

Supporting Information for

Synergetic Interfacial Passivation, Band Alignment, and

Long-Term Stability with Halide Optimized CsPbBr_xI_{3-x}

Nanocrystals for High Efficiency MAPbI₃ Solar Cells

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Experimental section

Materials and Reagents:

N, N-dimethylformamide (DMF), chlorobenzene, dimethyl sulfoxide (DMSO), lead bromide (PbBr_2 , 99.99%), caesium carbonate (CsCO_3 , 99.9%) and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. PbI_2 , MAI, bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI), 4-tertbutylpyridine (TBP) and Spiro-OMeTAD were purchased from Xian Polymer Light Technology Corp. Oleylamine (OLA, 70%), 1-octadecene (ODE, 90%) and methyl acetate were purchased from Alfa.

Device Fabrication:

Preparation of SnO_2 colloidal solution: $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CH}_4\text{N}_2\text{S}$ with the mass ratio of 3:1 were dissolved in 50 mL deionized water in the iodine flask with continuously magnetic stirring, exposing to air at 25 °C. After 24 hours, the yellow and clear colloidal SnO_2 solution was obtained.¹

Preparation of SnO_2 layer: The ITO glasses with the size of 1.5*2cm were sequentially cleaned by deionized water, ethanol, acetone and isopropanol by ultrasonic process for 20 min, and then dried by nitrogen. Before being used, the clean glasses were treated with the UV-Ozone cleaner for 15 min. The obtained SnO_2 solution was filtered with 0.22 μm PTFE filter before use. 65 μL of SnO_2 solution were spin-coated on ITO substrate at 3000 rpm for 30 s, and then annealed at 180 °C for 60 min. The SnO_2 layers were then treated with UV-ozone for 10 min before transferring into the glovebox for perovskite deposition.

Preparation of perovskite layer: The perovskite films were obtained by a one-step process. First, 553.2 mg PbI_2 and 190.8 mg $\text{CH}_3\text{NH}_3\text{I}$ were dissolved in the N, N-dimethylformamide (800 μL) and dimethylsulfoxide (200 μL) mixed solvent and stirred at 60 °C for 8 h. The perovskite precursor was filtered through a 0.22 μm pore PTFE filter. Then 35 μL of PbI_2 solution was spun on the SnO_2 / ITO substrate at 1000 rpm for 10 s and 5000 rpm for 30 s successively. During the second step, 100 μL of chlorobenzene was poured on the center of spinning substrate 20 s prior to the end of the program. Then the films were annealed at 70 °C for 2 min and 110 °C for 10 min.

Preparation of perovskite NCs layer:

Preparation of Cs-oleate: The preparation of the Cs-oleate was similar to the literature.² Then the Cs-oleate solution was stored in the refrigerator.

Synthesis of CsPbBr₃ NCs: 138 mg of PbBr₂ and 10mL ODE were loaded into a 50 mL three-necked flask. At the room temperature, nitrogen was used to clean impurities. Then the temperature of the solution was increased to 120 °C and kept for 70 min in vacuum. 1 mL of degassed OLA and OA were injected under nitrogen flowing. When the solution turned clear, the temperature of the solution was increased to 180 °C and 1 mL Cs-oleate was injected into the solution quickly. Five seconds later, the temperature of the solution was decreased to 15 °C in the ice-water bath.

Synthesis of CsPbBr_{1.2}I_{1.8} NCs: 55.36 mg of PbBr₂, 103.8 mg of PbI₂ and 10mL ODE were loaded into a 50 mL three-necked flask. At the room temperature, nitrogen was used to clean impurities. Then the temperature of the solution was increased to 120 °C and kept for 70 min in a vacuum. 1 mL of degassed OLA and OA were injected under nitrogen flowing. When the solution turned clear, the temperature of the solution was increased to 170 °C and 1 mL Cs-oleate was injected into the solution quickly. Five seconds later, the temperature of the solution was decreased to 15 °C in the ice-water bath.

