

Supporting Information

High- Efficiency Humidity-Stable Planar Perovskite Solar Cells Based On Atomic Layer Architecture

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Characterization

XRD, XPS, SEM and UV-Vis-NIR Spectroscopy

XRD analysis is carried out on the samples with an architecture of ALD Al₂O₃/perovskite/TiO₂/ITO/glass (top to bottom) using a PANalytical X'Pert Pro MRD x-ray diffractometer using Cu K α radiation ($\lambda=1.540598 \text{ \AA}$) in the 2θ range 10° to 60° at a scanning rate of $1.5^\circ \text{ min}^{-1}$. XPS measurements are carried out in a Thermo Scientific K-Alpha system, equipped with an Al x-ray source (K α , 1486.6 eV) without any pre-sputtering. Binding energy is corrected with respect to C 1s at 284.5 eV. SEM images are obtained using a FEI MK2 Helios Nanolab 600 system. The optical reflection spectra of the completed cells are measured by a Agilent Cary 5000 UV-VIS-NIR spectrometer equipped with an integrating sphere.

TEM and Elemental Mapping

Cross-sectional TEM samples of the stacks are prepared using a standard Focused Ion Beam lift-out procedure. In the transfer step, the samples are mounted on molybdenum support grids upon which the final thinning is performed. Mo grids are deliberately chosen, as inferior results were obtained when using copper support grids. In the latter case, Cu is redeposited on the sidewalls of the TEM lamella, leading to the formation of CuI crystals on the TEM sample surfaces and, as a result of that, void formation in the perovskite layer. The subsequent TEM studies are performed using a JEOL ARM 200 probe corrected TEM, operated at 200 kV, and equipped with a 100mm² Centurio SDD EDX detector. EDX mappings of 256*256 full spectra are acquired using a 0.1 ms dwell time, summing up over 37, 128 and 105 full frame acquisitions in **Figure 3**, **S4** and **S6**, respectively. Quantification of the EDX maps is performed using standard k-factors.

J-V and EQE measurements

A white light halogen lamp source in combination with interference filters is used to illuminate the perovskite solar cells. The J-V characteristics were measured using a Keithley 2400 source measuring unit at a scanning rate of 10 mV/s from -1.2 to 1 V. A stainless steel mask with openings

matching the cell area (0.16 cm^2) is used to limit the active area of the device (0.09 cm^2). Before each measurement, the exact light intensity is determined using a calibrated Si reference diode. All characterizations are done in a nitrogen filled glove box (0.1 ppm O_2 and $0.1 \text{ ppm H}_2\text{O}$) without exposure to ambient atmosphere. For the hysteresis measurements, the J-V curves are measured at a scan rate of 10 mV/s in forward (-0.2 to 1.2V) and backward (1.2 to -0.2 V) directions. During the aging study, the J-V characteristics are determined with a WACOM dual beam solar simulator under AM1.5 illumination using the same mask and measured using a Keithley 2400 source measuring unit at a scanning rate of 10 mV/s from 1.2 to -0.2 V . EQE under short circuit conditions is measured in air with an Optosolar (SR300) setup equipped with a 250 W xenon lamp and a Jobin Yvon iHR320 monochromator without bias illumination.

