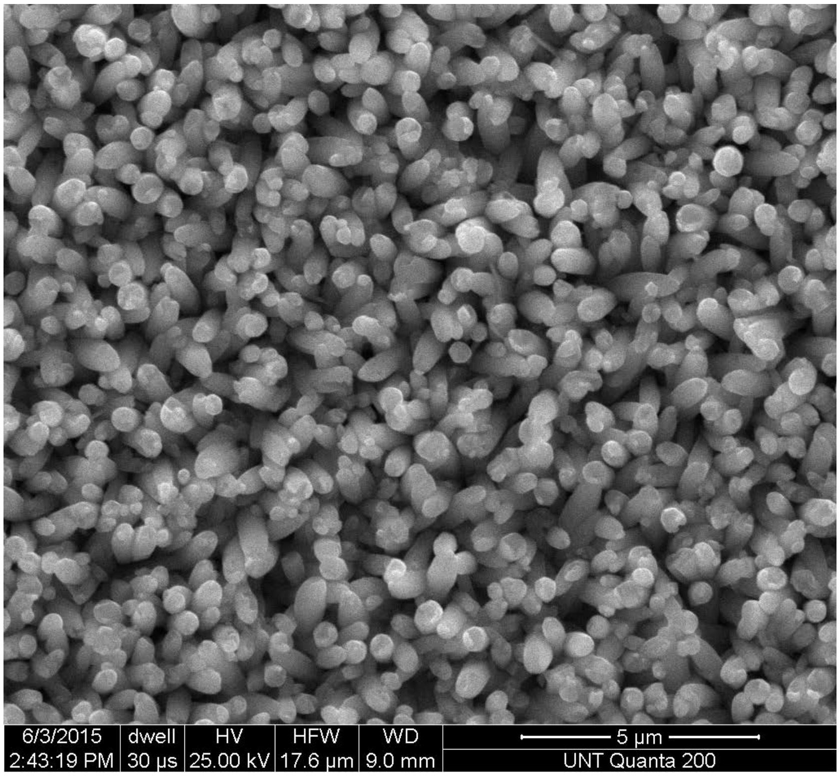

Figure S12. SEM image of Cu_2O nanorod film before sensitization with N3.

