

Supporting Information

Controlled Surface Decomposition Derived Passivation and Energy-Level Alignment Behaviors for High Performance Perovskite Solar Cells

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Materials Synthesis and Film Fabrication. All the raw reagents were purchased from Sinopharm and/or Sigma-Aldrich without further purification. Methylammonium iodide (MAI) was synthesized as we previously reported.^[1] by reacting 27.6 mL methylamine (27 ~ 32 wt% in ethanol) with 30 mL hydroiodic acid (HI, 45 wt% in water, Sinopharm) at 0 °C under argon atmosphere to prevent the oxidation of I⁻. HI was added to the solution dropwise while stirring. After stirring for 2 h, MAI powders were collected by evaporating the solvent using rotary evaporator at 60 °C. After which they were washed and purified with a mixture of ethanol and diethyl ether using air-pump filtration.

Device Fabrication: Fluorine-doped tin oxide (FTO) coated glass was patterned by etching with Zn powder and 1 M HCl diluted in distilled water. The etched substrate was then cleaned with ethanol, saturated KOH solution in isopropanol, and water and then dried with clean dry air. Subsequently, for inverted devices, the clean FTO glasses were placed on a hotplate at the temperature of 500 °C. 30 mL of an acetonitrile/ethanol (with 95: 5 volume ratio) solution of nickel acetylacetonate with 15 mol% magnesium was sprayed within 10 min by an air nozzle (with 0.2 mm caliber) onto the hot FTO glasses at a distance of about 20 cm above. The total metal ion concentration was set at 0.02 mol L⁻¹. After spraying, the film was further treated at 500 °C for another 20 min to promote NiO crystallization. In addition, for normal devices, a 20-nm thick compact SnO₂ hole-blocking layer was deposited on the FTO-glass by a modified spraying method, and annealed at 200 °C for 30 min in air. After cooling, the NiO or TiO₂ coated FTO glasses were transferred quickly to the N₂ filled glove box for MAPbI₃ perovskite layer deposition. The method for perovskite layer deposition was modified slightly from previous report: first, a 50 µL 1.33 M DMSO solution of PbI₂/MAI mixture was spread onto FTO glass with coated layer; then, the spin-coater was started at a rotation speed of 1000 rpm for 10 seconds and 5000 rpm for another 30 seconds. 300 µL chlorobenzene was drop-casted quickly 10 seconds before the 5000 rpm spin-coating finished. The perovskite films were then heated at 100 °C on a hotplate for 20 min. And the PEP post-treatment samples are transferred into the ALD reaction chamber for processing accordingly. Then, as for inverted devices, after cooling, a chlorobenzene (99.8%, Aldrich-Sigma) solution of PCBM ([6,6]-Phenyl-C61-butyric Acid Methyl Ester) (20 mg mL⁻¹) was spin-coated on top of the perovskite film at the rotation speed of 1500 rpm for 30 seconds. Subsequently, 50 µL isopropanol (99.8%, Aldrich-Sigma) solution of BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) (0.5 mg mL⁻¹) was drop-casted quickly onto the surface of PCBM layer at the rotation speed of 6000 rpm. For normal devices, the Spiro-OMeTAD hole-transporting layer was prepared by dissolving 72.3 mg of Spiro-OMeTAD in 1 mL of chlorobenzene, to which 28.8 µL of 4-tert-butylpyridine (96%, Aldrich-Sigma) and 17.5 µL of lithium bis(trifluoro-methanesulfonyl) imide (LITSFI, Aldrich-Sigma) solution (520 mg LITSFI (98%) in 1 mL acetonitrile (99.8%, Aldrich-Sigma)) were added. After complete dissolution, 30 µL of spiro-OMeTAD

solution was deposited by spin-coating (3000 rpm, 30 s). Finally, 100 nm thick Ag electrodes were thermally evaporated under vacuum to complete the PSC fabrication.

