

Supporting information for:

**Controllable self-induced passivation of hybrid lead iodide perovskites
toward high performance solar cells**

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Experimental section

Substrates preparation: A patterned FTO-coated glass ($13 \Omega/\text{sq}$, Aldrich) was etched by Zn powder and 2 M HCl diluted in deionized water. Subsequently, the substrates were cleaned with detergent diluted in deionized water, rinsed with deionized water, acetone and ethanol, and dried with clean dry air.

TiO₂ precursor solution: A 0.46 M titanium isopropoxide and 0.026 M HCl solution in ethanol was prepared separately. After that, the HCl solution was added dropwise to the titanium precursor solution under heavy stirring, giving a transparent TiO₂ precursor solution.

Device Fabrication: The etched FTO substrates were coated with TiO₂ precursor solution at 3,000 r.p.m. for 30 s, followed by annealing at 550 °C for 30 min in air to form a compact n-type layer of TiO₂(c-TiO₂). After cooling down, a solution of 400 mg/mL PbI₂ in DMF were spin coated on the FTO/c-TiO₂ substrates at 2,000 r.p.m. for 30s, and dried at 110 °C for 15 min. Then, the CH₃NH₃I powder was spread out around the PbI₂ coated substrates with a petridish covering on the top in a confined space, and heated at 150 °C for desired time. Both the deposition of PbI₂ film and treatment of PbI₂ film in CH₃NH₃I vapor are carried out in glovebox. Subsequently, the as-prepared substrates was washed with isopropanol, dried and annealed at 150 °C. The hole transport layer (HTL) was coated by spin coating at 2000 r.p.m for 30s, where a spiro-OMeTAD (Lumtec)/chlorobenzene (90 mg/1 mL) solution was employed with addition of 50 μL Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI, Sigma)/acetonitrile (170 mg/ 1 mL) and 20 μL tert-butylpyridine (tBP, Sigma). Finally, the electrode was deposited by thermal evaporation of gold under a pressure of 1×10^{-6} Torr. The active area was 0.12 cm^2 .

Characterizations. X-ray diffraction pattern (2θ scans) of perovskite deposited on the FTO/c-TiO₂ substrates were obtained by using an X-ray diffractometer (Panalytical X'Pert Pro), using Cu-K α radiation ($\lambda=1.54050\text{\AA}$). The SEM images were collected by using an emission SEM (The Nova 230 NanoSEM), where the electron beam accelerated at in the range of 500V to 30 kV. Scanning Kelvin Probe Microscopy was performed on grounded perovskite sample in air using a Bruker Dimension Icon Scanning Probe Microscope with an AC voltage of ~ 2 V. With the use of a lock-in amplifier, the electrostatic force arising from the surface potential difference between the AFM tip (Pt alloy is used in the current work) and device surface was measured. Through a feedback loop, this electrostatic force was nullified by a DC bias applied to the tip, while the DC bias served as a direct measurement of the surface potential. The photovoltaic performance was characterized in air without any encapsulation under AM1.5G illumination at 100 mW/cm^2 provided by a Oriel Sol3A solar simulator. A reference cell KG-5 filter diodes was used to determine the light intensity. Steady-state photoluminescence (PL) was analyzed using Horiba Jobin Yvon system with an excitation at 640 nm. Time-resolved photoluminescence was obtained using the time-correlated single-photon counting technique (PicoHarp 300), and the excitation was provided by a picosecond diode laser at the wavelength of 640 nm with a repetition frequency of 1 MHz (PDL 800B).

