

Supporting Information for:

Improved stability of perovskite solar cells in ambient air by controlling mesoporous layer

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1. Experimental details

Solar cell fabrication:

Fluorine doped tin oxide (FTO) glasses (NSG, 14 Ω) were ultrasonically cleaned by ethanol and acetone for 20 min sequentially, and then treated by O₂ plasma for 6 min. The compact TiO₂ (c-TiO₂) film was formed by spin-coating 0.15 M titanium diisopropoxide bis (acetylacetonate) (75 wt% in isopropanol, TCI) in *n*-butanol on the FTO substrates at 2500 rpm for 30 s, then dried at 125 °C for 10 min and annealed at 550 °C in air for 30 min. After that, the substrates were immersed in 40 mM TiCl₄ aqueous solution for 30 min at 70 °C and washed with distilled water, followed by annealing at 500 °C for 30 min in air. The m-TiO₂ layer was deposited by spin coating a commercial TiO₂ paste (Dyesol 18NRT) diluted in ethanol (1:5, weight ratio) at 5000 rpm for 30 s, and annealed at 500 °C for 30 min. To control the thickness of m-TiO₂ layer, different spin-coating times were introduced. The perovskite film was prepared using the widely used two-step method: PbI₂ solution (1 M) in N, N-dimethylformamide (DMF) was spin-cast on the m-TiO₂ layer followed by immersing in CH₃NH₃I solution and the subsequent thermal treatment. The hole-transporting material (HTM) layer was then deposited by spin coating a solution of spiro-MeOTAD (Lumtech) at 4000 rpm for 30 s. Finally, 80 nm-thick gold electrodes were deposited by electron beam

evaporation through a shadow mask. All of the devices were fabricated under ambient air with humidity about 50% and then stored in dry air environment without sealing and maintaining the humidity of ~15% before measurements.

Device characterization:

Absorption spectra of perovskite films were recorded using a Shimadzu UV 2550 UV-Visible spectrophotometer. The morphologies were investigated using a field-emission scanning electron microscopy (SEM) (Hitachi S-4800), and the crystallinity of the perovskite films was characterized by an X-ray diffraction (XRD) (Rigaku Ultima IV) with Cu $K\alpha$ radiation in a 2θ range of 10 - 35°. Photovoltaic $J-V$ measurements were performed under AM 1.5G illumination at the intensity of 100 mW cm⁻² using a 300 W Xenon solar simulator (Newport) equipped with a Keithley 2420 source meter. The incident photon to electron conversion efficiency (IPCE) was measured using a power source (Newport, 300 W xenon lamp, 66920) with a monochromator (Newport, Cornerstone 260) and an optical power meter (Newport, 2936-R). Electrochemical impedance spectra (EIS) measurements were carried out on CHI660 under 1 sun illumination with different DC bias voltage from 0.4 to 1.0 V. A small AC voltage perturbation of 10 mV was applied during the measurement at frequency ranging from 1 Hz to 1 MHz. The spectra were fitted using Z-View software. The time-resolved PL (TRPL) spectra were recorded on a fluorescence spectrometer (FLS980, Edinburgh Photonics) excited by picosecond pulsed diode lasers (375 nm).