Synthesis of CsPbBr_{0.9}I_{2.1} NCs: 41.4 mg of PbBr₂, 121.3 mg of PbI₂ and 10mL ODE were loaded into a 50 mL three-necked flask. At the room temperature, nitrogen was used to clean impurities. Then the temperature of the solution was increased to 120 °C and kept for 70 min in a vacuum. 1 mL of degassed OLA and OA were injected under nitrogen flowing. When the solution turned clear, the temperature of the solution was increased to 170 °C and 1 mL Cs-oleate was injected into the solution quickly. Five seconds later, the temperature of the solution was decreased to 15 °C in the ice-water bath.

Synthesis of CsPbI₃ NCs: 173.3 mg of PbI₂ and 10mL ODE were loaded into a 50 mL three-necked flask. At the room temperature, nitrogen was used to clean impurities. Then the temperature of the solution was increased to 120 °C and kept for 70 min in a vacuum. 1 mL of degassed OLA and OA were injected under nitrogen flowing. When

the solution turned clear, the temperature of the solution was increased to 160 °C and 1 mL Cs-oleate was injected into the solution quickly. Five seconds later, the temperature of the solution was decreased to 15 °C in the ice-water bath.

Purification of perovskite NCs: The reaction mixture was firstly centrifuged for 10 min at 5000 rpm. The precipitate at the bottom of the centrifuge tube was dissolved in 2 mL toluene and 3 mL ethyl acetate and then centrifuged again for 10 min at 10 000 rpm. Then the clean precipitate was dissolved in 3 mL toluene and centrifuged for 1 min at 3000 rpm. The supernatant was filtered through a 0.22 µm pore PTFE filter. The clean NCs solution was stored in a glove-box.

NCs layer: 30 µL of NCs solution are spin-coated onto the MAPbI₃ perovskite films at 4000 rpm for 30 s and then transferred to the hot plate at 50 °C for 5 min.

Preparation of Spiro-OMeTAD layer: 20 µL Spiro-OMeTAD solution prepared by dissolving 72.3 mg Spiro-OMeTAD, 17.5 µL Li-TFSI solution (520 mg in 1 mL acetonitrile) and 28.8 µL tert-butylpyridine in 1 mL CB was spin-coated on the NCs layer at 4000 rpm for 30s.

Preparation of back electrode: About 90 nm Ag was deposited by thermal evaporation. The active area of each device was 0.32 cm².

Characterization

The X-ray diffraction (XRD) spectra were conducted on a Rigaku D/max-2500 X-ray diffraction meter with Cu K α radiation ($\lambda=1.5418\text{\AA}$). The TEM images were obtained by using FEI - Model: Tecnai G2 F30. The SEM images and EDS were obtained by using HITACHI Regulus8100 Scanning Electron Microscope. The UV-vis absorption spectra were carried out by using Shimadzu UV-3600 UV-vis spectrophotometer. The UPS measurement were obtained by thermo scientific NEXSA. The PL spectra were obtained using an FLS980 spectrometer (Edinburgh Instruments Co., Ltd.), and the excitation wavelength was 450 nm. The AFM were performed using Dimension Icon (Veeco Instruments/bruker, German) under ambient conditions. The time-resolved photoluminescence (TRPL) measurement was carried out by Fluo Time 300 (picoquant GmbH) with the 450 nm laser (LDH-P-C-405, Pico Quant GmbH). The current density-

voltage (J-V) characteristics of fabricated devices were measured using Keithley 2400 Source Meter under Air Mass 1.5 Global (AM 1.5 G) with an Oriel 300 W solar simulator intensity of 100 mW/cm². The EQE spectra were conducted by using Crowntech QTest Station 1000 AD. TAS measurements were performed on Femtosecond Ti:Sapphire Laser System (Coherent, America). The contact angle measurement were obtained by Attension Theta Lite at ambient conditions. Electrochemical impedance spectroscopy (EIS) measurements were achieved on the CHI660E electrochemical workstation in the frequency range from 82 kHz to 1 Hz under an open circuit.

