

Supporting Information for

Smooth perovskite thin films and efficient perovskite solar cells prepared by the hybrid deposition method

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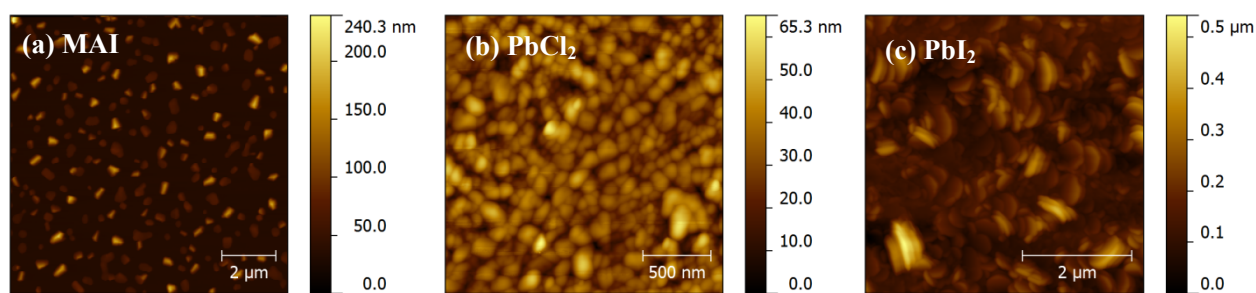


Fig. S1 AFM topographic images of (a) MAI (average thickness = 100 nm), (b) 100 nm PbCl₂ and (c) 100 nm PbI₂ films prepared by the hybrid deposition method on Si substrates. The MAI layer partially covers the substrate, indicating the Volmer-Weber or Stranski-Krastanov mode growth. The PbCl₂ and PbI₂ layers show uniform and complete coverage on the substrate, but different morphologies. The PbCl₂ layer shows round grains with small *RMS* roughness of 8.51 nm. The PbI₂ layer shows uniform plate-like structures with much larger *RMS* roughness of 63.6 nm.

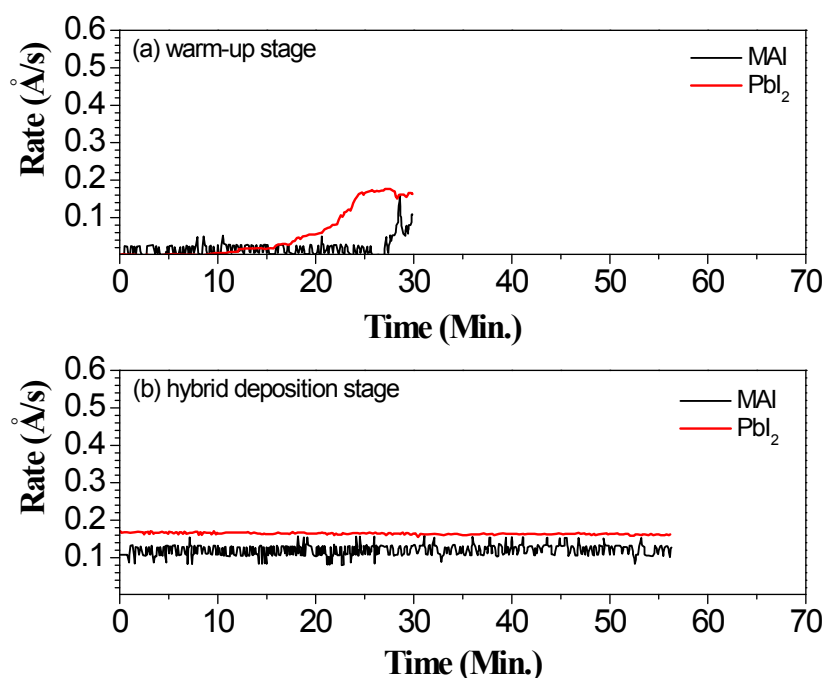


Fig. S2 Evaporation rate reading from sensor 1 for PbI₂ and sensor 2 for MAI during (a) warming up stage and (b) hybrid deposition stage. The digitalization of sensor 2 is caused by the natural vibration induced by the small values of the density, z-factor, and tooling factor parameters, rather than the instability of MAI rate. From (a), we can see that sensor 2 has no reading during heating PbI₂. Also sensor 1 is still stable during heating MAI. This indicates that the two sensors have no cross-talking in our hybrid deposition method. From (b), we can see that the deposition rates of individual materials are very stable during the whole hybrid deposition process.