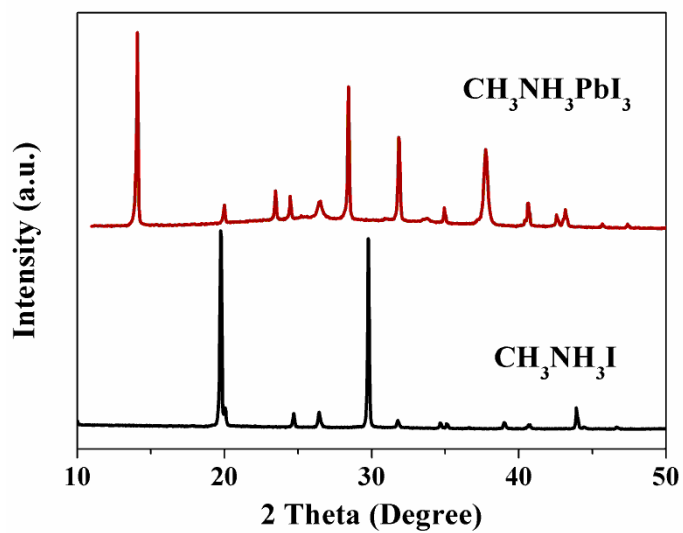


Figure S1: X-ray Diffraction of $\text{CH}_3\text{NH}_3\text{I}$ and pristine $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. The pattern shows that the $\text{CH}_3\text{NH}_3\text{I}$ doesn't match with pristine $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, which indicates no obvious excessive $\text{CH}_3\text{NH}_3\text{I}$ in the pristine film.

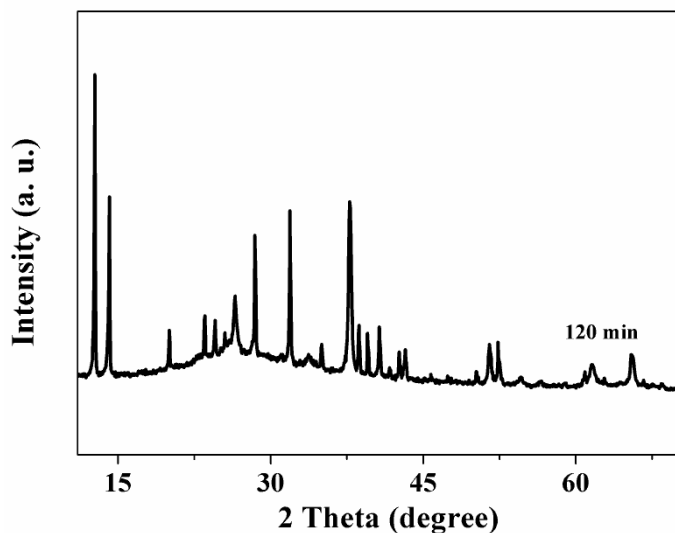


Figure S2: X-ray Diffraction of the perovskite thin film by annealing $\text{CH}_3\text{NH}_3\text{PbI}_3$ at 150 °C for 120 min.

According to Figure S2, the intensity for PbI_2 phase is further enhanced, and the PbI_2 phase becomes dominant. This result is consistent with the composition evolution of the perovskite film along the thermal annealing, investigated by the series X-ray diffraction (XRD) measurement. It is also worthy to point out that the presence of large amount of PbI_2 in the perovskite film leads to a decreased J-V performance, as shown in Figure 1 in the manuscript.

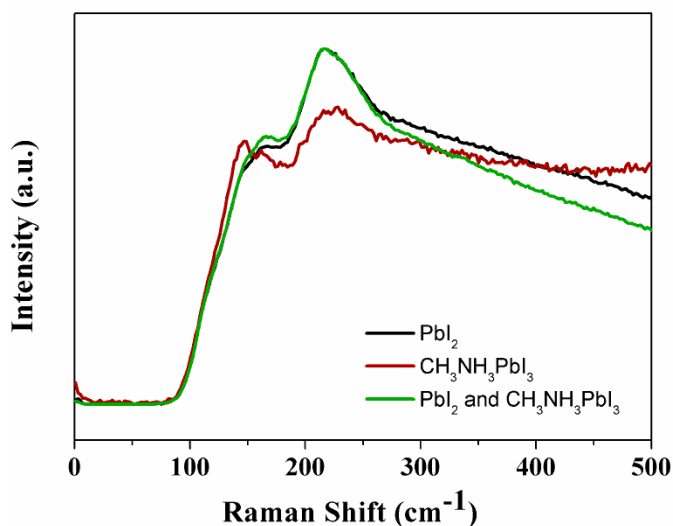


Figure S3: Raman spectroscopy characterization of different films upon 514 nm excitation, including PbI₂ film, the pristine perovskite film (CH₃NH₃PbI₃), and the post-annealed perovskite film (co-existence of PbI₂ and CH₃NH₃PbI₃).

We conducted Raman spectroscopic measurement to examine the PbI₂ species in the perovskite grains. As shown in Figure S3, we provided Raman characterization on different samples under 514 nm laser excitation, including the PbI₂ film, the perovskite film, and the post-annealed perovskite film (the co-existence of PbI₂ and perovskite phases). The PbI₂ film exhibits a strong peak at 216 cm⁻¹ with a shoulder at 166 cm⁻¹. The pristine perovskite film, without any post-annealing, exhibits a set of peaks located at 148 cm⁻¹, 162 cm⁻¹ and 226 cm⁻¹. While the annealed perovskite film (the co-existence of PbI₂ and perovskite phases) shows decreased peak intensity at 148 cm⁻¹ and increased peak intensity at around 166 cm⁻¹. The enhanced signal at 166 cm⁻¹ probably suggests the formation of PbI₂ species in the perovskite film.