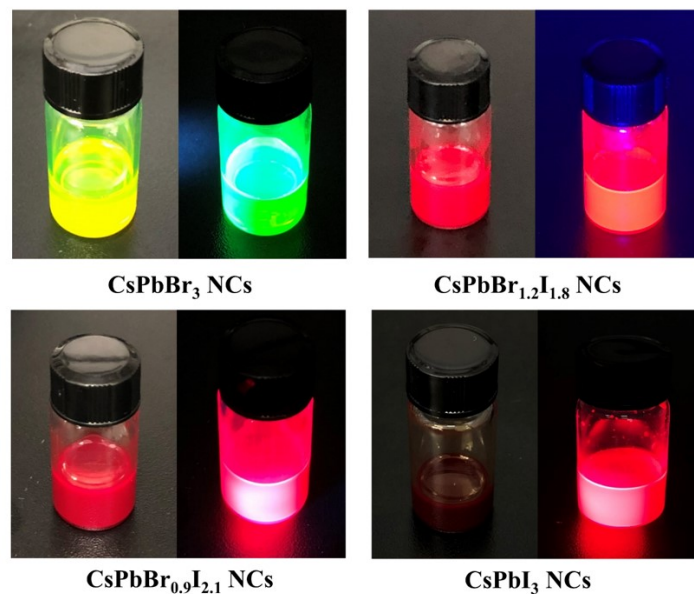


Figure S1. The photos of the different NCs under 365 nm UV illumination.

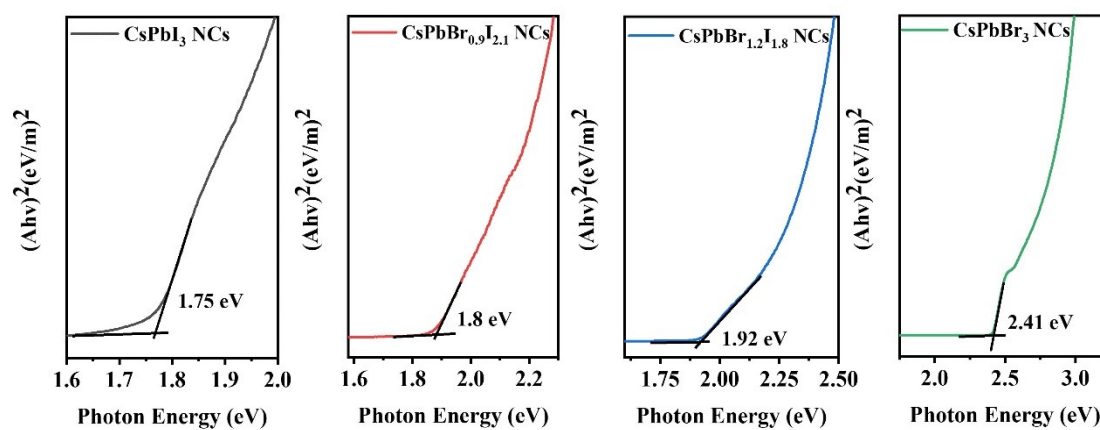


Figure S2. The optical band gaps of NCs derived from the Tauc plots for $x = 0, 0.9, 1, 2$ and 3 , respectively.

