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Supporting information

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for

3 Elimination of unstable residual lead iodide near the buried interface

4 for the stability improvement of perovskite solar cells

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35 Experimental Section

36 Materials. The SnO₂ colloid precursor was purchased from Alfa Aesar. FAI, methylammonium bromide (MABr), and methylammonium chloride (MACl) were 37 purchased 38 from Greatcellsolar. PbI₂, CsBr, 2,2',7,7'-tetrakis[N,N-bis(pmethoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD), and Poly(bis(4-phenyl) 39 (2,4,6-trimethylphenyl) amine) (PTAA) were purchased from Xi'an Polymer Light 40 Technology Corp. All solvents were purchased from Sigma-Aldrich Inc. 41

Solar cell fabrication. The indium tin oxide (ITO) substrates were washed by 42 ultrasonic with ultrapure water, ethanol, and isopropanol for 30 minutes, respectively, 43 and then treated with a UV-O₃ machine for 20 minutes. The SnO₂ precursor was 44 prepared by mixing SnO_2 colloidal dispersion and ultrapure water (1:5). To obtain the 45 pre-embedded SnO₂-FAI precursor, FAI powder was dissolved in SnO₂ precursor 46 with a concentration of 60 mM. Similarly, for the pre-embedded SnO₂-FAI-CsBr 47 precursor, FAI and CsBr powder were dissolved in SnO₂ with a concentration of 52.5 48 mM and 7.5 mM. Both the pre-embedded halide colloid precursors were freshly 49 prepared and stirred for 2 hours. The pre-embedded A-cation halides precursor was 50 deposited on the ITO at a speed of 3000 rpm for 30 s with 1500 rpm s⁻¹ and annealed 51 in ambient air at a temperature of 150 °C for 30 min. For the perovskite layer, the PbI₂ 52 precursor (691.5 mg PbI₂ in the 1 mL mixture solvent of N,N-dimethylformamide 53 (DMF) and dimethyl sulfoxide (DMSO) with a volume ratio of 9:1) was stirred at 70 54 °C and was spin-coated at a speed of 2000 rpm for 30 s with 1000 rpm s⁻¹. The 55 56 organic salt solution (65 mg of FAI, 5 mg of MACl, and 5 mg of MABr in 1 mL

57 isopropanol) was spin-coated at the same speed as PbI₂ in an N₂ glove box. Then, the films were placed on the hot plate with a temperature of 150 °C for 15 min in the 58 atmosphere (30%-40% relative humidity). For the hole transport layer, the spiro-59 OMeTAD precursor (72.3 mg spiro-OMeTAD, 30 µL 4-tert-butylpyridine solution, 60 and 35 µL bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI) in 1 mL 61 chlorobenzene) was deposited at 3000 rpm for 30 s with 1500 rpm s⁻¹. For the 62 stability test, the PTAA precursor (20 mg PTAA, 16 µL 4-tert-butylpyridine, and 30 63 µL Li-TFSI in chlorobenzene), as the hole-transport layer, was deposited with the 64 65 same speed as the spiro-OMeTAD solution. Finally, a 100 nm gold electrode was thermally evaporated under the vacuum. 66

Module fabrication. For module (substrate size: 6.7×6.7 cm) fabrication, the same 67 68 spin coating procedure was used, using 350 µL pre-embedded precursor, 300 µL PbI₂ precursor and 350 µL organic salt solution. After the deposition of the perovskite 69 layer, the hole-transport layer was deposited with 300 µl spiro-OMeTAD precursor. 70 71 Finally, a 100 nm gold electrode was thermally evaporated under the vacuum. The temperature was 25 ± 2 °C and the humidity was $40 \pm 5\%$ RH during the laser 72 processing. Regarding the laser etching for module fabrication, the P1, P2 and P3 73 were ablated by laser (JPT OPTO-ELECTRONICS Co., China) with a wavelength of 74 532 nm and minimal pulse duration of 18 ns. The average power was 7 W and the 75 frequency was 50 kHz. The laser pulse energy was adjusted by rotating the polaroid 76 77 without changing any optical path. The inactive P1-P2-P3 interconnection area or 78 dead area width W_d and the active area width W_a of our module is 0.6mm and 7.5mm,

79 respectively. This geometric fill factor (GFF), or ratio of active area to aperture area is

$$W_a$$

80 given by $\overline{W_a + Wd}$. Thus, the GFF of our modules is 92.6%.

Device Encapsulation. First, a cover glass was covered on the top surface of PSCs to provide mechanical protection by sealing devices with bynel sealant at 135 °C for 10 min along its edge carefully. And then, the edges of the devices were further encapsulated by butyl rubber/aluminum tape. After that, the fabricated PSCs were performed for the operational stability test.