Materials and Device Characterization. XRD spectra were measured by a Bruker-AXS Micro diffractometer (D8 ADVANCE) with Cu K α radiation (1.5406Å). The optical absorbance spectra were measured by UV-vis/NIR spectrophotometer (U-4100, Hitachi). Top view, cross-section SEM images and energy disperse spectroscopy (EDS) were obtained with a field-emission scanning electron microscope (S-4800, Hitachi). FT-Raman spectroscopy were carried out at the wavelength excitation of 532nm using a FT Raman Thermo Scientific™ DXR. Steady photoluminescence (PL) spectra were recorded on a Perkin LS-55 fluorescence spectrometer excited at 500 nm. Time-resolved photoluminescence (TRPL) experiments were performed with a Fluorolog using a pulsed source either at 406 nm (NanoLED 402-LH from Horiba, pulse width <200 ps, 11 pJ/pulse, approx. 1 mm² spot size) or at 460 nm (Ps diode lasers BDS-SM, pulse with < 100 ps, from photonic solutions, 0.2 pJ/pulse, approx. 1 mm² spot size), and the signal was recorded at 780 nm using the Time-Correlated Single Photon Counting (TCSPC) technique. The samples were excited from the mesoporous SiO₂ side under ambient conditions. A mono-exponential fitting was used to analyze the background-corrected PL decay signal. Transient photovoltage decay measurements were done on a home-made system. I–V curves of the as fabricated PSCs with different scanning directions were measured using a 2400 Sourcemeeter (Keithley, USA) under simulated one-sun AM 1.5G 100 mW cm⁻² intensity (Oriel Sol3A Class AAA, Newport, USA). The maximum-power output stability of the PSCs was measured by monitoring the J output at the maximum-power V bias. The typical active area of PSCs is 0.09 cm² defined by a metal mask. The intensity of the one-sun AM 1.5G illumination was calibrated using a Si-reference cell certified by the National Renewable Energy Laboratory.

Supplementary Figures:

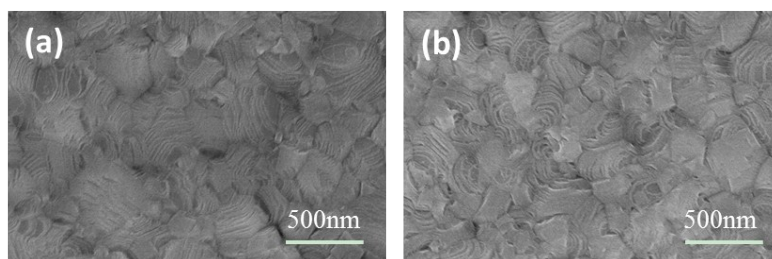


Figure S1. SEM images of perovskite films with 20- (a) and 40-cycle (b) PHEP treatment, respectively.

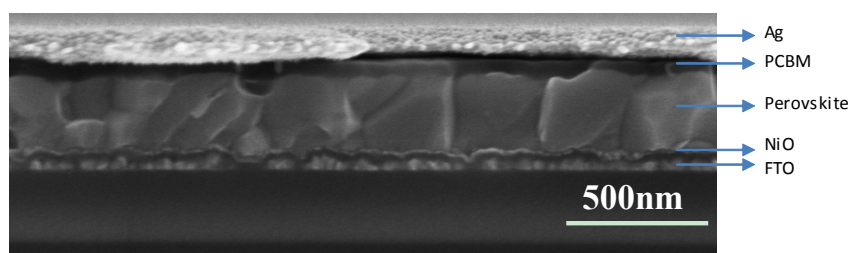


Figure S2. Cross-sectional SEM image of MAPbI₃ film with 10-cycle PHEP treatment.

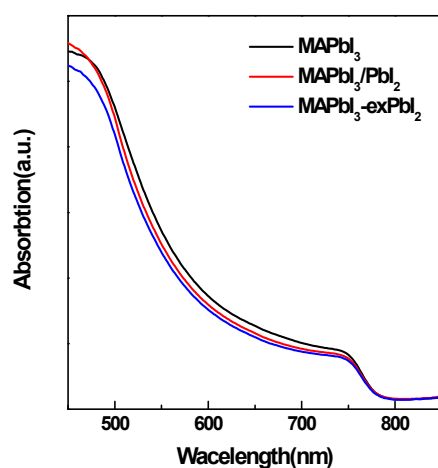


Figure S3. UV-Vis absorption of the MAPbI₃, MAPbI₃/PbI₂ and MAPbI₃-exPbI₂ films.

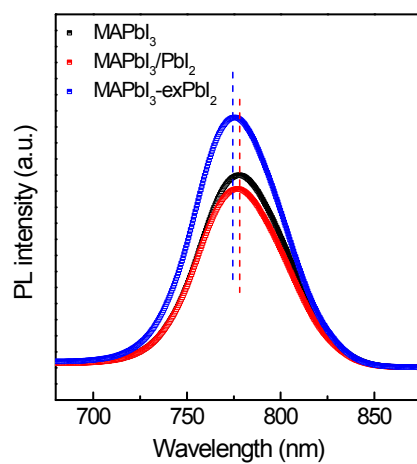


Figure S4. PL intensity of the MAPbI₃, MAPbI₃/PbI₂ and MAPbI₃-exPbI₂ films.

