

Supporting Information for

Position-locking of volatile reaction products by atmosphere and capping layers slows down photodecomposition of methylammonium lead triiodide perovskite

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The wide range X-ray diffraction (XRD) measurements of a PbI_2 film and the pristine PEDOT:PSS/ MAPbI_3 perovskite films before and after illumination treatments in different environmental conditions are shown in Fig S1. The XRD peaks appeared at 14.2° , 20.1° , 23.6° , 24.6° and 28.5° correspond to the (110), (200), (211), (202) and (220) planes of the perovskite tetragonal structure, according the PDF card [PDF 01-084-7607 (ICDD, 2018)]. Peak at 12.7° is assigned to be the (001) plane of the PbI_2 hexagonal structure [PDF 00-007-0235 (ICDD, 1957)].

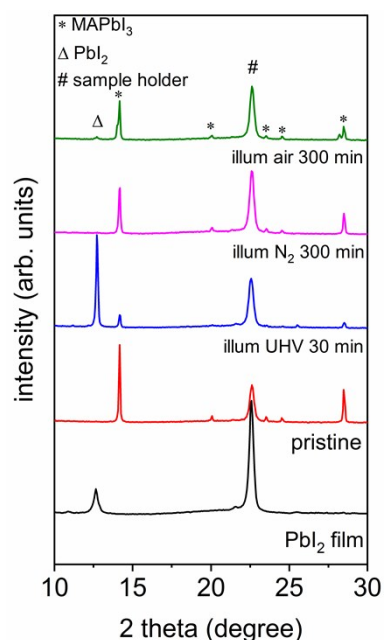


Fig S1. X-ray diffraction patterns of a PbI_2 film, and the pristine MAPbI_3 perovskite films before and after illumination treatment in different environmental conditions. Symbol “ Δ ” and “*” corresponds the peak positions of PbI_2 and MAPbI_3 , respectively. PbI_2 (001) peak position accords to PDF 00-007-0235 (ICDD, 1957) and MAPbI_3 peaks to PDF 01-084-7607 (ICDD, 2018).

X-ray photoelectron spectroscopy (XPS) spectra of the PEDOT:PSS/MAPbI₃ films before and after illumination treatments in UHV, N₂ and ambient air conditions are shown in Fig S2, Fig S3 and Fig S4, respectively. We note that in all cases, C 1s spectra consist of two peaks at 285.8 eV (C_H) and 284.4 eV (C_L) for all pristine perovskite samples with C_H being much higher than C_L in intensity. Here, the C_H peak is assigned to be the CH₃NH₃⁺ from perovskite structure, and the C_L is possibly due to the presence of CH₃NH₂, according to previous reports.^{1,2} Therefore, quantitative analyses of the stoichiometry upon illumination treatments were conducted using the C 1s (peaks of C_H), N 1s, Pb 4f 7/2 and I 3d5/2 peaks, as displayed in Fig 1c.

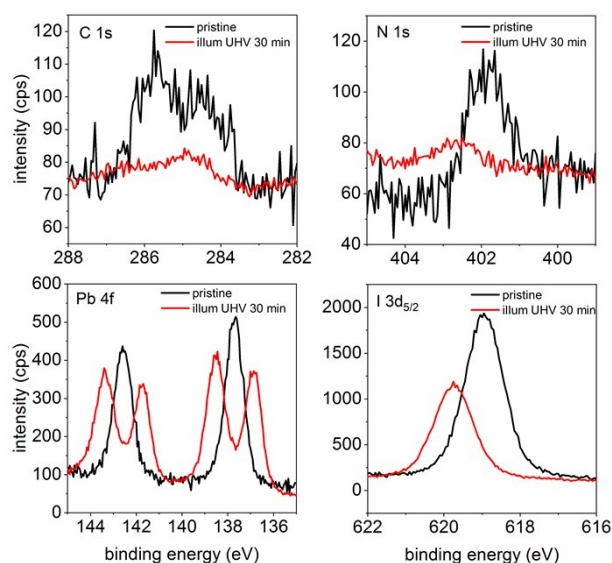


Fig S2. XPS core levels spectra of C 1s, N 1s, Pb 4f and I 3d_{5/2} of the PEDOT:PSS/MAPbI₃ films before (black line) and after illumination treatment (red line) in UHV condition for 30 min. Spectra were recorded at JPS-9030 UHV system.