2. Cross-section morphology of the perovskite films

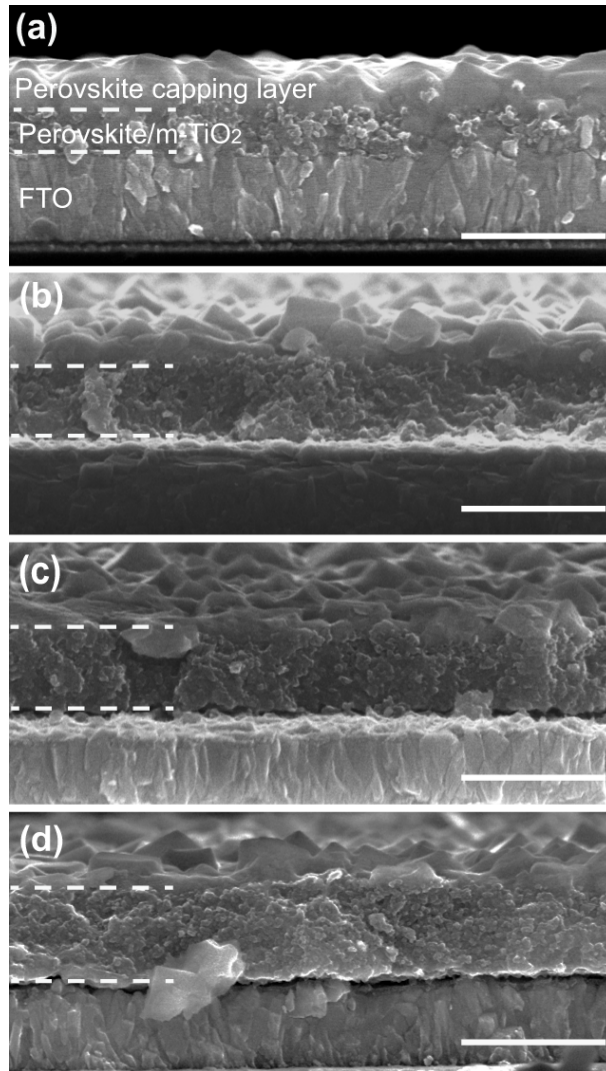


Figure S1. Cross-section SEM images of the perovskite films on different thicknesses of m-TiO₂ layer by changing spin-coating times: (a) 1 time, (b) 2 times, (c) 3 times and (d) 4 times. Scale bar represents 500 nm.

3. Histogram of PCE for samples with 160-nm thick m-TiO₂ layer

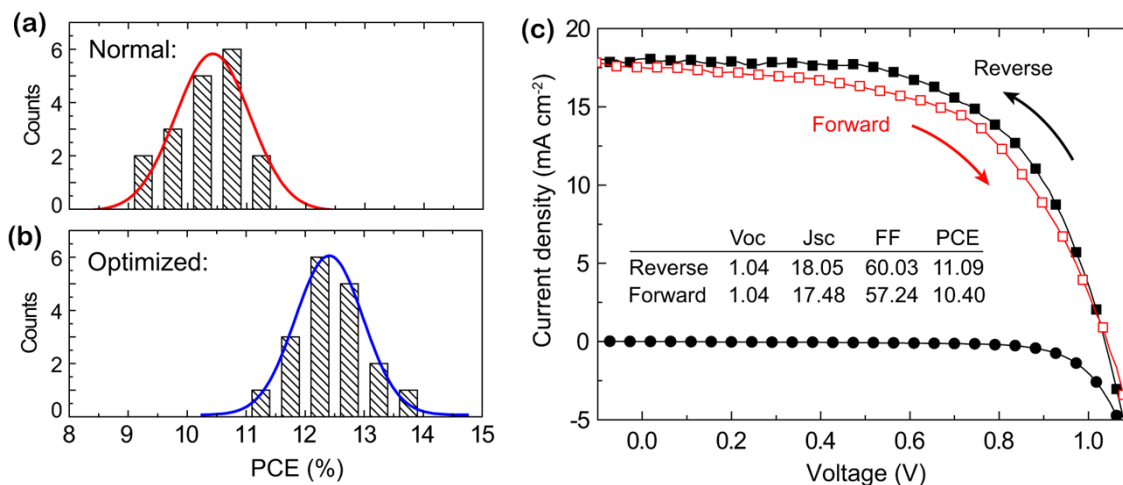


Figure S2. Histogram of solar cell efficiency of 18 samples (a) without and (b) with optimization. In this work, the most efficient cells were realized on the devices configured by m-TiO₂ with the thickness of ~160 nm and achieved the PCE of 11.09% (10.43% in average), as shown in (a). With optimized perovskite layer, 13.76% PCE (12.41% in average) can be obtained as shown in (b). (c) J - V curves measured by reverse- and forward-scan for a typical device configured with 160 nm-thick m-TiO₂ layer. The scan rate was 150 mV/s.

4. IPCE spectra for the devices with different thickness of m-TiO₂ layer

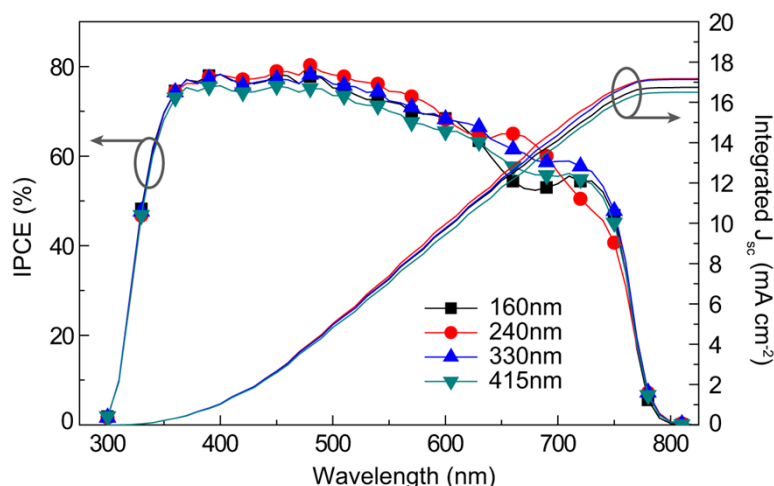


Figure S3 m-TiO₂-thickness dependence of the IPCE response for the perovskite solar cells. The integrated photocurrent density J_{sc} from IPCE spectra was also shown in the figure with a value of 16.74, 17.19, 17.12, and 16.51 mA cm⁻² for the device with 160, 240, 330 and 415 nm-thick m-TiO₂ layer, respectively. The integrated J_{sc} from IPCE matched well with the J-V measurement results, and also undergo a slight increase and then decrease trend.

