A Residual Strain Regulation Strategy Based on Quantum Dots for Efficient Perovskite Solar Cells

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Experimental section

Chemicals

All reagents were used as received without further purification. Cs_2CO_3 (99.9%), oleic acid (OA, 90%), CsCl (99.99%), chlorobenzene (CB 99.9%) and MeOAc (anhydrous 99%) were obtained from Sigma-Aldrich. Octadecene (ODE, 90%), oleylamine (OAm, 90%), octane (98%) and Aqueous suspensions of tin oxide nanoparticles (SnO_2: 15% mass in H_2O colloidal dispersion) were obtained from Alfa Aesar. PbI_2 (99.99%), poly-(3,4-ethylenedioxythiophene)-poly (styrene sulfonic acid ester) (PEDOT: PSS, 1.3-1.7wt% solution in water) and PCBM (99.9%) were obtained from Xi'an Polymer Light Technology Corp. Dimethyl sulfoxide (DMSO, 99.9%), Dimethylformamide (DMF) was obtained from J&K. Spiro-OMeTAD (99.8%) were obtained from Ningbo Borun New Material Co., Ltd.

Synthesis and Purification of $CsPbI_3$ QDs

Synthesis of Cs Oleate Precursor. Cesium oleate was prepared by adding Cs_2CO_3

(0.25 g), ODE (25 mL), OA (1 mL) in to a 50 mL three-neck flask; it was degassed and dried under vacuum for 1 h at 120 ℃ until a clear solution was obtained.

Synthesis of $CsPbI_3$ QDs. PbI_2 (0.5 g) and ODE (25 mL) were loaded into a 50 mL 3-neck flask and heated to 120 °C under vacuum for 30 min, then OA (2.5 mL), OAm (2.5 mL) were injected into the system under the protection of N_2. The flask was put under vacuum again until the PbI_2 completely dissolved (30 min). The temperature was increased to 165 °C and Cs-oleate solution (4 mL) was quickly injected and after 5 s the solution was immediately cooled down to room temperature by immersing the flask in an ice water bath. For first-time purification, the synthesized $CsPbI_2$ QDs were precipitated by adding methyl acetate (MeOAc) at the volume ratio of QDs reaction solution: MeOAc was 1:3 and then centrifuged at 8500 rpm for 3 min. For two-times purification, the precipitate of first-time purification was redispersed in 5 mL of hexane and precipitated by adding 10 mL of MeOAc, it was centrifuged again for 3 min at 8000 rpm. As for the three times of purification, the precipitate of two-time purification was redispersed in 1mL of hexane and precipitated by adding 2 mL of MeOAc, it was centrifuged again for 3 min at 8000 rpm. Finally, the one/two/three times-purified $CsPbI_3$ QDs were redispersed in hexane and stored in a freezer at 4 ℃ for device fabrication.

Synthesis of FAX (X= I. Cl): FAX was synthesized by reacting FAAc with HX (X=I, Cl) (molar ratio FAAc: HX=1:1.1) at 0℃, where HX was slowly dropped into a round-bottomed flask filled with FAAc. After stirring for 3 h, the product was recovered by evaporating the solvent at 60 ℃ using a rotary evaporator. The solids were washed with ether and recrystallized from ethanol, and the process was repeated at least three times. Finally, white precipitate was dried under vacuum oven for 24 h and then stored in glovebox filled with nitrogen.

Synthesis of $FAPbI_3$ crystal: FAI (3.44 g) was reacted with PbI_2 (9.22 g) in 16 mL 1,4-butyrolactone at 165 ℃ for 90 min. The supernatant was removed and a moderate

amount of ACN was added to the product, which was shocked for 1 min to wash the product. The washing process was repeated at least 3 times. Then add an appropriate amount of ether to wash the product. Finally, the product was dried in vacuum over for 24 h at room temperature and then stored in glovebox filled with nitrogen.

