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Supporting Information:

Monolayer $MAPbI_3$ film for high-efficiency solar cells via coordination and heating assistance process

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1. Result and Discussion

The TiO_2 electron transport layer was deposited on the 450 °C FTO substrate by spray pyrolysis method, annealing 30min. The precursor of TiO_2 was dissolved in ethanol at a 1:20 volume ratio, and was charged into a nozzle after ultrasonic 10min. Figure S1 show the top-view SEM images of the annealed TiO_2 films. The dense TiO_2 film with 30nm thick was obtained by spray pyrolysis method, as shown in Figure S1 (a). In order to increase the fill factor and decrease the hysteresis, a mesoporous TiO_2 layer with 100-150nm thick was spin-coated on the dense TiO_2 layer, as shown in Figure S1 (b).

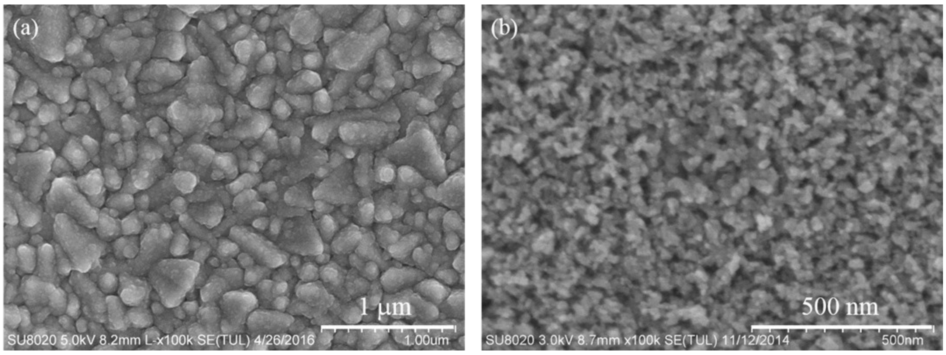


Figure S1. The top-view SEM images of the annealed TiO_2 films. (a) The dense TiO_2 film prepared by spray pyrolysis method; (b) the mesoporous TiO_2 film prepared by spin-coating.

Figure S2 shows millimeter-scale crystalline grains with a unique leaf-like pattern radiating from the center of the grain. However, under high magnification, the large grains still consist of many small particles, and there are large number of voids on the film. Therefore, it suggests that the crystallization rate should be retarded in order to form high quality perovskite films with large size grains by hot-casting method.

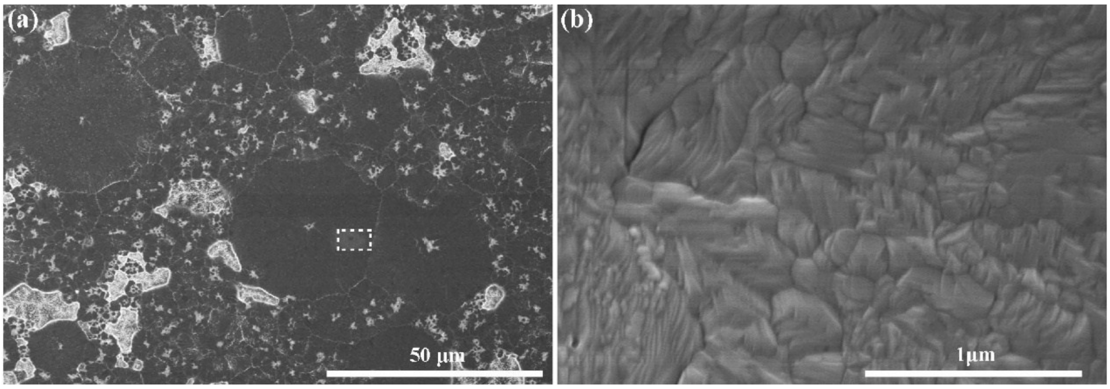


Figure S2. Surface SEM images of perovskite films prepared by the hot-casting method without MACl in the standard precursorat 150 °C. The dotted rectangle indicates the selected area of high magnification SEM.