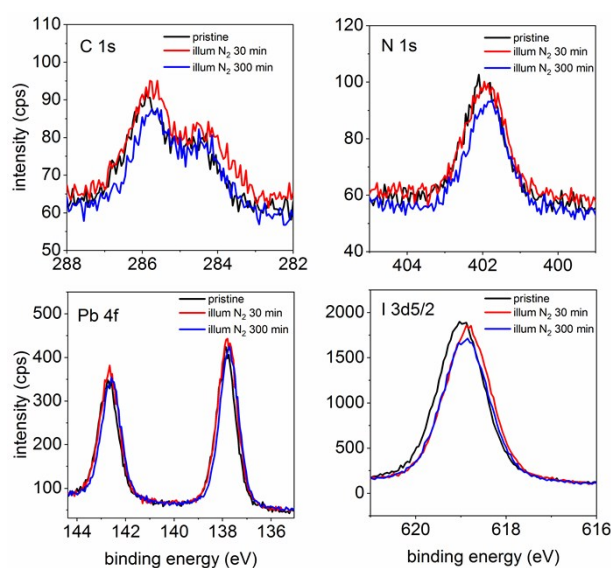


Fig S3. XPS core levels spectra of C 1s, N 1s, Pb 4f and I 3d_{5/2} of the PEDOT:PSS/MAPbI₃ films before (black line) and after illumination treatment in N₂ condition for 30 min (red line) and 300 min (blue line), respectively. Spectra were recorded at JPS-9030 UHV system.

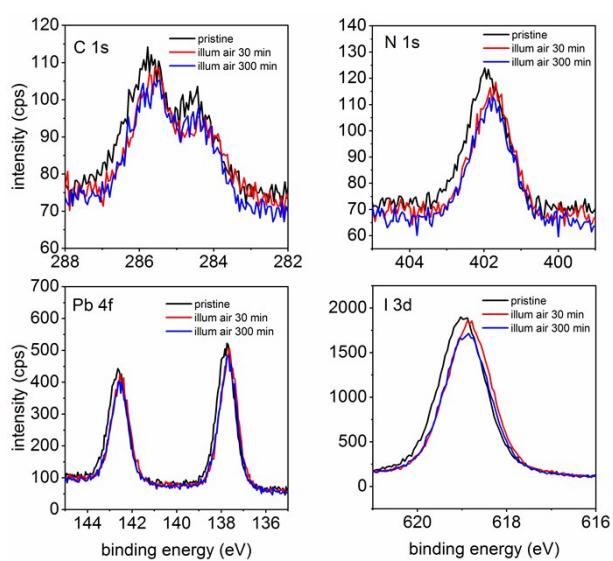


Fig S4. XPS core levels spectra of C 1s, N 1s, Pb 4f and I 3d_{5/2} of the PEDOT:PSS/MAPbI₃ films before (black line) and after illumination treatment in ambient air condition for 30 min (red line) and 300 min (blue line), respectively. Spectra were recorded at JPS-9030 UHV system.

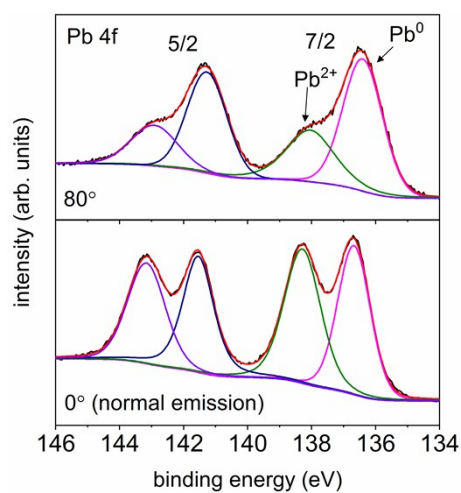


Fig S5. Angle-dependent XPS spectra of the Pb 4f core levels of the PEDOT:PSS/ MAPbI₃ films after illumination treatment in UHV condition for 30 min.