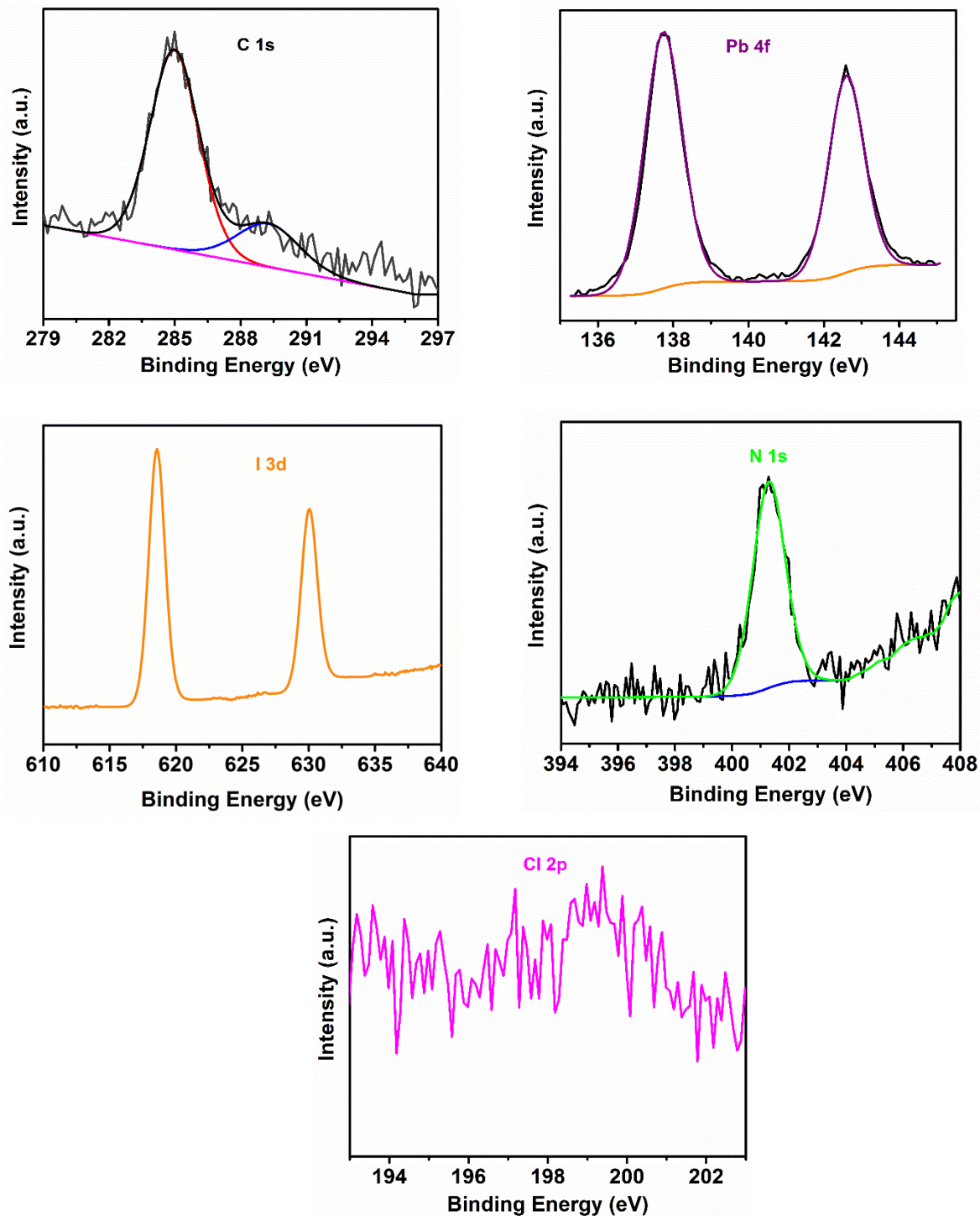


Figure S1. XPS spectra of C, Pb, I, N and Cl elements after the deposition of ALD Al₂O₃ on top of the perovskite film.

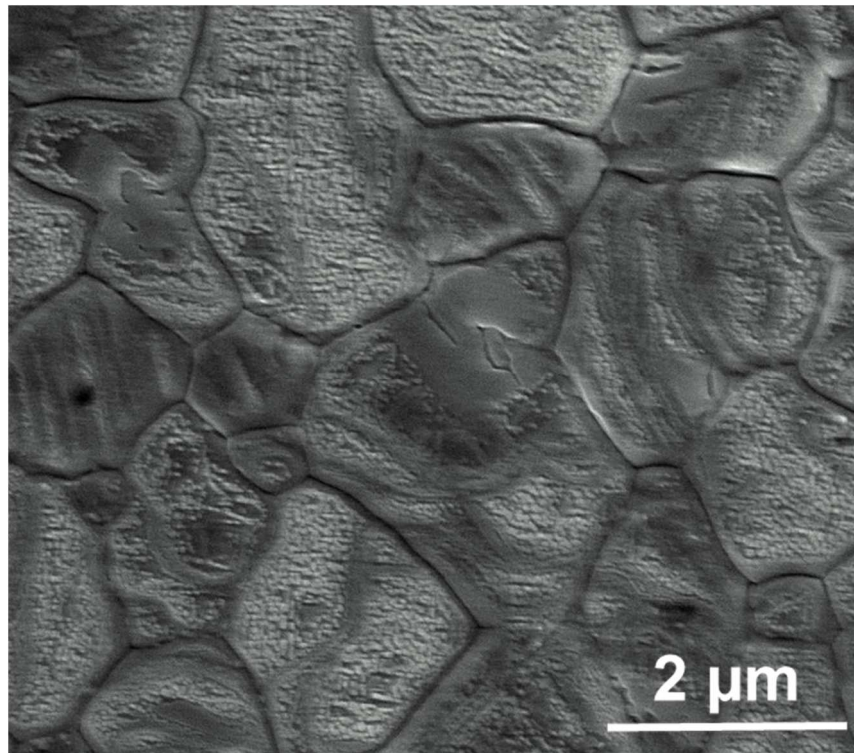


Figure S2. Top view SEM image of the perovskite film.