5. Electrochemical impedance spectra (EIS) measurement

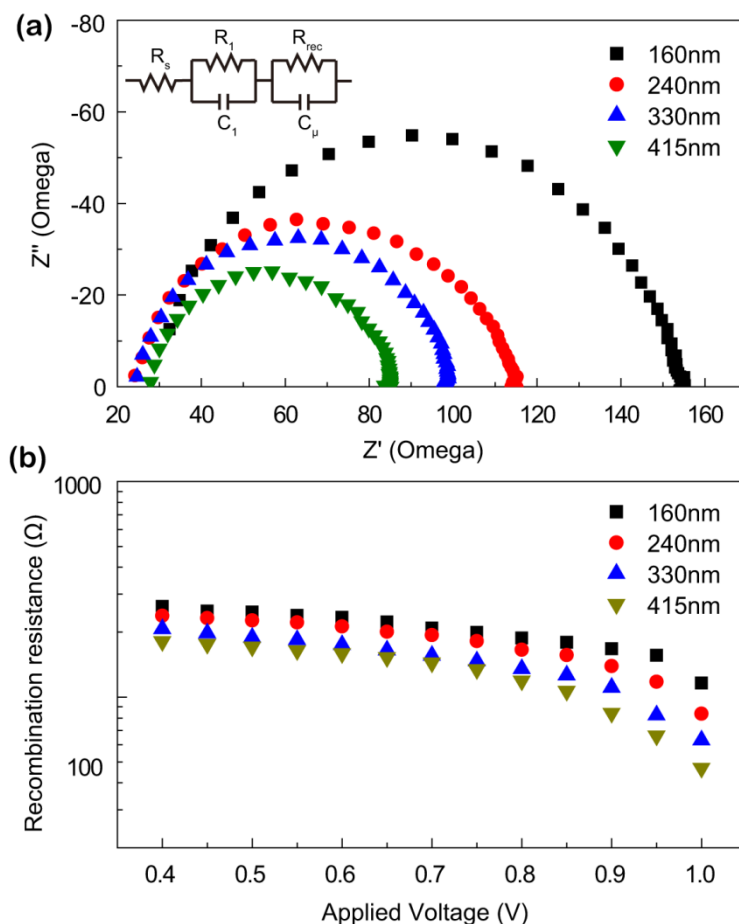


Figure. S4 (a) EIS of the cells with different thickness of m-TiO₂ layer under AM 1.5G illumination (100 mW cm⁻²) and 1.0 V bias. (b) Recombination resistance (R_{rec}) estimated from the EIS measurements as a function of the applied voltage (0.4 - 1.0 V) to the devices. The EIS spectra is fitted using transmission line model¹ and R_{rec} is extracted and plotted as a function of the applied voltage bias. Equivalent circuit is shown in inset of (a). R_l and C_l represent the hole transport resistance and capacitance through the hole transport material (HTM) layer.

