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Supplementary Information for

Scaling Behavior of Moisture-induced Grain Degradation in Polycrystalline Hybrid Perovskite Thin Films

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Methods

Perovskite sample fabrication. All the perovskite devices were fabricated in glovebox with oxygen level lower than 100 particle per million. All the samples, including the samples for STEM/EDS measurements, had a 20 nm thick PTAA layer before the fabrication of perovskite film. Five methods were used to fabricate $MAPbI_3$ films in this study. In interdiffusion method, PbI_2 and MAI solutions were sequentially spun onto the substrates, followed by a thermal annealing driven diffusion process. The concentration of PbI_2 and MAI were 650 mg/ml and 65 mg/ml, respectively. The films were annealed at 100 °C for different durations. In one-step spin-coating method, the perovskite precursor solution was prepared by mixing 460 mg PbI_2 with 159 mg MAI in 700 μL Dimethylformamide (DMF). The precursor solution was spin-coated on PTAA layer with 6000 RPM. During spinning process, 15μL toluene anti-solvent was casted on perovskite film to accelerate nucleation of perovskite grain. The details of Doctor Blading method could be found in our previous paper.[1] In short, the perovskite precursor solution was prepared by mixing 400 mg PbI_2 with 138 mg MAI in 1 mL DMF. 5% and 10 % volume ratio of Dimethyl sulfoxide (DMSO) was added into the precursor solution to tune the grain size of the coated films. In Drop coating method, the perovskite precursor solution was prepared by following the same way in Doctor blading method. 5-10 μL precursor solution was dropped on the substrate. Then the substrate was titled back and forth to form a uniform thin layer of solution. Then the films were annealed at 140 °C for 1 min, followed by annealing at 100 °C for 60 min. In vapor assisted solution process method, 60% PbI_2 solution was spin coated on top of PTAA film with spinning speed of 6000 RPM. Then the PbI_2 film was thermally annealed at 70 °C for 10 min. The PbI_2 films were tightly sealed in a glass bottle with MAI particles around the films. After that, the glass bottle was put on a hot plate with 200 °C for 120 min.

HRTEM and STEM/EDS measurement: The HRTEM and STEM/EDS measurements were conducted using FEI OSIRIS microscope operated at 200 kV accelerating voltage equipped with an energy dispersive spectrometer. Two typical types of specimens were prepared. The cross-sectional samples shown in Fig. 3 of the manuscript were prepared by using focused-ion-beam equipment (FEI Helios 660). A Pt layer of 2-3 μm thick was deposited on the surface of the sample prior to the FIB cross-sections preparation. A low current beam and low accelerating voltage of 15 pA and 5 kV were used in the whole milling process to minimize the thermal damage caused by ion beam. The other type of specimens shown in Fig. 4 of the manuscript were prepared by directly solution processing of the perovskite on a special TEM grids with a 400 nm Si_3N_4 window, which was purchased from TEMwindows company. Deposition of perovskite film on the gird followed the method described in the sample fabrication section. Before the STEM measurement, the Si_3N_4 window was further ion milled by FIB to thinner the Si_3N_4 layer for better contrast in STEM.

Relative humidity control: For all the humidity studies, the perovskite samples were stored at room temperature in a controlled-humidity glass flask. The setup we used is shown in Supplementary Fig. 4. The relative humidity was tuned to the desired values by adjusting the N_2 gas flow and the hot plate temperature. The hot plate temperature was set to ~30 ℃, so that the required N_2 flow speed could be low to minimize the non-uniform humidity distribution in the flask. The humidity was in-situ measured by a probe of humidity meter which was placed in the flask. The humidity was controlled to 85 ± 5 % for the degradation study.

Figure S1 A recently took photograph of a single crystal. This crystal has been stored in air without encapsulation for more than 2 years. A photograph of this crystal was shown in our paper published about 2 year ago.[2]

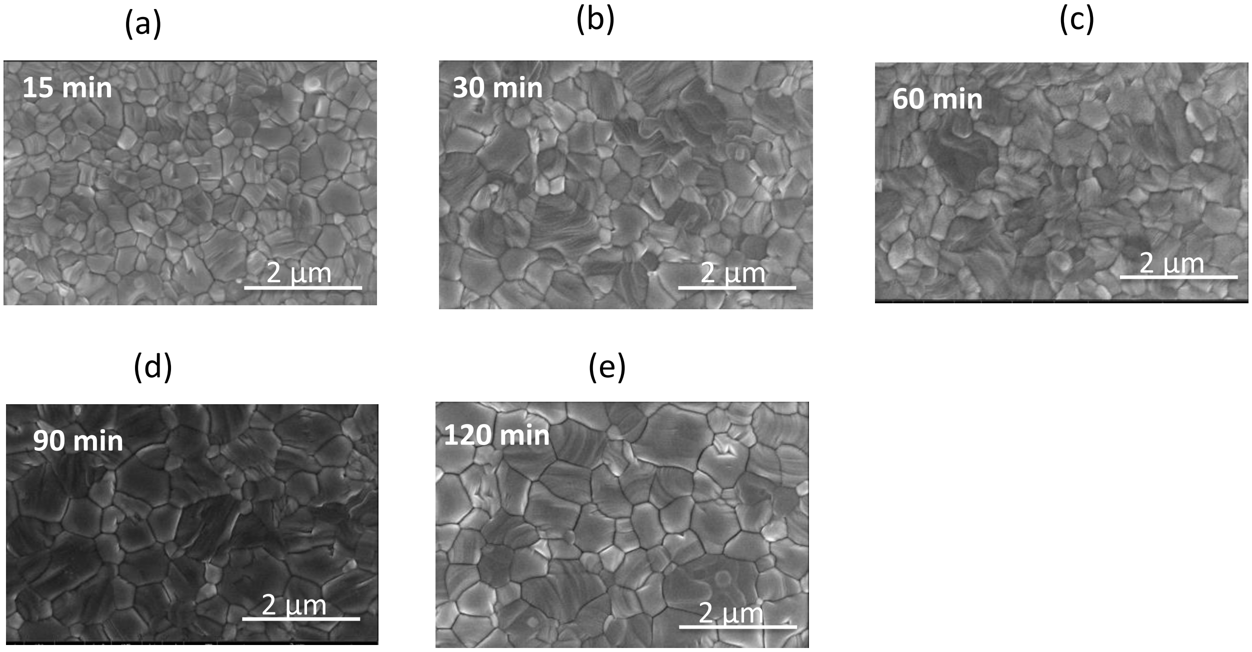

Figure S2 Scanning electron microscopy (SEM) images of perovskite films with different annealing times of 15 min (a), 30 min (b), 60 min (c), 90 min (d), 120 min (d).