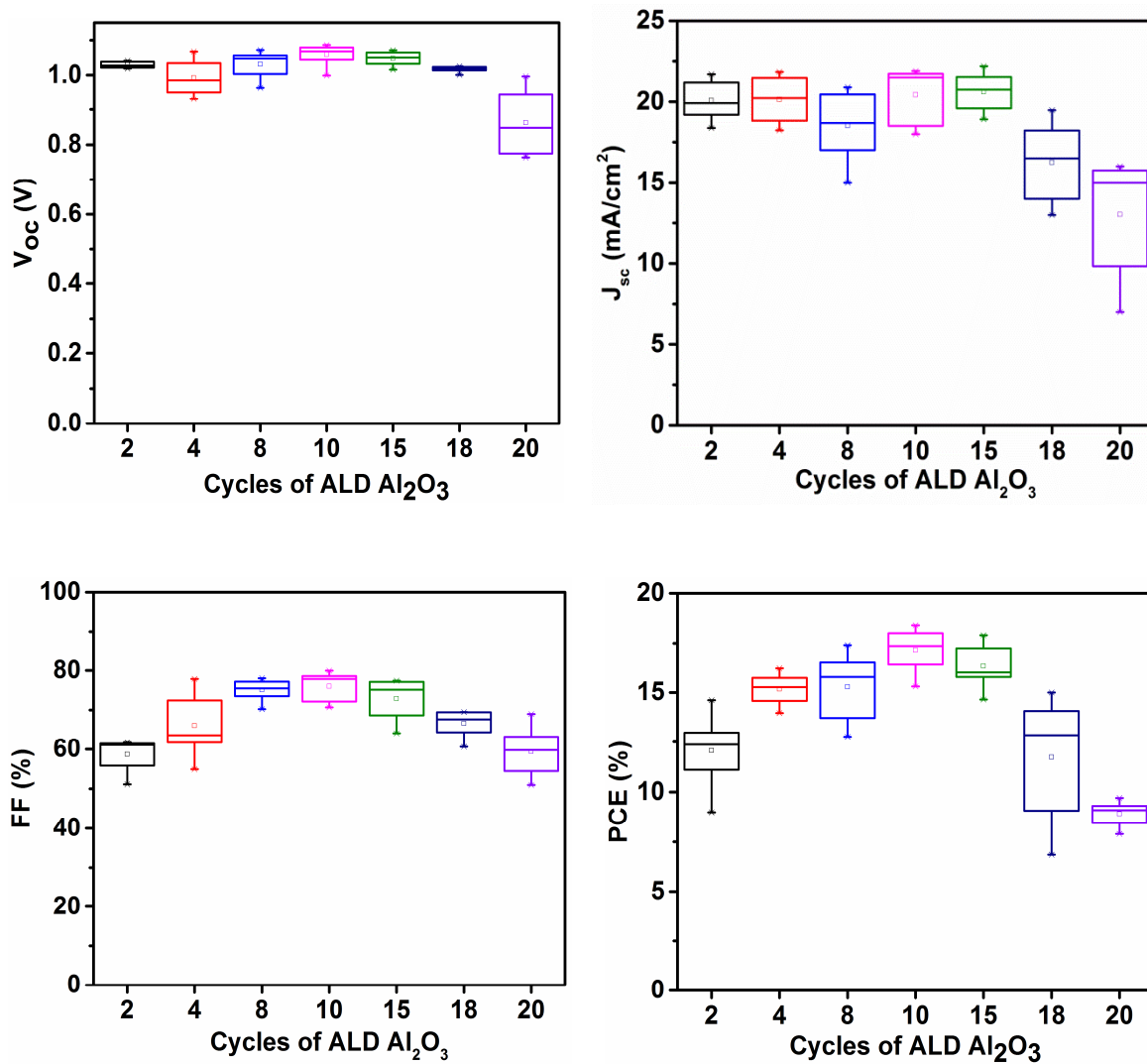


Figure S3. Box plot showing the PV parameters of the perovskite devices employing different cycles of ALD Al₂O₃ at the perovskite/HTL interface.

