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ARTICLE

Supporting Information

Crystallization Manipulation and Morphology Evolution for Highly Efficient Perovskite Solar Cells Fabrications via Hydration Water Induced Intermediate Phase Formations under Heat Assisted Spin-coating

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Experimental Section

Materials: PEDOT: PSS (P VP AI4083) was purchased from Heraeus Clevios. Lead acetate trihydrate ($\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$) was purchased from Aladdin Industrial Corporation. Methylamine iodide (MAI) was purchased from Xi'an Polymer Light Technology Corporation. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was purchased from SunaTech Inc. PC_{61}BM was purchased from Nano-C Tech. DMF, isopropyl alcohol (IPA), and chlorobenzene (CB), were purchased from Sigma-Aldrich. ITO and ITO-PEN was purchased from Wu Han Jinge Solar Energy Technology Co. Ltd. China.

Fabrication of $3\text{MAI}:\text{PbAc}_2 \cdot x\text{H}_2\text{O}$ precursor solution: $3\text{MAI}:\text{PbAc}_2 \cdot x\text{H}_2\text{O}$ precursor solutions were prepared according to a previously reported method.¹ To generate the $3\text{MAI}:\text{PbAc}_2 \cdot x\text{H}_2\text{O}$ precursor solution with x equal to 0, $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ was first heated to 110 °C for 12h in the glove box to get anhydrous PbAc_2 . $\text{PbAc}_2 \cdot x\text{H}_2\text{O}$ was then obtained by mixing PbAc_2 with $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ at a molar ratio of $(3-x):x$. Finally, MAI and $\text{PbAc}_2 \cdot x\text{H}_2\text{O}$ were dissolved in anhydrous N, N-dimethylformamide at a 3:1 molar ratio with the concentration of 45 wt%.

Fabrication of Perovskite Solar Cells: The device structure is ITO glass (ITO-PEN)/PEDOT: PSS/Perovskite/PCBM/BCP/Ag. ITO glass or ITO-PEN substrates was sequential ultrasonic washed in detergent, deionized water, acetone, and isopropanol. Then, the substrate was dried in an oven and treated in an ultraviolet-ozone chamber for 20 min. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios P VP AI4083) aqueous solution filtered through a 0.45 μm filter tip was spin-coated at 4000 rpm for 50 s on the ITO glass or ITO-PEN substrate, and then baked at 130 °C for 20 min in air. Subsequently, the substrate was transferred to the nitrogen-filled glove-box. Perovskite films were spin-coated from the prepared precursor solution with different temperatures from 70 °C to 95 °C at a speed of 4000 rpm for 50 s by heat assisted spin-coating process (HASP), where the substrate temperature was kept at 90 °C, and annealed on the hot plate at 90 °C for 10 min. For the conventional one-step process (abbreviated as CP), both the perovskite precursor solvent temperature and the substrate temperature were kept at room temperature, and annealed on the hot plate at 90 °C for 10 min. The spin-coating time was varied for optimization according to the temperature and DMF atmosphere in the glovebox. The PC_{61}BM (dissolved in CB, 20 mg mL^{-1}) was spin-coated on top of the perovskite layer at 1000 rpm for 30 s. After that, BCP in IPA was spin-coated at 2000 rpm. Finally, metal silver (100 nm) electrode was thermally evaporated in the vacuum chamber with the pressure of $< 4 \times 10^{-4}$ Pa through a shadow mask. The photoactive areas of the devices are 0.08 cm^2 and 1.2 cm^2 respectively.

We have optimized the experimental conditions by changing the precursor temperatures and keeping the substrate temperature constant. Alternatively, we can also optimize the experimental condition by changing the substrate temperature and keeping the precursor solution temperature constant. Actually we started our experiment work in both ways and found their results were consistent. Thus in this paper we only present our result in the first way.

Characterization of Perovskite Solar Cells: The J-V measurement of the devices under AM1.5G solar 100 mW cm^{-2} simulator illumination (Enlitech Solar Simulator SS-F5-3A) was performed on a computer-

controlled Keithley 2400 Source Measure Unit in air (60% humidity) at room temperature without encapsulation. The external quantum efficiency (EQE) was measured under ambient atmosphere at room temperature using a DSR100UV-B spectrometer with an SR830 lock-in amplifier. The steady-state J_{sc} was measured by recording device photo current under 0.85 V bias. Then steady-state PCE was obtained by multiplying the measured current with 0.85 V bias voltage. A xenon lamp was used as the light source.