Lift-off process for the perovskite film. The PTAA solution (40 mg mL⁻¹, in 86 chlorobenzene) was spin-coated on the substrates at 1500 rpm for 25 s with 750 rpm 87 s⁻¹ and annealed at 150 °C for 15 min. After that, the SnO₂ precursor was deposited 88 on it. It is worth noting that the PTAA layer is as thick as possible, while the SnO₂ 89 90 layer is as thin as possible. Since a \sim 5 nm thick SnO₂ layer is enough thin for beam transmission of the high-energy electron, we could clearly observe the structure of 91 perovskite by SEM. Subsequently, the perovskite solution was deposited and then 92 93 covered by the copper electrode. The obtained film was soaked in chlorobenzene for 2 hours and separated from the substrate due to the dissolution of the PTAA layer. 94

95 Fabrication of space charge limited current devices. The structure of the device was 96 ITO/SnO₂(FAI-CsBr)/Perovskite/PCBM/BCP/Ag. The preparation of the electron 97 transport layer and perovskite layer are the same procedure as that of the previous cell 98 devices. Then, the PCBM solution (20 mg mL⁻¹, in chlorobenzene) was spin-coated 99 on top of the perovskite film at 2000 rpm for 30 s with 1000 rpm s⁻¹, and annealed at 100 70 °C for 10 min. Sequentially, the saturated solution of BCP in methanol was spin101 coated on PCBM at 6000 rpm for 30 s with 3000 rpm s⁻¹, and annealed at 70 °C for 102 10 min. Finally, The device was completed by thermally evaporating Ag (100 nm) in 103 a vacuum chamber ($\leq 3 \times 10^{-4}$ Pa).

104 Space charge limited current (SCLC) based on electron-only devices 105 ITO/SnO₂(FAI-CsBr)/Perovskite/PCBM/BCP/Ag is used to quantify the effect of 106 buried interface on defects density. The ohmic region, trap-filled region and SCLC 107 region can be seen in the curves. The trap-filling limit voltage (V_{TFL}) is defined as the 108 intersection of the ohmic region and the trap-filled region, and the defect density (N_t) 109 in a perovskite device can be calculated using the following equation:^[1, 2]

$$N_t = \frac{2\varepsilon_0 \varepsilon V_{TFL}}{qL^2} \tag{1}$$

111 where ε_0 and ε are the vacuum permittivity and the relative dielectric constant of 112 perovskite, *q* is the electron charge, and *L* (~570nm) is the thickness of the 113 corresponding perovskite films. The V_{TFL} of the pristine and target films are 0.119V 114 and 0.308V, respectively. According to the above equation, the defect density N_t of 115 the pristine and target films can be calculated as 3.46×10^{15} and $1.33 \times 10^{15} cm^{-3}$.

116 *Characterization and Measurements.* The XRD characterizations were recorded on 117 an Empyrean X-ray diffractometer with Cu K α radiation (PANalytical B.V. Co., 118 Netherlands). The grazing incident X-ray diffraction (GIXRD) was determined using 119 an X-ray diffractometer (XRD, Rigaku Smartlab) with Cu k α wavelength $\lambda = 1.54$ Å. 120 The top-viewing and the cross-sectional images of the samples were monitored by a 121 field-emission SEM (FEI NOVA NanoSEM 450). The XPS spectra were recorded on 122 an AXIS-ULTRA DLD-600 W Ultra spectrometer (Kratos Co., Japan). The time123 resolved photoluminescence spectrum (TRPL) was obtained by a fluorescence spectrometer with an excitation wavelength of 478 nm (DeltaFlex, HORIBA). TOF-124 125 SIMS depth profiles were carried out using an IonToF TOF-SIMS 5 instrument 126 (IONTOF Co., Germany). The current density-voltage (J-V) curves were recorded with a black mask with an active area of 0.0928 cm^2 for small size PSCs and 9.66 cm^2 127 for mini-modules by a solar simulator (Oriel, model 9119) with an AM1.5G spectrum 128 and the simulated light intensity was calibrated with a silicon photodiode (Enlitech). 129 The scanning speed for both forward and reverse scans was 0.01 V s⁻¹. The EQE 130 131 spectra were measured in DC mode by the EQE system (Saifan, China) using monochromatic light of 1×10¹⁶ photons cm⁻². The grazing incidence wide-angle X-132 ray scattering (GIWAXS) measurements were performed at beamline BL14B1 of the 133 134 Shanghai Synchrotron Radiation Facility. The space charge limited current (SCLC) plots were obtained by a CHI1000c multichannel electrochemistry workstation 135 (Chenhua, Co., China). The LBIC measurement was performed by a laser with a 136 137 wavelength of 405 nm, and this device was fixed on a micro-spectral measurement system, ProSp-Micro40-VIS (Hangzhou SPL Photonics Co., LTD, China), together 138 139 with a spectrograph (Ocean Insight, USA). The film light aging was measured by xenon lamp aging tester (APKJ, China) with a wavelength from 290 to 800 nm. The 140 operation stability of the devices was measured in ambient with a multi-channel 141 142 automated stability testing system (91PVKSolar Co., Ltd).