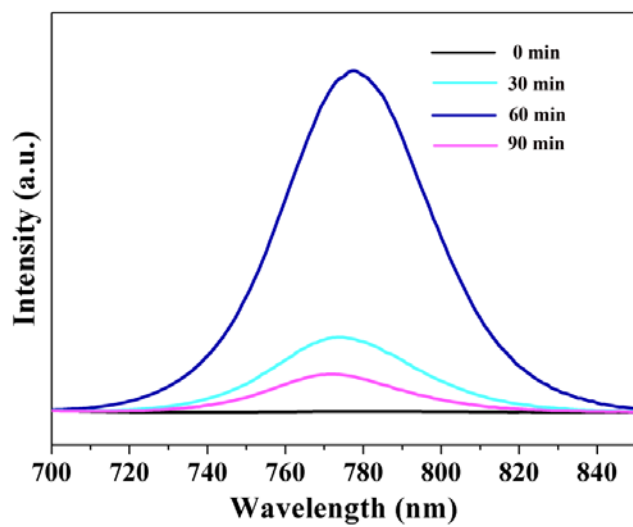


Figure S4: Steady-state Photoluminescence (PL) measurement of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films on glass substrate with different post-annealing time, under 640 nm excitation .

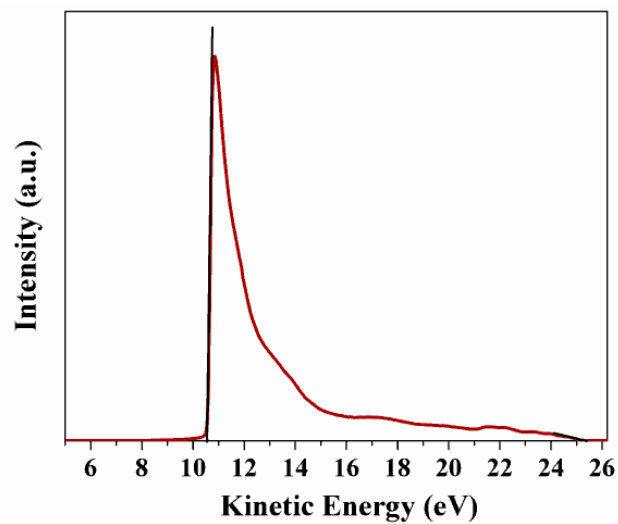


Figure S5: Photoemission cutoff obtained via UPS of PbI_2 film. The Fermi level and VBM of PbI_2 are measured to be 5.05 eV and 5.75 eV, respectively. Considering its bandgap of 2.3 eV, the CBM of PbI_2 is calculated to be 3.45 eV.

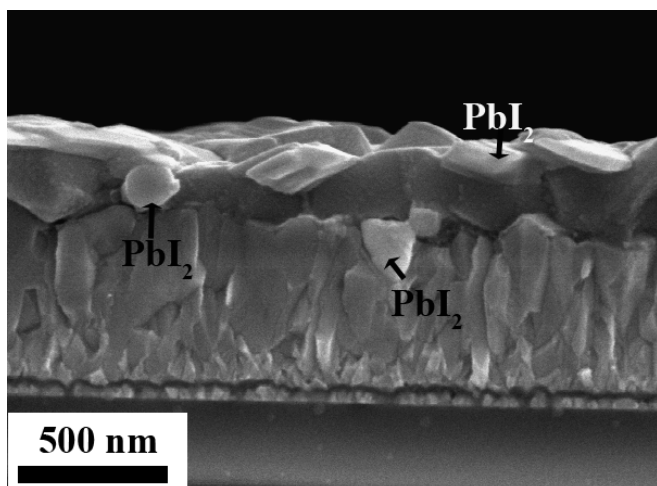


Figure S6: Cross-sectional SEM image of CH₃NH₃PbI₃ film annealed at 150 °C for 60 min. The species with light contrast is speculated to be PbI₂ species, and it appears in the grain boundary, the interfaces of perovskite/TiO₂, and perovskite/HTM.

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