Figure S3 shows the SEM images at a lower magnification for both hot-casting and spin-coating perovskite films using 0.5M and 0.75M MACl, respectively. At 0.5M-MACl, the films show large grain sizes with a compact film morphology and minimum amount of pinhole formation. However, a large number of pinholes/voids appear for both spin- and blade-coated films when 0.75M-MACl is used. The pinholes/voids in the perovskite films prepared by HAP is less than that of the spin-coating with different concentration of MACl. The formation of the voids is probably caused by the release of excess MACl during annealing.

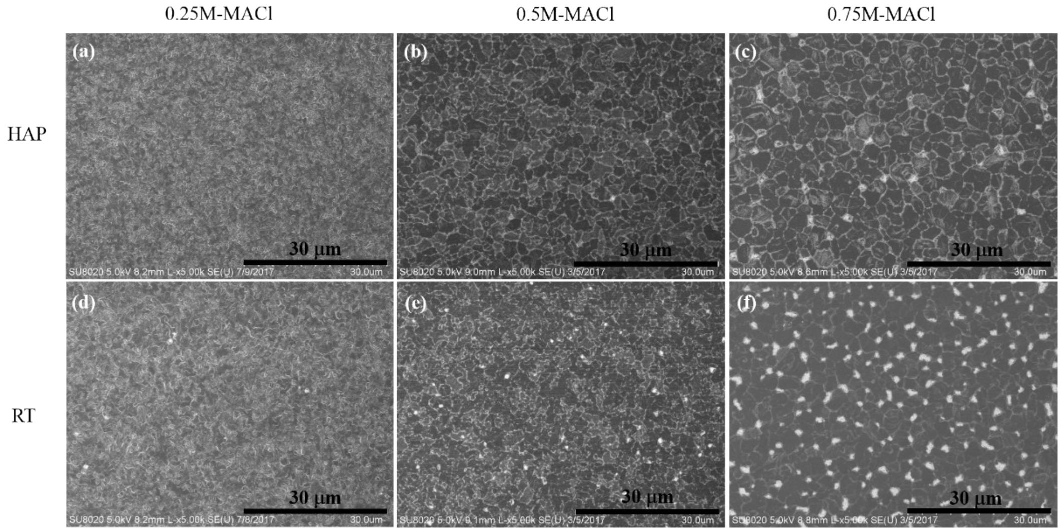


Figure S3. The SEM images at a lower magnification for both hot-casting and spin-coating perovskite films using0.25, 0.5, 0.75 M MACl, respectively.