144 Fig S1. Depth-resolved GIWAXD patterns of a-b) pristine and c-d) target films with

145 incident angle of 0.3° and 0.5° , respectively.



147 Fig S2. The ratio of PbI₂/perovskite characteristic peak in the GIWAXD results for

148 pristine and target films with different incident angles.



- 149
- 150 Fig S3. Top view SEM images of a) pristine and b) target films after 7 days UV light
- 151 illumination aging.



153 Fig S4. X-ray photoelectron spectroscopy (XPS) results of the bottom interface for

154 target film before and after 7 days UV light illumination aging.



156 Fig S5. X-ray diffraction image of target film before and after UV light illumination.



158 Fig S6. XRD pattern evolutions of aging perovskite films with and without pre-

159 embedded A-cation halides under UV illumination exposed to N_2 atmosphere.



161 Fig S7. Fitted line of $2\theta - \sin^2(\psi)$ from GIXRD spectra with different ψ values at the

162 depth of 500 nm for pristine film and target film, respectively.



164 **Fig S8.** a-b) Grazing incident X-ray diffraction (GIXRD) spectrums at different tilt 165 angles at the depth of 200 nm for the pristine and target films, respectively. c) Fitted 166 line of 2θ -sin²(ψ) from GIXRD spectra with different ψ values for the pristine and 167 target films, respectively.



169 Fig S9. a) UV-vis absorption spectra of the pristine and target perovskite films. b)

170 Bandgap of corresponding perovskites extracted from UV-vis absorption spectra.



Fig S10. 85°C thermal stability test for the device.



- 175 Fig S11. Optical photo of perovskite solar module.



177 Fig S12. *J-V* curves of perovskite solar modules based on the pristine and target films.



179 Fig S13. Statistical distributions of PCEs for 30 perovskite modules.



181 Fig S14. Mott-Schottky plots of pristine and target devices.



183 Fig S15. N_t distribution as a function of defect energy level E_{ω} for the pristine and

184 target devices measured by TAS characterization.



186 Fig S16. The representative dark J-V curves of electron-only device with a 187 configuration of ITO/SnO₂/Perovskite/PCBM/BCP/Ag. Three regions can be 188 identified according to different values of the slope n: n = 1 represents the ohmic 189 regime, n = 2 represents the SCLC regime (child), and n > 3 represents the trap-filled 190 limited regime (TFL).



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193 Fig S17. Normalized time-resolved photoluminescence (TRPL) decay of pristine and

194 target films.



196 Fig S18. EQE of EL results for the pristine and target devices while operating as197 LEDs.



199 Fig S19. Transient photocurrent (TPC) decay results for the pristine and target PSCs.



201 Fig S20. Transient photovoltage (TPV) decay results for the pristine and target202 devices.

Concentration	$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	PCE (%)
0 mM	1.145	24.30	78.92	21.96
20 mM	1.158	24.77	79.98	22.95
40 mM	1.162	25.19	81.28	23.81
60 mM	1.163	25.41	81.95	24.22
80 mM	1.162	25.23	80.78	23.68

203 Table S1. The photovoltaic performance parameters of devices with different204 concentration of pre-embedded A-cation halides.

FAI:CsBr	$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	PCE (%)
0:1	1.159	24.21	79.86	22.41
1:1	1.161	24.91	80.59	23.32
3:1	1.162	25.31	81.75	24.04
6:1	1.163	25.44	81.88	24.23
9:1	1.162	25.28	81.42	23.93
1:0	1.159	24.64	80.88	23.09

206 Table S2. The photovoltaic performance parameters of devices with different pre-207 embedded FAI:CsBr ratios.

Depth (nm)	(hkl)	Speed	ψ (°)	ω(°)
			5	1.8313
			15	1.8933
200 nm	(012)	0.8	25	2.0273
			35	2.2617
			45	2.6573
			5	3.4807
			15	3.6065
500 nm	(012)	0.8	25	3.8835
			35	4.3772
			45	5.2423

Table S3. Instrument angles (ψ , ω) setting parameters of GIXRD residual strain

210 gradient measurements.

	-		
Depth (nm)	Films	Slope	Strain (MPa)
200 nm	Pristine	-0.0205	15.2227
	Target	-0.0149	11.0461
500 nm	Pristine	-0.1758	130.379
	Target	-0.0118	8.73900

212 Table S4. The slope of the residual strain fitting line is measured by GIXRD and

213 strain is calculated by equation (2) for the tensile strain pristine film and strain-free

214 target film at the depth of 200 nm, and 500 nm.

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