Device Fabrication

FTO glass was cleaned with deionized water, ethanol, and isopropanol. The electron transporting layer were prepared by spin-coating the SnO_2 aqueous solution (3 wt% in DI water) on the cleaned substrates at 3000 rpm for 30 s, following with a thermal treatment at 180 °C for 30 min. The 1.2 M solution was prepared by dissolving the pre-synthesized $FAPbI_3$ crystal, FACl, CsCl in DMF and DMSO cosolvent (DMF: DMSO = 12:1 v/v). The perovskite solution was spin-coated on the SnO_2-coated FTO substrate at 1000 rpm for 5 s and 5000 rpm for 20 s. The antisolvent toluene was dropped 10 s before the end of spin coating. For the device with QDs, different treating times of QDs in toluene were used as the anti-solvent. Subsequently, the sample was annealed at 150 ℃ for 20 min. Then, a hole transporting layer (HTL) solution of 72.3 mg of spiro-OMeTAD, 28.8 μL of 4-tert-butylpyridine and 17.5 μL of Li-TFSI (pre-dissolved in acetonitrile) in chlorobenzene was spin-coated on the top of perovskite film with 4000 rpm for 30 s. In the end, Ag electrode (80 nm) was fabricated by thermal evaporation.

Characterization

The transmission electron microscope (TEM) images of $CsPbI_3$ QDs were obtained by JEM-2100F. The optical properties of the samples were measured by an UV–vis spectrophotometer (UV-2550). The steady-state PL and PLQY were obtained by HoribaFluoroMax-4 fluorescence spectrometer of Shimadzu Instruments. XRD patterns of perovskite films and QDs were measured using PANalytical X-Rert PRO MPD. The GIXRD measurements were characterized using a Rigaku SmartLab. Top-view surface morphology of films was performed using Gemini 500. XPS spectra were recorded using an X-ray photoelectron spectrometer (Thermo Scientific ESCALAB 250Xi), AFM topography images were acquired on a Bruker Dimension

Icon instrument. The TRPL measurements were carried out using the Edinburgh FLS1000. The photocurrent density-voltage (J-V) characteristics of solar cells were measured under AM 1.5G illumination at 100 mW/cm^2 (Newport Sol3A solar simulators) using a Keithley 2450 source meter. The incident photon conversion efficiency (IPCE) measurements were obtained with an IPCE measurement kit (Newport).

Density functional theory (DFT) calculations

The first-principles density-functional theory (DFT) [1] calculations were performed using the Vienna ab initio simulation package (VASP)[2,3]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[4] was chosen for electronic structure calculations and geometry relaxation. The projector-augmented wave (PAW) [5] potentials were used to treat interactions between ion cores and valance electrons. The reciprocal space is meshed using Monkhorst-Pack method [6]. The plane wave kinetic energy cutoff 400 eV and 5×5×5 mesh for reciprocal space was chosen in geometry relaxation and force fields calculations along with the PBE functional. The total energy convergence criterion is set to be 10-4 eV and the force is converged within 0.02 eV/Å.

