

Supporting Information for

Core-Shell CdS-Cu₂S Nanorod Array Solar Cells

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Experimental details:

CdS Nanorod Growth. CdS nanorods were prepared in a 45 mL Teflon-lined stainless steel autoclave at 200°C for 4 hours after charging the autoclaves with 35 mL of precursor solution and clean, pre-scored conductive substrates on glass. The conductive substrates were cleaned by rinsing in deionized water followed by etching in 0.01 M HCl for 30 seconds and thorough rinsing in deionized water. Conductive substrates were placed to stand vertically with the conductive side facing down. The precursor solution was prepared by dissolving 0.259 g cadmium nitrate tetrahydrate (Aldrich, 99.999%) in deionized water followed by 0.192 g thiourea (Aldrich, ACS grade, >99.0%) and 34.6 mg of glutathione, reduced form (TCI, >97%) for 35 mL of stock solution. The amount of glutathione could be used to vary the diameter and length of nanorods. The oven was preheated to 200°C. After the autoclaves were allowed to cool, the CdS array-coated substrates were washed under a gentle stream of deionized water. After this reaction, it was found that the CdS array could be placed back into the autoclave with a fresh stock solution to enlarge the existing nanorods by performing the reaction again. The CdS nanorods used for devices reported in this work were enlarged one time with this approach. However, depending on the concentration of glutathione, this could also result on particle growth on the nanowires or the nucleation of new CdS nanorods. The CdS array coated substrates were carefully broken along the scored lines into individual chips of about 1 cm².

Device Fabrication.

The as-grown CdS nanorod arrays were coated in 20 nm of Al₂O₃ at 200°C in a home-built ALD system. After functionalizing the surface with hexamethyldisilazane (HMDS),

PMMA (C4, Microchem) was spin coated onto the chip with an initial spin rate of 500 rpm with a ramp rate of 500 rpm/sec for 40 seconds followed by an increase in rate to 2500 rpm with a ramp rate of 500 rpm/sec for 60 seconds. Within several minutes, the sample was annealed at 120°C for 10 minutes on an equilibrated hotplate. After annealing, the surface was functionalized again with HMDS, and I-line photoresist was spin coated at a rate of 4000 rpm with a 3000 rpm/sec ramp rate for 40 seconds. The sample was baked at 90°C for 90 seconds. The active conversion area was defined using photolithography, and the PMMA was removed from the conversion areas by timed O₂ plasma etching at a power of 50W and a pressure of 180 millitorr for several minutes. The depth of the etch was verified by SEM on a control CdS array coated with PMMA. Active areas fabricated ranged from about 20 to 2500 μm². The ALD Al₂O₃ was removed by etching in 10:1 buffered hydrofluoric acid (BHF) solution for 60 seconds followed by a rinse in deionized water and annealing at 170°C in Ar for 30 minutes to ensure adhesion of the PMMA to the surface of the CdS after the removal of the Al₂O₃. At this point, cation exchange was performed on these samples as previously described. After cation exchange, 1 nm of ALD Al₂O₃ was deposited at 50°C to serve as a protection layer. Afterwards, the HMDS-functionalized surface was coated with I-line photoresist as described above and the area for the contacts was patterned using photolithography. The ITO top contact was deposited in a sputterer with a RF ITO target. The base pressure was less than 1e-5 torr, the power for deposition was 75W, and the deposition time was 6 minutes. During deposition, the Ar gas flow was 10 cm³/min while the O₂ flow was 2.4 cm³/min. To perform liftoff of the ITO, the edges of the sample were carefully scratched, and the chip was soaked for 1 hour in isopropanol before the chip was sonicated for 1-2

seconds to remove excess ITO to prevent the formation of high pressure tetragonal phases of Cu_2S . After liftoff, the chips were dried under a stream of nitrogen and annealed in air at 200°C for 5 minutes. Afterwards, devices were stored in nitrogen inside a desiccator (Plas Labs, 862-CGA) with ambient temperature and light until measurement in ambient air. All fabrication described here was completed during the same day.

