Supporting Information

Vapor assisted crystallization control toward high performance perovskite photovoltaics with over 18% efficiency in open air

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S1. Photo of the vapor assisted depositing setup

Figure S1. (a) Photo of the vapor assisted depositing equipment during the vapor reaction with a PbI₂ substrate; (b) Temperature distribution of the inner glass tube (reaction chamber) along the vapor transportation direction when the heating temperature is 150 °C (measured by thermocouple). The measured temperature at the MAI source region is 149.0 \pm 1.0 °C. By evaluating the crystal quality and PV performance, the suitable growth region (substrate position) was schematically shown in the figure with a temperature range from ~142.5 - 144.5 °C. The actual temperature on the surface of PbI₂ substrate in the reaction process of this region was measured to be ~139.0 to 141.2 °C, which is about 2-3 °C lower than the chamber temperature (open circles and green line in the figure).

S2. As prepared large scale and uniform perovskite films



Figure S2. (a)-(d) SEM images of the prepared perovskite film in different magnifications.

S3. Photoluminescence (PL) mapping characterization

Figure S3. (a) Optical microscope (OM) images of the large scale perovskite film; (b) Photoluminescence (PL) mapping of perovskite film in (a); (c) PL spectra with comparison to the absorbance spectra.

S4. Morphology evolution of the PbI₂ substrate after vapor reaction

Figure S4. SEM images of (a) PbI_2 layer and (b) the subsequently prepared perovskite film after vapor-assisted reaction, and their corresponding cross-sectional morphologies shown in (c) and (d), respectively. After the vapor-assisted reaction, an obvious volume expansion from PbI_2 film (~150-nm thick) to $CH_3NH_3PbI_3$ film (~395-nm thick) can be resolved from the cross-sectional SEM images.

S5. Temperature dependent perovskite growth

As shown in Figure S5, distinctly different surface morphologies of the as-prepared perovskite films have been obtained by employing different heating temperature. Under lower temperature at 140 °C, a much smooth surface has been prepared as seen in Figure S5a, while a rough surface with larger crystal domains was obtained under 150 °C. As the temperature continuously increased to 160 °C, the average size of crystal domains undergoes a slight decrement. Undoubtedly, this morphology evolution should originate from the controlled diffusion rate and depth of MAI molecules diffusing into PbI₂ substrate under different temperatures. The lower reaction temperature would lead a slower reaction rate and a much smooth surface. Additionally, the limited migration kinetic energy and diffusion distance under

lower temperatures would cause the existing of unreacted PbI₂, as identified by the XRD pattern shown in Figure S5b. While high temperatures would result in a much rapid reaction rate and rough surface morphology, as shown in Figure S5a (150 and 160 °C). However, under the situation of 160 °C, although the raised temperature can further improve the migration kinetic energy of MAI with a longer diffusion distance, which can ensure the complete reaction of PbI₂ to perovskite, the simultaneously increased reaction rate would lead to a decreased crystal domain in size (Figure S5a-III) and a poorer crystallinity, as demonstrated by the XRD patterns shown in Figure S5b. The PV performance of the devices based on these films shown in Figure S5c also indicated that the 150 °C is the optimized heating temperature for high-quality perovskite films in photovoltaic application.

Figure S5. (a) Surface morphology evolution of the perovskite film as a function of the heating temperature: 140, 150 and 160 °C; (b) the corresponding XRD patterns of the films in (a). (c) J-V curves of the perovskite solar cells fabricated using the perovskite films in (a).

Growth temperature (°C)	$V_{\rm oc}\left({ m V} ight)$	$J_{\rm sc}$ (mA cm ⁻²)	FF	PCE (%)
140	0.99	21.88	0.74	16.04
150	1.05	21.90	0.74	17.07
160	1.02	20.27	0.65	13.34

Table S1. Summarized PV parameters of the *J-V* curves shown in Figure S5c.

S6. Substrate position dependent perovskite growth behaviors

Figure S6. (a) Schematically shows three typical substrate location (A, B and C) in the reaction chamber; (b) Absorption spectra of the PbI₂ substrates that located at different positions (A, B and C sites illustrated in (a)) after reaction with MAI vapor for 60 min and 150 min, respectively. (c) Device PCE performance of the perovskite films prepared at different position of the reaction chamber. The average PCE value is $16.31\pm0.57\%$, $16.28\pm0.68\%$, and $14.01\pm1.36\%$ for A, B and C sites, respectively (12 devices).