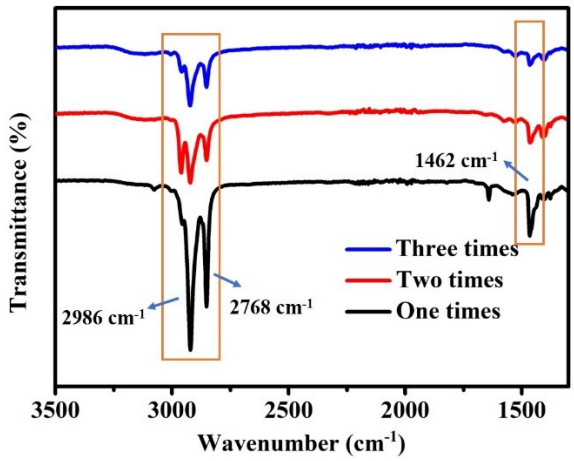

Figure S1. FTIR spectrum of the one-, two-, three- times treated $CsPbI_3$ QDs

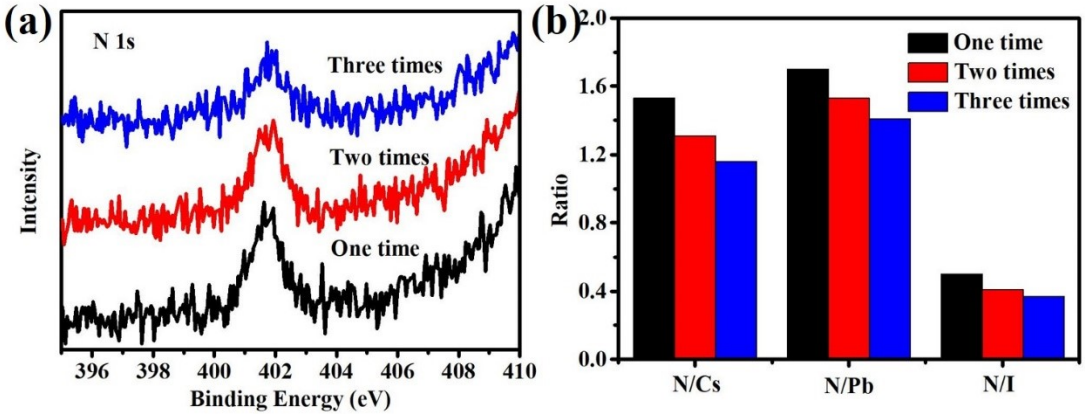

Figure S2. a) N 1s XPS spectra of the one-, two-, three- times treated $CsPbI_3$ QDs. b) Relative nitrogen content of $CsPbI_3$ QD films with different purifying cycles plotted by XPS data.

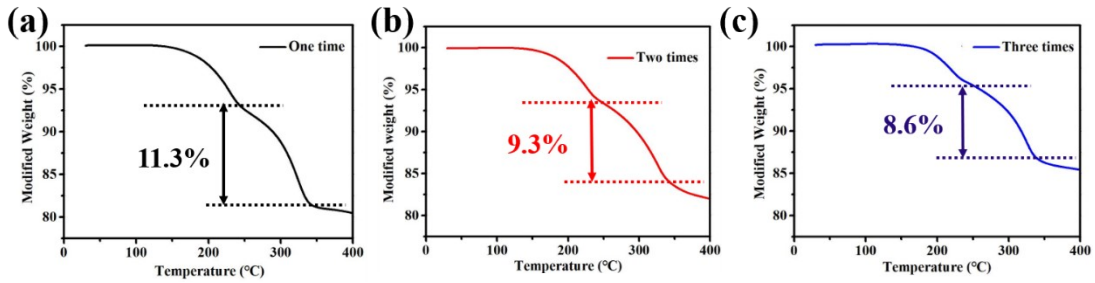

Figure S3. The thermal gravimetric analysis (TGA) curves of $CsPbI_3$ QDs after one two and three -times treatment.