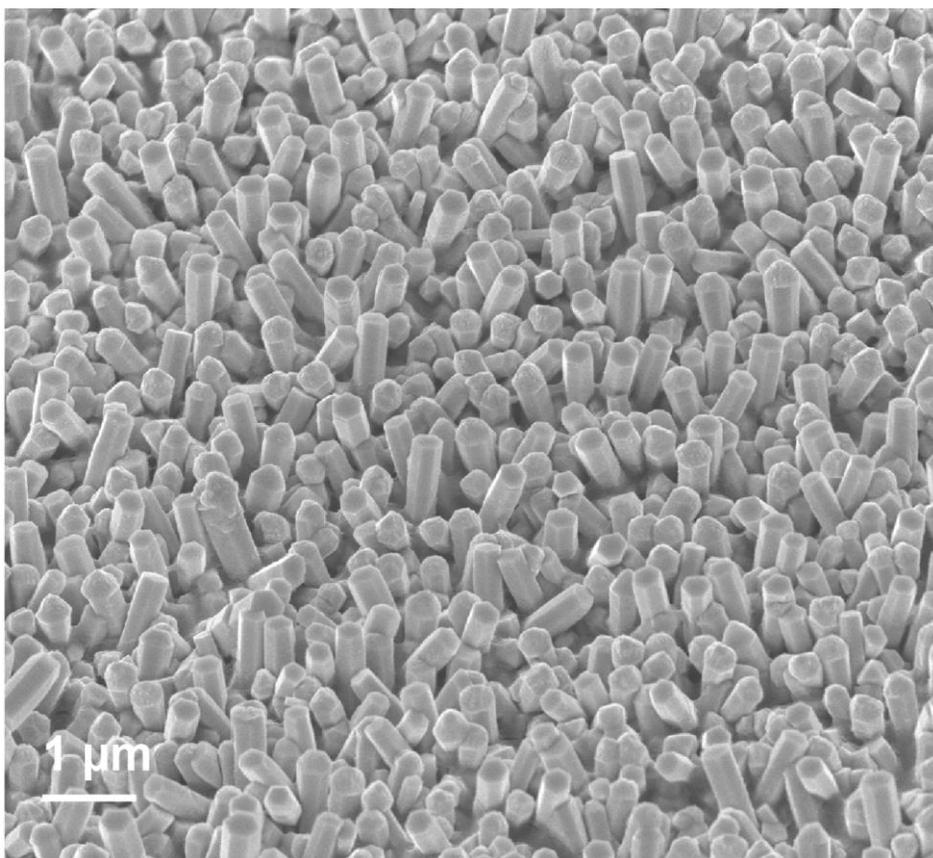


Figure S1. SEM image of a CdS nanorod array that has been filled with poly(methyl methacrylate) (PMMA) and subsequently partially etched in O₂ plasma.

Device Name	Open Circuit Voltage (V)	Fill Factor	Jsc (mA/cm ²)	Efficiency (%)
TiA_3	0.42	0.70	10.0	2.9
TiA_4	0.45	0.68	12.5	3.8
TiA_5	0.44	0.67	7.9	2.3
TiA_6	0.40	0.65	14.3	3.7
TiA_7	0.44	0.62	10.6	2.9
TiA_8	0.40	0.69	7.1	2.0
TiA_9	0.42	0.68	6.8	1.9
TiA_10	0.44	0.64	4.8	1.9
TiA_11	0.42	0.71	11.7	2.6
TiA_12	0.42	0.71	6.6	2.0
TiA_13	0.42	0.69	11.8	3.4
TiA_14	0.42	0.70	8.3	2.4
TiA_15	0.42	0.71	7.1	2.1
TiA_17	0.42	0.64	8.5	2.3
TiA_18	0.42	0.66	8.3	2.3
TiB_1	0.44	0.70	9.1	2.8
TiB_4	0.44	0.73	8.2	2.7
TiB_5	0.40	0.60	6.2	1.5
TiB_6	0.42	0.60	6.5	1.6
TiB_7	0.44	0.71	12.1	3.8
TiB_8	0.40	0.69	7.1	2.0
TiB_9	0.44	0.72	9.2	2.9
TiB_10	0.42	0.68	8.8	2.5
TiB_11	0.40	0.71	9.5	2.7
TiB_12	0.44	0.73	7.4	2.4
TiB_13	0.44	0.64	9.9	2.8
TiC_1	0.42	0.60	8.3	2.1
TiC_2	0.46	0.68	8.9	2.8
TiC_4	0.40	0.57	10.6	2.4
TiC_6	0.42	0.49	6.9	1.4
Averages	0.42	0.67	8.8	2.5
Standard Deviation	0.02	0.05	2.2	0.6