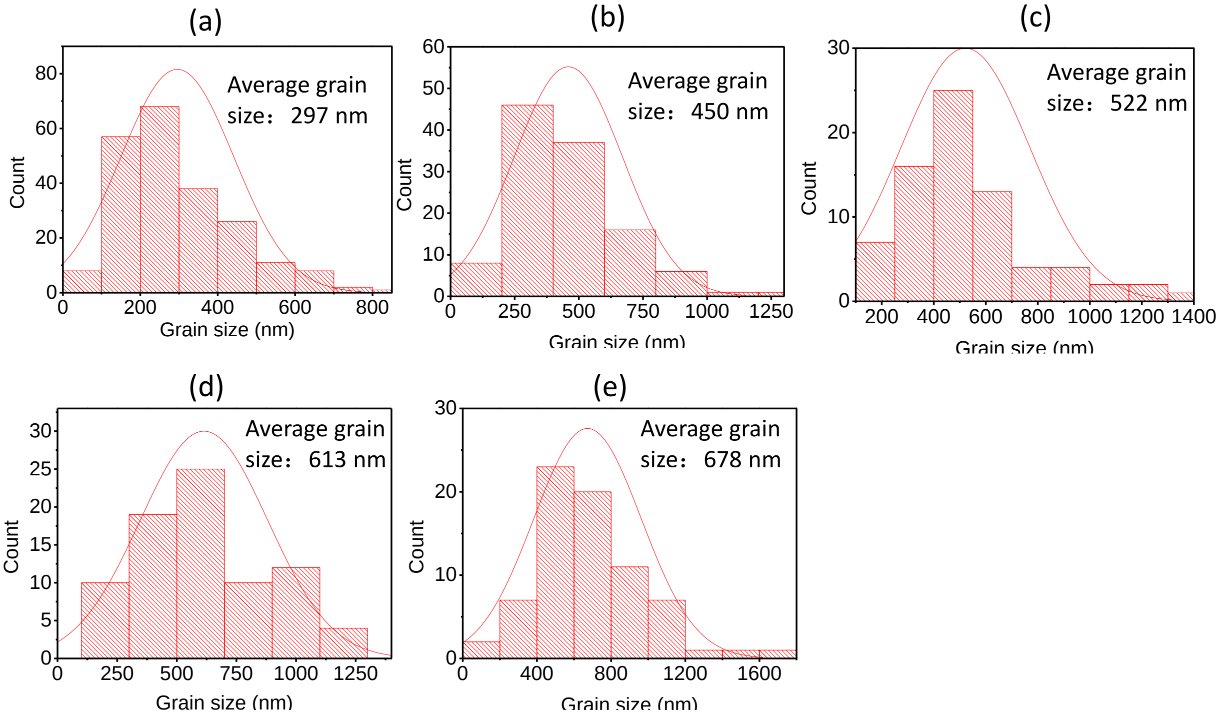

Figure S3 Corresponding grain size statistics of perovskite films shown in Figure S2. The grain size of each film was analyzed by Nano Measure software. The grains have irregular shapes. In order to get accurate size distribution, all the grain size were measured in the same lateral direction, and all grains in the SEM images were included in the statistics without selection. The average grain size was derived by fitting the data with Gauss distribution.

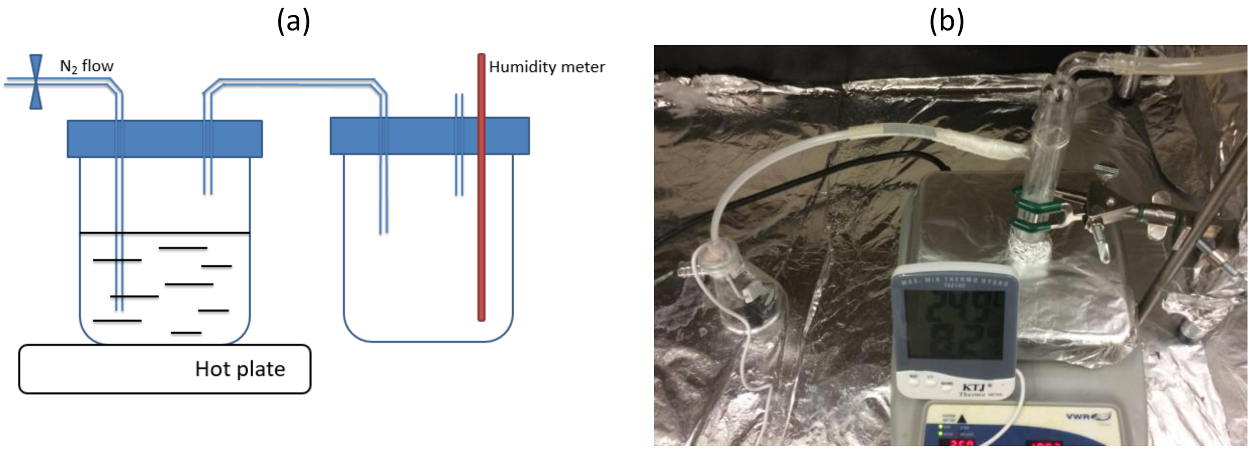

Figure S4 Schematic diagram (a) and photo image (b) of the home-made humidity system. The humidity was in-situ measured by a probe of humidity meter which was placed in the flask. The hot plate temperature was set to ~30 ℃, so that the required N_2 flow speed could be low to minimize the non-uniform humidity distribution in the flask.