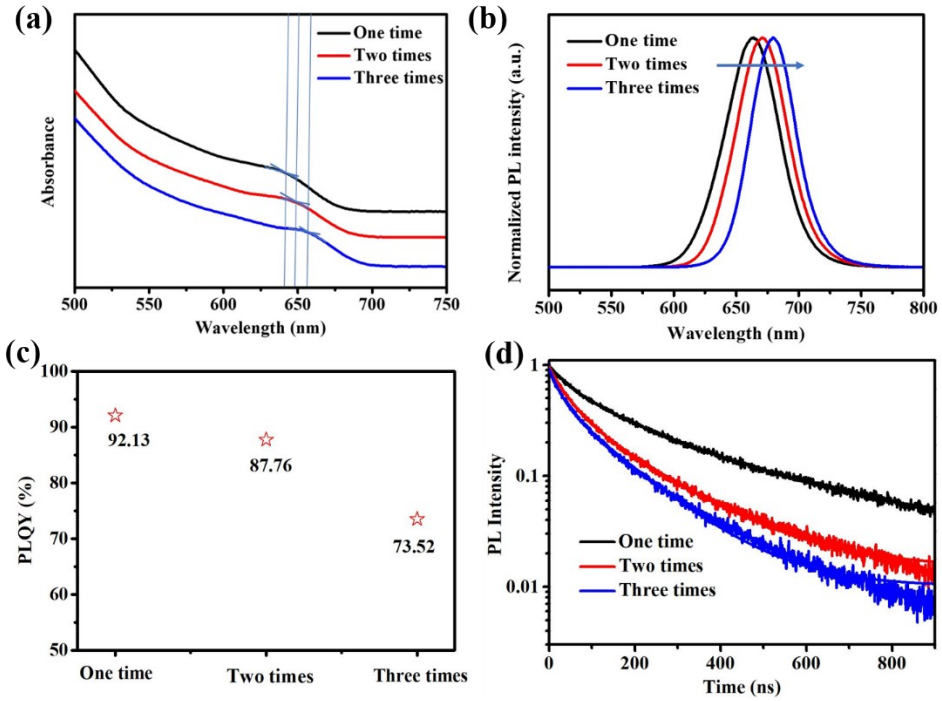

Figure S4 a) UV-vis absorption, b) PL spectra, c) PLQY, d) PL lifetime of the one, two, and three-times treatments of $CsPbI_3$ QDs.

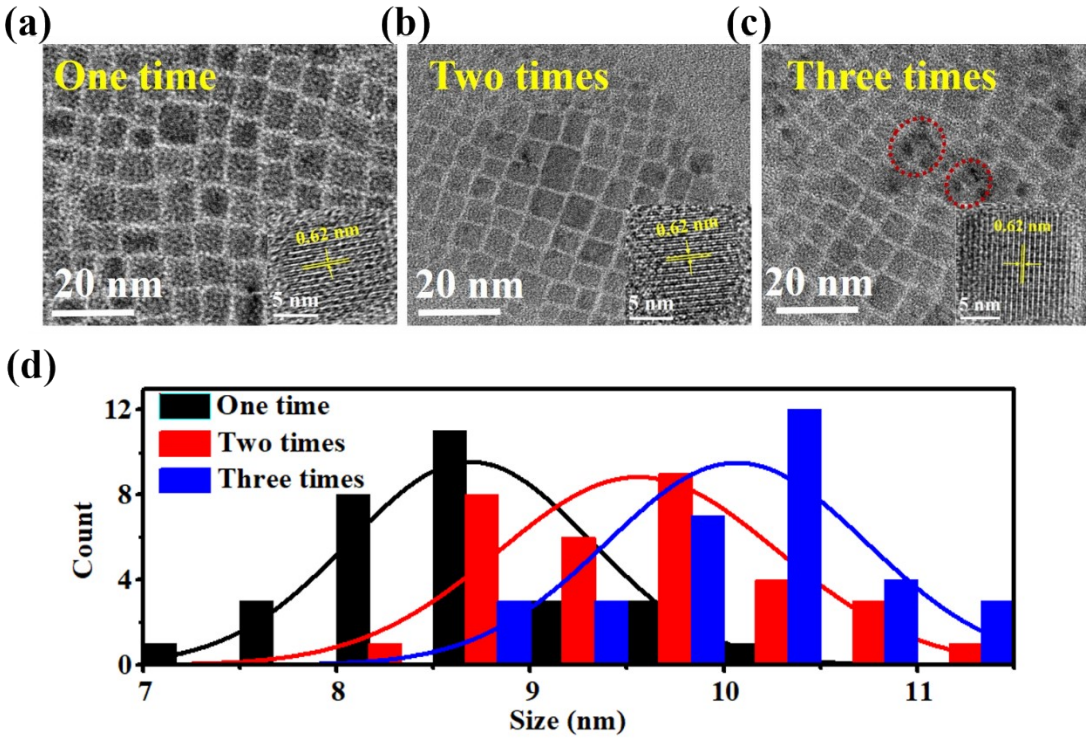

Figure S5 a-c) TEM images and d) The crystal size distribution of the one, two, three-times treatments of $CsPbI_3$ QDs.