Table S2. Table of Representative Solar Cells. The efficiency and short circuit current density of each solar cell is calculated with based on the area of each individual solar cell with the average area of 24 μm^2 for the devices shown in this table. Although devices with areas up to 2500 μm^2 were fabricated, peak efficiency generally dropped with increasing size because of the formation of shunt paths over large areas of the nanorod array.

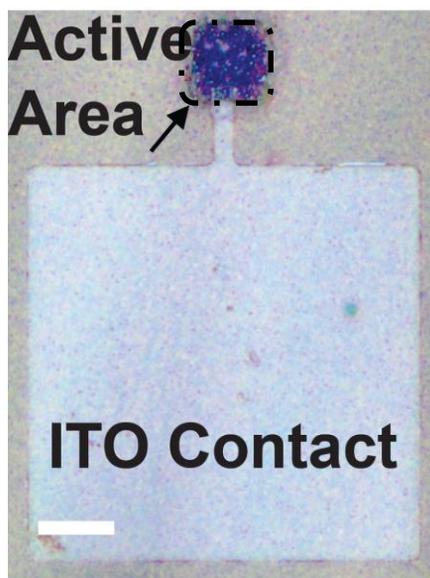


Figure S3. Optical image of a finished photovoltaic device. Scale bar is 10 μm .