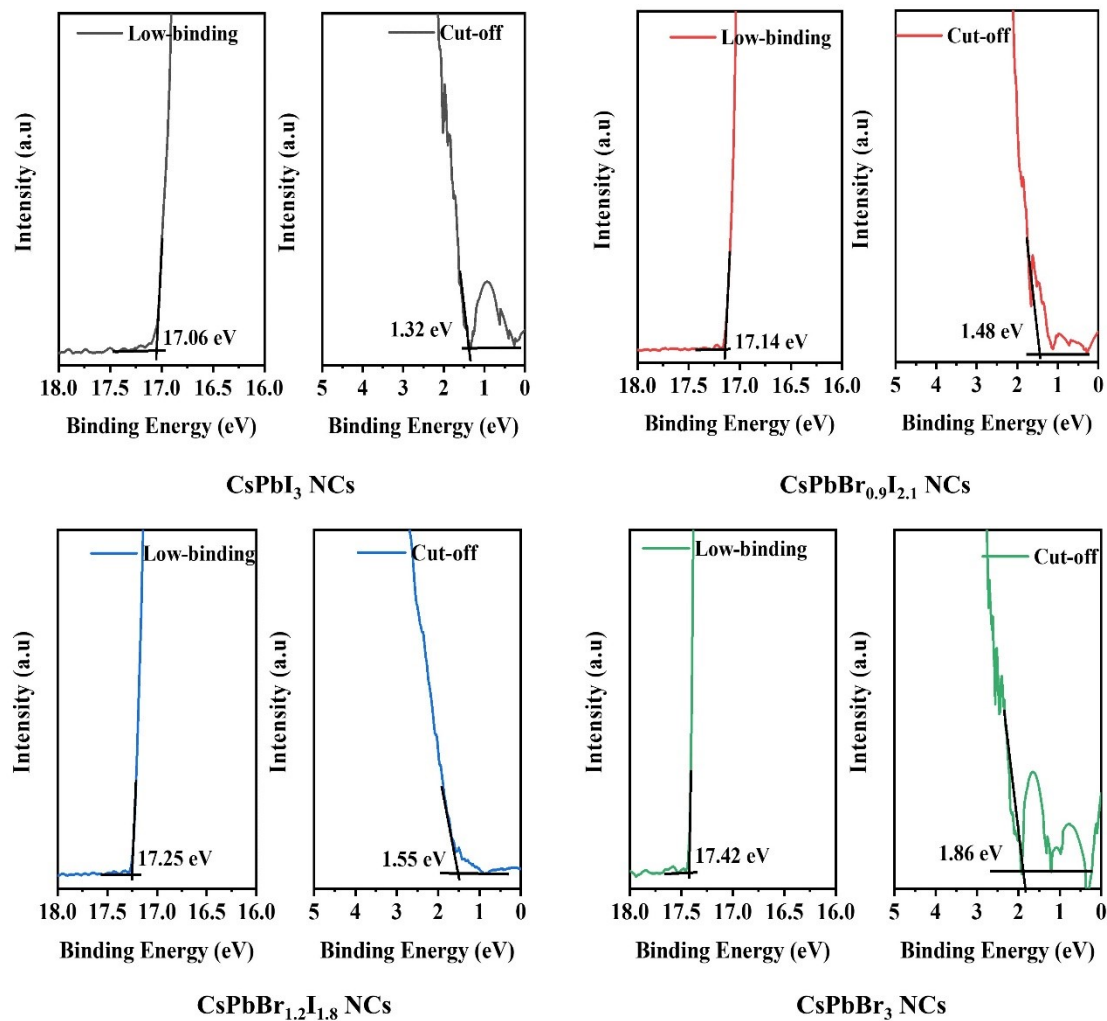


Figure S3. The ultraviolet photoelectron spectroscopy (UPS) of NCs for $x = 0, 0.9, 1.2$ and 3 , respectively.

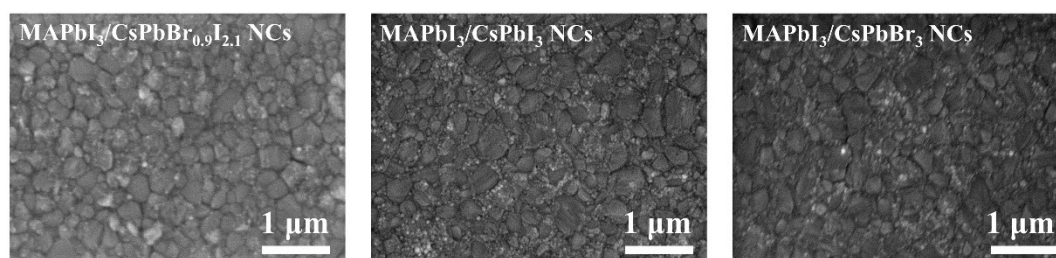
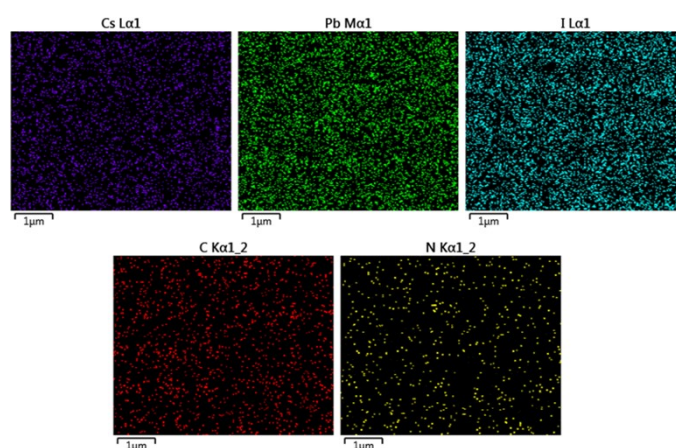