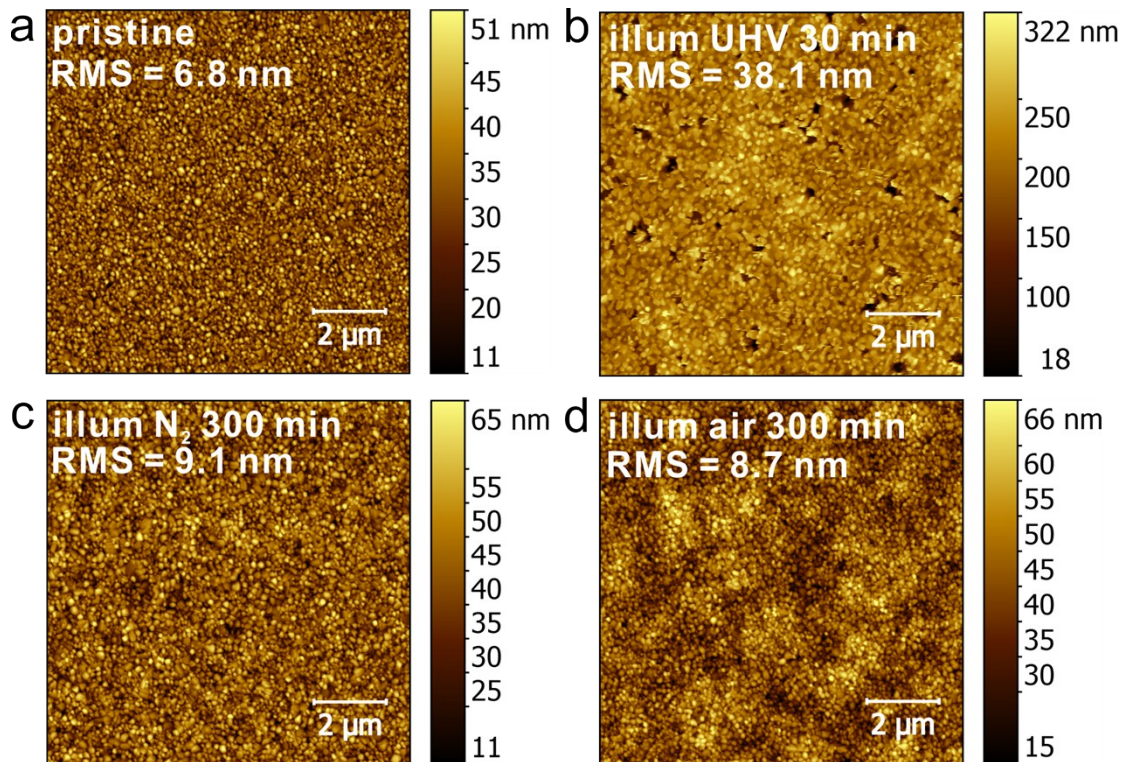


Fig S6. AFM morphology of the (a) pristine PEDOT:PSS/ MAPbI₃ films and after illumination treatments in (b) UHV for 30 min, (c) N₂ and (d) ambient air for 300 min.