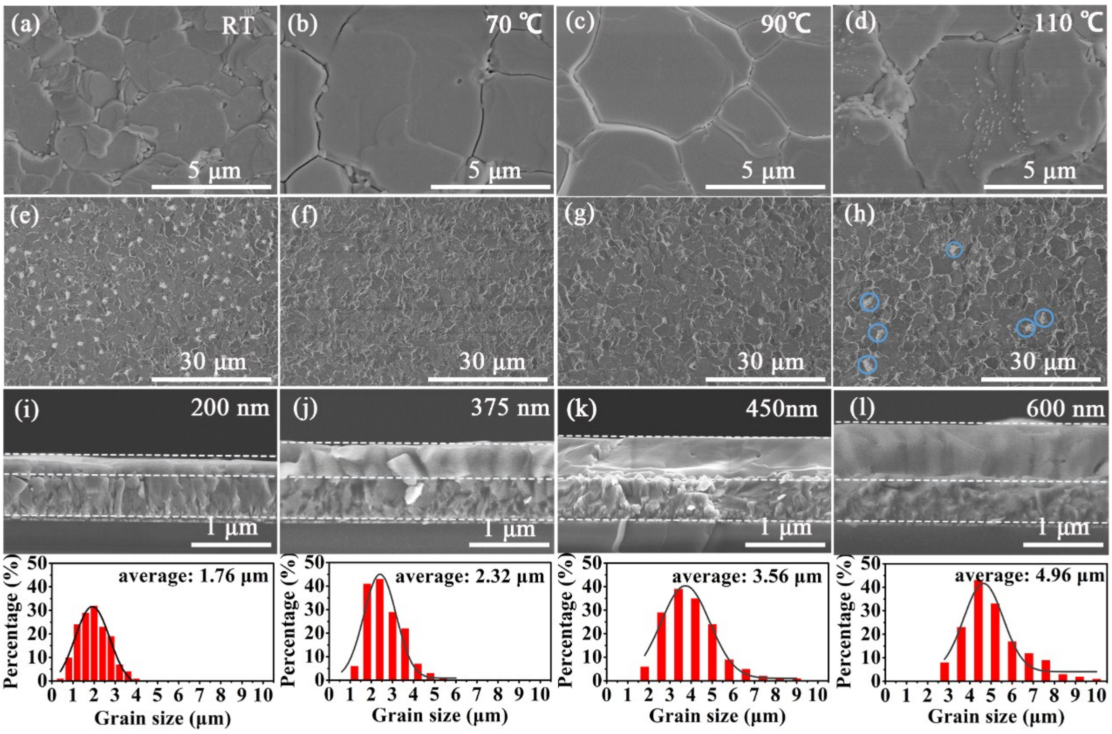


Figure S4. Characterization of perovskite films prepared with spin-coating at room temperature (RT) and hot-casting process (HAP) at 70, 90, and 110 °C with MACl in the precursor solution. (a)–(h) Surface SEM images of perovskite films with different temperature as indicated. (i)–(l) Cross SEM images of perovskite films deposited on FTO substrate with different film thicknesses as indicated. The FTO layers and the different-thickness perovskite layers are indicated by the dashed lines.

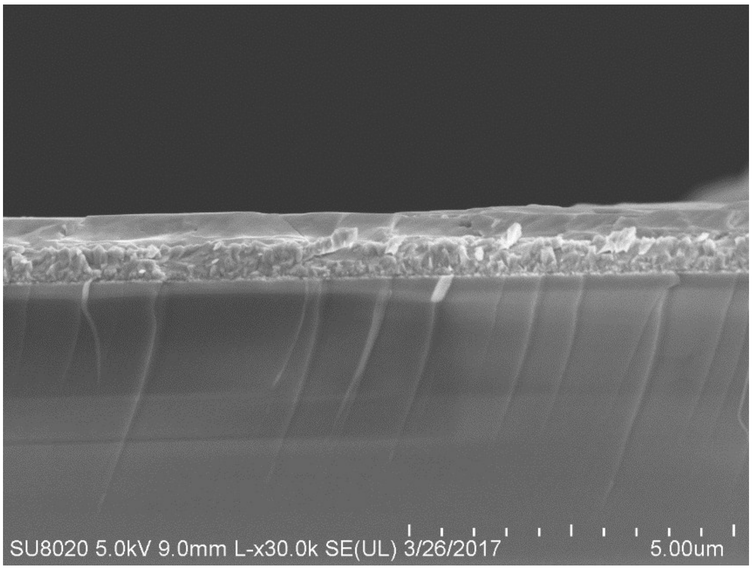


Figure S5. The cross SEM of perovskite films prepared by MACl-HAP at 90 °C.

Before spin-coating, the substrate is heated to a desired temperature for 10 min. After that, the hot substrates (70, 90, and 110 °C) are transferred from the hot plate to the spin coater chuck and the spin coating process is started immediately. The temperature was monitored using an IR thermal gun to monitor the temperature change of the film during the entire process (**Figure. S4 (a)**). The color change of the film at different temperatures was captured by a video during the spin coating (**Figure. S4 (b)**). When the substrate is 70 °C, the film dries within the 6~7 s and temperature quenches rapidly to about 50 °C. At the same time there is a change in color of the film from yellow to dark brown, which indicates the formation of the perovskite phase. With the increase of temperature, the crystal transition time of perovskite also accelerates. When the temperature rose to 110 °C, the color of the perovskite film shown gray-black and the roughness increased. At this time, the formation mechanism of the perovskite film is changed from the “multistage formation mechanism” to the “direct formation mechanism.[1] As a comparison, control samples were prepared with the same precursor solution by spin-coating at RT.