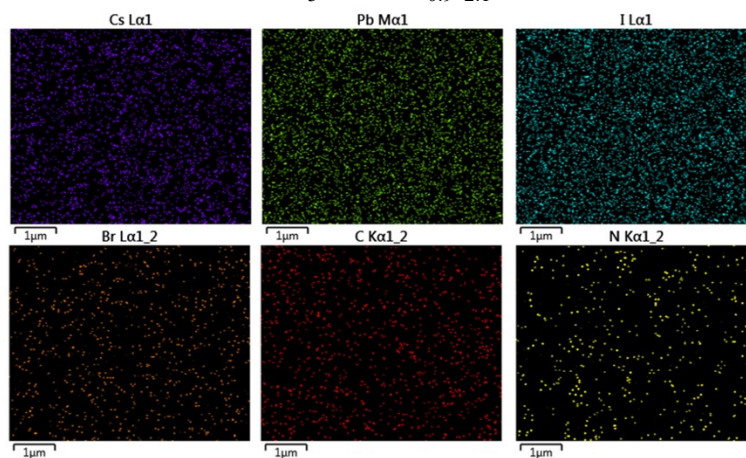
Figure S4. The scanning electron microscopy (SEM) images of MAPbI₃ films after CsPbBr_{0.9}I_{2.1}, CsPbBr_{1.2}I_{1.8} and CsPbBr₃ NCs treatment.

MAPbI₃/CsPbI₃ NCs



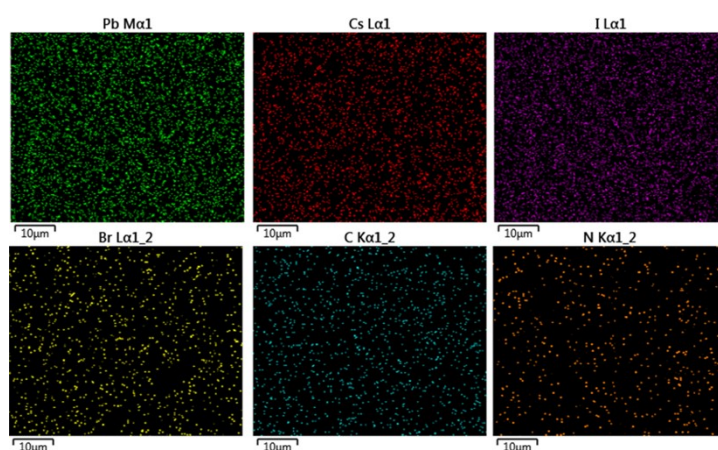
Element	C	N	Cs	Pb	Br	I
Ratio of the element (%)	49.54	12.48	0.48	10.03	0	27.47
Quality of the element (wt%)	9.30	2.73	1.00	32.48	0	54.48