Other Characterizations: The TGA was carried out by utilizing thermogravimetric analyzer (FR-TGA-10). The AFM images were obtained by the Bruker Dimension Icon in the ScanAsyst mode. The time-resolved PL spectra were measured at 760 nm on the excitation at 470 nm by the fluorescence spectrophotometer (Horiba-FM-2015, France). Scanning electron microscopy (SEM) images were obtained by field-emission SEM (FEI Nova_Nano SEM 430). The X-ray diffraction patterns were obtained by Bruker ECO D8 (Bruker, Germany). The ultraviolet–visible (UV–vis) absorption spectra of the perovskite films were obtained by the spectrophotometer (Perkin Elmer Lambda 750).

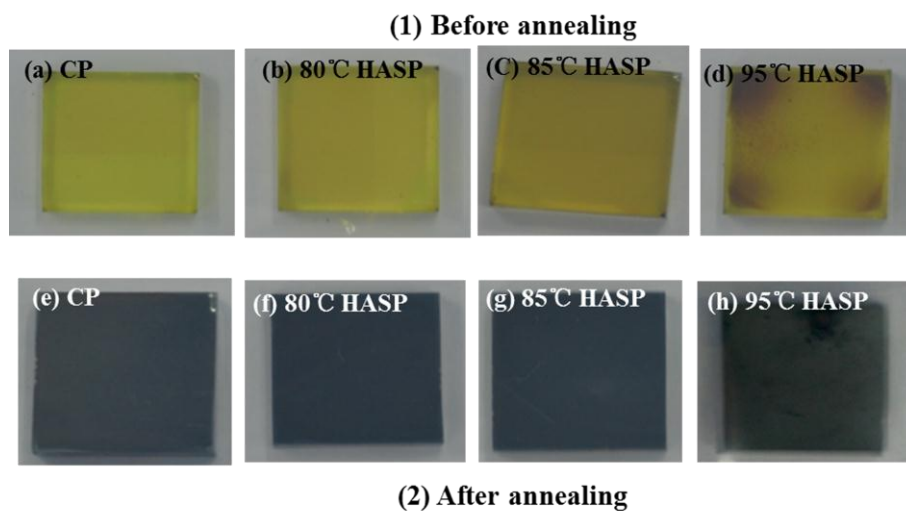


Figure S1. (1) before thermal annealing, (2) after thermal annealing, the image of the perovskite films prepared 3MAI:PbAc₂•3H₂O precursor solution via CP and HASP method contains different temperature of perovskite precursor solution, a,e) CP; b,f) 80 °C HASP; c,g) 85 °C HASP; d,h) 95 °C HASP.

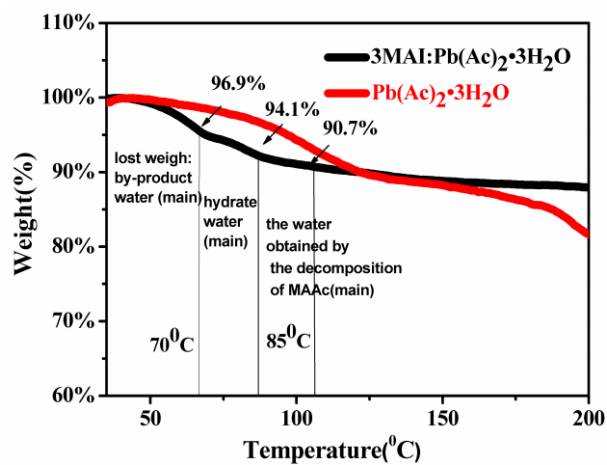


Figure S2. The thermogravimetry analysis (TGA) of $3\text{MAI}:\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ precursor powder and $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ powder.

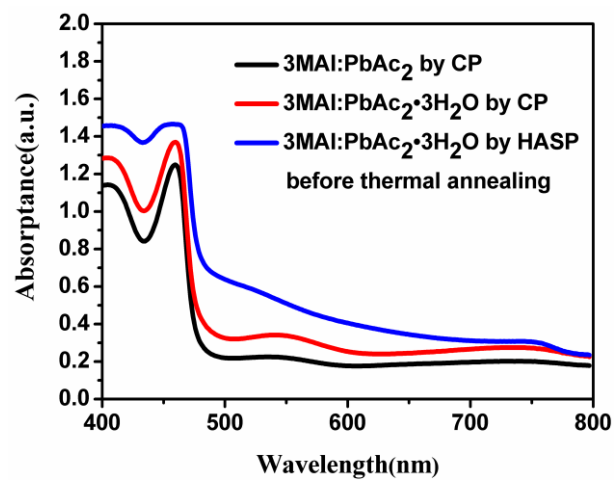


Figure S3. UV--vis spectra for perovskite films prepared with different contents of hydration water in the precursor solutions by the CP or HASP methods (the precursor solution temperature was maintained at 85 °C, the substrate temperature was pre-heated at 90 °C) before thermal annealing.