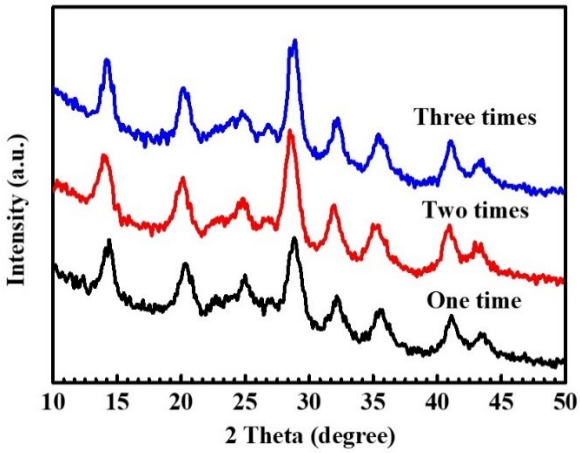

Figure S6. XRD spectra of the one-, two-, three-times treated $CsPbI_3$ QDs

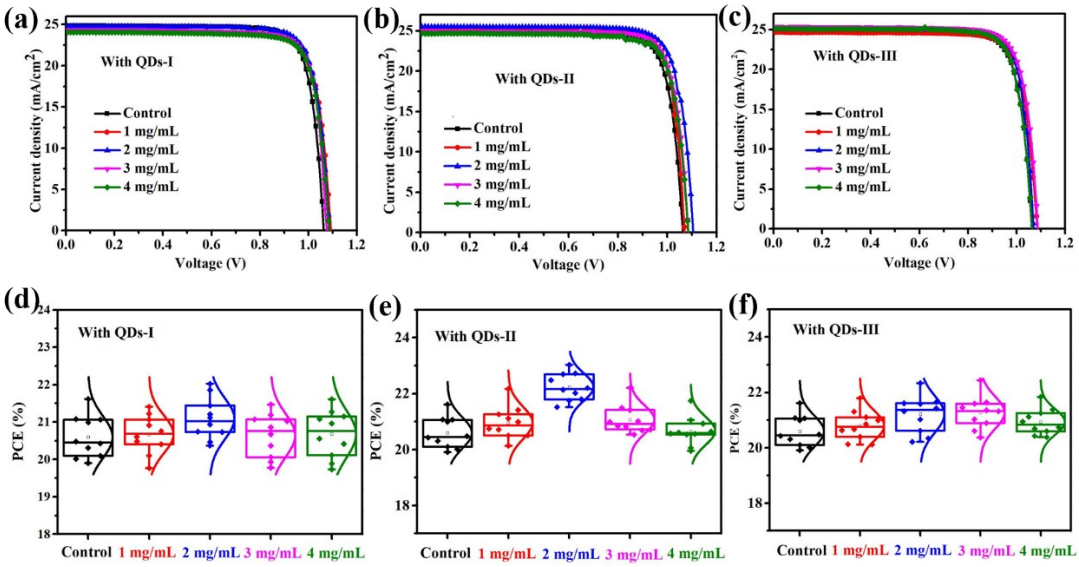

Figure S7. a-c) J-V curve and d-e) PCE statistics of PSCs treated with different concentrations of QDs-I, QDs-II and QDs-III in toluene.

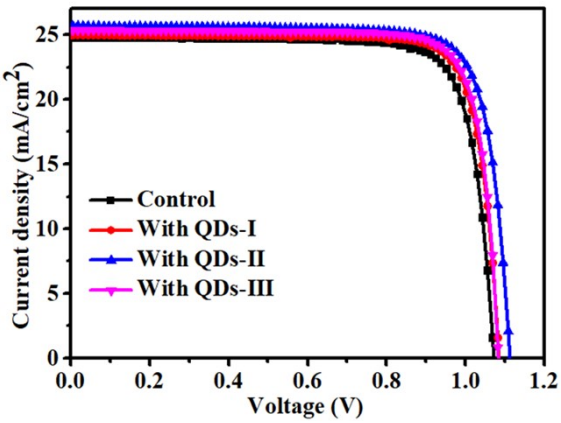

Figure S8. *J-V* curves from the best-performing devices without and with QDs treatment.