MAPbI₃/CsPbBr_{0.9}I_{2.1} NCs



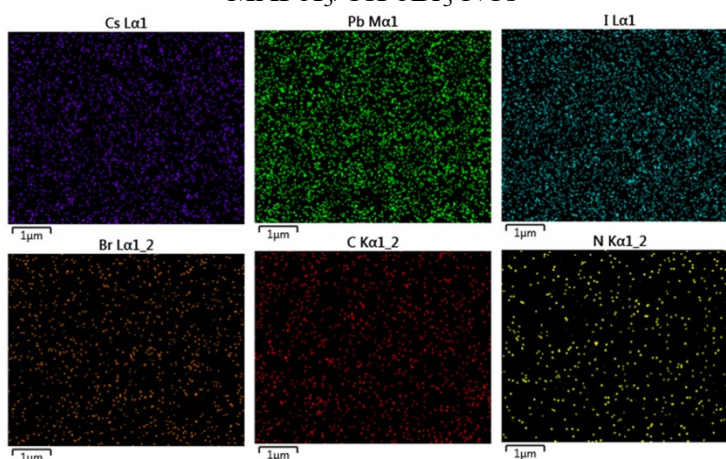
Element	C	N	Cs	Pb	Br	I
Ratio of the element (%)	43.95	8.83	0.67	11.79	1.44	33.33
Quality of the element (wt%)	7.01	1.64	1.18	32.44	1.53	56.19

MAPbI₃/CsPbBr_{1.2}I_{1.8} NCs



Element	C	N	Cs	Pb	Br	I
Ratio of the element (%)	51.75	6.05	0.88	10.25	3.38	27.7
Quality of the element (wt%)	9.23	1.26	1.74	31.54	4.01	52.22

MAPbI₃/CsPbBr₃ NCs



Element	C	N	Cs	Pb	Br	I
Ratio of the element (%)	49.84	9.88	0.63	9.85	1.71	28.10
Quality of the element (wt%)	9.12	2.11	1.27	31.09	2.08	54.33

Figure S5. The EDS elemental mapping images of CsPbBr_xI_{1-x} NCs modified perovskite film.

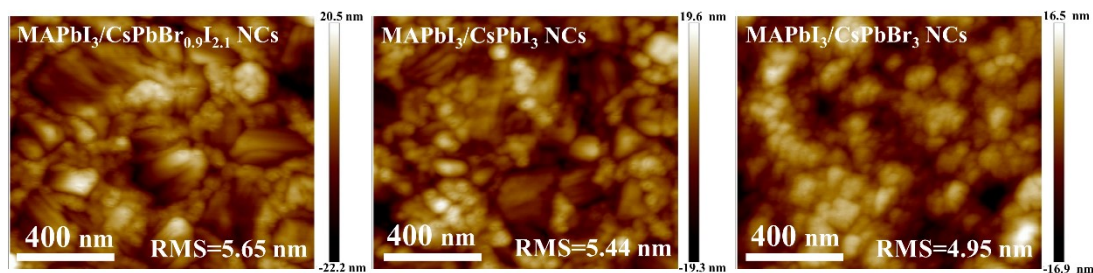


Figure S6. The atomic force microscopy (AFM) images of MAPbI₃ films after CsPbBr_{0.9}I_{2.1}, CsPbBr_{1.2}I_{1.8} and CsPbBr₃ NCs treatment.

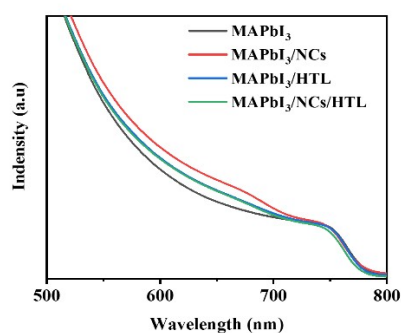


Figure S7. The UV-vis absorption measurement of the NCs interfacial layer on the perovskite layer with and without HTL

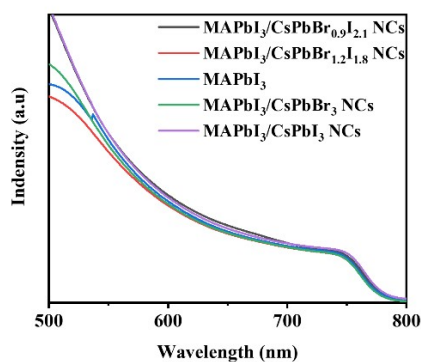


Figure S8. The UV-vis absorption measurement of the perovskite layers treated by different Br/I ratio of NCs