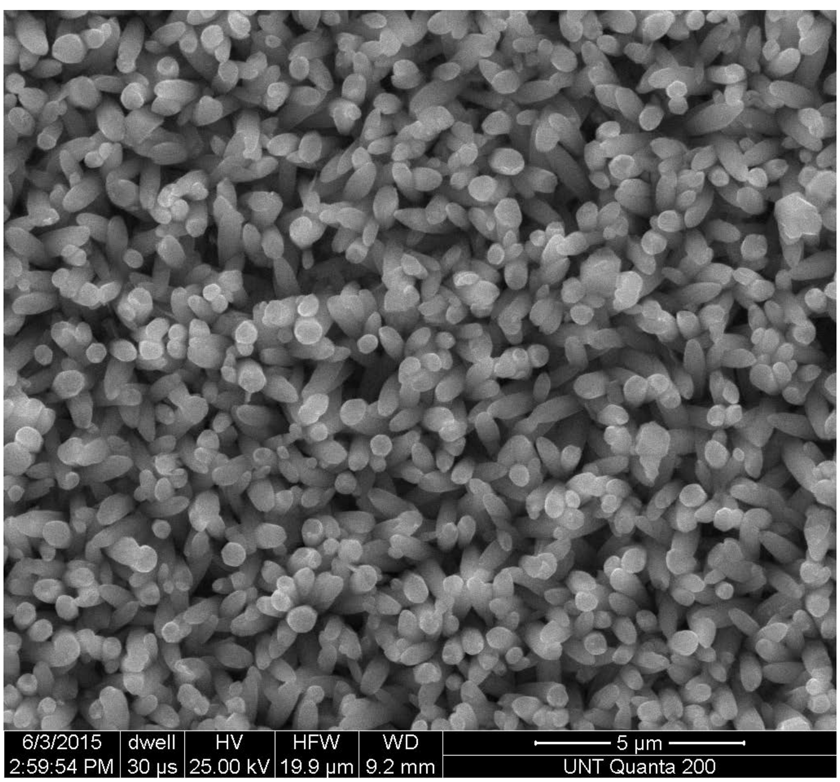

Figure S13. SEM image of Cu_2O nanorod film after sensitization with PTCDA

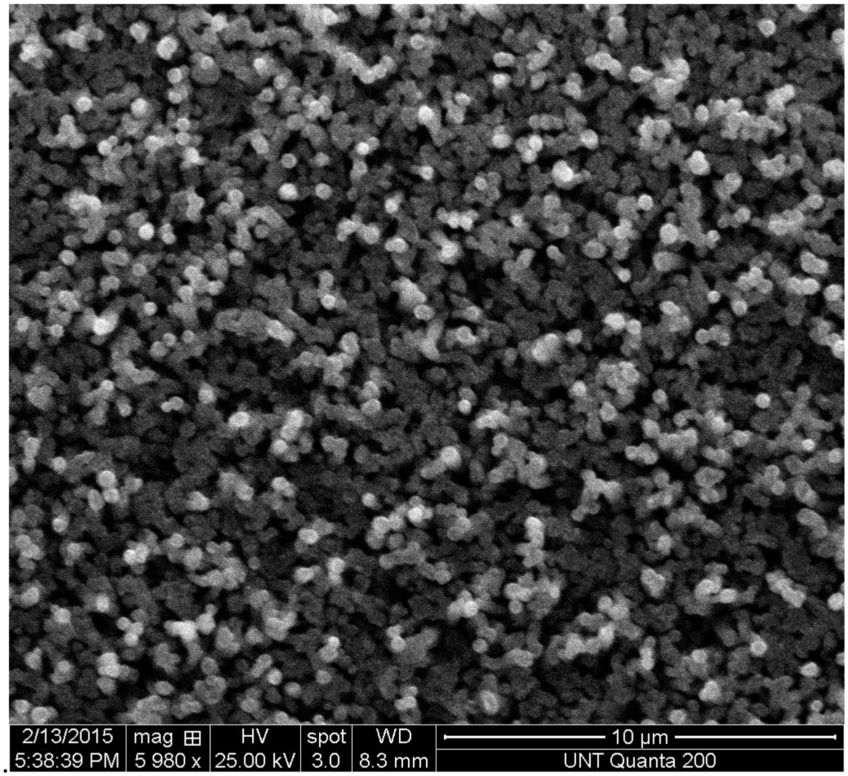

Figure S14. SEM image of Cu_2O nanorod film before sensitization with N3.

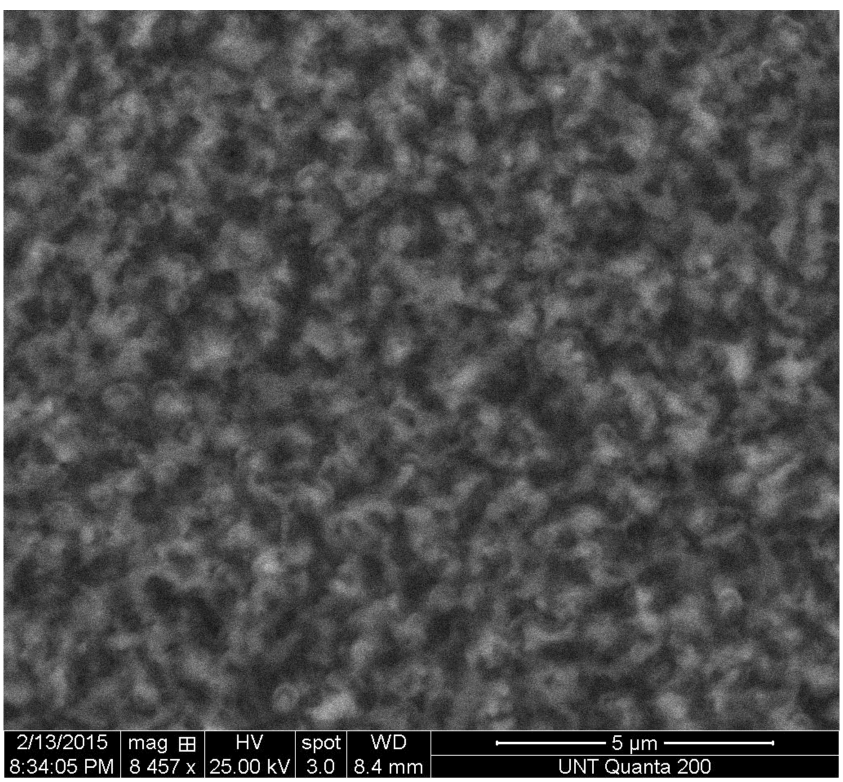

Figure S15. SEM image of Cu_2O nanorod film after 24 h sensitization with N3.