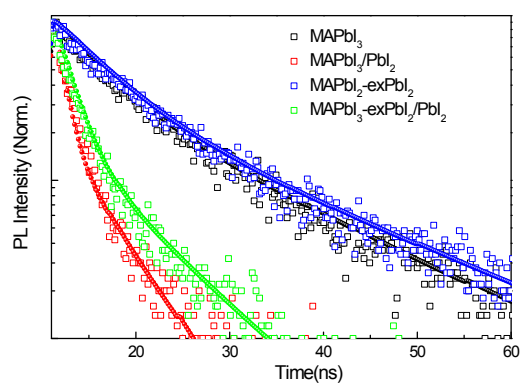


Figure S5. PL lifetime decay of the MAPbI₃, MAPbI₃/PbI₂, MAPbI₃-exPbI₂ and MAPbI₃-exPbI₂/PbI₂ films. MAPbI₃-exPbI₂/PbI₂ film is the MAPbI₃-exPbI₂ film with 10-cycle PHEP treatment.

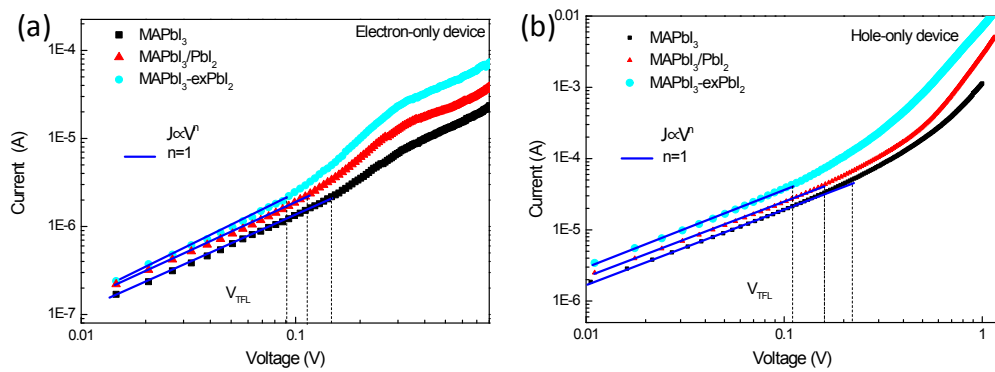


Figure S6. J-V curves of (a) electron-only device FTO/TiO₂/MAPbI₃(or MAPbI₃/PbI₂ or MAPbI₃-exPbI₂)/PCBM/Au. and (b) hole-only device FTO/NiO/MAPbI₃(or MAPbI₃/PbI₂ or MAPbI₃-exPbI₂)/Spiro-OMeTAD/Au.

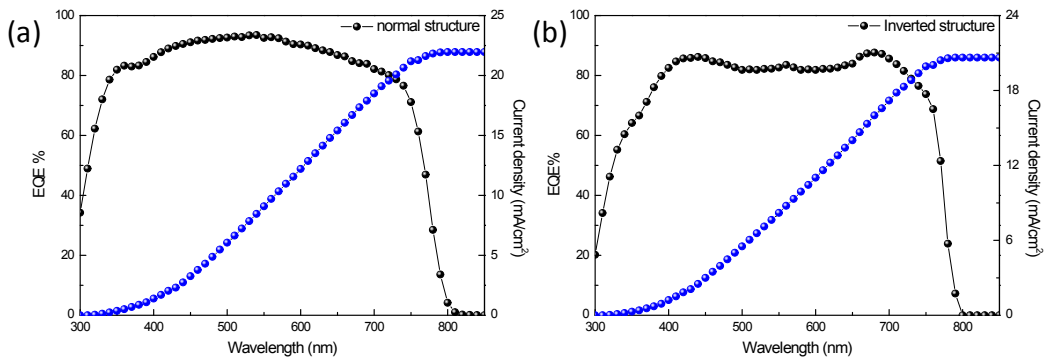


Figure S7. EQE spectrum of the devices with normal (a) and inverted (b) structure.

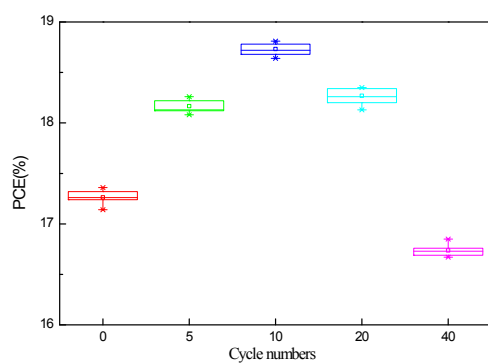


Figure S8. The efficiency distribution of inverted solar cells with different cycles PHEP treatment .

Table S1. Reported photovoltaic parameters of similar structure solar cells in inverted structure.