The results indicated that there is a little difference in the reaction for the substrates located at different positions: a relative slight slow reaction rate is performed on the substrate which is farther away to the MAI source. As show in Figure S6b, after reaction with MAI vapor for 60 min, the substrate located in A site presents a slight stronger absorbance than that in B, but shows much stronger than that in C site. After the full reaction duration for 150 min (including the in-situ annealing process), the absorbance (dash lines) for the prepared perovskite films

located at A and B sites seem almost no difference, while the absorption for C-site sample is still much low, indicating the incomplete of PbI_2 to perovskite. With considering the acceptable position dependent PCE deviation, the suitable growth region was optimized as illustrated in Figure S1b and S6a.

S7. Air-flow rate dependent perovskite growth behaviors

Figure S7. (a) Air-flow rate dependent growth durations for PbI_2 substrates to fully change into dark brown color; (b) Absorption spectra of the PbI_2 substrates reacted with MAI vapor source at different air-flow rates for 30 min. (c)-(f) show the SEM images of the perovskite films fabricated by adopting different air-flow rates in the vapor-solid reaction process: 3.50, 4.34, 5.72 and 6.70 m/s, respectively. The measured average crystal domain size is 255, 340, 420 and

425 nm, separately.

According to the results shown above, it can be concluded that the vapor-solid reaction rate decreased as the air-flow rate increased, while obtained perovskite crystal domains' size increased accordingly. Considering the crystal quality (crystal domains' size) and growth rate, 5.72 m/s is adopted as the optimized air-flow rate in the perovskite films' fabrication.

S8. Posting-annealing effect induced crystallinity evolution

Figure S8. XRD patterns of the samples grown *via* vapor-assisted method for only 90 min and 90-min growth followed by a subsequent post-annealing treatment in air for 20 min.

S9. Growth duration dependent morphology evolution

Figure S9. (a)-(f) surface and (g)-(l) cross-sectional SEM images of the PbI_2 substrates reacted with MAI vapor for different time: 0, 30, 60, 90, 120 and 150 minutes, respectively. The Photographs of substrates were also shown in inset. The scale bars are 500 nm.

S10. Vapor-assisted reaction duration dependent PV performance

Figure S10. Statistics of the vapor-assisted reaction duration dependent PV performance (a batch of 12 devices): (a) V_{oc} , (b) J_{sc} , (c) FF and (d) PCE. The corresponding average values with standard deviations (S. D) were shown in **Table S2**.

 Durations	$V_{\rm oc}\left({ m V} ight)$	$J_{\rm sc}$ (mA cm ⁻²)	FF	PCE (%)
 30 min	1.02 ± 0.01	5.49 ± 0.75	0.65 ± 0.04	3.64 ± 0.64
60 min	0.97 ± 0.01	16.91 ± 0.76	0.67 ± 0.03	11.01 ± 0.93
90 min	0.99 ± 0.01	19.48 ± 1.04	0.66 ± 0.02	12.80 ± 0.67
120 min	1.03 ± 0.01	20.76 ± 0.93	0.70 ± 0.03	14.82 ± 0.65
150 min	1.04 ± 0.02	21.36 ± 0.45	0.74 ± 0.02	16.49 ± 0.73
180 min	1.00 ± 0.01	19.34 ± 1.25	0.66 ± 0.03	12.79 ± 1.24

Table S2. Summarized PV parameters in Figure S10 with standard deviations

Figure S11. (a) PCE statistics of the PSCs fully fabricated in open-air by the vapor-assisted method at different humidity (a batch of 12 devices). The obtained average PCE was $16.43 \pm 0.98\%$ at RH of 35%, $16.40 \pm 0.99\%$ at RH of 45% and $16.14 \pm 0.89\%$ at RH of 60%, respectively. (b) XRD patterns for the corresponding perovskite films that in (a). As evidenced by the XRD patterns in (b), there are no obvious changes in the crystallinity of the corresponding perovskite films at different humidity. As discussed in the main article, the main reason is that the modified heating method can effectively prevent the moisture attack in the perovskite films. Therefore, the proposed vapor-assisted depositing process in this work exhibit superior environment tolerance in open air.