In our hybrid deposition method, the perovskite formation is based on a chemical reaction between metal halide and MAI vapor. Because the vapor pressure of MAI is relatively high, its vapor fills the entire chamber once heated to a certain sublimation temperature. Proper calibration of the quartz crystal monitor geometrical parameter (i.e., tooling factor) would allow the determination of the absolute rate corresponding to the substrate position. Although sensor 2 is located in a different location, which is far away from the substrate position, it can still detect the arbitrary nominal deposition rate. Initially, we tried calibrating the quartz crystal monitor (sensor 2) by setting the density and z-factor to be 1.0 g/cm³ and 1.0, respectively, as already reported previously [1, 2]. However, we were unable to calibrate the tooling factor by the standard ways of measuring the thickness of deposited MAI film by AFM or profilometer. We have observed that MAI film grows as patches (islands) instead of a uniform flat film even on an extremely flat surface of silicon wafer (with a thin layer of native oxide) showing roughness of approximately 1 Å. Thus, an alternative procedure has been adopted. Our methodology is based on the MAI vapor pressure and flow inside the chamber. Because a fixed shutter (Part ⑤ in Fig. 1) was mounted between sensor 2 and MAI source in our system, the detected nominal rate of MAI by sensor 2 would become relatively small. Thus, sensor 2 in our system serves to monitor indirectly the deposition rate of MAI by time evolution during heating and perovskite formation, but cannot quantify the absolute MAI amount to the substrate. Subsequently, we set the parameters of sensor 2 to be relatively small values (density = 0.2 g/cm³, z-factor = 0.2, and tooling factor = 3) to enhance the signal-to-noise ratio and minimize the influence to the sensor 1. In this case, we can monitor and control the nominal rate of MAI by sensor 2. We prepared several batches of samples by changing the relatively deposition rate ratios of metal halide and MAI. The nominal rate of MAI during the hybrid deposition was varied keeping the metal halide rate constant. The optimum conditions were found by characterizing the film quality using XRD and AFM techniques.

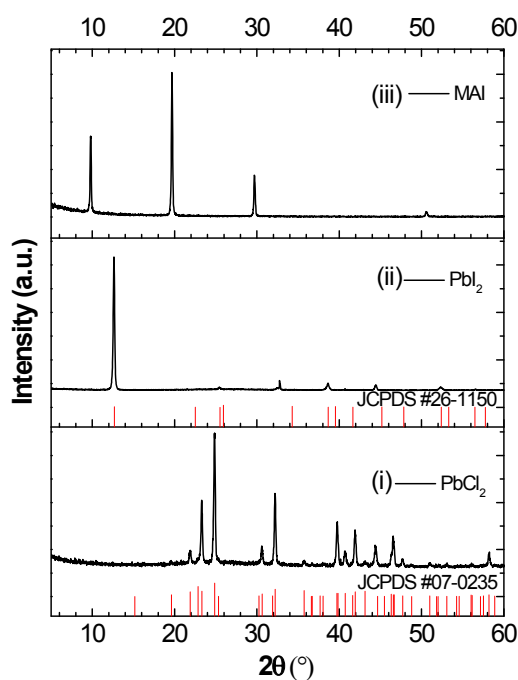


Fig. S3 XRD spectra of 100 nm PbCl_2 , 100 nm PbI_2 , and nominal 100 nm MAI films deposited by the hybrid deposition method on Si substrates. The red vertical lines correspond to the XRD patterns for the standard values of JCPDS files no. 07-0235 for PbCl_2 and no. 26-1150 for PbI_2 . The PbCl_2 layer shows multiple peaks, corresponding to the orthorhombic structure. The PbI_2 film shows the (001) plane of hexagonal structure as the main diffraction peak. The MAI film shows three diffraction peaks at 9.7° , 19.5° , and 29.5° .