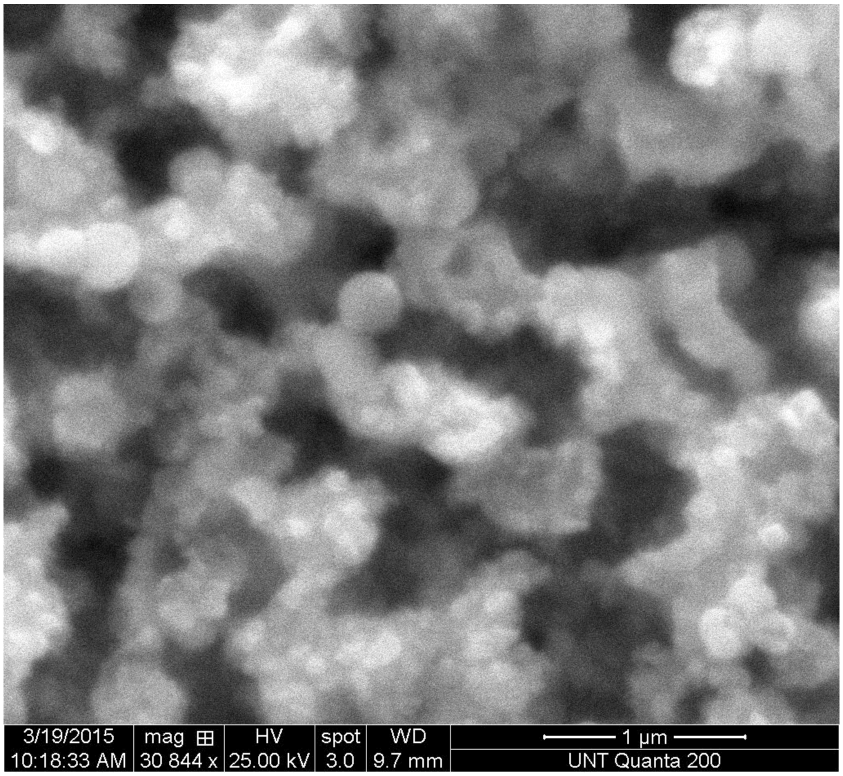

Figure S16. SEM image of Cu_2O nanorod film after 6 h sensitization with N3.

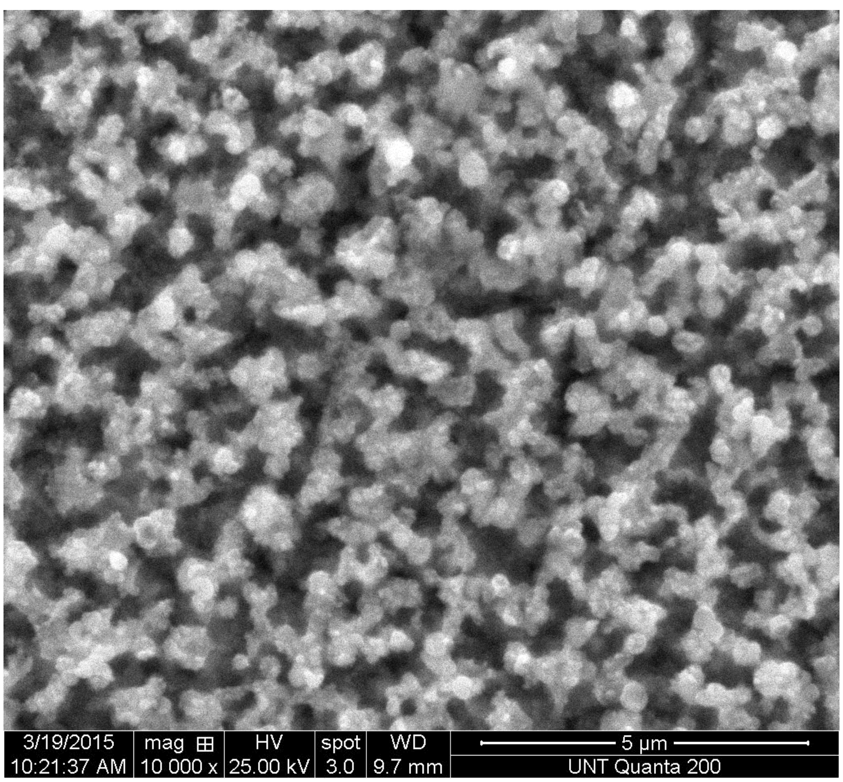

Figure S17. SEM image of Cu_2O nanorod film after 6 h sensitization with N3.