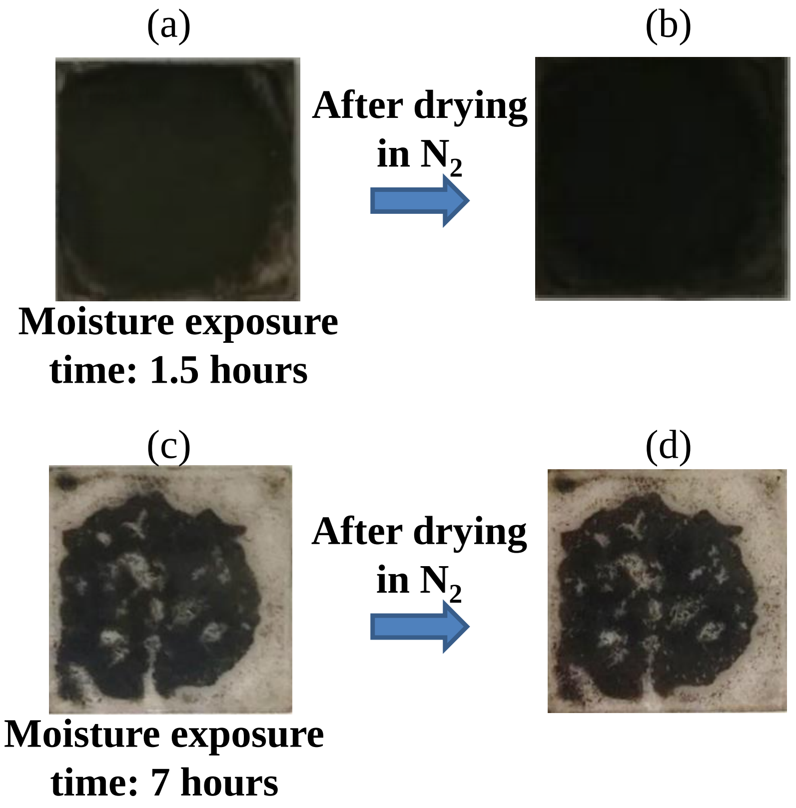

Figure S5 Photographs showing the reversible and irreversible degradation processes of perovskite films. For the films degraded in N_2 with 85% humidity for 1.5 hour when the degraded area was around 5%-10% of the total area (a), the decoloring-process could be recovered after it was stored in dry nitrogen for 2 hours (b). However, the films stored in humid N_2 for 7 hours, which degraded over 30% of the total area (c), couldn’t recover after it was stored in dry nitrogen for 2 hours (d).

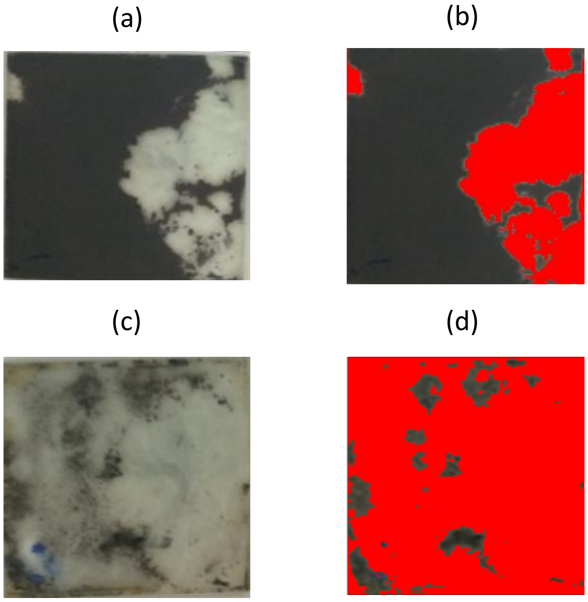

Figure S6 Method of degradation percentage calculation. Photo images of (a) and (c) were analyzed by software Image J. The original white color region in (a) and (c) was marked as red color by the software as shown in (b) and (d). The degradation percentage was defined as the ratio of red area to the whole area of the film.