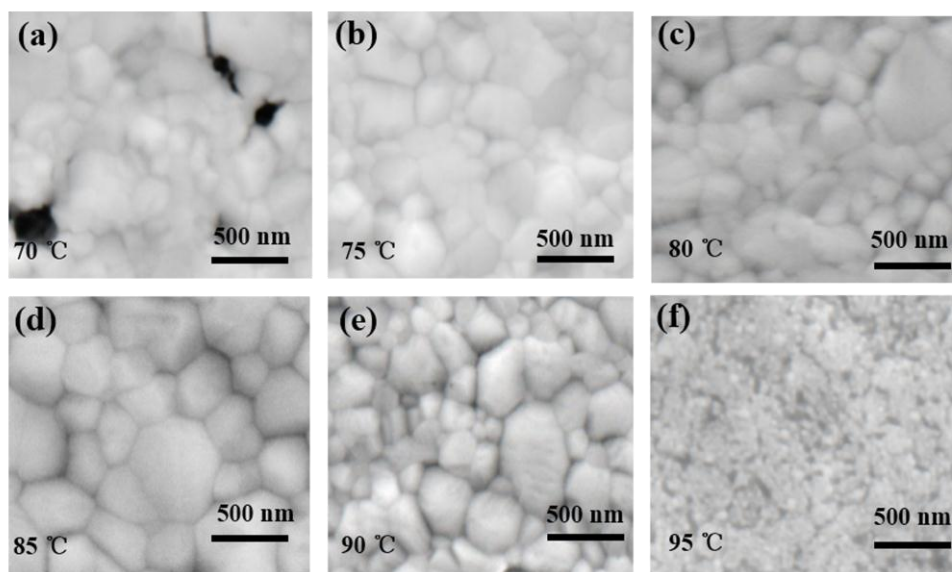


Figure S4. Surface SEM images of the perovskite films fabricated by the heat-assisted spin-coating processing (HASP) from 3MAI:PbAc₂•2.8H₂O precursor solution with different precursor solution temperatures (the substrate temperature was maintained at 90 °C) : a) 70 °C; b) 75 °C; c) 80 °C; d) 85 °C; e) 90 °C; f) 95 °C.

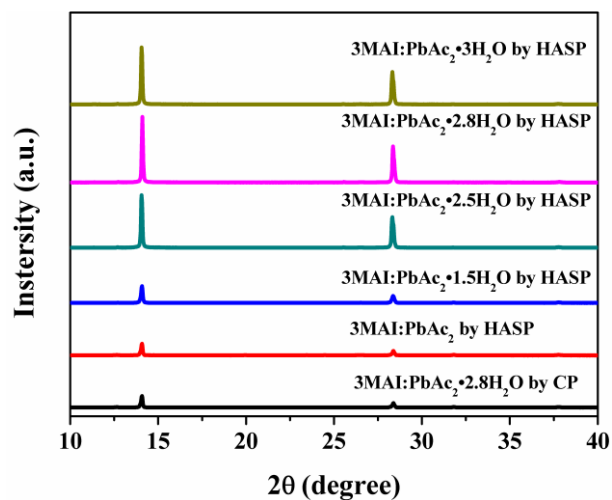


Figure S5. The XRD patterns for perovskite films prepared with different contents of hydration water in the precursor solutions by the CP or HASP methods (the precursor solution temperature was maintained at 85 °C, the substrate temperature was maintained at 90 °C).

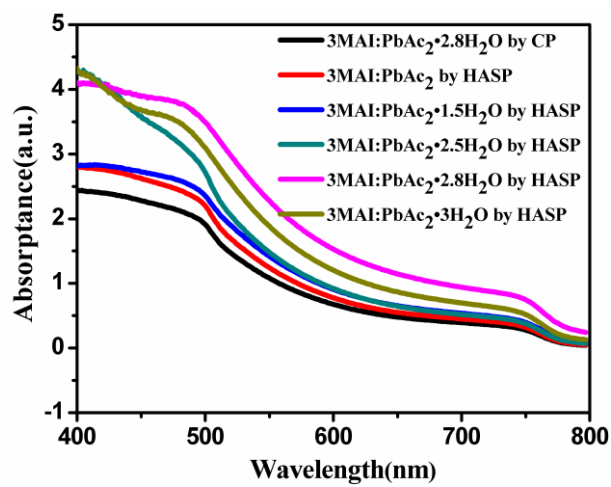


Figure S6. UV--vis spectra for perovskite films prepared with different contents of hydration water in the precursor solutions by the CP or HASP methods (the precursor solution temperature was maintained at 85 °C, the substrate temperature was maintained at 90 °C).