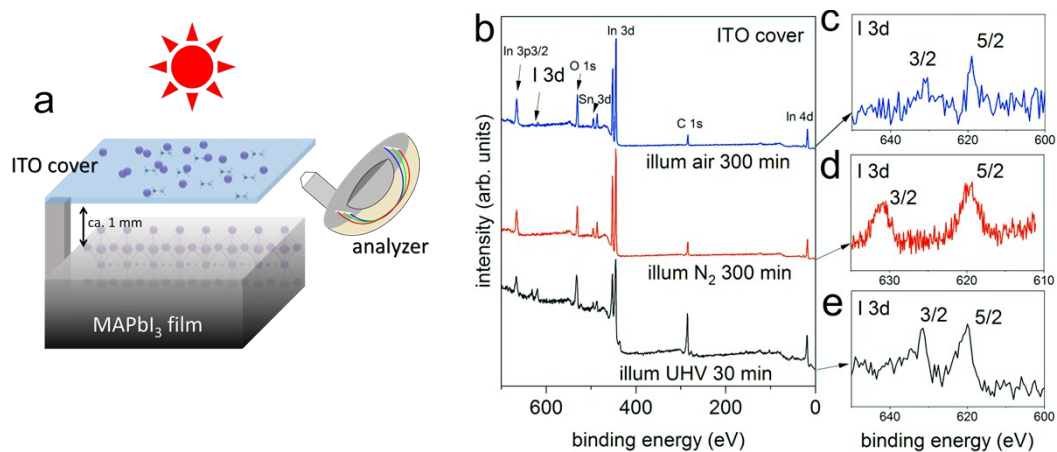


Fig S7. (a) Schematic illustration of ITO covers mounted on top of the perovskite films during illumination process. (b) XPS survey spectra of the ITO covers as illustrated in (a) during illumination treatments in UHV, N₂ and ambient air conditions. (c), (d) and (e) are the magnified spectra of the corresponding ITO covers in UHV, N₂ and air, respectively, in the energy region of iodine.

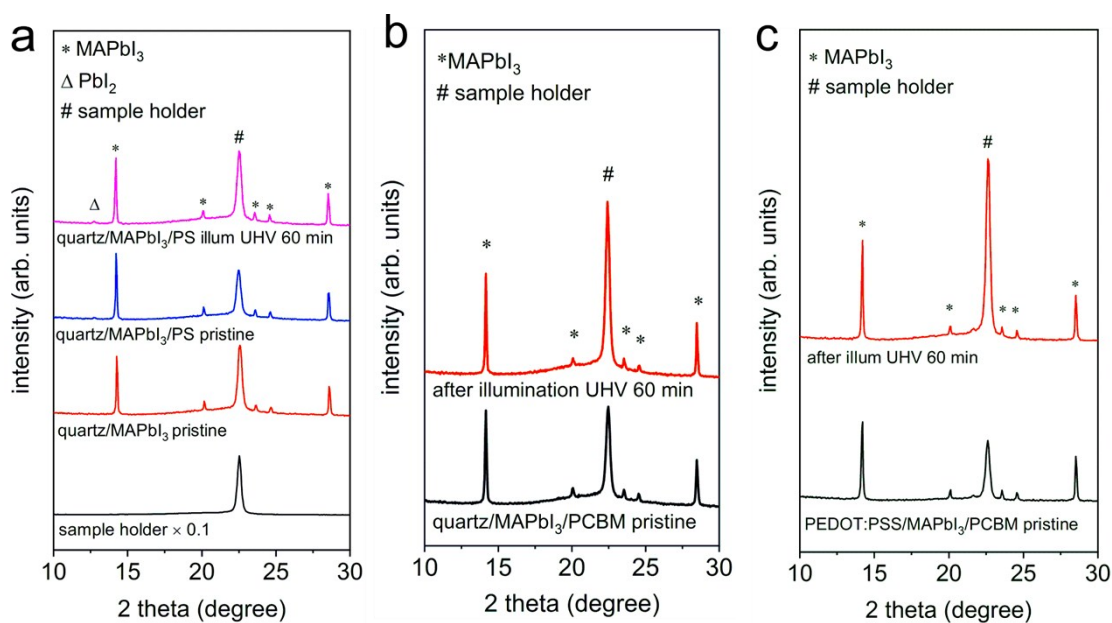
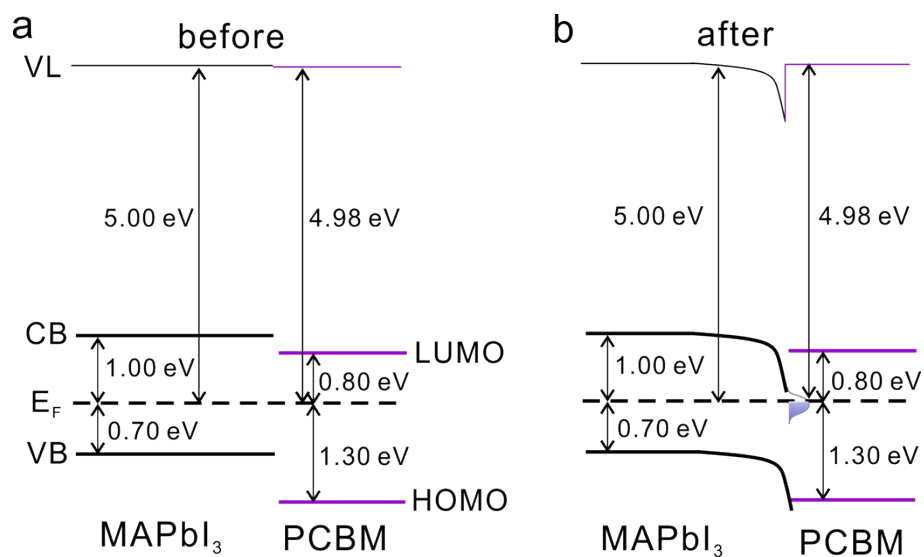
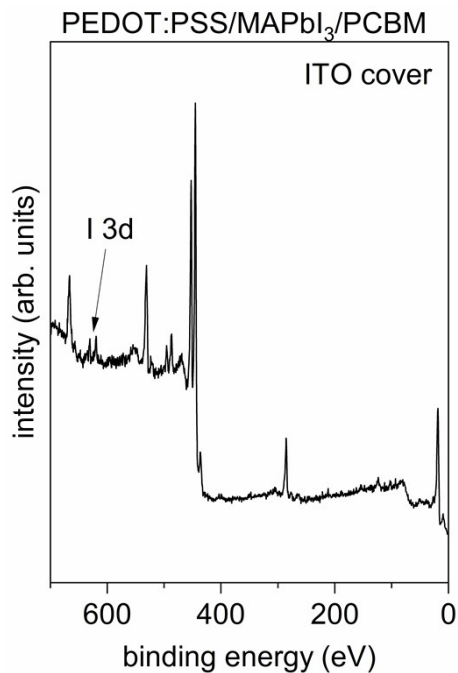