S12. Photograph and crystallinity of the prepared PbI₂ substrates

Figure S12. The photograph images of the spin-coated PbI₂ films before and after heating treatment when using (a) bare PbI₂ and (b) PbI₂:DMSO = 1:1 in DMF solution as precursors, respectively (spin-coating speed was 5000 rpm for 30 s). Here, for the conventional PbI₂ film, the substrates were heated at 100 °C for 5 min, while the PbI₂ (DMSO) films were heated at 60 °C for 10 min and then at 100 °C for another 10 min, which was used to fully remove the DMSO. (c) and (d) show the corresponding XRD patterns comparison for the samples in (a) and (b). When comparing with the traditional coated PbI₂ film shown in (a), a more transparent feature can be seen on the spin-coated PbI₂ film using PbI₂:DMSO = 1:1 in DMF solution as precursor, as seen in (b). The XRD characterization results well indicated that in the spin-coated PbI₂ (DMSO) film there was only an intermediate PbI₂ (DMSO) phase as resolved at diffraction peak of about 9.9° instead of PbI₂ related peak. After heating treatment, the DMSO was removed and a mesoporous structure of PbI₂ layer was formed as seen in Figure 4d of the main article. The obtained film thickness is measured to be about 150 nm and 220 nm for the conventional and mesoporous PbI₂, respectively.

S13. Thermal gravimetric analysis (TGA) of PbI₂(DMSO)

Figure S13. Thermal gravimetric analysis (TGA) of (a) the synthesized $PbI_2(DMSO)$ powder¹ and (b) the scraped powder from the spin-coated $PbI_2(DMSO)$ film on the substrate after the thermal treatment. The measurements were performed on SDT-Q600 (TA Instruments) Simultaneous TGA/DSC instrument at 5 °C per minute heating rate from 25 °C -200 °C. The TGA feature shown in (a) well agrees with the previous report¹ and indicates that the DMSO started decomposing from PbI₂(DMSO) complex at temperature about 80 °C and was fully removed at about 136 °C. The constant TGA curve without weight-loss shown in (b) indicated that the DMSO has been completely removed in the thermal treated PbI₂(DMSO) film, leaving only PbI₂ on the substrate.

S14. Hysteresis property of the conventional PbI_2 layer based PSC device

Figure S14. (a) *J-V* curves of a conventional PbI_2 layer based PSC measured under forward and reverse scans. The measurement was taken in air ambient at humidity of about 60%.

S15. J-V curves for a PSC device measured under different scan rates

Figure S15. *J-V* curves for a fabricated perovskite solar cell measured under different scan rates: 250, 188, 150, 100, 75 and 50 mV/s. The corresponding PV parameters extracted from *J-V* curves are shown in **Table S3**.

Scan rate (mV/s)	$V_{\rm oc}$ (V)	$J_{\rm sc}$ (mA cm ⁻²)	FF	PCE (%)
250	1.04	22.30	0.79	18.35
188	1.05	22.02	0.79	18.22
150	1.05	21.91	0.79	18.27
100	1.05	21.77	0.80	18.20
75	1.05	21.79	0.79	18.16
50	1.05	21.66	0.79	18.00

Table S3. Summarized PV parameters of the *J-V* curves shown in Figure S15.

S16. Long-term stability comparison with the solution process device

Figure S16. (a) Long-term stability comparison for the typical devices fabricated by vaporassisted method and conventional two-step solution based method². All of the devices were fabricated under ambient air with relative humidity (RH) about 40% and then stored in drying cabinet with maintained RH about 15% before measurements. (b) and (c) shows the corresponding *J-V* curves for the freshly fabricated devices and aged devices, separately. The PV parameters were summarized in Table S4.

Cell	$V_{\rm oc}\left({ m V} ight)$	$J_{\rm sc}$ (mA cm ⁻²)	FF	PCE (%)
Vapor-assisted (fresh)	1.05	21.98	0.75	17.38
Solution method (fresh)	1.04	21.11	0.73	15.86
Vapor-assisted (aged)	1.05	21.05	0.70	15.61
Solution method (aged)	1.00	15.78	0.52	8.32

Table S4. PV parameters of the PSC devices shown in Figure S16.

References:

- 1. W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Science*, 2015, aaa9272.
- 2. J. Yin, J. Cao, X. He, S. F. Yuan, S. B. Sun, J. Li, N. F. Zheng and L. W. Lin, *J. Mater. Chem. A*, 2015, **3**, 16860-16866.