## Supporting Information

## High-Air-Flow-Velocity Assisted Intermediate Phase Engineering for Controlled Crystallization of Mixed Perovskite in High Efficiency Photovoltaics

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## **Experimental section**

*Device Fabrication:* Fluorine-doped tin oxide (FTO, Yingkou OPV Tech New Energy Co., Ltd, 15  $\Omega$ /sq,) was patterned by etching with Zn powder and HCl solution, Then the FTO glass cleaned by deionized water and rinsed sequentially with deionized water, isopropanol and deionized water, finally dried with clean dry air. SnO<sub>2</sub> electron transfer layer was prepared through a low-temperature solution process: 22.565 mg SnCl<sub>2</sub>·2H<sub>2</sub>O (Alfa, dihydrate, ACS, 98.0-103.0%) was dissolved in 1 ml isopropanol. The 0.1 mol L<sup>-1</sup> precursor solution was spin coated on FTO glass with a spin rate of 3000 rpm for 30 s, followed by an annealing process at 200°C for 45 min.

The perovskite precursor was prepared by a two-step method. Precursor A: 507.7 mg PbI<sub>2</sub> (Alfa, 99.9985%), 80.7 mg PbBr<sub>2</sub> (Alfa, 99.999%), 172 mg HC(NH<sub>2</sub>)<sub>2</sub>I (Xi'an Polymer Light Technology Corp), and 22 mg CH<sub>3</sub>NH<sub>3</sub>Br (Xi'an Polymer Light Technology Corp) were first dissolved in 1 ml mixed solvent with DMF (Sigma, anhydrous, 99.8%) and DMSO (Sigma, anhydrous, 99.9%) (4:1, volume ratio). Precursor B: 194.9 mg CsI (Alfa, 99.999%) was dissolved in 500  $\mu$ l DMSO. The two solutions were both stirring at 60 °C for 1 h and then precursor B was added into precursor A with a volume ratio 1:19. The mixed precursor was stirring at 60 °C for 1 h again and cooled to room temperature. Perovskite film was fabricated by spin-coating the above precursor in a two-step program: first at 1000 rpm for 5 s and then at 4000 rpm for 65 s. During the second step, the spinning substrate was poured with 250  $\mu$ L of chlorobenzene (Sigma, 99.8%) 45 s prior the end of the program. The substrate was

placed on a hotplate under 85°C for 30 min. The annealing procedure was chosen based on a systematic comparison of different temperature and time. Hole transport layer (HTL) precursor consisting 72.3 mg spiro-OMeTAD, 17.5  $\mu$ L lithium bis(trifluoromethylsulphonyl)imide (Sigma, 99.95%) acetonitrile solution (520 mg mL<sup>-1</sup>), 28.8  $\mu$ L 4-tert-butylpyridine (Sigma, 96%), and 20  $\mu$ L FK 209 Co(III) TFSI salt (Dyesol) acetonitrile solution (300 mg mL<sup>-1</sup>) in 1 ml chlorobenzene. Then, HTM layer was deposited atop perovskite by spin-coating at 3000 rpm for 30 s. Finally, 60 nm Ag was thermally evaporated on the top of HTL.

Film and Device Characterization: Sample microscopic morphologies were characterized by scanning electron microscopy (SEM, FEI QUANTA 450) and atomic force microscopy (AFM, ICON2-SYS). Absorbance spectra were measured by a UVvis spectrophotometer (PerkinElmer Lambda 950). The Crystallinity of perovskite was examined by XRD (D/MAX-2400, Japan) analysis with Cu K $\alpha$  radiation ( $\gamma = 0.1541$ nm). Composition in perovskite film was tested by infrared spectroscopy (IR, EQUINOX55). Electrochemical impedance spectroscopy (EIS) measurements were conducted with an electrochemical workstation (Zennium Zahner, Germany) with a 20 mV amplitude of AC perturbation ranging from 100 mHz to 2 MHz. J-V curves of PSCs were obtained using a Keithley 2450 source meter scanning the devices at 0.1 V/s under simulated AM 1.5 G illumination (100 mW cm<sup>-2</sup>, Solar3A, Newport). Fluorescence spectra (PL) were recorded by Edinburgh LP 920 Laser Flash spectrometer and all the samples were excited using 404 nm light. Transient absorption (TA) setup was based on a regenerative amplified Ti:sapphire laser system from Coherent (800 nm, 35 fs, 6 mJ/pulse, and 1 kHz repetition rate), nonlinear frequency mixing techniques and the Helios spectrometer (Ultrafast Systems LLC). All the samples were excited using 370 nm light.