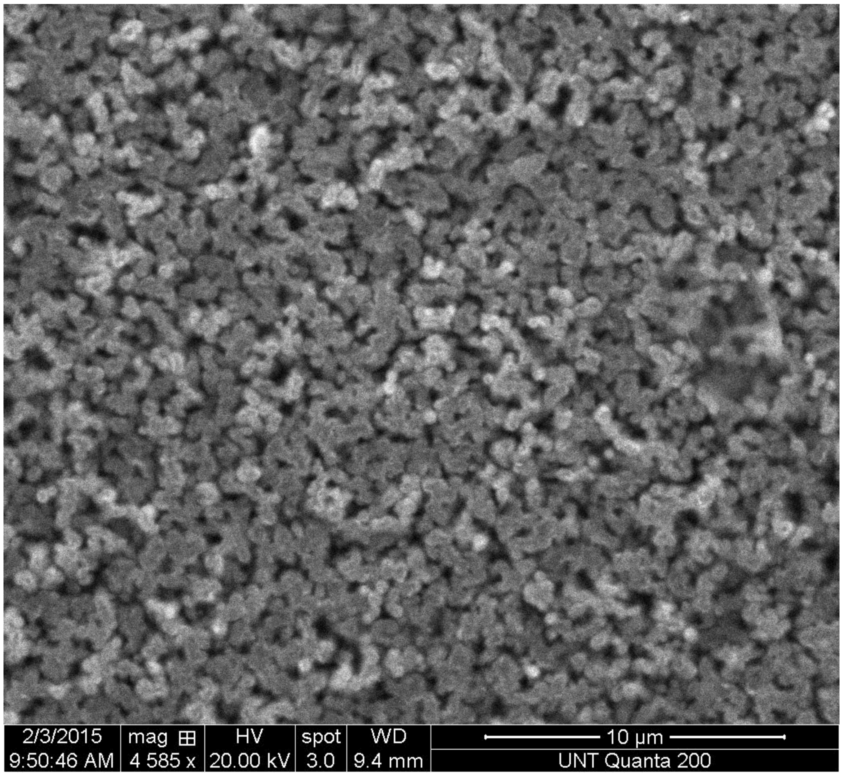

Figure S18. SEM image of Cu_2O nanorod film before sensitization with 1-adamantanecarboxylic acid.

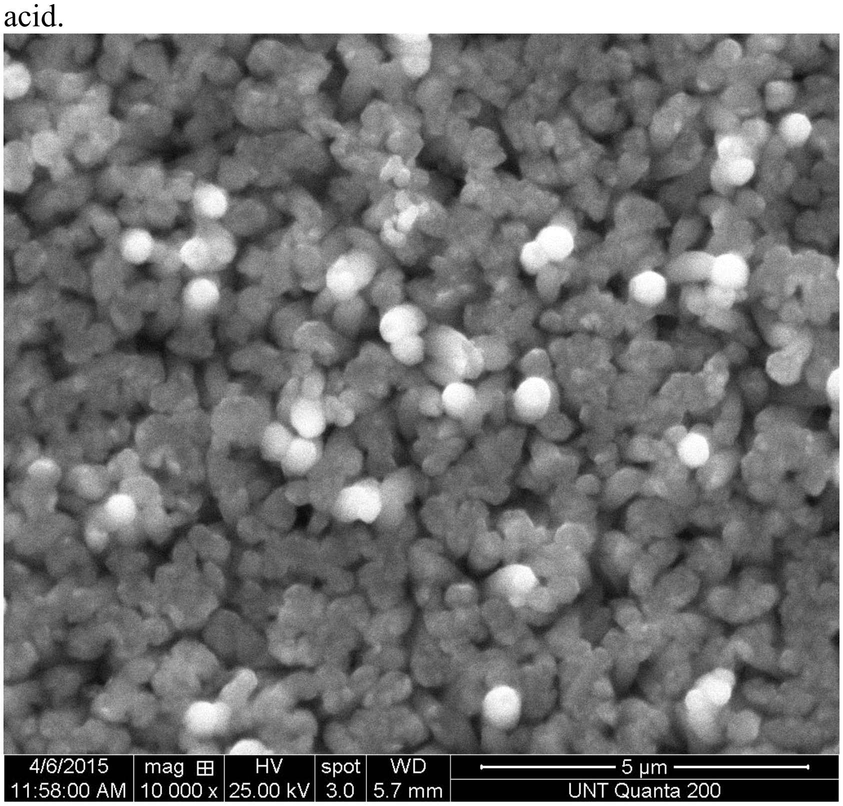

Figure S19. SEM image of Cu_2O nanorod film after 24 h sensitization with -adamantanecarboxylic acid.