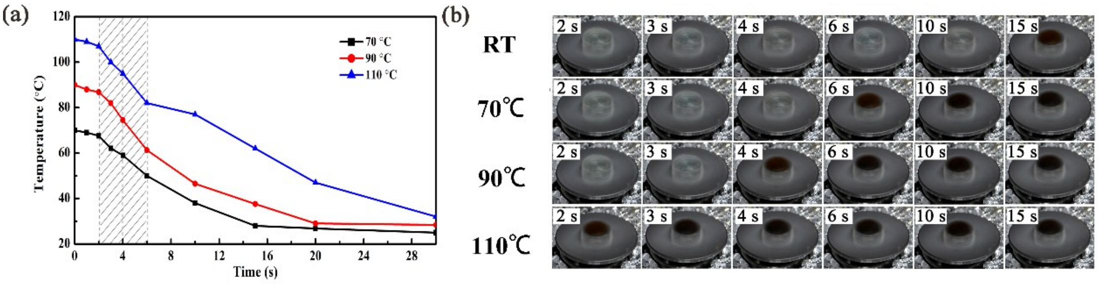


Figure S6. (a) The temperature change of the film was monitored by an IR thermal gun during the entire process; (b) a change in color of the film from transparent to dark brown captured by a video.

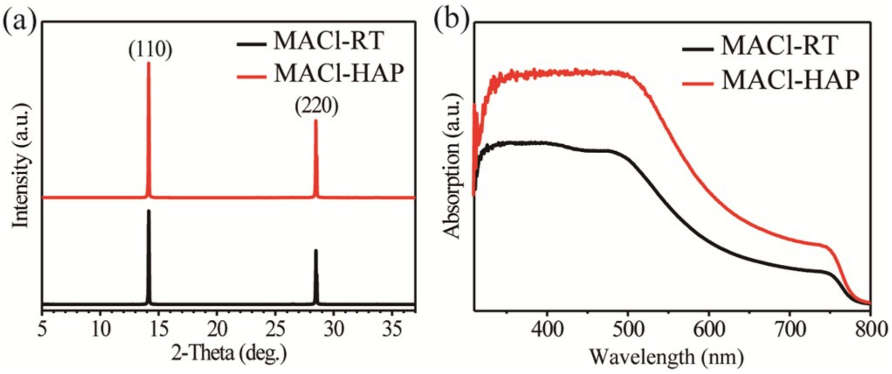


Figure S7 (a) XRD patterns of the films after the annealing process. (b) The absorption spectra of the film after the annealing process.

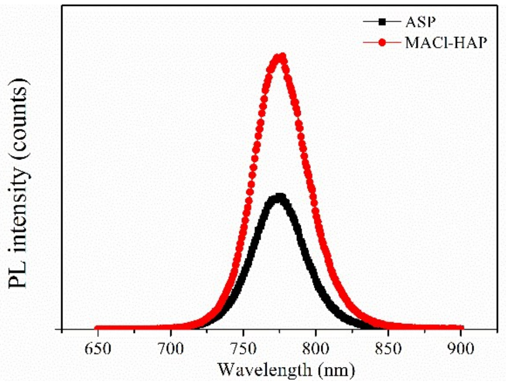
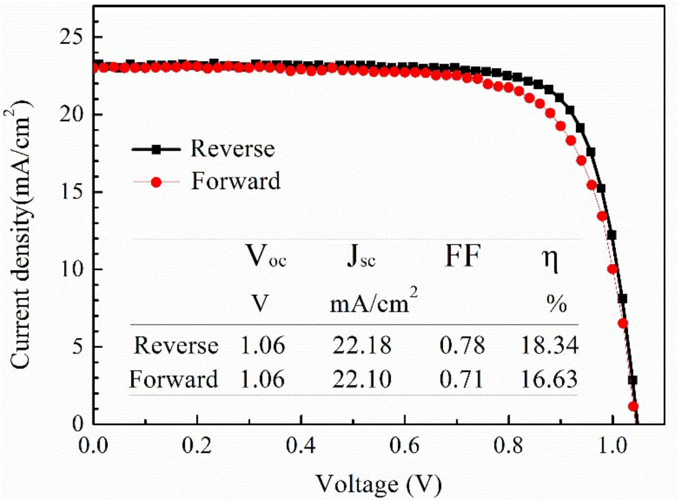


Figure S8. The steady state PL spectra of perovskite films prepared by ASP and MACl-HAP on glass substrate. The excitation wavelength is 375 nm.