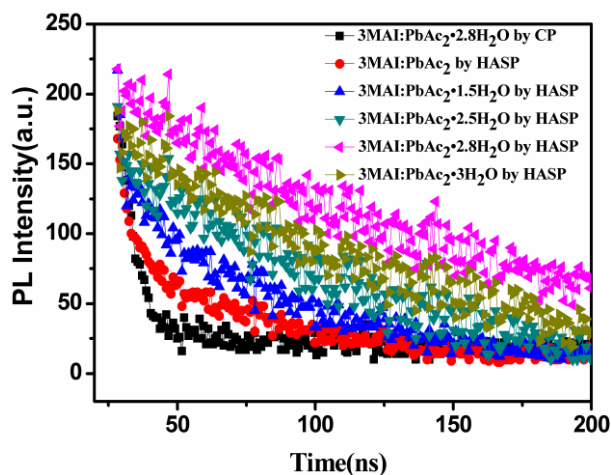


Figure S7. Time-resolved photoluminescence (PL) measurements (TRPL) for perovskite films deposited to ITO/PEDOT:PSS substrate prepared with different ratios of hydration water in the precursor solutions by the CP and HASP methods (the precursor solution temperature was maintained at 85 °C, the substrate temperature was pre-heated at 90 °C). TRPL dynamics was performed by monitoring the PL from the bulk perovskite (excited from side of the capping layer) at 760 nm.

Table S1. The obtained carrier lifetime of the perovskite films prepared with different contents of hydration water in the precursor solutions by the CP or HASP method (the precursor solution temperature was maintained at 85 °C, the substrate temperature was maintained at 90 °C).

Sample	3MAI:PbAc ₂ •2.8H ₂ O by CP	3MAI:PbAc ₂ by HASP	3MAI:PbAc ₂ •1.5H ₂ O by HASP
Lifetime(ns)	33	39	53
Sample	3MAI:PbAc ₂ •2.5H ₂ O by HASP	3MAI:PbAc ₂ •2.8H ₂ O by HASP	3MAI:PbAc ₂ •3H ₂ O by HASP
Lifetime(ns)	92	125	110

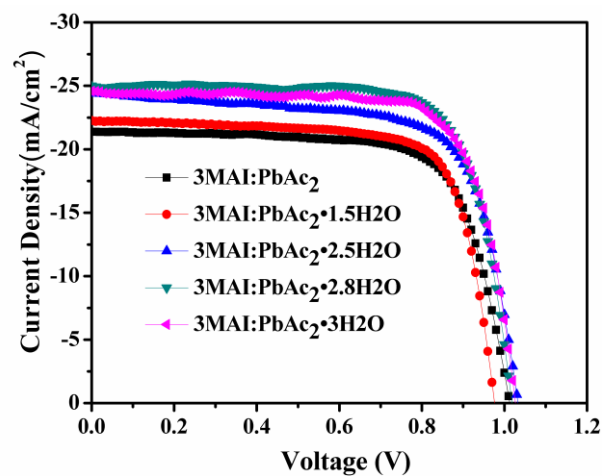


Figure S8. J-V curves of the perovskite solar cells based on different contents of hydration water in precursor solutions by the HASP (the precursor solution temperature was maintained at 85 °C, the substrate temperature was pre-heated at 90 °C), measured under an AM1.5G illumination of 100 mw cm⁻².

Table S2. Photovoltaic parameters of the best cells for each batch with different contents of hydration water in the precursor solution prepared by the HASP method (the precursor solution temperature was maintained at 85 °C, the substrate temperature was maintained at 90 °C). Each batch has 10 devices. The measurement was done under standard AM 1.5G illumination of 100 mW cm⁻² with active area of 0.08 cm².

