

Supporting Information

Defects Passivation Engineering of Chalcogenide Quantum Dots via In-Situ Fluorination Treatment

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Experimental section

Chemicals

Cadmium oxide (CdO, 99.99%) and tellurium powder (Te, metals basis, 99.9%) were purchased from Aladdin, oleic acid (OA, 80-90%), selenium powder (Se, 200 mesh, 99.99%), N, N-dimethylformamide (DMF, 99.5%), 1-octadecene (ODE, 90%), dichloromethane (CH₂Cl₂, 99.5%), hexane (97.0%), sodium hydroxide (NaOH, 96%), and trioctylphosphine (TOP, 90%) were received from J&K Chemical. 3-mercaptopropionic acid (MPA, 99%) and paraffin liquid (chemical grade) were purchased from Macklin. All reagents were used without further treatment.

Synthesis of oil-soluble CdSeTe QDs with in-situ fluorination treatment

According to our previous report, oil-soluble CdSeTe QDs were synthesized *via* the one-pot solvent hot process.¹ The first step was to obtain Cd precursor solution (5.0 mL, 0.1 M) by dissolving CdO powder in OA under nitrogen shielding. The Se precursor (0.65 mL, 0.1 M) was obtained by dissolving Se powder in TOP and heating it under a nitrogen atmosphere at 300 °C. Te precursor (0.35 mL, 0.1 M) was also obtained via Te powder dissolved in TOP, followed by heating under nitrogen at 200 °C. Secondly, the Cd precursor with a specific content of BF molecular additive was added to the mixed solution of Se/Te precursors and held, stirring for one h. The feed molar ratio of Se to Te in CdSeTe QDs for photodetectors is 0.65:0.35. Subsequently, the mixed solution was heated to 320 °C for 10 min. The QDs were finally centrifugated with methanol and dispersed in a toluene solution (~ 20 mg/mL), defined as the target sample. In comparison, the control sample was obtained as the as-prepared CdSeTe QDs without in-situ fluorination treatment in the solution.

Fabrication of CdSeTe QDs self-powered photodetectors

For the assembly of QDs-based photodetectors, a 50 nm thick TiO₂ blocking layer (c-TiO₂) was deposited on an FTO glass by spraying 20 mM titanium diisopropoxide bis(acetylacetonate) solution at 450 °C. The m-TiO₂ (TiO₂ paste/ethanol = 1:5) solution was spin-coated on the c-TiO₂ layer at 3500 rpm for 20 s and then annealed at 500 °C for 30 min. The oil-soluble CdSeTe QDs (30 mg/ml) were spin-coated on the surface of the TiO₂ layer. The oil-soluble CdSeTe QD solution was dipped into the 2.0 M MPA methanol solution for 1.0 min and then washed with methanol to remove the redundant ligand by dropping methanol twice to complete the solid-state ligand exchange. To obtain the moderate thickness of QDs film, ten cycles of the processes were repeated to deposit sufficient QDs on the TiO₂ films. After the QDs depositing, the PF2 polymer solution for the hole-transparent layer was spin-coated at 4000 rpm/min for 30 s. Finally, 100 nm of the silver electrode was thermally evaporated under a high vacuum.

Fabrication of CdSeTe QD-sensitized solar cells

For the assembly of QD-based solar cells, TiO₂ mesoporous film electrodes with a thickness of $10 \pm 1.5 \mu\text{m}$ were prepared through the screen printing method.² According to our previous report, oil-soluble CdSeTe QDs were transferred to an aqueous solution using the NOBF₄/MPA ligand exchange method at a concentration of 30mg/ml.³ QDs were deposited on a TiO₂ photoanode and held for 4 hours. Then, the device was alternately immersed in Zn (OAc)₂ methanol solution and Na₂S aqueous solution for 60 seconds using successive ionic layer absorption and reaction, repeating four cycles to form a ZnS passivation layer. The sandwich solar cell was assembled from QD-sensitized photoanode and Cu₂S/brass CE. Cu₂S/Brass CE is prepared by soaking copper sheets in a 10% HCl aqueous solution at 90 °C for 30 minutes, then rinsing with deionized water and ethanol. Dissolve 2.0 M Na₂S, 2.0 M S, and 0.2 M KCl in water by ultrasound to obtain a polysulfide electrolyte.