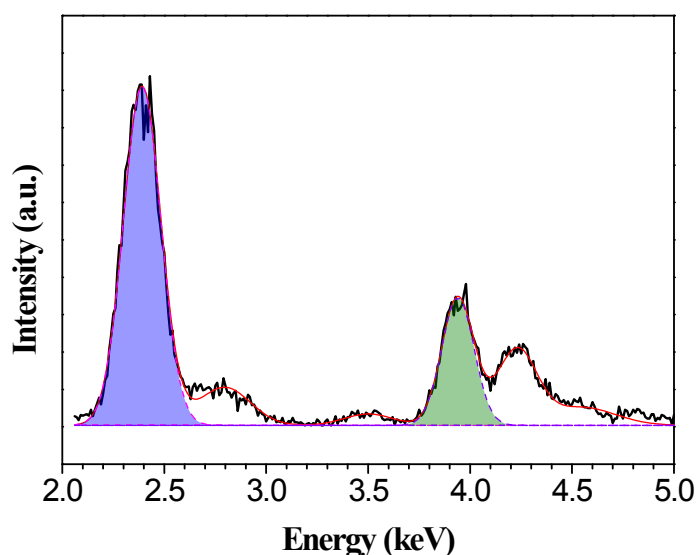


Fig. S4 XRF spectra of perovskite film (*film 4*) prepared by the hybrid deposition method on Si substrate. The peak at 2.39 keV corresponds to the $\text{Pb-M}\alpha_1$ fluorescence peak. The peaks at 3.95, 4.23, 4.50, and 4.93 keV correspond to $\text{I-L}\alpha_1$, $\text{I-L}\beta_1$, $\text{I-L}\beta_2$, and $\text{I-L}\gamma_1$ fluorescence peaks, respectively. Spectra were fitted with Gaussian functions for each emission line. After fitting, the atomic ratio of I/Pb was derived to be ~ 3.01 , suggesting that this perovskite film has well matched stoichiometry.

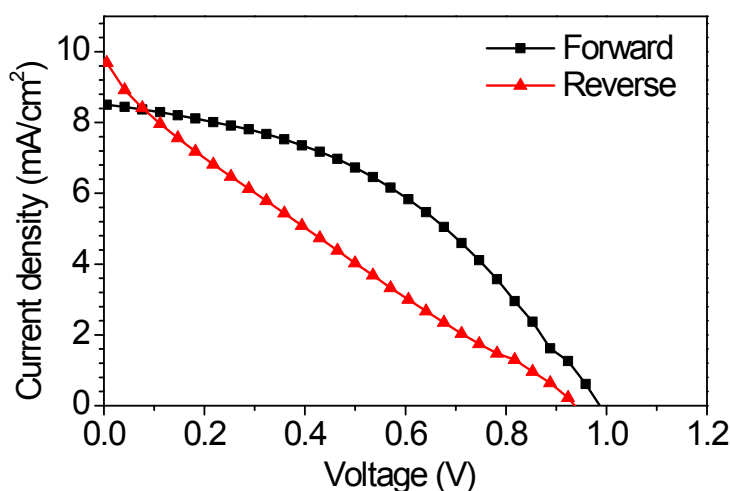


Fig. S5 J - V characteristic curves for a PSC measured under different scan directions showing the hysteresis. The voltage sweeping from forward bias to short circuit and from short circuit to open circuit are denoted as “Forward” and “Reverse”, respectively. For the forward scan, the photovoltaic parameters of V_{oc} , J_{sc} , FF and PCE are 979 mV, 8.49 mA/cm², 42.54%, and 3.53%, respectively, whereas 927 mV, 9.82 mA/cm², 22.39% and 2.04% for the reverse scan. The scan rate is fixed at 0.17 V/s. The higher PCE is found from forward scan. As comparison, a lower PCE of ~40% decrease is determined when measured from reverse scan.