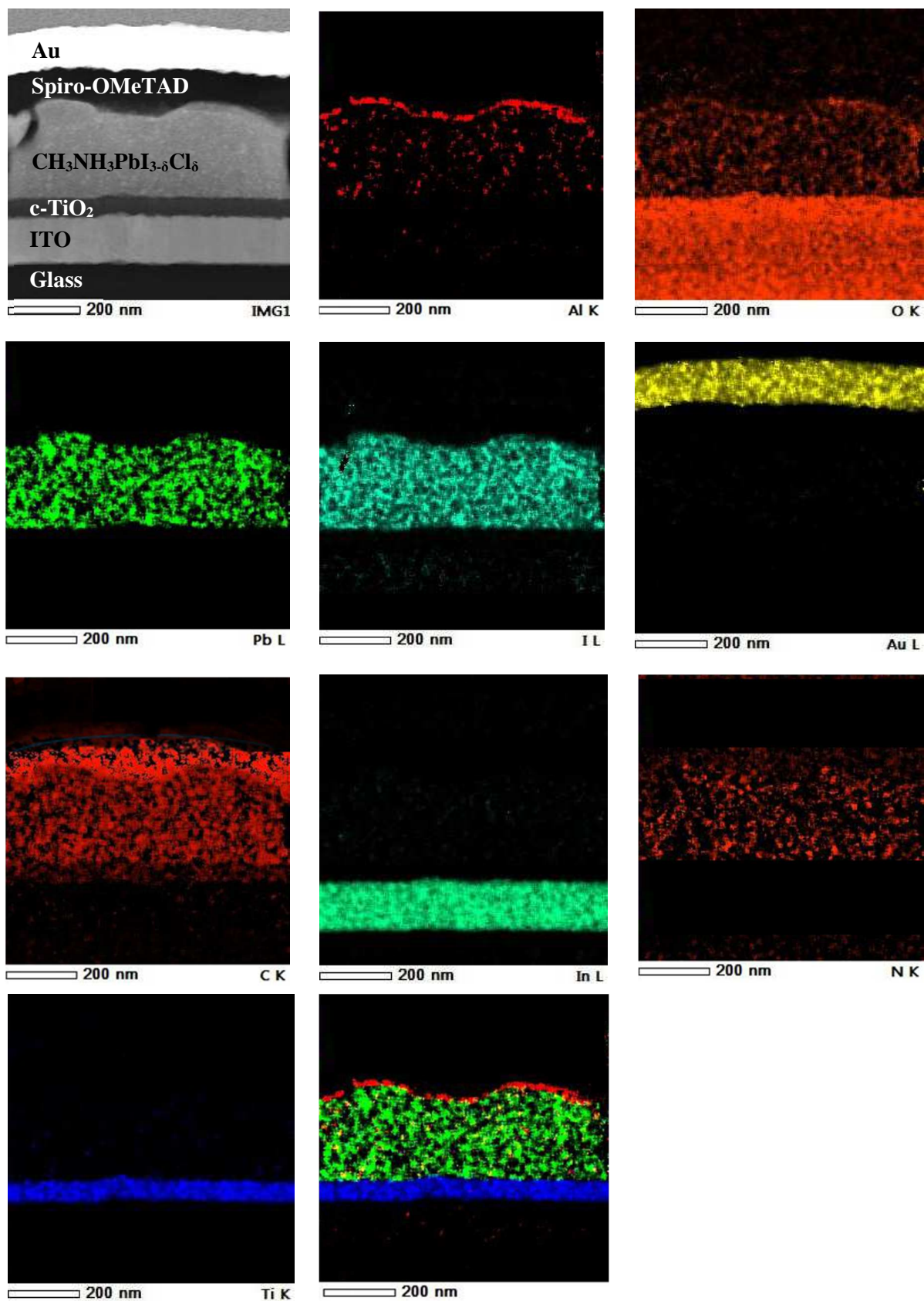


Figure S4. High angle annular dark field (HAADF) scanning TEM image of the device layer stack and the corresponding individual and overlapped elemental maps of Al, O, Pb, I, C, N, Ti and In and Au.

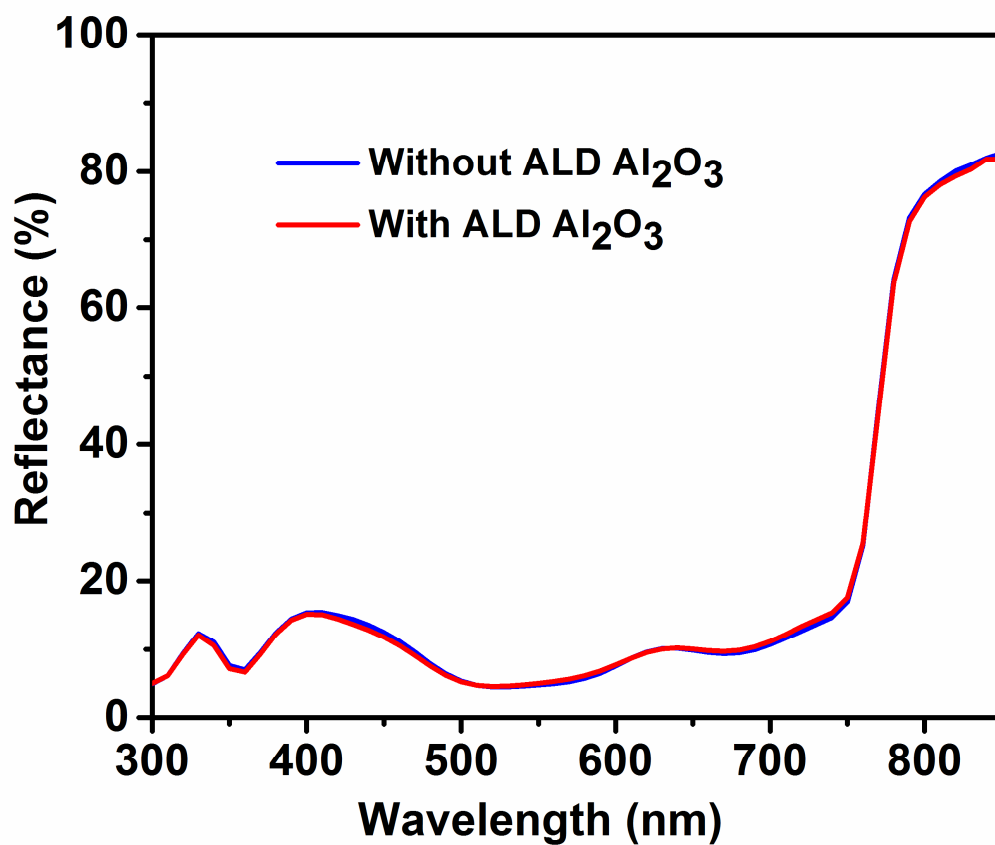


Figure S5. Reflectance spectra of the perovskite devices with and without the ALD Al₂O₃.