**Figure S1.** (a) The blue line represents the place we choose to analyze the pressure distribution quantitatively. (b) Corresponding pressure distributions based on HAFV and LAFV respectively.



**Figure S2.** Grain size distributions of perovskite films based on (a) HAFV, and (b) LAFV. (c) XRD patterns, (d) absorbance spectra, and (e) photoluminescence spectra of m-perovskite films based on HAFV and LAFV respectively.



**Figure S3.** Entire SEM images of perovskite films based on HAFV and LAFV with different post-spinning time without annealing.

We would like to emphasize that a precise control over the degree of intermediate phase decomposition under HAFV is also an essential precondition for high-qualified perovskite film. Excessive decomposition in HAFV-(20s + 90s) sample generate too many seed crystals so that some of them have to precipitate right upon others when the substrate is fully covered causing multilayer growth. Thus lots of dislocations and voids are created in the bulk and the crystallinity is also suppressed delivering bad device performance. All in all, it is vital to carry out a precise control over the aerodynamics

to keep the right balance between formation and decomposition of intermediate phase. From the comparative XRD results related to both HAFV and LAFV samples before and after annealing for 60s we can suggest that only the optimized combination of 20s for FSP and 45s for SSP under HAFV can perform the fastest crystal growth under annealing with the largest grain size and the least bulk and surface defects. Photogenerated carriers can transport freely both in the vertical and horizontal directions without the serious interruption of GBs. Since prolonging the time of the second subprocess plays the similar role with enhancing the air velocity, the discussion above should also be the explanation of the infeasibility of stronger air turbulence generated by the metal disk with more fans.



**Figure S4.** XRD patterns of perovskite films based on (a-i) LAFV, and (j-r) HAFV with different post-spinning time and annealing time.



**Figure S5.** IR spectrum of perovskite films based on LAFV and HAFV with different post-spinning time respectively.

In the case of HAFV, one interesting fact is that more solvent molecules are retained rather than being thoroughly removed due to the need for formation of high quality intermediate phase. Considering the deficient reports with respect to the accurate crystal structure of this intermediate phase, we can only conjecture that it contains structural units of PbX, MAX, FAX, CsX, and DMSO with unknown stoichiometric ratio. The peak intensities of S=O (DMSO) stretch vibration is obviously higher for the sample based on HAFV when comparing to the one based on LAFV. Moreover, the stretch vibration wavenumber of S=O (normally at 1042 cm<sup>-1</sup>) has shifted to 1018 cm<sup>-1</sup>, suggesting the solvent molecules are in coordination with other ions in the intermediate phase.<sup>[1]</sup>



**Figure S6.** (a) XRD patterns of final perovskite films based on LAFV and HAFV with different post-spinning time. (b, c) SEM surface images of final perovskite films based on LAFV and HAFV with a post-spinning time of 5s. (d, e) Cross-sectional SEM images of final perovskite films based on LAFV and HAFV with a post-spinning time of 5s.



**Figure S7.** (a) Nyquist plots of HAFV based device under different forward biases. (b) *C*-f plots of HAFV based device under different forward biases. (c) Nyquist plots of LAFV based device under different forward biases. (d) *C*-*f* plot of LAFV based devices under different forward biases.

Sample	Voc V	J <sub>SC</sub> mA cm <sup>-2</sup>	FF %	PCE %
LAFV-(20s + 5s)	0.86	19.87	38.1	6.41
HAFV-(20s + 5s)	1.10	21.22	63.3	14.74
LAFV-(20s + 45s)	1.09	22.09	65.1	15.49
HAFV-(20s+45s)	1.10	22.63	77.0	19.19

**Table S1.** The performance of PSCs based on HAFV and LAFV with different postspinning time.

**Table S2.** Biexponential fitting decay profiles of HAFV and LAFV based FTO/SnO<sub>2</sub>/Perovskite configurations.

Sample	$ au_1$ [ns]	<b>A</b> 1	$ au_2$ [ns]	<b>A</b> 2	$ au_m^{\mathbf{a})}$ [ns]
HAFV	25.26	81.5	289.43	18.5	216.13
LAFV	24.72	87.5	255.49	12.5	162.30
a) 1.C	•				

<sup>a)</sup> $\boldsymbol{\tau}_m$ : mean lifetime;

 $\boldsymbol{\tau}_m$  is calculated as

$$\boldsymbol{\tau}_m = \frac{A_1\boldsymbol{\tau}_1^2 + A_2\boldsymbol{\tau}_2^2}{A_1\boldsymbol{\tau}_1 + A_2\boldsymbol{\tau}_2}$$

## References

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