Characterization

The UV-visible absorption spectra were collected using a spectrometer (PerkinElmer Lambda 950). The emission spectra were obtained with a fluorescence spectrophotometer (Cary Eclipse Varian) under the excitation wavelength at 350 nm. The PL lifetime was obtained using an Edinburgh LifeSpec spectrometer fitted with a single-photon counter. The samples were stimulated at 375 nm using a picosecond pulsed diode laser. Samples for TEM imaging were prepared by drop-casting QDs onto a thin carbon-supported copper TEM grid. HAADF-STEM images were acquired using a Thermo Fisher Scientific Talos F200X microscope, both operating at 200 kV. The inner electrons or valence electrons of the atoms or molecules of the samples were determined by PHI5000 Versaprobe III XPS. XPS samples were prepared by drop-casting a solution of QDs on silicon wafers. Al k rays ($h\nu = 1486.6$ eV) were employed for the excitation source, and the adventitious C1s peak at 284.80 eV was used as the energy standard for charging correction. XRD measurements were done using a PAN analytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu K α ceramic X-ray tube, with a power of PIXcel3D 2 \times 2 area detector, and running at 45 kV and 40 mA. The current density-voltage (J - V) curves of the self-powered photodetectors were measured by a Keithley 2400 source meter lit under the AM 1.5G spectrum from a 3A solar simulator. The intensity of the light was calibrated to 100 mW/cm 2 using an NREL Si solar reference stack. A black metal mask was utilized to form a photoactive zone of 0.0375 cm 2 . External quantum efficiency (EQE) curves were carried out on a Keithley 2000 multimeter under the irradiation of a 300 W tungsten lamp with a Spectral DK240 monochromator. The current density-voltage (J - V) curves of solar cells were measured by a Keithley 2400 source meter lit under the AM 1.5G spectrum from a 3A solar simulator. The intensity of the light was calibrated to 100 mW/cm 2 using an NREL Si solar reference stack. The photoactive area of

the solar cells is 0.235 cm^2 . External quantum efficiency (EQE) curves were carried out on a Keithley 2400 multimeter under the irradiation of a 300 W tungsten lamp with a Spectral DK240 monochromator. Characterization *via* Electrochemical Impedance Spectroscopy (EIS) was done with an electrochemical workstation (Zahner). In the dark situation, EIS spectra were recorded at a forward bias range between 0.35 and 0.65 V by applying a sinusoidal signal of 20 mV AC.