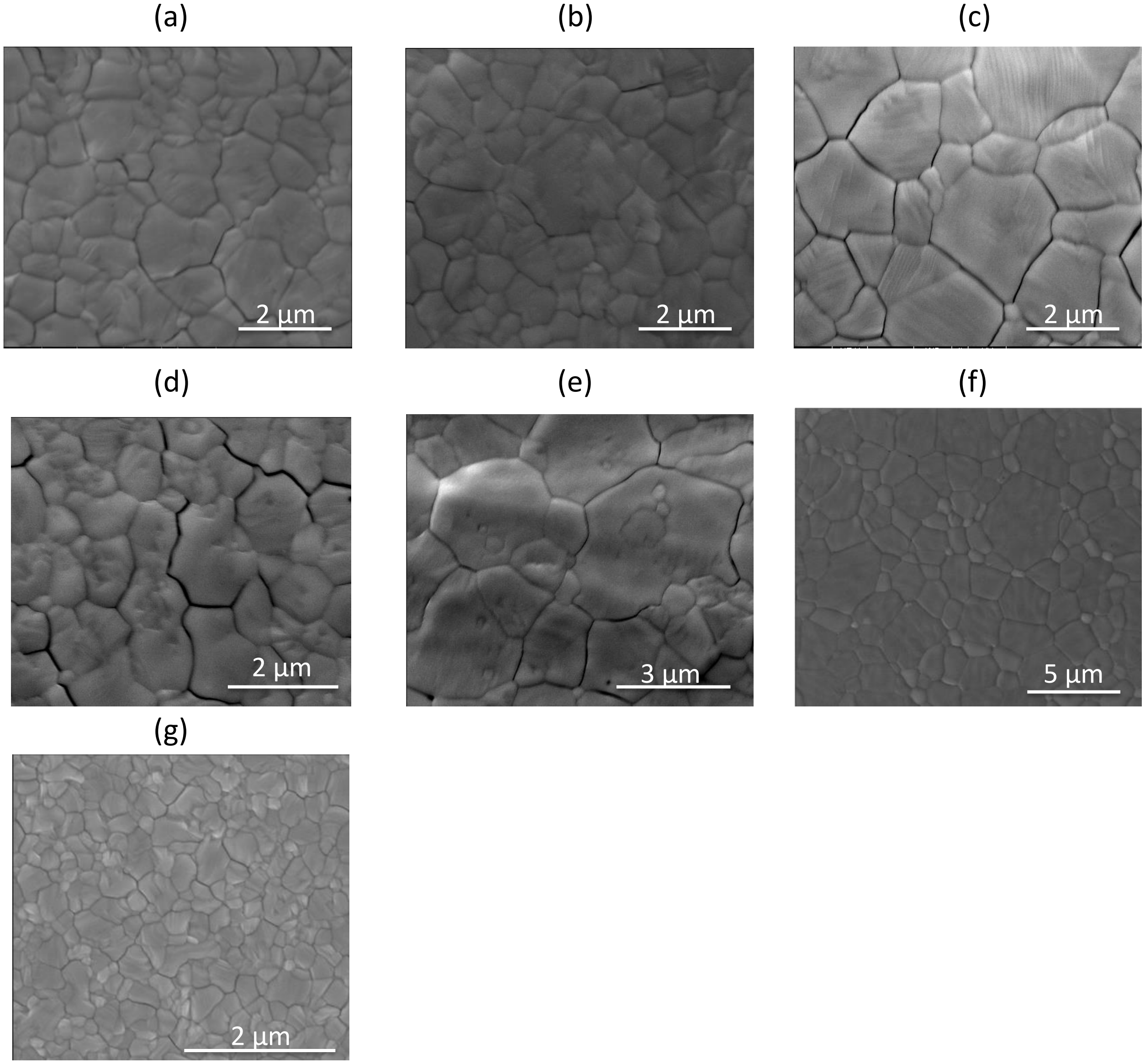

Figure S7 SEM images perovskite films fabricated by doctor blading (a, b, c), drop coating (d, e), vapor assisted deposition (f), one step spin coating (g). The precursor solutions for perovskite films in (a), (b), (c) were made by pure dimethylformamide (DMF), 95% volume ratio of DMF with 5% Dimethyl sulfoxide (DMSO), 90% volume ratio of DMF with 10% DMSO, respectively. The precursor solutions for perovskite films in (d) and (e) were DMF and 90% volume ratio of DMF with 10% DMSO, respectively.

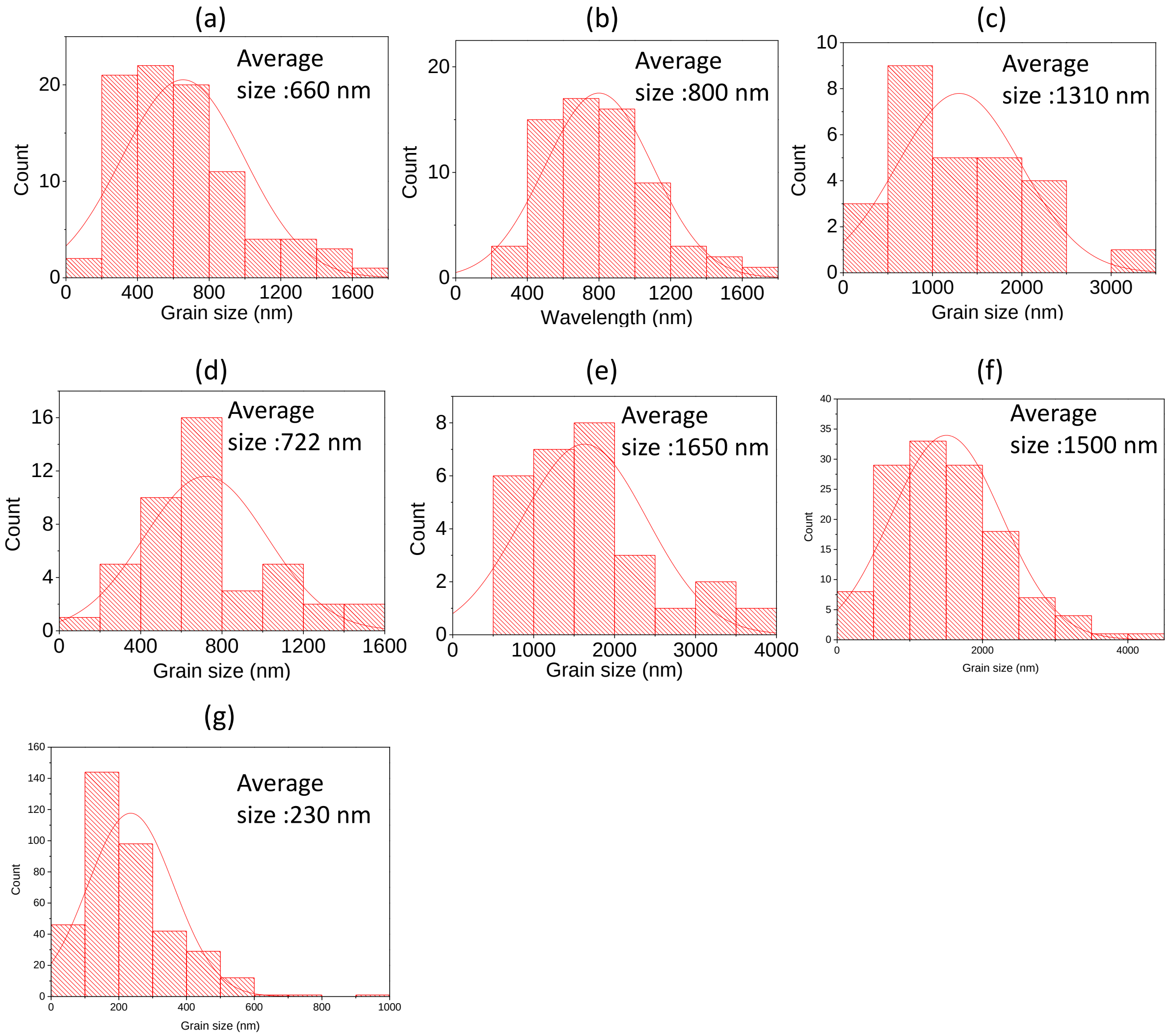

Figure S8 Corresponding grain size statistics of perovskite films shown Figure S7. The grain size of each film was analyzed by Nano Measure software. The grains have irregular shapes. In order to get accurate size distribution, all the grain size were measured in the same lateral direction, and all grains in the SEM images were included in the statistics without selection. The average grain size was derived by fitting the data with Gauss distribution.