6. Long-term PCE stability of the devices

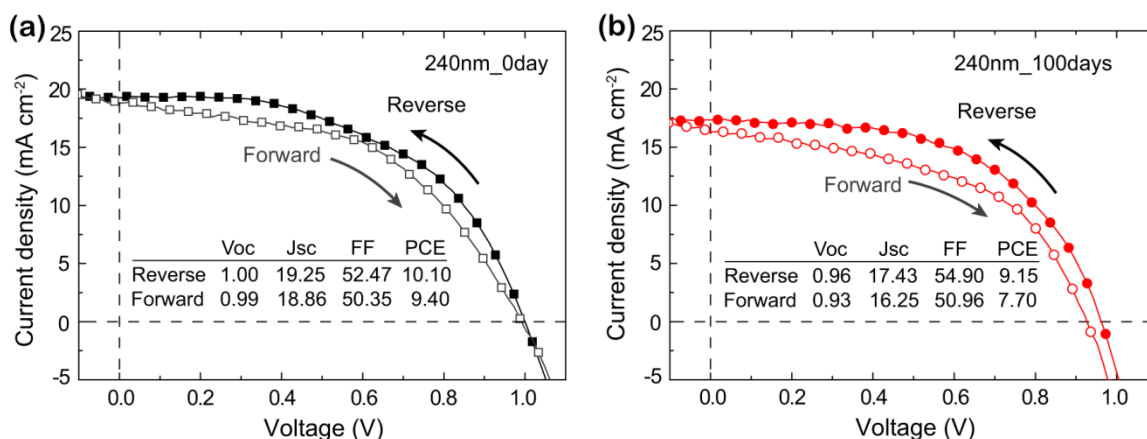


Figure S5. (a) and (b) show the J - V curves for the same device with 240-nm- m - TiO_2 layer that measured immediately and after 100 days of ageing, respectively. The PV parameters measured by reverse- and forward-scan are summarized in inset. The devices were stored in air ambient with controlled humidity of $\sim 15\%$ and without sealing. A maximum of 9.15% PCE still can be obtained on this structure even after 100 days (~ 2400 hours).

7. Time-resolved PL (TRPL) measurement

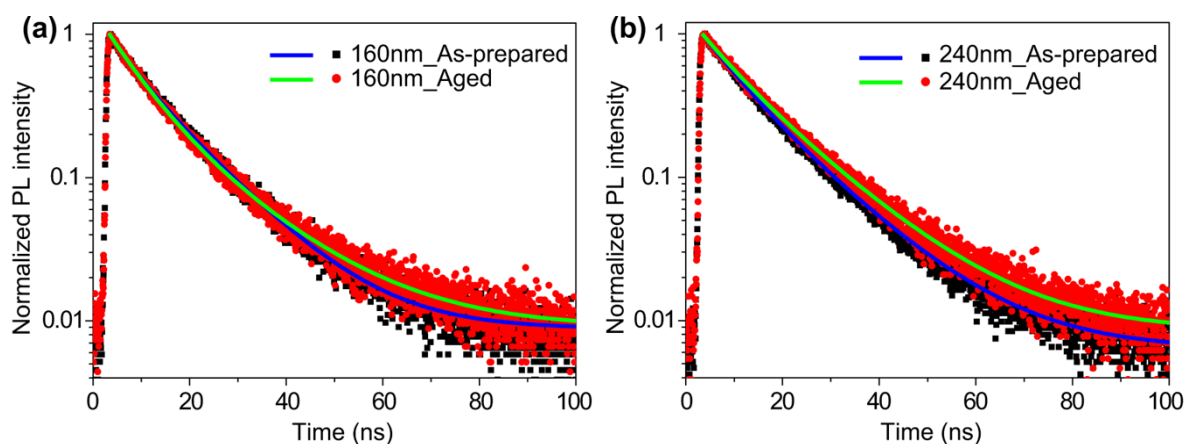


Figure S6. Time-resolved photoluminescence (TRPL) spectra of the perovskite films configured with (a) 160 nm- and (b) 240 nm- thick m - TiO_2 layer before and after aging (7 days) in air under controlled humidity ($\sim 15\%$).

In order to further evaluate the charges transportation process for the cells with different thickness of m - TiO_2 layer after aging, time-resolved photoluminescence (TRPL) were carried out to determine the carriers' lifetime in perovskite film as shown in Figure S6. The curves can

be well fitted using two-component exponential decay and the results were summarized in Table S1. According to the previous report,^{2,3} the fast decay component (τ_1) should attribute to the injection of free carriers in the perovskite crystals to the charges collection materials, while the longer part (τ_2) should be the recombination of free carriers in the radiative channel.

As demonstrated by Wang *et al.*,⁴ the slowed injection rates ($1/\tau_1$) was undoubtedly originated from the increased PbI₂ grains in the perovskite layer for all of the aged samples. The longer recombination lifetimes (τ_2) also indicates the increased carriers' accumulation effect in perovskite layer induced by more generated PbI₂ after aging for the cells.³ However, less slowed recombination lifetime for the PSCs with thicker m-TiO₂ layer after aging was presented. This demonstrated that a better charges transportation process still can be maintained, which is consistent with the photocurrent response measurement. These results well support the decay mechanisms mentioned in the manuscript.

Table S1. Fitted TRPL parameters for the different perovskite films. The relative intensity ratio for each fraction is also shown in the table.

Samples	τ_1 (ns)	τ_2 (ns)
160 nm-As prepared	4.83 (30%)	12.62 (70%)
160 nm-Aged	7.16 (48%)	17.35 (52%)
240 nm-As prepared	7.18 (36%)	14.46 (64%)
240 nm-Aged	7.21 (50%)	15.24 (50%)

References:

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