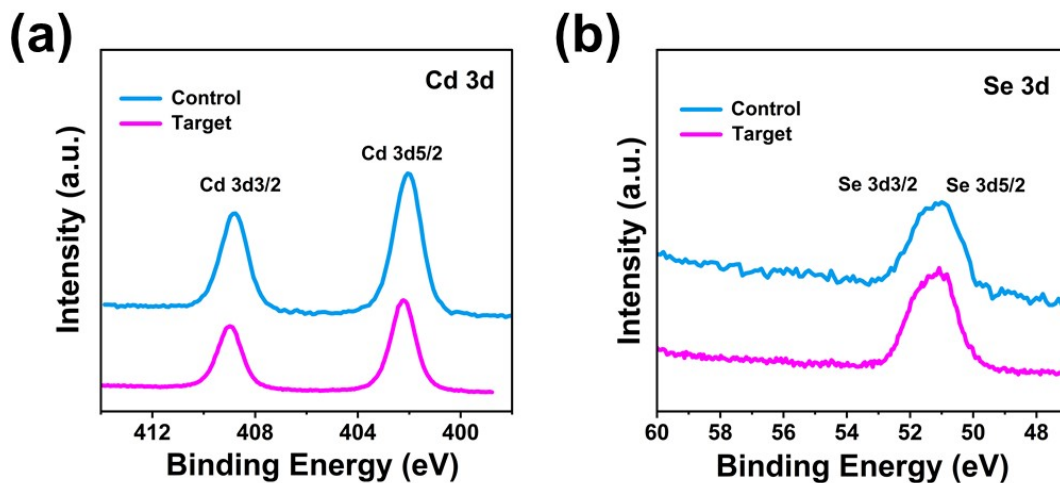


Fig. S1 X-ray photoelectron spectroscopy (XPS) spectra of Cd 3d, Se 3d, and Te 3d for control and target CdSeTe QDs.

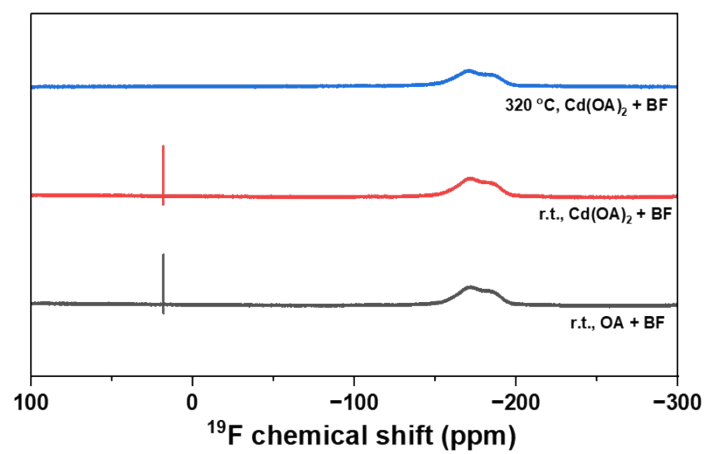


Fig. S2 ^{19}F NMR spectroscopy of benzene carbonyl fluoride to explain the proposed reaction mechanism.

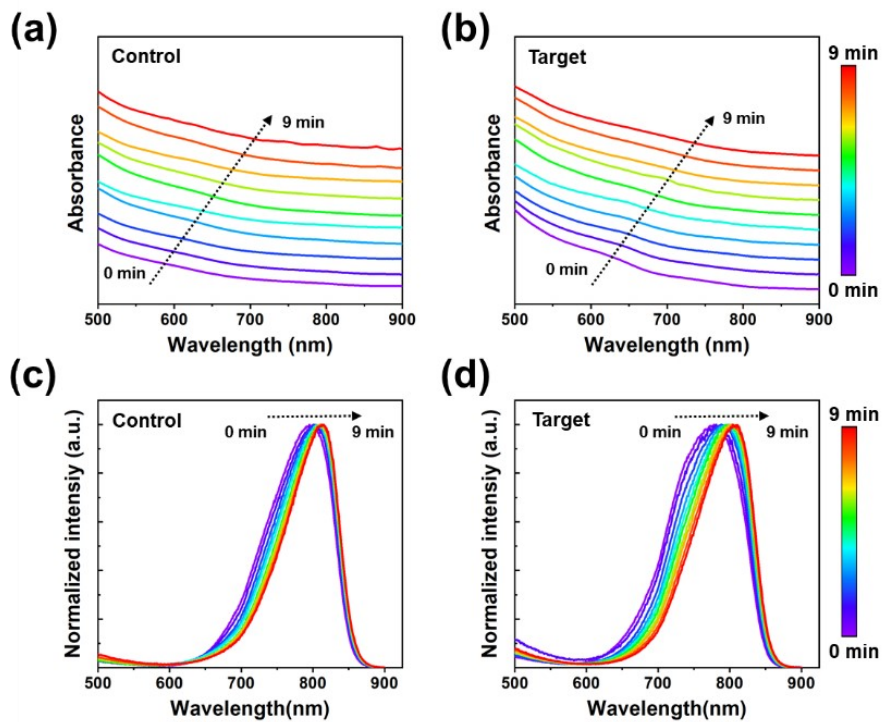


Fig. S3 The UV-Vis absorption (a, b) and PL emission (c, d) spectra of the target and control CdSeTe QDs with and without in-situ fluorination treatment as a function of reaction time at an interval of one minute, respectively.