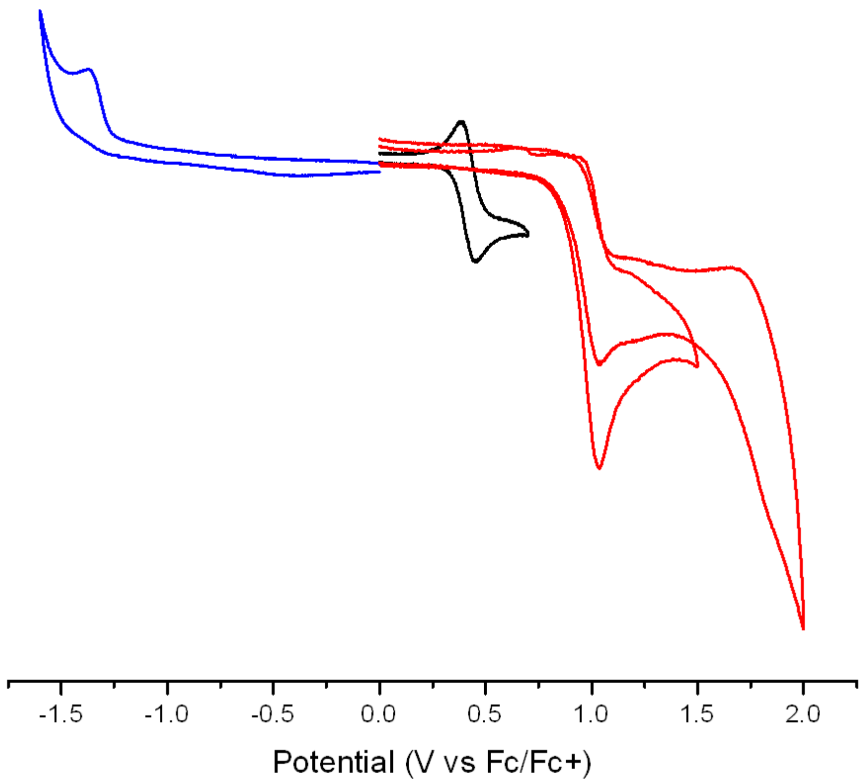

Figure S20. Cyclic voltammogram of Coumarin C343 in acetonitrile containing 0.1 M (*t*-$Bu_4N)ClO_4$ @ scan rate = 50mV/s.

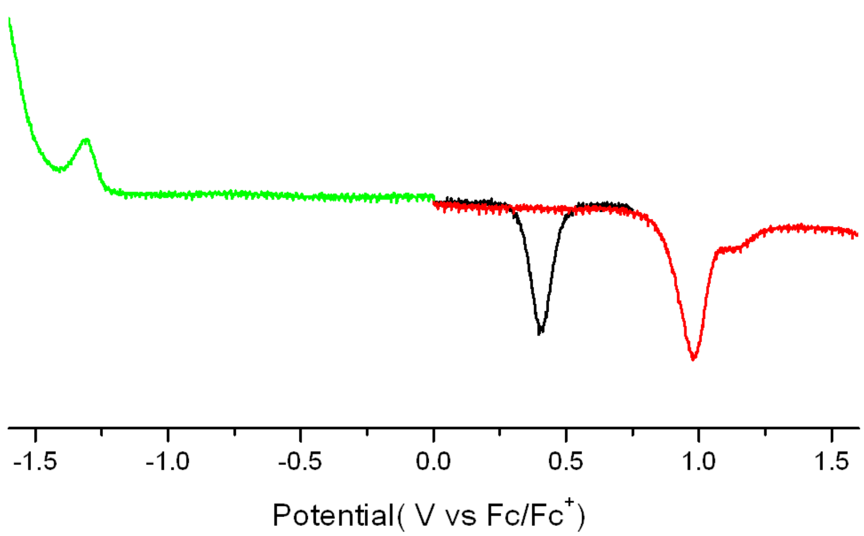

Figure S21. Differential pulse voltammogram of Coumarin C343 in acetonitrile containing 0.1 M (*t*-$Bu_4N)ClO_4$ @ Scan rate = 20mV/s

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