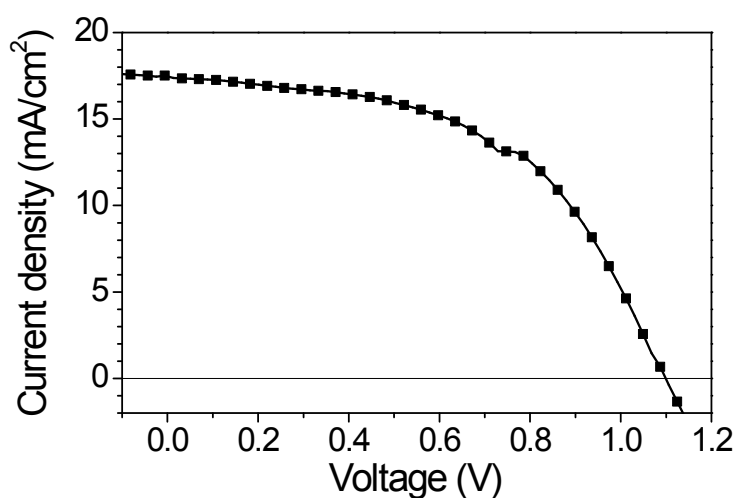


Fig. S6 J - V curve of the PSC with ~170 nm perovskite layer prepared by the hybrid deposition method. The device shows a V_{oc} 1.098 V, a J_{sc} 19.92 mA/cm², a FF 52.44%, and an overall PCE of 11.48%.

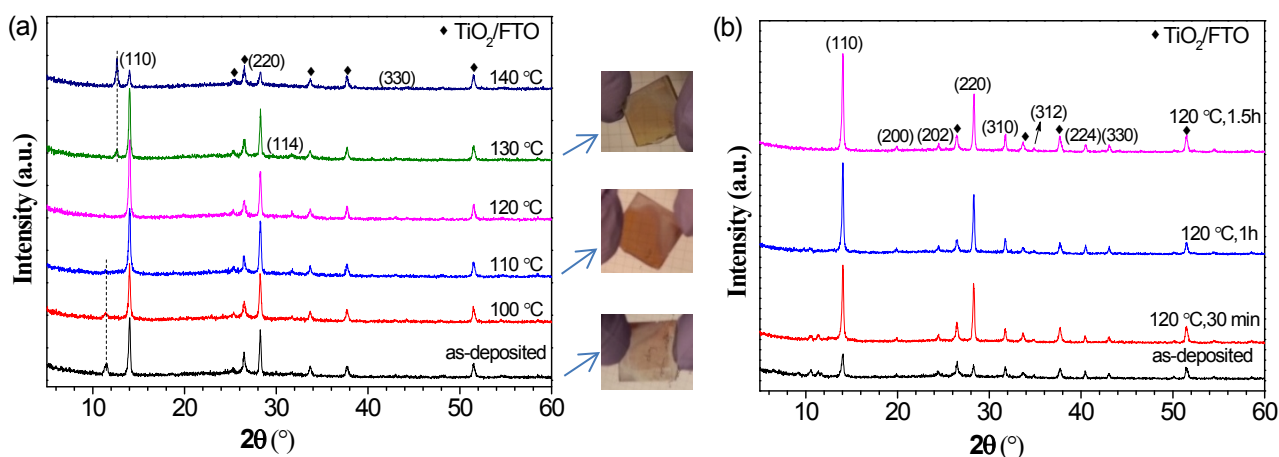


Fig. S7 XRD spectra of as-deposited non-stoichiometric perovskite films by the hybrid deposition method from (a) PbCl_2 :MAI and the subsequently post-annealed films from 100 to 140 °C with increments of 10 °C and 30 min annealing time at each temperature; and from (b) PbI_2 :MAI and the subsequently post-annealed films at 120 °C with increment of 30 min in annealing time. The annealing time of 30 min, 1 h, and 1.5 h in (b) indicates the total annealing time performed on the sample.

The as-deposited film (Fig. S7(a)) shows the (110), (220) and (330) diffraction peaks of perovskite and an additional diffraction peak at 11.4° , suggesting that this film has slight excess of MAI. From the sample picture, we can see that the as-deposited sample shows a little bit brown-red color (the light color is caused by very thin thickness of ~ 50 nm). With increasing the post-annealing temperature from 100 to 120 °C, the intensity of 11.4° peak gradually decreases and it finally disappears, suggesting that the H_2O -incorporated complex is removed from the film. Simultaneously, the intensity of the diffraction peaks of perovskite increases and the film color turns much darker with characteristic brown-red color. When the temperature is increased to 130 °C, the PbI_2 (001) diffraction peak appears, and the peak intensity increases with further increase of the annealing temperature. Meanwhile, the intensity of perovskite peaks weakens. This demonstrates that the high temperature decomposes the $\text{CH}_3\text{NH}_3\text{PbI}_3$ to PbI_2 . After the appearance of PbI_2 , the sample showed a characteristic yellow color.