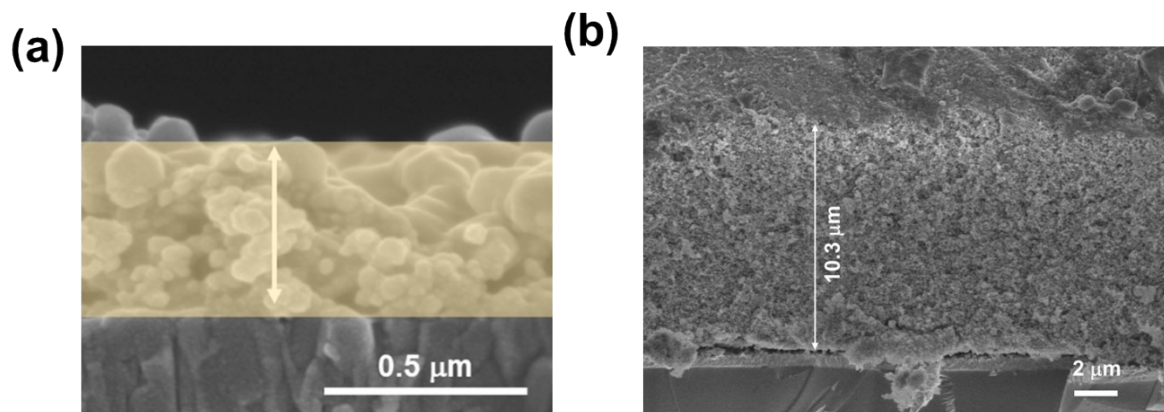


Fig. S4 Cross-section SEM images of the (a) QDs photodetector device and (b) QDs-sensitized TiO₂ photoanode for solar cells, respectively.

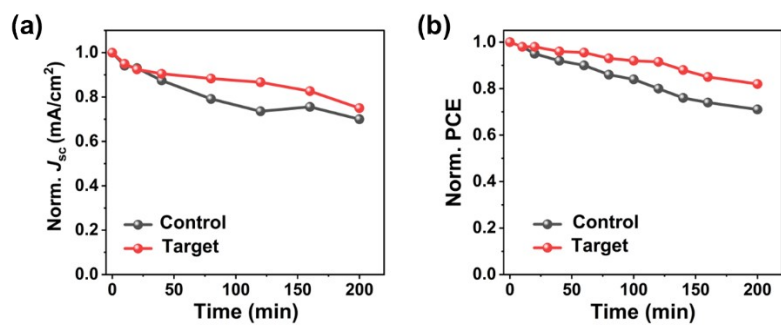


Fig. S5 The stability of the CdSeTe QDs-based photodetector (a) and solar cells (b) during continuous operation under standard sunlight illumination.

Table S1 The values of the band edge level of the control and target CdSeTe QDs calculated according to the UPS and UV measurements.

QDs	First E_{cutoff} (eV)	Secondary E_{cutoff} (eV)	E_{g} (eV)	E_{F} (eV)	E_{v} (eV)	E_{c} (eV)
Control	0.43	16.36	1.84	-4.86	-5.29	-3.45
Target	0.29	16.10	1.78	-5.12	-5.41	-3.63

Table S2 Comparison of photovoltaic performance of Cd-based photodetectors, which have been reported in the literature.