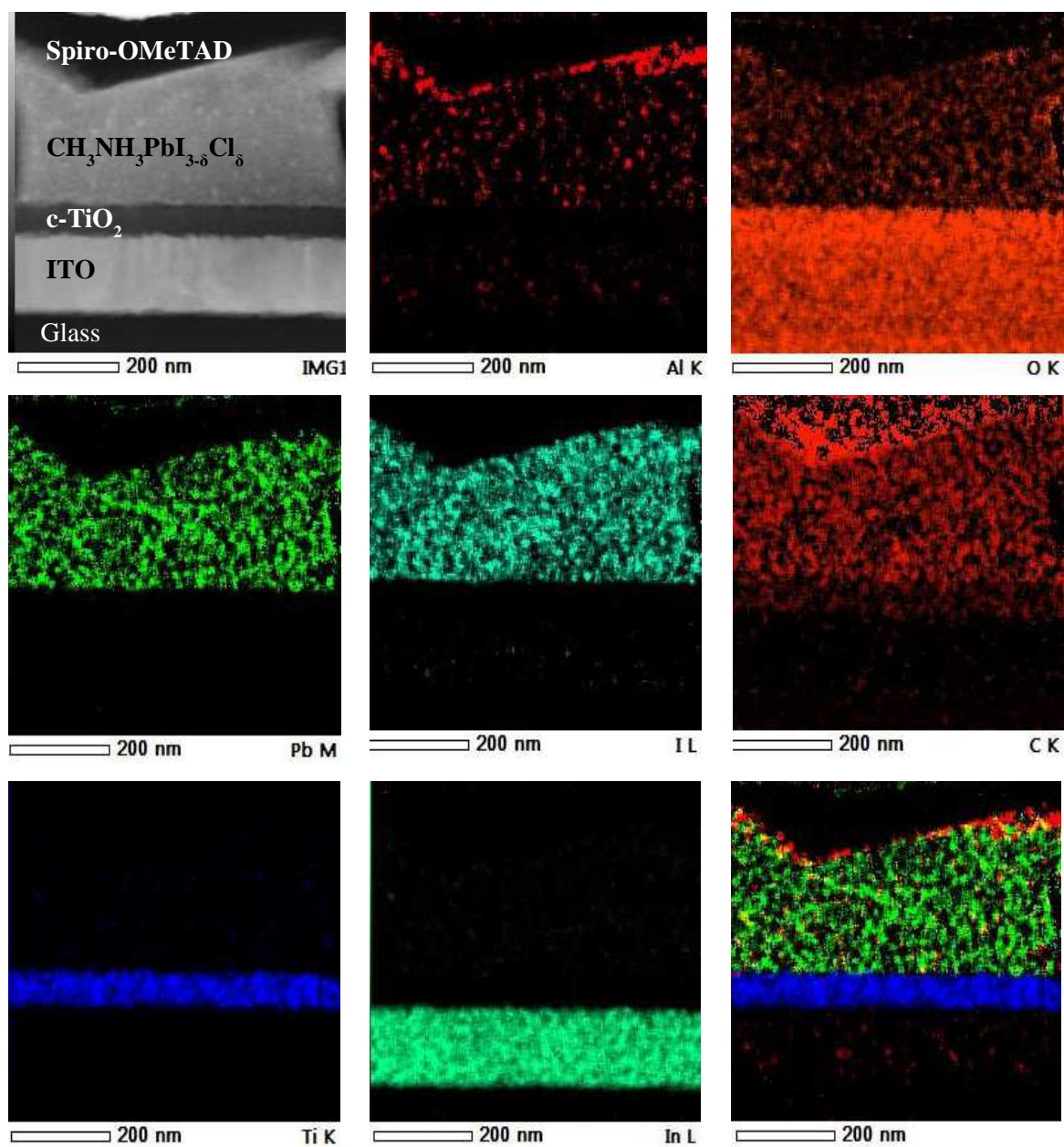


Figure S6. High angle annular dark field (HAADF) scanning TEM image of the device layer stack and the corresponding individual and overlapped elemental maps of Al, O, Pb, I, C, Ti and In.