	V_{oc} V	J_{sc} mA/cm^2	FF	η %
Reverse	1.06	22.18	0.78	18.34
Forward	1.06	22.10	0.71	16.63

Figure S9. Current density-voltage curves of the perovskite solar cells with different scanning direction. The scanning range is from -0.05 V to 1.2 V, while the scanning rate is 50 mV/s. All the photovoltaic parameters of the different scanning direction curves are listed.

In order to investigate the long-term stability of PSCs, we tested the PCE of PSCs (without encapsulation) which stored in ambient environment (20-30% humidity). Figure S9 shows the normalized PCE of PSCs prepared by ASP and MACl-HAP methods, respectively. The stability of MACl-HAP is better than that of ASP, the PCE can retain 80% after expose in ambient environment (20-30% humidity) after 120 h. In our case, the degradation of PCE should be mainly attributed to the reaction between Ag electrode and perovskite film due to the diffusion of Ag, which have been studied by the literature.[1, 2] As shown the insert in Figure S9, after the long-term air- storage tests, the color of Ag electrode changed from silver to light yellow for the PSCs prepared from ASP, while it retains silver for the PSCs prepared from HAP-MACl. It indicate that the degradation rate of PSCs prepared from MACl-HAP is suppressed due the high-quality of perovskite films. Moreover, the long-term stability should be further improved by using Au electrode.

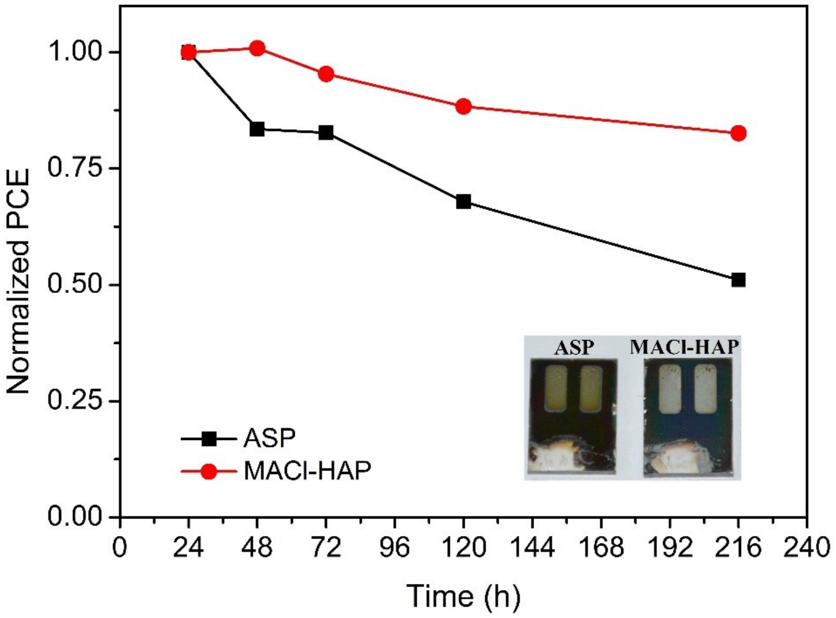


Figure S10. The long-term air-storage stability of the unencapsulated PSCs prepared by ASP and MACl-HAP in ambient environment (20-30% humidity), respectively. The insert is the photographs of PSCs prepared from ASP and MACl-HAP after the tests, respectively.

Reference

[1] Chang C, Huang Y, Tsao C, et al. Formation Mechanism and Control of Perovskite Films from Solution to Crystalline Phase Studied by in Situ Synchrotron Scattering[J]. ACS Applied Materials & Interfaces, 2016,8(40):26712-26721.

[2] Y. Kato, L. K. Ono, M. V. Lee, S. Wang, S. R. Raga and Y. Qi, Advanced Materials Interfaces, 2015, 2, 1500195.

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