Device type	champion	Voc(V)	Jsc(mA cm ⁻²)	FF	PCE (%)
3MAI:PbAc ₂	reverse	0.99	21.24	0.71	14.93
	forward	1.01	21.36	0.72	15.62
	average	1.00	21.30	0.71	15.28
3MAI:PbAc ₂ •1.5H ₂ O	reverse	0.99	22.01	0.73	15.90
	forward	0.98	22.26	0.74	16.14
	average	0.98	22.14	0.73	16.02
3MAI:PbAc ₂ •2.5H ₂ O	reverse	1.03	24.36	0.69	17.31
	forward	1.03	24.44	0.70	17.74
	average	1.03	24.40	0.69	17.52
3MAI:PbAc ₂ •2.8H ₂ O	reverse	1.02	24.95	0.75	19.08
	forward	1.02	25.00	0.75	19.12
	average	1.02	24.98	0.75	19.10
3MAI:PbAc ₂ •3H ₂ O	reverse	1.02	24.32	0.73	18.11
	forward	1.02	24.67	0.74	18.62
	average	1.02	24.49	0.73	18.36

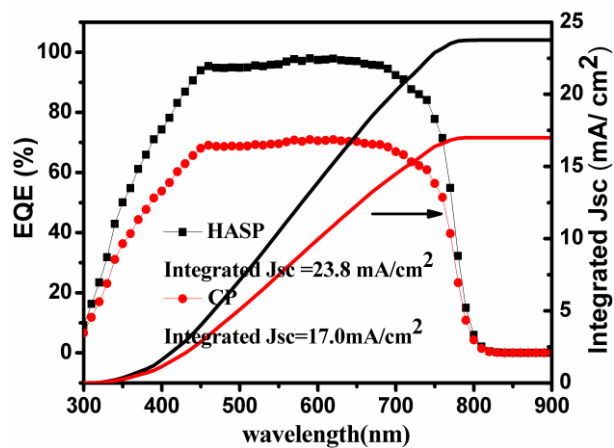


Figure S9. IPCE curves of the cells fabricated using 3MAI:PbAc₂•2.8H₂O precursor solution by the CP (red) or HASP (black) method (the precursor solution temperature was maintained at 85 °C, the substrate temperature was pre-heated at 90 °C).

Table S3. Photovoltaic parameters recorded at a scanning rate of 50 mV s⁻¹ in forward direction for a batch of ten 3MAI:PbAc₂•2.8H₂O-based perovskite devices fabricated by conventional process (CP) measured with an active area of 0.08 cm² under standard AM 1.5G illumination of 100 mW cm⁻².

Device	Voc(V)	Jsc(mA cm ⁻²)	FF	PCE (%)
1	0.85	17.68	0.64	9.61
2	0.89	17.77	0.63	9.96
3	0.89	18.01	0.66	10.57
4	0.84	17.52	0.62	9.12
5	0.85	17.61	0.61	9.13
6	0.84	18.04	0.63	9.54
7	0.86	18.04	0.65	10.08
8	0.87	18.10	0.67	10.55
9	0.88	18.13	0.68	10.84
10	0.90	18.18	0.69	11.28
average	0.86±0.04	17.90±0.28	0.64±0.05	10.36±0.93

Table S4. Photovoltaic parameters recorded at a scanning rate of 50 mV s⁻¹ in forward direction for a batch of ten 3MAI:PbAc₂•2.8H₂O-based perovskite devices fabricated by heat assisted spin-coating processing (HASP) measured with an active area of 0.08 cm² under standard AM 1.5G illumination of 100 mW cm⁻².

Device	Voc(V)	Jsc(mA cm ⁻²)	FF	PCE (%)
1	1.02	24.53	0.74	18.51
2	1.01	24.10	0.72	17.52
3	0.99	3.89	0.71	16.79
4	1.02	24.23	0.73	18.04
5	1.03	23.87	0.72	17.70
6	1.02	24.76	0.72	18.18
7	1.03	24.79	0.73	18.63
8	1.02	24.92	0.74	18.80
9	1.02	25.00	0.75	19.12
10	1.04	23.78	0.73	18.05
average	1.02±0.02	24.4±0.68	0.73±0.02	18.23±0.91

Table S5 Material inventory of 1 m² of PSCs with structure of PEN-ITO/PEDOT:PSS/CH₃NH₃PbI₃/PCBM/BCP/Ag.

Materials	Thickness	Weight(g/m ²)	Power (W/m ²)
PEN-ITO	1.6 um	5.3	(one-sun) 1000W/m ² ×PCE
PEDOT:PSS	50 nm	1.8×10 ⁻⁴	
CH ₃ NH ₃ PbI ₃	400 nm	0.6	=1000×14.87% W/m ²
PCBM/BCP	50 nm	8×10 ⁻⁵	
Ag	100 nm	1.2×10 ⁻³	=148.7 W/m ²
Total		5.9015	

Power-per-Weight = Power/Weight =148.7/ 5.9015 W/g =25.20 W/g

References

- (1) Ling, L; Yuan, S. J; Wang, P. F; Zhang, H. T; Tu, L; Wang, J; Zhan, Y. Q; Zheng, L. R. *Adv. Funct. Mater.* **2016**, 26, 5028.