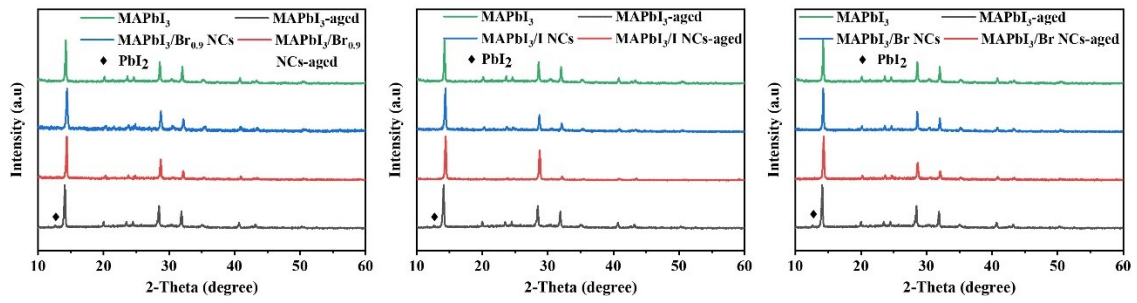


Figure S9. XRD patterns of the fresh and 5 days-aged MAPbI₃ films with and without CsPbBr_{0.9}I_{2.1}, CsPbBr_{1.2}I_{1.8} and CsPbBr₃ NCs treatment.

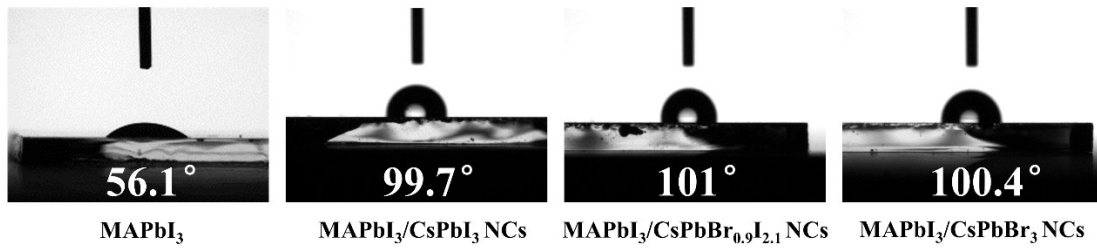


Figure S10. The contact angle of water for the perovskite / NCs stacks.

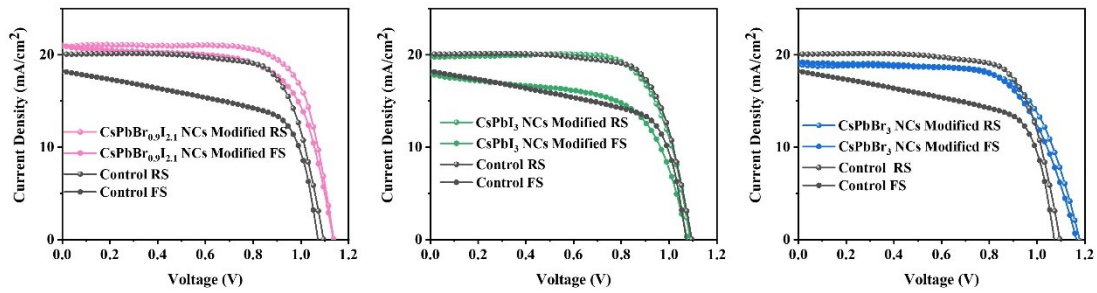


Figure S11. J-V curves for the NCs treatment and control devices with both forward and reverse scan directions

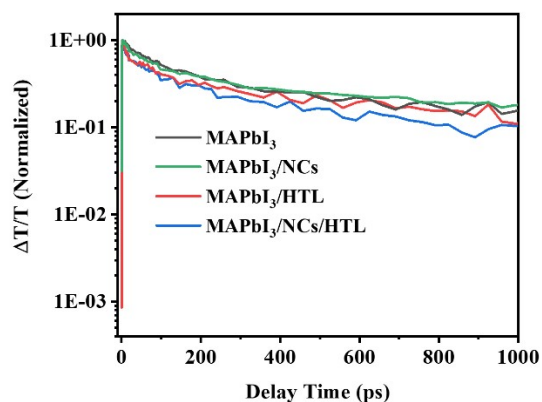


Figure S12. The decay dynamics of PB2 peaks of corresponding films at 730 nm.