In Fig. S7(b), the as-deposited film shows also the 11.4° diffraction peak in addition to the perovskite diffraction peaks. At 120 °C annealing for 30 min, even though the intensity of perovskite peaks increases, the peak at 11.4° could not be removed, suggesting that the 30 min post-annealing is not enough for removing the H_2O -incorporated complex. When the annealing time is extended to 1 h, the 11.4° peak disappears. With further increasing the post-annealing time to 1.5 h, there is no change in the XRD features. This suggests that the optimized annealing condition is 120 °C for 1 h for the non-stoichiometric perovskite films with excessive MAI.

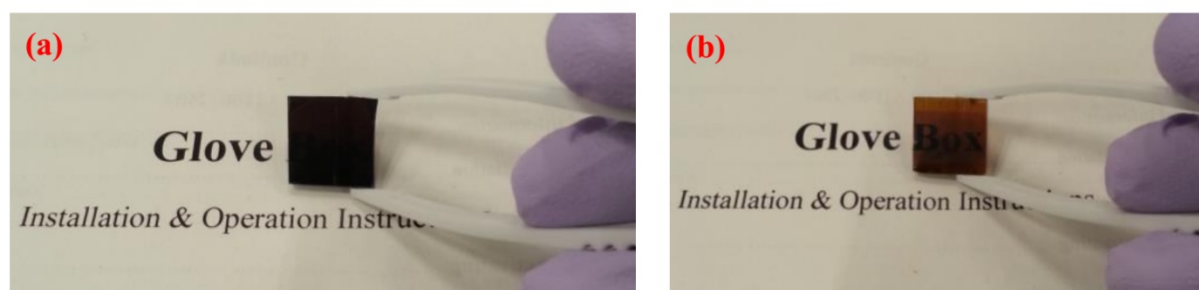


Fig. S8 Photos of perovskite films prepared by (a) the solution method and (b) the hybrid deposition method. The film prepared by the hybrid deposition method is semi-transparent, while the solution-processed perovskite film is dark and opaque.

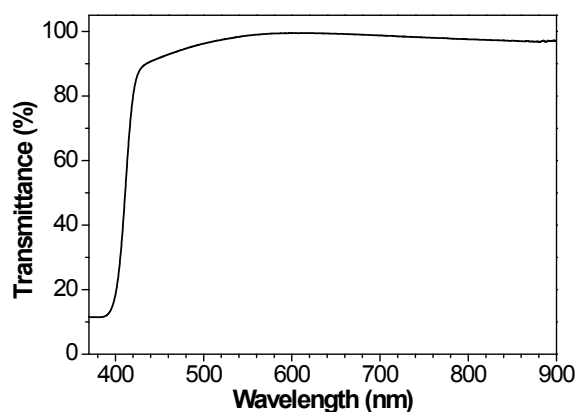


Fig. S9 Transmittance of 100 nm-thick spiro-MeOTAD HTL layer on glass substrate. The transmittance of glass substrate has been subtracted. The spiro-MeOTAD HTL layer is highly transparent in the visible range.

Table S1. Photovoltaic performance of semi-transparent PSCs with different thicknesses of perovskite layer

Thickness	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
50 nm	1.05	10.75	56.2	6.37
110 nm	1.01	12.85	66.6	8.64
135 nm	1.09	16.98	53.5	9.86

References:

- [1] M. Z. Liu, M. B. Johnston, and H. J. Snaith. Efficient Planar Heterojunction Perovskite Solar Cells by Vapor Deposition. *Nature*, 2013, **501**, 395-398.
- [2] A. S. Subbiah, A. Halder, S. Ghosh, N. Mahuli, G. Hodes, and S. K. Sarkar. Inorganic Hole Conducting Layers for Perovskite-Based Solar Cells. *J. Phys. Chem. Lett.*, 2014, **5**, 1748-1753.