Fig S8. X-ray diffraction patterns of (a) a reference sample holder, the pristine quartz/MAPbI₃/PS films, (b) the pristine quartz/MAPbI₃/PCBM films and (c) the pristine PEDOT:PSS/MAPbI₃/PCBM films before and after illumination treatment in UHV condition for 60min. Symbol “ Δ ” and “*” corresponds the peak positions of PbI₂



and MAPbI₃, respectively. “#” refers to the peak of the sample holder.

Fig S9. The energy level diagrams at the MAPbI₃/PCBM interface before and after illumination treatment in UHV condition for 60 min. Electronic bandgaps of 1.70 eV for MAPbI₃³ and of 2.1 eV for PCBM⁴ are assumed according



to previous reports. CB, VB and VL denote conduction bands, valence bands and vacuum level, respectively. LUMO and HOMO stand for lowest unoccupied and highest occupied molecular orbitals, respectively. E_F refers to Fermi level at 0 binding energy.

Fig S10. XPS survey spectrum of the ITO cover mounted on top of the PEDOT:PSS/MAPbI₃/PCBM film during light exposure in UHV condition. Iodine 3d peaks are indicated.

XRD patterns of the MAPbI₃ perovskite films prepared at the MAI/PbI₂ molar ratios of 1:1 and 1:0.95 are shown in Fig. S11. Clearly, the perovskite sample using the 1:1 ratio exhibits noticeable PbI₂ species in the film, as illustrated by the PbI₂ (001) peak at 12.7°. In comparison, by reducing the PbI₂ content by 0.05 percent, the formation of PbI₂ can be prevented.

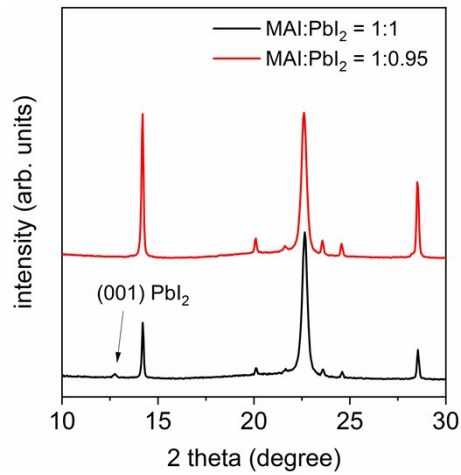


Fig. S11 XRD patterns of the MAPbI₃ perovskite films prepared at the MAI/PbI₂ molar ratios of 1:1 and 1:0.95.

References

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