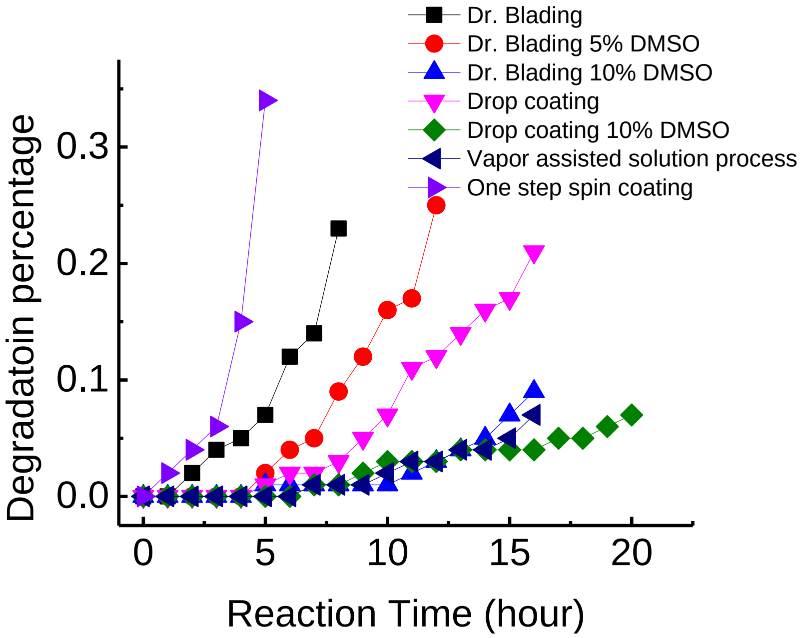

Figure S9 Degradation percentage of perovskite films fabricated by one step spin-coating, doctor blading, drop coating and vapor assisted deposition.

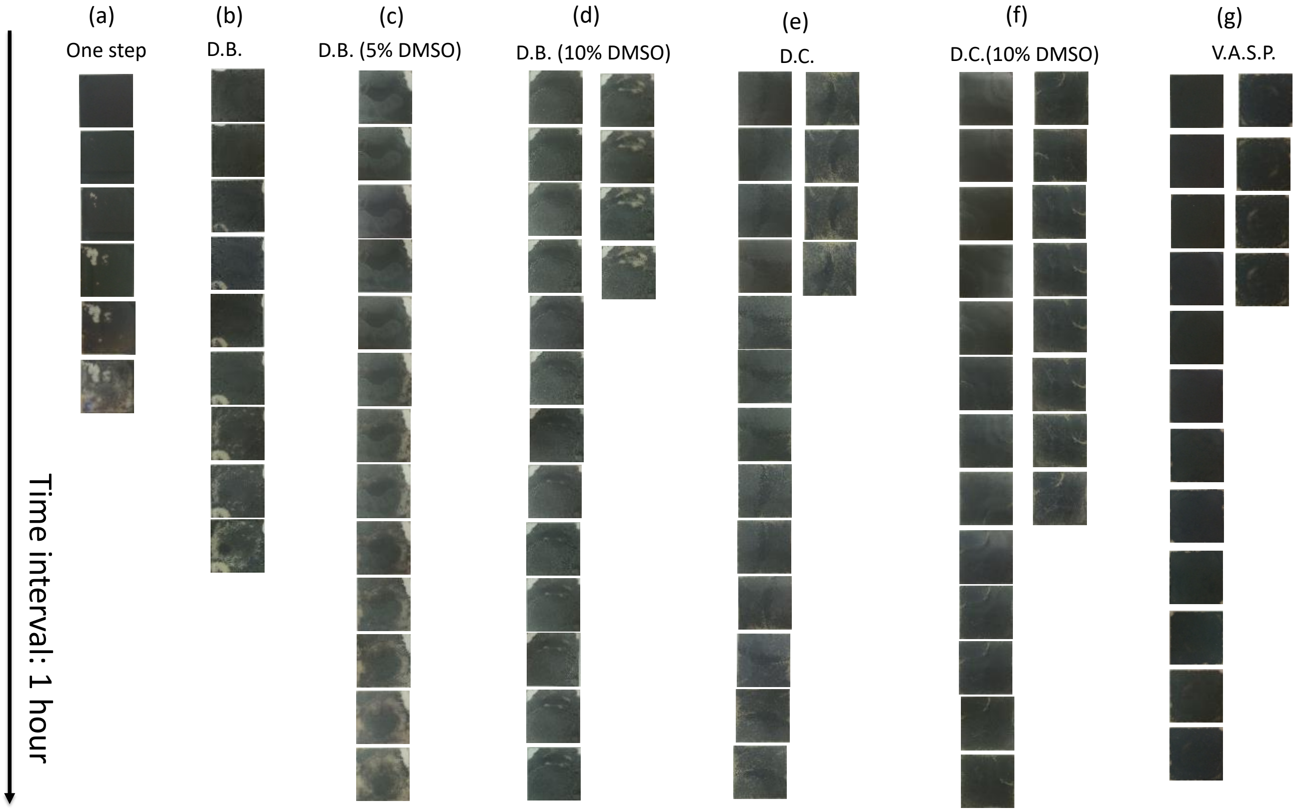

Figure S10 Photo images recording the moisture induced degradation of perovskite films fabricated by one-step spin coating (a), doctor blading (b-d), drop-coating (e-f) and vapor assisted solution process (g).