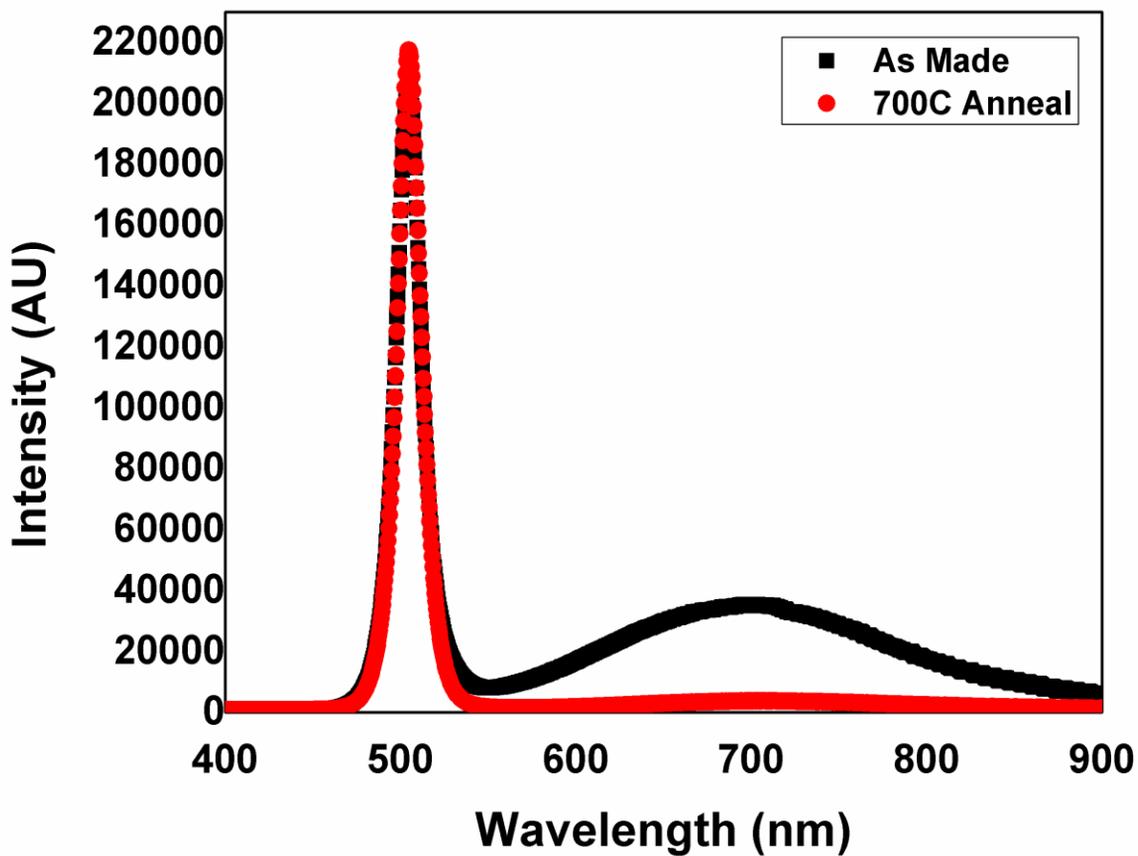


Figure S4. Photoluminescence of solution-grown CdS coated with Al₂O₃ before and after annealing at 700C in Ar gas.

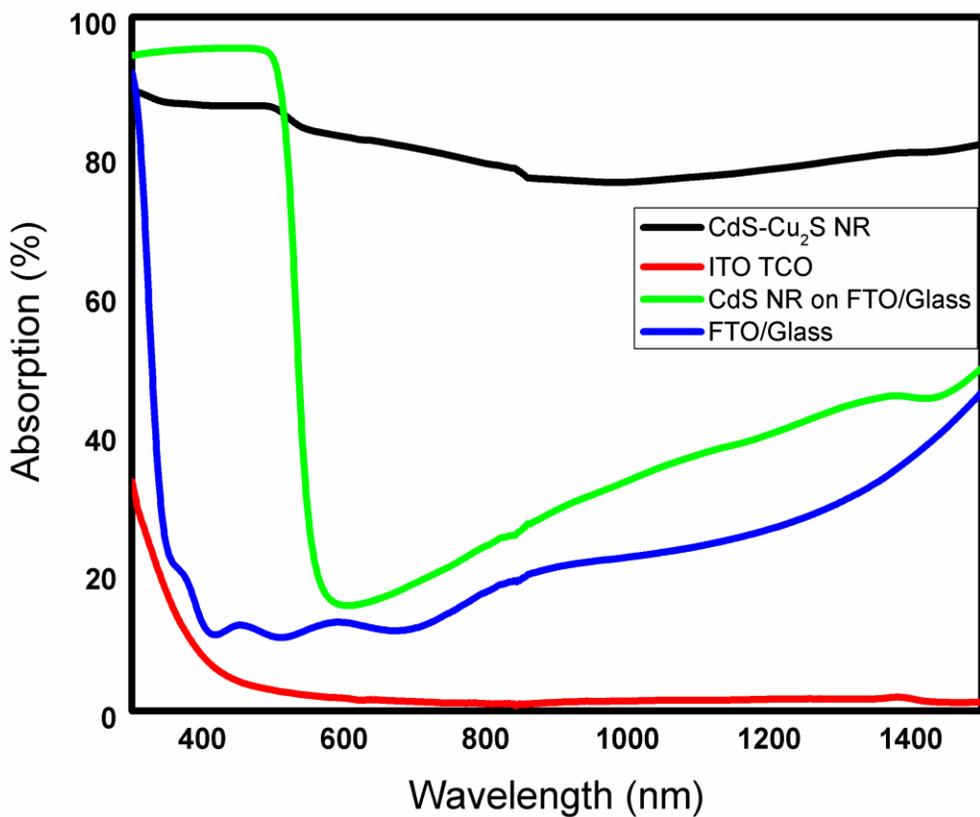


Figure S5. UV-vis absorption of the FTO/glass substrate, CdS nanorod array on FTO/glass substrate, CdS-Cu₂S nanorod array defined by PMMA on FTO/glass substrate, and ITO on quartz used as the top contact. Notches in the curves around 840 nm are artifacts of switching detectors.