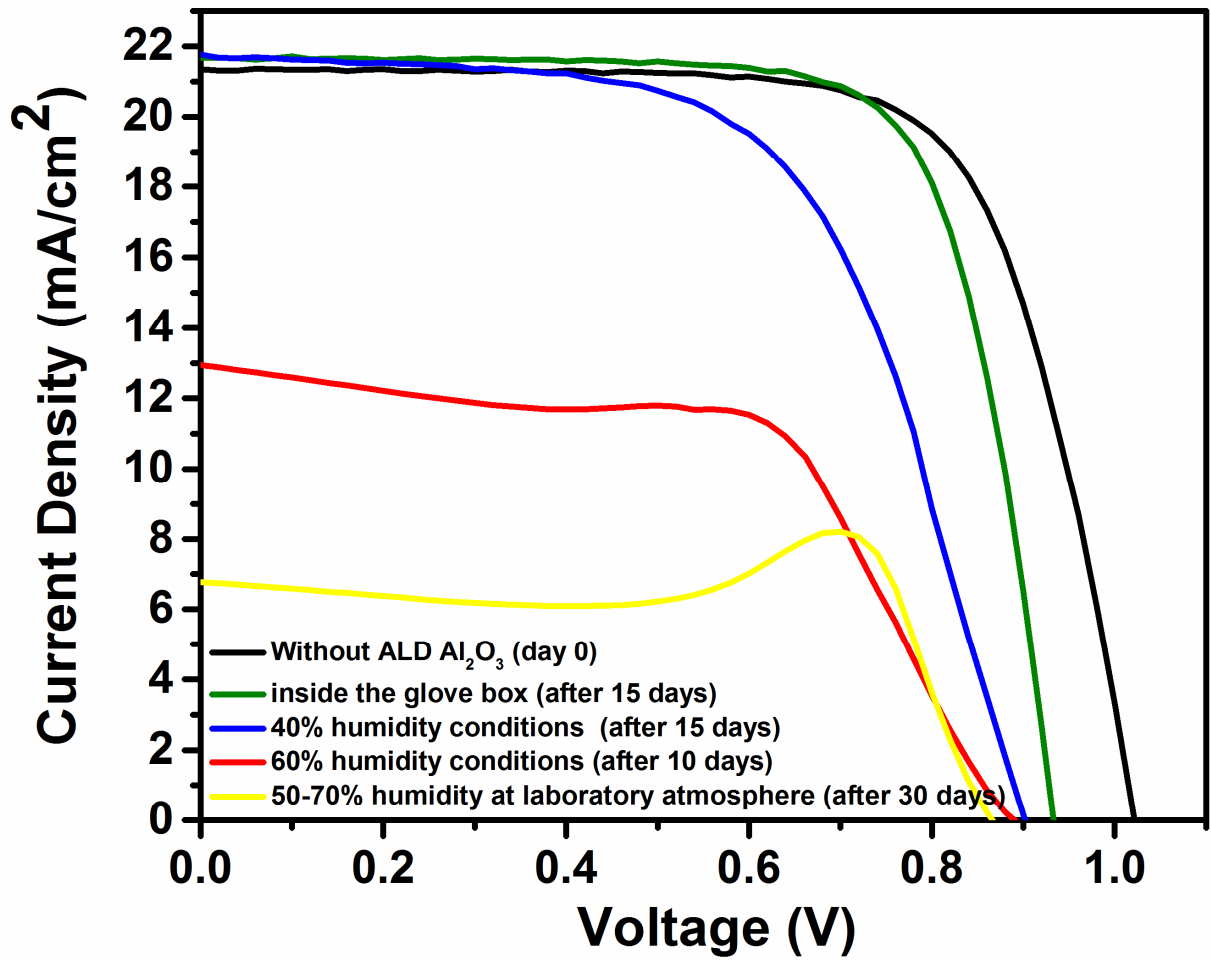


Figure S7. J-V curves of the perovskite device before and after exposure to varied humidity conditions.