Device structure	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Ref.
FTO/NiMgLiO/CH ₃ NH ₃ PbI ₃ /PCBM/TiO ₂ /Ag	1.12	22.6	76	19.2	[2]
FTO/NiO/CH ₃ NH ₃ PbI ₃ /C ₆₀ /SnO ₂ NC _s /Ag	1.12	21.8	77	18.8	[3]
ITO/NiO _x /CH ₃ NH ₃ PbI ₃ /PCBM/LiF/Al	1.06	20.2	81	17.3	[4]
ITO/NiO _x /CH ₃ NH ₃ PbI ₃ /C ₆₀ /Bis-C ₆₀ /Ag	1.03	21.8	78	17.6	[5]
ITO/PTAA/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Cu	1.04	22.5	73	17.1	[6]
ITO/PTAA/FA _{0.83} MA _{0.17} Pb(I _{0.6} Br _{0.4}) ₃ /PCBM/BCP/Cu	1.12	17.1	66	12.6	[6]
ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ /PCBM/Au	1.10	20.9	79	18.1	[7]
FTO/NiO/CH ₃ NH ₃ PbI ₃ /PbI ₂ /PCBM/Ag	1.13	21.5	77	18.7	This work

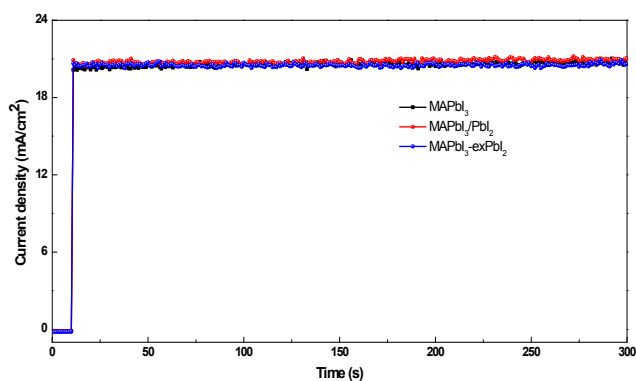


Figure S9. Stabilized current density output of the invert structured MAPbI₃, MAPbI₃/PbI₂ and MAPbI₃-exPbI₂ solar cells.

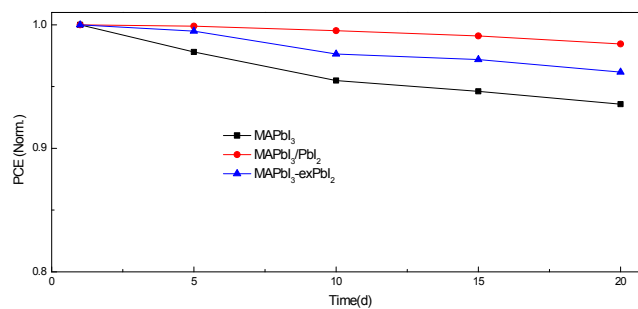


Figure S10. Stability of the inverted MAPbI₃, MAPbI₃/PbI₂ and MAPbI₃-exPbI₂ solar cells. The cells were kept in dark under a humidity of 20%.

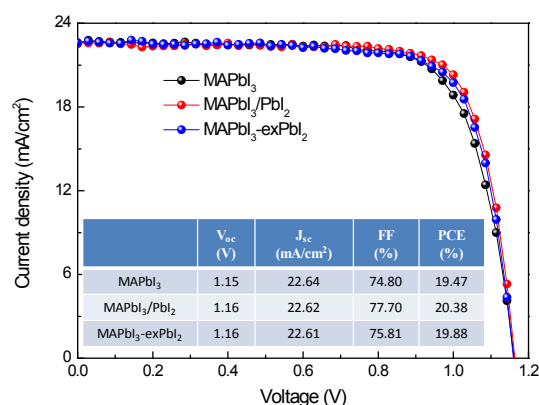


Figure S11. Reverse J-V curves of normal structured MAPbI₃, MAPbI₃/PbI₂ and MAPbI₃-exPbI₂ solar cells. Inset shows the photovoltaic parameters extracted from the J-V curves.

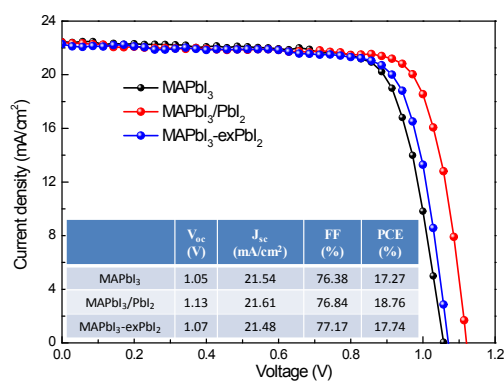


Figure S12. Reverse J-V curves of inverted structured MAPbI₃, MAPbI₃/PbI₂ and MAPbI₃-exPbI₂ solar cells. Inset shows the photovoltaic parameters extracted from the J-V curves.

References

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