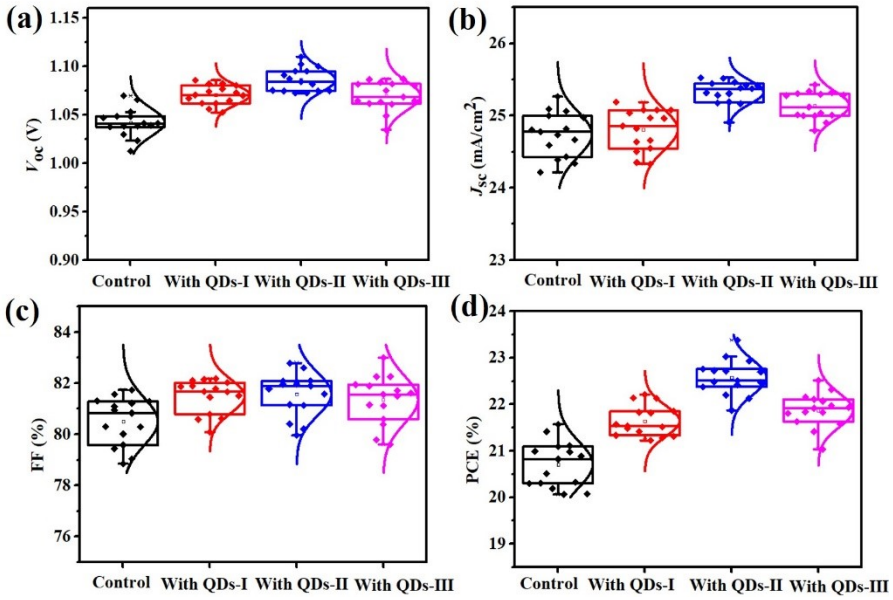

Figure S9. Statistical PCE, V_{OC}, FF and J_{SC} distribution for 20 devices fabricated without and with QDs treatment.

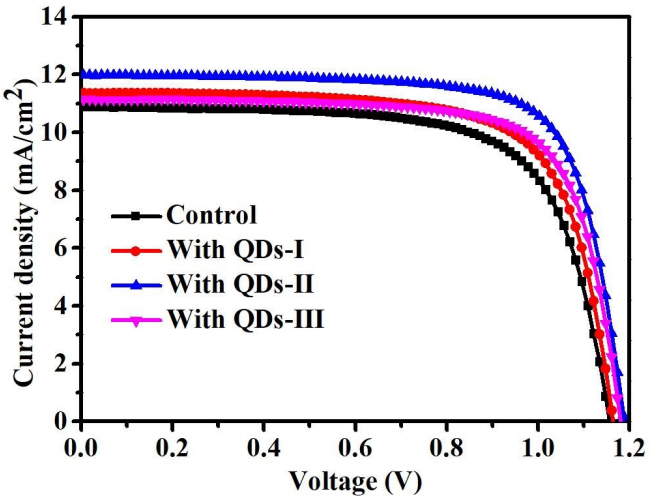

Figure S10. *J-V* curves of $CsPbIBr_2$ solar cells without and with QDs-I, QDs-II, and QDs-III treatment.

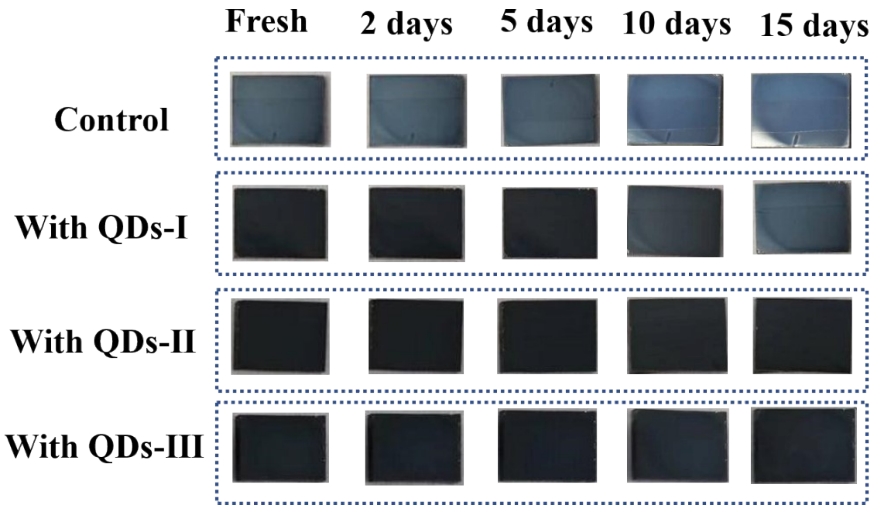

Figure S11. photographic images showing the stability of perovskite film without and with QDs-I, II, III treatment, stored under dark and relative humidity (RH) 50-55% conditions for 15 days.