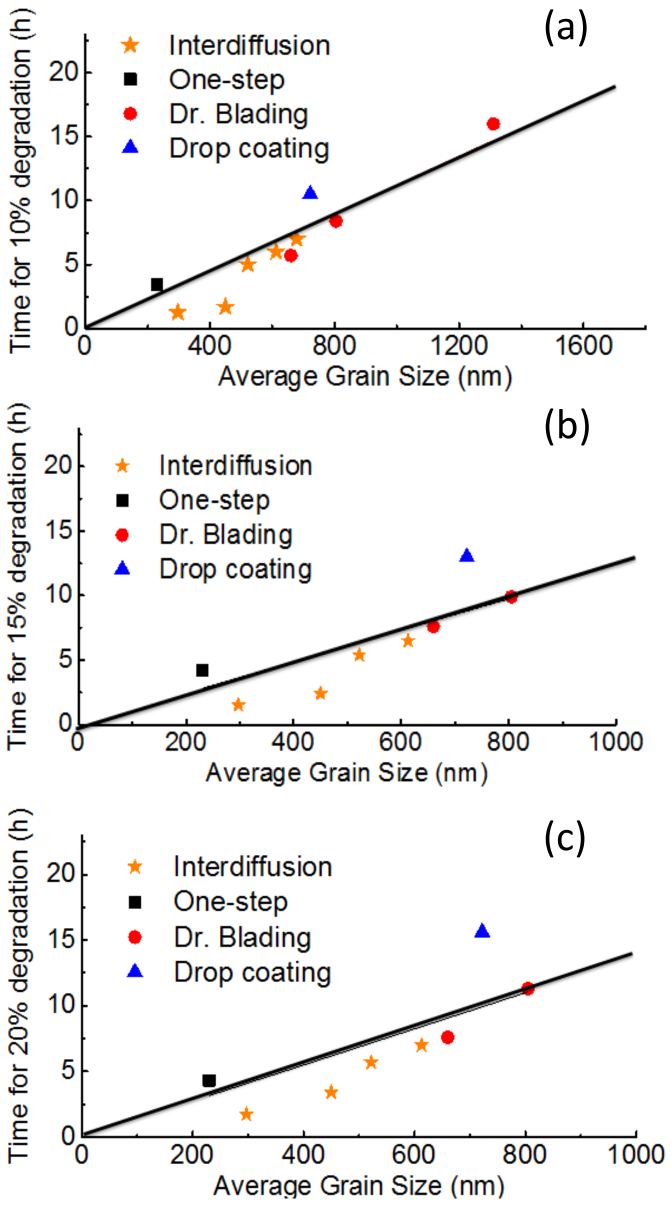

Figure S11 Time needed for 10% (a), 15% (b) and 20% (c) degradation of the perovskite films with different grain sizes which were fabricated by different methods. The solid lines in the figures are fitted lines with fixed zero intercept. All the points in the figures located around a straight line and could be fitted with R-squared values of 0.95 (a), 0.91 (b) and 0.89 (c).

Scaling behavior theory: As shown in the Figure 1c of the manuscript, moisture induced degradation rate of perovskite films showed a linear relationship with the grain size. To find out the function between grain size and degradation, we assumed perovskite grains are all cubic as shown in the Figure S12. The total number of perovskite grains in the film is N. Each grain has grain size of a which represents the average grain size we derived in the experiment. The degraded area of each grain follows the equation:

$$\mathit{\Delta} S = 4N * a * \mathit{\Delta} a \qquad (1)$$

,where $\mathit{\Delta} a$ is the degradation of the grain in one direction. The degradation of grain involves water molecule reaction/diffusion from grain boundary to the grain interior. Assuming the degradation speed is v, then $\mathit{\Delta} a$ follows the equation:

$$\Delta a = v * t \qquad (2)$$

$$\Delta S = 4N * a * v * t \qquad (3)$$

,where t is time for degradation. The total area of the film follows:

$$S = N * a^2 \qquad (4)$$

The degradation rate equals to ratio of degraded area to the whole area

$$\frac{\Delta S}{S} = \frac{4v*t}{a} = 5\% \qquad (5)$$

Time needed for 5% degradation of the film follows the equation:

$$t_{5\%} = \frac{a}{4v} * \frac{\Delta S}{S} = \frac{a}{80v} \qquad (6)$$

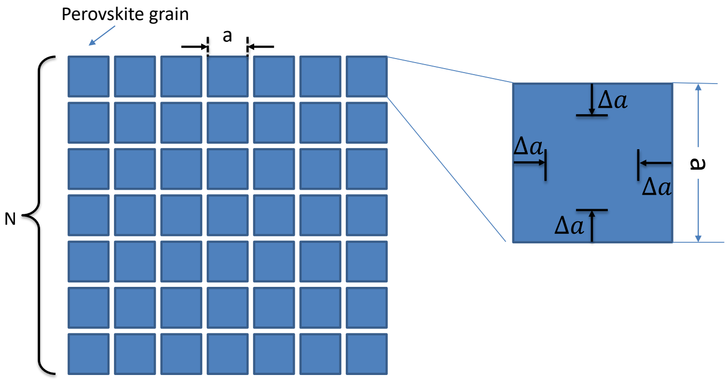

Figure S12 Schematic diagram shows perovskite grains and grain boundary

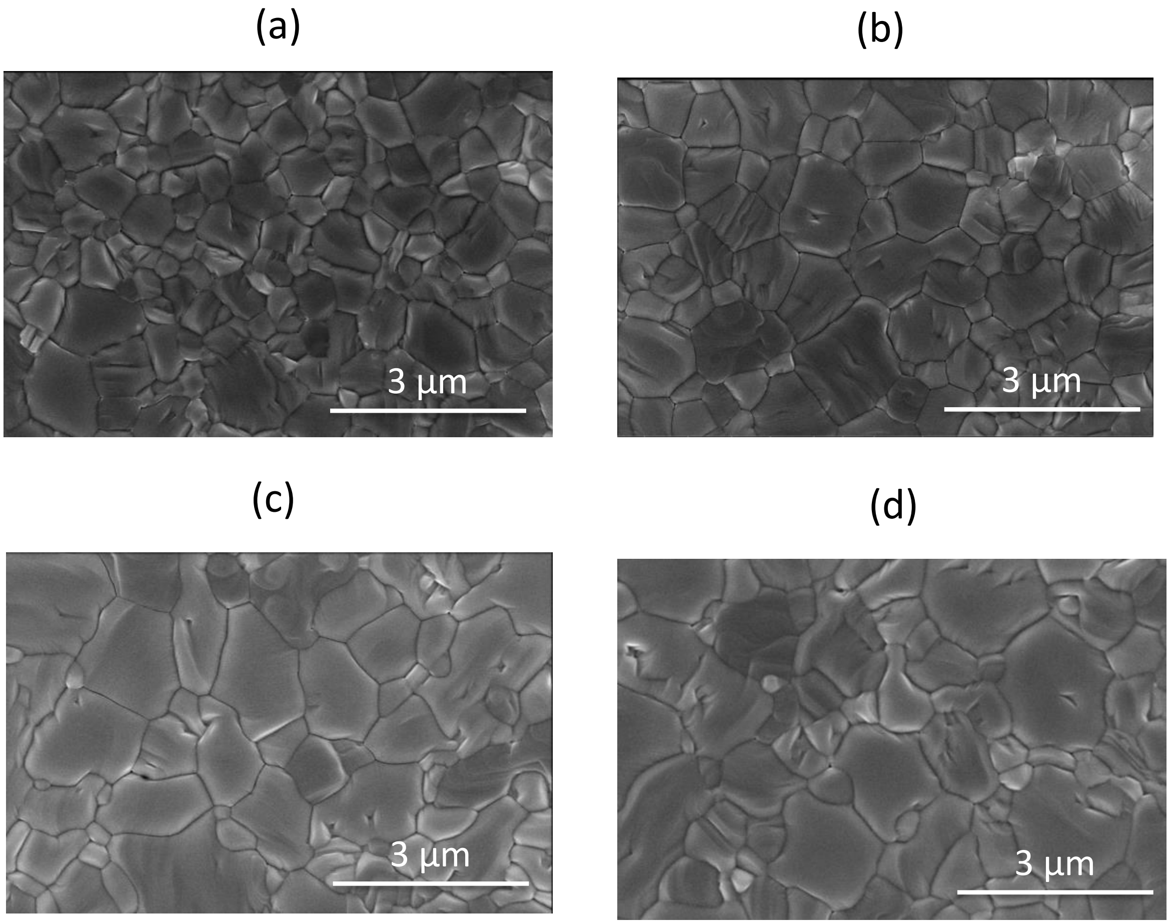

Figure S13 SEM image of perovskite film with film thickness of 450 nm (a), 650 nm (b), 800 nm (c) and 1000 nm (d). The average grain sizes of these films were fitted to be 660 nm, 760 nm, 844 nm and 840 nm, respectively.

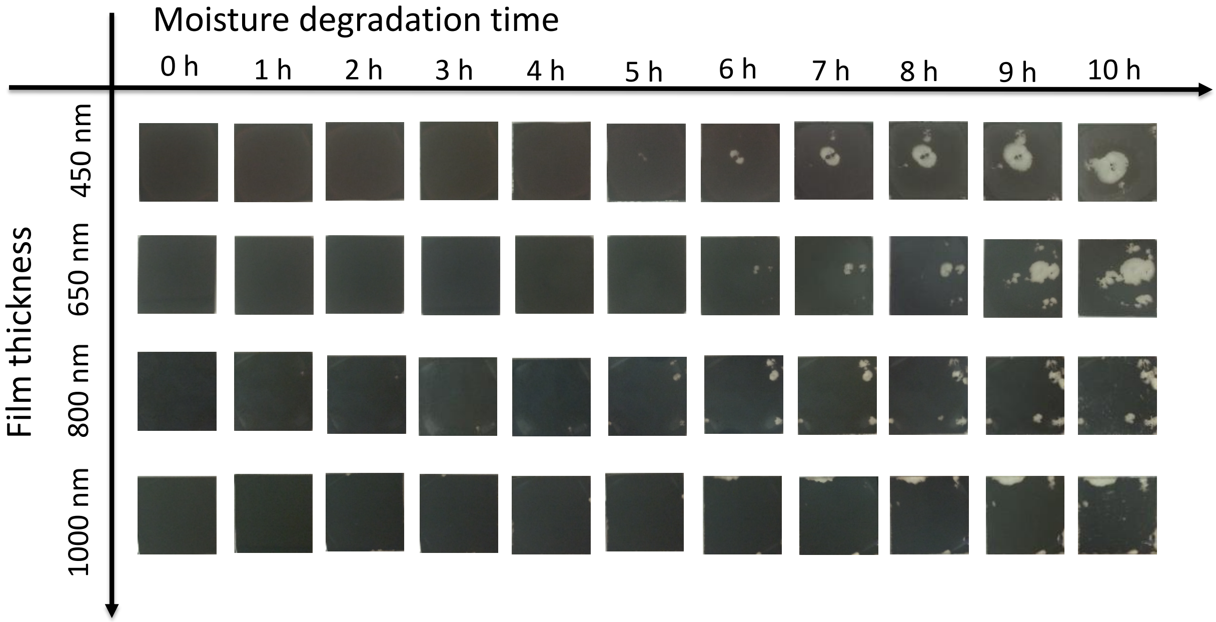

Figure S14 Photographic images recording the moisture induced degradation of perovskite films with different thickness. The films were made by interdiffusion method. The thickness was varied by tuning the precursor solution concentration.[3] The thickness was measured by step-profiler.