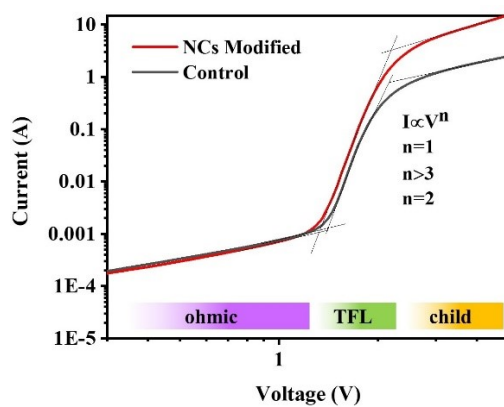


Figure S13. Current-Voltage (I-V) characteristics of the corresponding electron-only devices.

Table S1. Photovoltaic parameters of the control and CsPbBr_xI_{1-x} NCs treatment device.

Device	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	η (%)
CsPbBr _{1.2} I _{1.8} NCs Modified	1.13	22.70	0.75	19.16
CsPbBr _{0.9} I _{2.1} NCs Modified	1.14	20.85	0.73	17.52
Control	1.10	20.12	0.70	16.06
CsPbI ₃ NCs Modified	1.09	19.78	0.72	15.58
CsPbBr ₃ NCs Modified	1.17	18.87	0.68	15.08

Table S2. The grain size statistics of CsPbBr_xI_{1-x} NCs modified perovskite film.

Sample	MAPbI ₃	MAPbI ₃ /CsPbBr ₃ NCs	MAPbI ₃ /CsPbBr _{1.2} I _{1.8} NCs	MAPbI ₃ /CsPbBr _{0.9} I _{2.1} NCs	MAPbI ₃ /CsPbI ₃ NCs
Mean (nm)	374.05	387.96	337.03	403.32	370.99
Standard Deviation (nm)	103.20	129.83	80.5	96.92	112.43

Table S3. Photovoltaic parameters of the control and optimized device measured at forward and reverse scans.

Device	Scan Direction	V _{oc} (mV)	J _{sc} (mA cm ⁻²)	FF	η (%)	Hysteresis Index
Control	Reverse	1.10	20.12	0.70	16.06	0.28
	Forward	1.07	18.22	0.54	11.54	
NCs Modified	Reverse	1.13	22.70	0.75	19.16	0.06
	Forward	1.10	21.96	0.74	17.95	

Table S4. Lifetime fitted by the TRPL result of the bare and NCs treatment perovskite films with and without HTL layer.

Samples	τ_1 (ns)	τ_2 (ns)	A_1	A_2	τ_{ave} (ns)
MAPbI ₃	5.61	23.43	0.73	0.27	16.35
MAPbI ₃ /NCs	5.46	18.75	0.80	0.20	11.61
MAPbI ₃ /HTL	4.76	14.18	0.77	0.21	8.98
MAPbI ₃ /NCs/HTL	3.16	10.18	0.75	0.25	6.80

Table S5. The parameters of the series resistance (R_s) and the recombination resistance (R_{rec}) fitted by the Nyquist plots of the devices with and without the modification of CsPbBr_{1.2}I_{1.8} NCs.

Device	R_s (Ω)	R_{rec} (Ω)
Control	41.47	110680
NCs Modified	39.47	179420

References

- 1 G. Yang, C. Chen, F. Yao, Z. Chen, Q. Zhang, X. Zheng, J. Ma, H. Lei, P. Qin, L. Xiong, W. Ke, G. Li, Y. Yan and G. Fang, *Advanced Materials*, 2018, **30**, 1–9.
- 2 H. Yang, W. Yin, W. Dong, L. Gao, C. H. Tan, W. Li, X. Zhang and J. Zhang, *Journal of Materials Chemistry C*, 2020, **8**, 14439–14445.