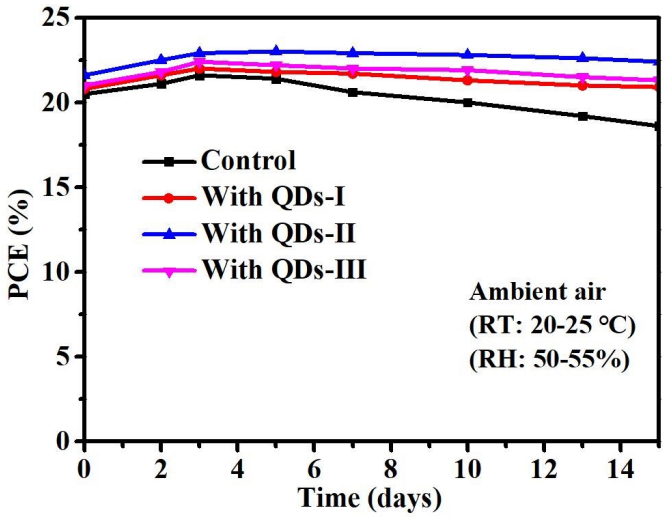

Figure S12. Long-time stability of $FA_{0.95}Cs_{0.05}PbI_3$ solar cells without and with QDs-I, II, III treatment (20-25 ℃, RH: 50-55%).

Table S1 The parameters of PL lifetime by fitting the TRPL spectroscopy of the $CsPbI_3$ QDs after one, two, and three times-treatment.

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	Average τ (ns)
One time	0.40	52	0.60	251	227
Two times	0.54	39	0.46	166	138
Three times	0.47	26	0.53	133	117

Table S2. Photovoltaic parameters of PSCs treated with different concentrations of QDs-I in toluene.

Sample (QDs-I)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (%)
Control	1.06	24.9	81.8	21.6
1 mg/mL	1.09	24.2	80.9	21.4
2 mg/mL	1.08	24.8	82.0	22.0
3 mg/mL	1.07	24.4	82.0	21.5
4 mg/mL	1.08	24.1	81.6	21.3

Table S3. Photovoltaic parameters of PSCs treated with different concentrations of QDs-II in toluene.

Sample (QDs-II)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (%)
Control	1.06	24.9	81.8	21.6
1 mg/mL	1.07	25.1	83.4	22.3
2 mg/mL	1.10	25.5	82.1	23.0
3 mg/mL	1.08	24.9	82.2	22.2
4 mg/mL	1.08	24.7	81.4	21.7

Table S4. Photovoltaic parameters of PSCs treated with different concentrations of QDs-III in toluene.

Sample (QDs-III)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (%)
Control	1.06	24.9	81.8	21.6
1 mg/mL	1.08	24.6	81.6	21.8
2 mg/mL	1.07	25.0	82.8	22.1
3 mg/mL	1.08	25.3	81.6	22.4
4 mg/mL	1.06	25.1	81.9	21.8

Table S5 Photovoltaic parameters of PSCs based $FAPbI_3$ film without and with QDs-I, II, III treatment

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (%)
Control	1.07	24.8	81.3	21.6
With QDs-I	1.08	24.9	82.2	22.2
With QDs-II	1.11	25.6	82.0	23.3
With QDs-III	1.08	25.3	82.2	22.5

Table S6 Photovoltaic parameters of CsPbIBr2 solar cells without and with QDs-I, QDs-II, and QDs-III treatment.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (%)
Control	1.15	10.9	69.5	8.76
With QDs-I	1.16	11.4	71.3	9.42
With QDs-II	1.19	11.9	74.5	10.6
With QDs-III	1.18	11.1	73.7	9.69

Table S7 The parameters of PL lifetime by fitting the TRPL spectroscopy of the control film and QDs-I, II, III-treated film.

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	Average τ (ns)
Control	0.59	151	0.41	917	770
With QDs-I	0.49	196	0.51	1551	1404
With QDs-II	0.34	263	0.66	1564	1460
With QDs-III	0.57	289	0.43	1031	830

Reference

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