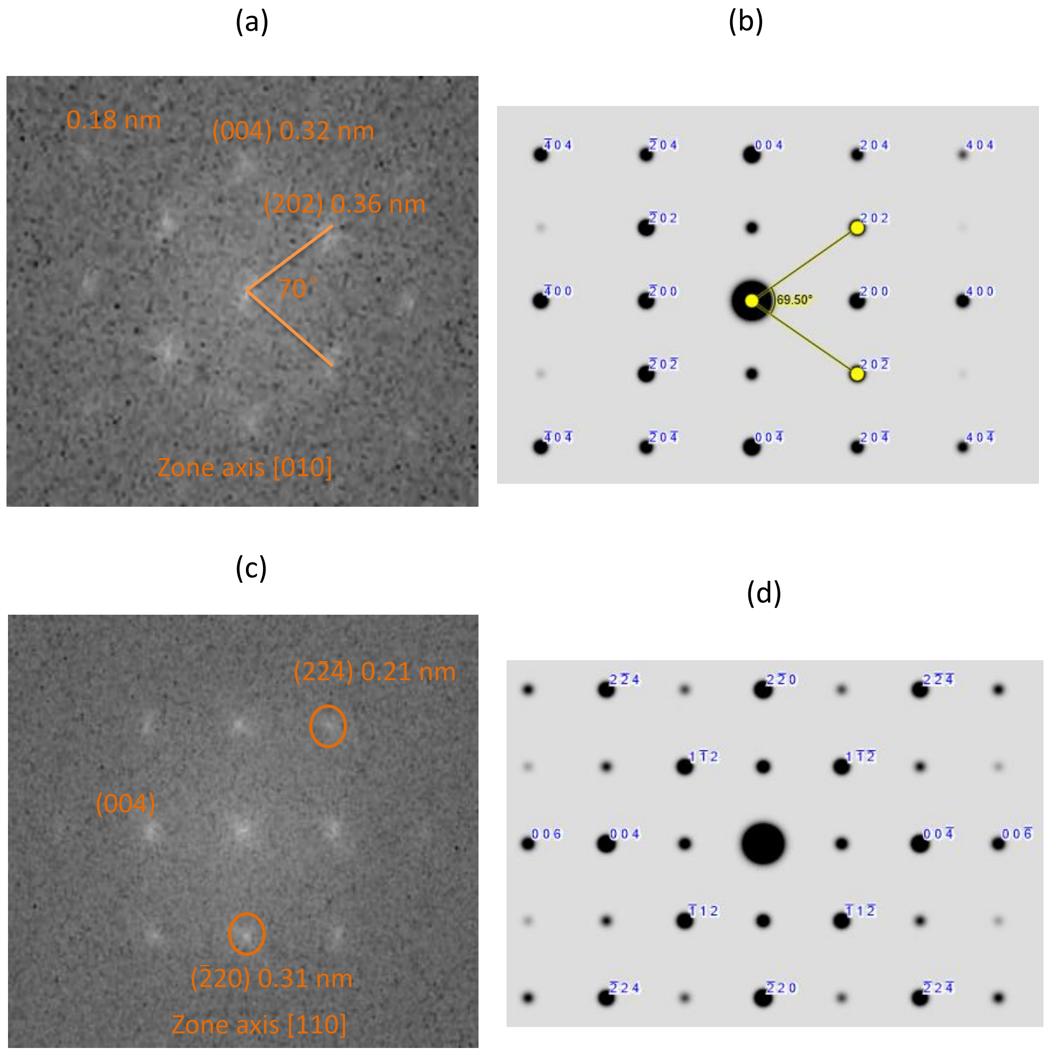

Figure S15 fast Fourier transformation (FFT) patterns of grain 1 (a) and grain 2 (c) in Figure 2c of the manuscript. Software Crystalmaker was used to simulate the electron diffraction patterns of $MAPbI_3$ with zone axis of [010] and [110], which show excellent agreement with the FFT results. There are missing refractions of {200} in zone axis of [010] and {112} and {020} in [110] in experimental results compared with computer generated ones due to quite low intensity in electron diffractions of organic-inorganic halide compounds.[4]

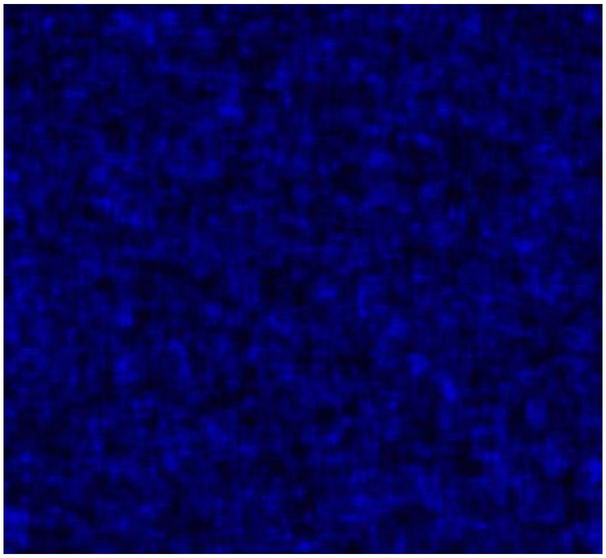

Figure S16 EDS analysis of oxygen element distribution of perovskite film before moisture degradation. The signal was weak and random, indicating negligible water existed in the film before degradation.

Reference

1. Y. Deng, E. Peng, Y. Shao, Z. Xiao, Q. Dong and J. Huang, *Energy. Environ. Sci.*, 2015, **8**, 1544-1550.
2. Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao and J. Huang, *Science*, 2015, **347**, 967-970.
3. Z. Xiao, Q. Dong, C. Bi, Y. Shao, Y. Yuan and J. Huang, *Adv. Mater.*, 2014, **26**, 6503-6509.
4. D.-Y. Son, J.-W. Lee, Y. J. Choi, I.-H. Jang, S. Lee, P. J. Yoo, H. Shin, N. Ahn, M. Choi and D. Kim, *Nature Energy*, 2016, **1**, 16081.