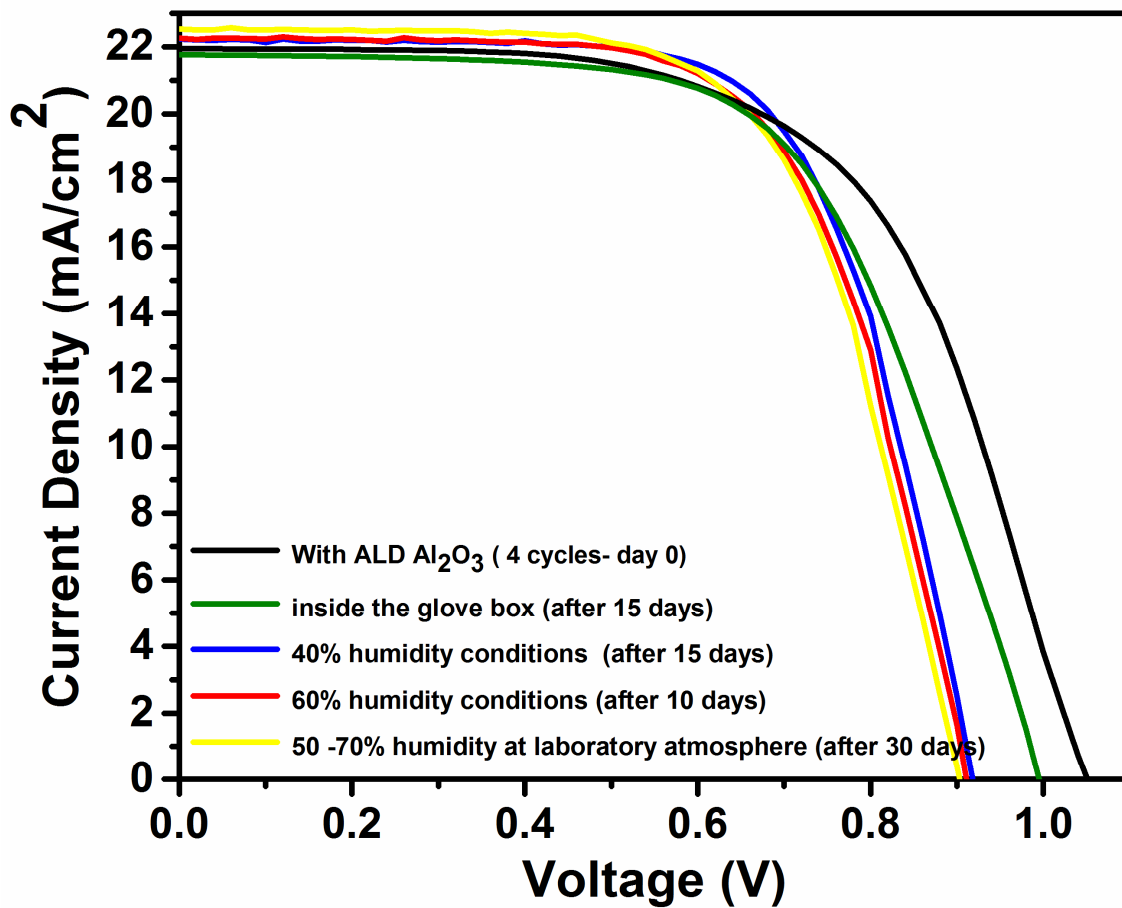


Figure S8. J-V curves of the perovskite/ ALD Al₂O₃ (4 cycles) device before and after exposure to varied humidity conditions.