QDs	R (AW^{-1})	D* ($\text{cmHz}^{1/2}\text{W}^{-1}$)	$I_{\text{on}}/I_{\text{off}}$	References
CdSe	1.7	4.46×10^{10}	143	<i>ACS Nano</i> 2011, 5, 7627
CdSe	0.1	3.1×10^9	250	<i>Nano Letters</i> 2007, 7, 2999
CdTe/ZnSe	1.6×10^{-3}	--	36	<i>Adv. Electron. Mater.</i> 2015, 1, 1400050
CdSe	76	2.75×10^{10}	1285	<i>J. Alloys Compd.</i> 2017, 726, 214
CdSeTe	15	2.0×10^{12}	--	<i>Nanomaterials</i> 2019, 9, 1738
CdSeTe	0.053	8.0×10^{13}	--	<i>J. Phys. Chem. Lett.</i> 2018, 9, 3285
CdSeTe	45	2.6×10^{12}	9.9×10^5	<i>Nanoscale</i> , 2019,11, 9626
CdSeTe	0.046	--	8.3×10^6	<i>J. Mater. Chem. C</i> , 2019,7, 6266

Table S3 Comparison of photovoltaic performance of CdSeTe QD-based sensitized solar cells, which have been reported in the literature.

QDs	J_{sc}	V_{oc}	FF	PCE (%)	References
CdSeTe/ZrOCl ₂	20.69	0.700	0.62	9.13	<i>Chem. Mater.</i> 2015, 27, 8398
CdSeTe/CdS	20.82	0.713	0.64	9.48	<i>J. Phys. Chem. C</i> 2015, 119, 28800
CdSeTe/CdSe	21.04	0.720	0.64	9.73	<i>Chem. Mater.</i> 2016, 28, 2323
Cl passivated-CdSeTe	21.20	0.702	0.648	9.64	<i>J. Mater. Chem. A</i> , 2016, 4, 877
Mn ²⁺ doped CdSeTe	20.87	0.688	0.655	9.40	<i>J. Mater. Chem. A</i> 2016, 4, 18976
ZnS/Ga(OH) ₃ passivated CdSeTe	3.78	0.593	0.56	1.25	<i>Sol. Energy Mater Sol.</i> 2016, 157, 161
CdS/CdSe/CdSeTe/ZnS	20.50	0.643	0.56	7.4	<i>Electrochimica Acta</i> 2017, 247, 899
CdSeTe/ZnS/SiO ₂	20.30	0.608	0.51	6.40	<i>J. Alloys Compd.</i> 2017, 728, 1058
CdSeTe	32.25	0.629	0.41	8.28	<i>Solar Energy</i> 2020, 197, 519
CdSeTe	10.05	0.641	0.54	3.46	<i>Solar Energy</i> 2020, 206, 741
CdSeTe/NOBF ₄ -MPA	21.49	0.687	0.68	10.02	<i>Chem. Eng. J.</i> 2023, 474, 145657

Table S4 Fitted impedance values at 0.8 V forward bias for the solar cells based on the control and target CdSeTe QDs.

QDs	R_s (Ω)	C_μ (mF/cm ²)	R_{rec} (Ω cm ²)
Control	4.1	4.8	5.1
Target	3.7	7.8	6.9

Reference

1. Yin, F.; Zou, X.; Chen, M.; Sun, Z.; Bao, X.; Du, Z.; Tang, J., Promoting the efficiency of quantum dots-based solar cells via the Cu:ZnSeS intermediate passivation layer. *Journal of Materials Research and Technology* **2022**, *21*, 1974-1983.
2. Chen, M.; Yin, F.; Du, Z.; Sun, Z.; Zou, X.; Bao, X.; Pan, Z.; Tang, J., MOF-derived CuxS double-faced-decorated carbon nanosheets as high-performance and stable counter electrodes for quantum dots solar cells. *Journal of Colloid and Interface Science* **2022**, *628*, 22-30.
3. Sun, Z.; Hou, Q.; Zhang, R.; Cheng, J.; Kong, J.; Wang, K.; Liu, F.; Du, Z.; Tang, J., Facile surface pseudohalide pretreatment of quantum dots for efficient photovoltaics. *Chemical Engineering Journal* **2023**, *474*, 145657.