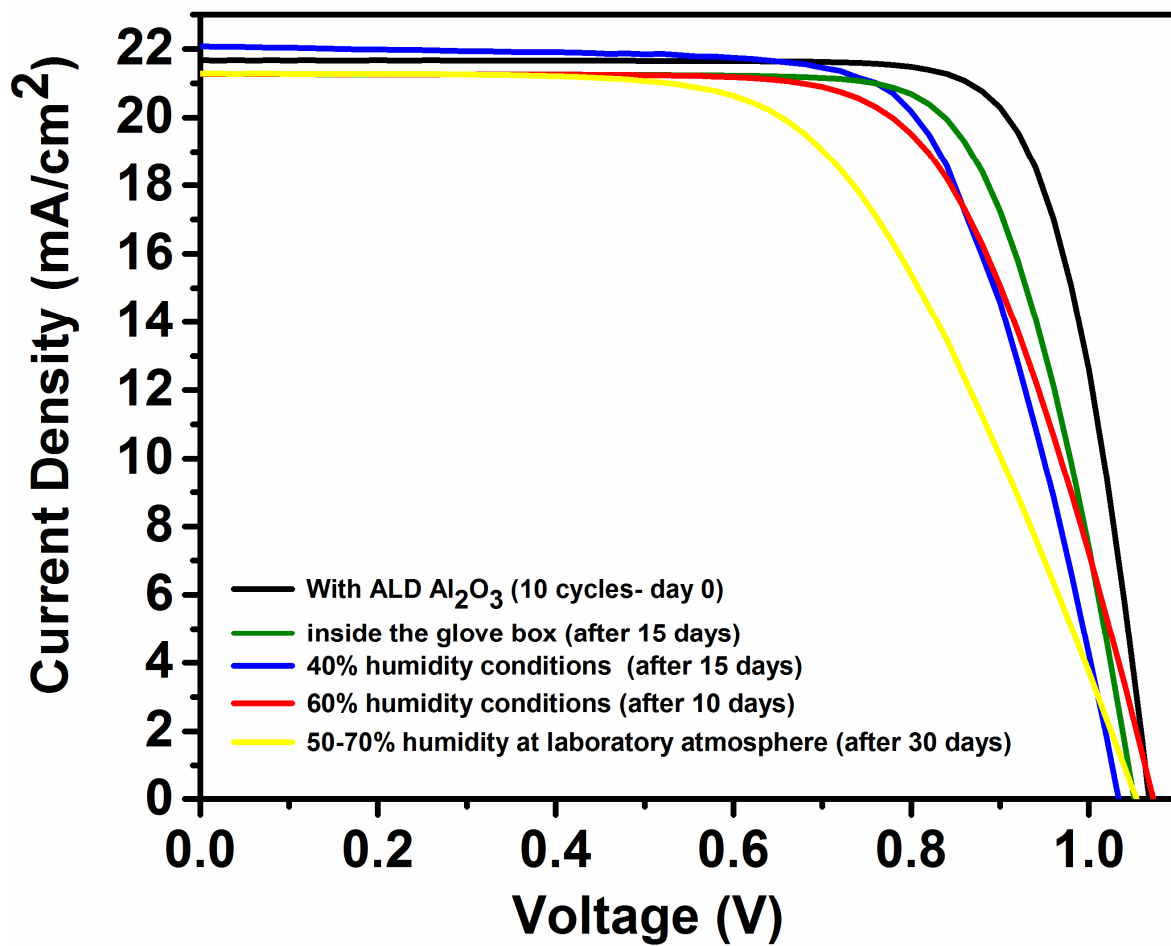


Figure S9. J-V curves of the perovskite/ ALD Al₂O₃ (10 cycles) device before and after exposure to varied humidity conditions.

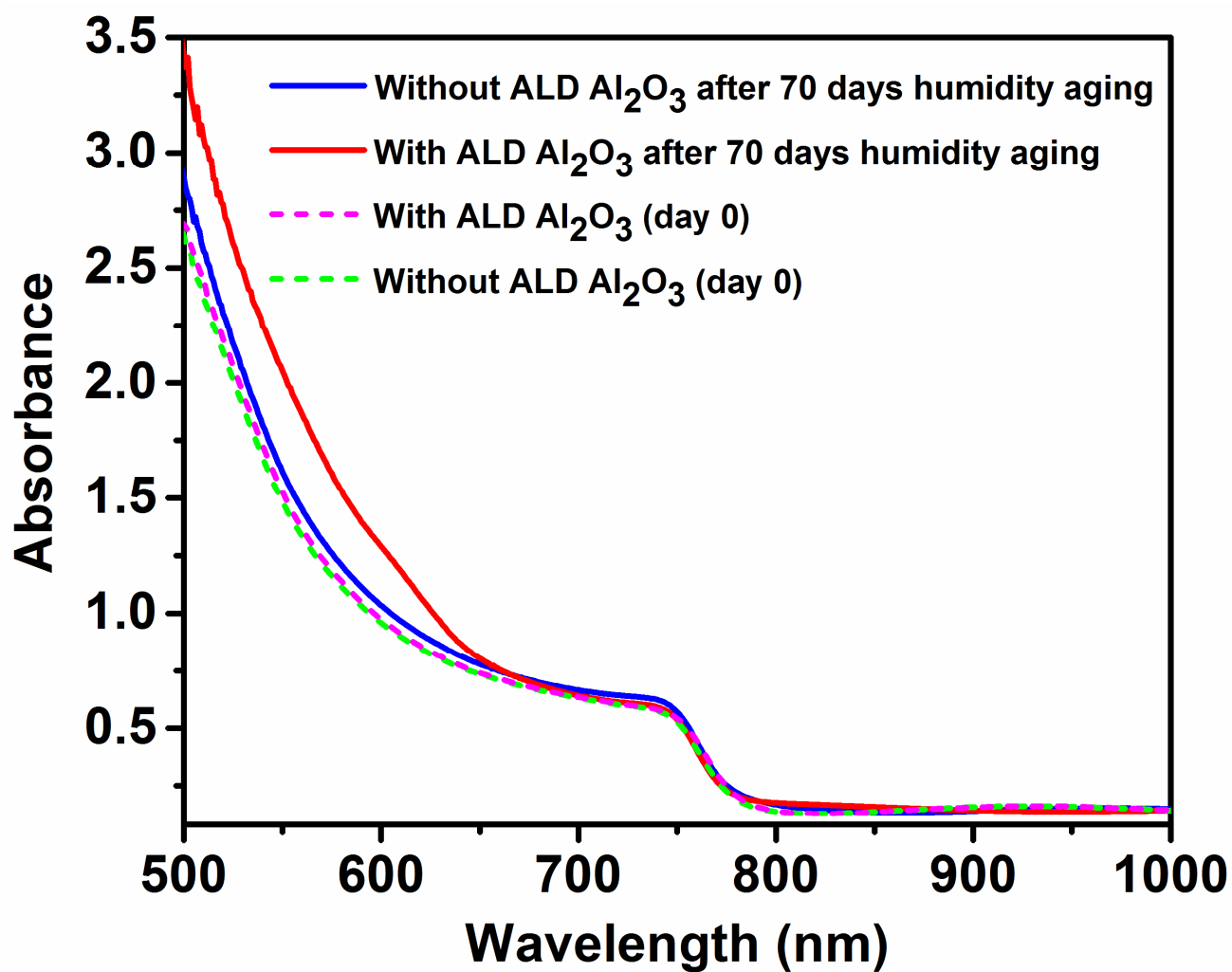


Figure S10. Absorbance spectra of the perovskite films with and without ALD Al₂O₃ at day 0 and after 70 days of humidity aging.