

## **Supporting Information**

### **Humidity-Insensitive Fabrication of Efficient CsPbI<sub>3</sub> Solar Cells in Ambient Air**

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## Experimental

*Control:* The experiments under  $RH < 1\text{ppm}$  ( $RH=0\%$ ) were prepared in a commercial nitrogen-filled glovebox with circulating filtration system. The experiments under  $RH < 30\%$ ,  $RH=30\% \sim 60\%$  and  $RH > 60\%$  were processed in open air.

*Preparation of  $TiO_2$  layer:* The clean FTO-coated glass substrate was immersed in a 45 mM  $TiCl_4$  aqueous solution for 60 min at 70 °C and washed with distilled water and ethanol, followed by annealing at 200 °C for 30 min in air to form a compact layer.

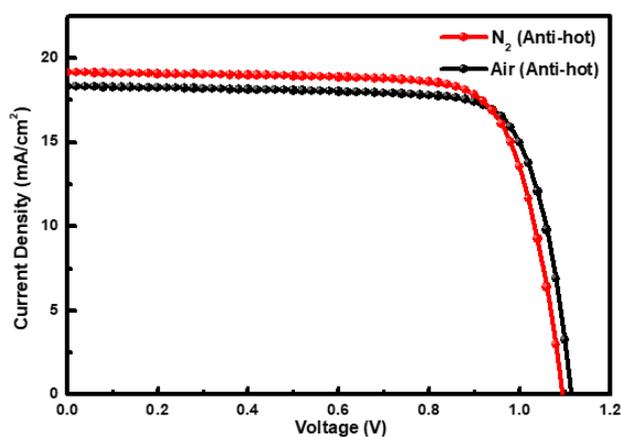
*Fabricated  $CsPbI_3$  PSCs:* The  $CsPbI_3$  precursor solutions and HTL solution were prepared according to the procedure as reported:<sup>[1]</sup> For the Anti-hot method: At first, the  $O_2$ -plasma-treated  $TiO_2$  substrate was heated on the heating stage at 85 °C for 5 minutes before spin-coating. Secondly, the  $CsPbI_3$  layer was prepared via one-step spin-coating onto substrate at 1500 rpm for 10 s and then was increased to 4000 rpm for 40 s. The anti-solvents MA was sprayed into  $CsPbI_3$  films at 25 s. Finally, the films were annealed at 150 °C for 70 minutes for grains growth in open air. Other contrast samples were all fabricated under the same parameters with different conditions. All these steps were operated in the open environment with different humidity. The HTL film was deposited by spin-coating the HTL solution onto the  $CsPbI_3$  film at 5000 rpm for 30 s, with following to anneal on the heating stage about 5min in 75 °C. After spin-coating, a 100-nm-thick gold electrode was then thermally evaporated onto the HTL-coated film.

*Characterization:* The SEM micrographs, EDS and cross-section SEM images of device were characterized by FESEM (SEM, Jeol SU-8020). Absorbance spectra were collected using a Shimadzu UV-3600. The PL spectra were measured using a PicoQuant

FluoTime 300. XRD patterns of the samples were obtained using a D/Max-3c diffractometer (DX-2700) with Cu K $\alpha$ . The J-V measurement was performed via the solar simulator (SS-F5-3A, Enlitech). The EQE data were obtained by using the solar-cell spectral-response measurement system (QE-R3011, Enlitech).

### Reference:

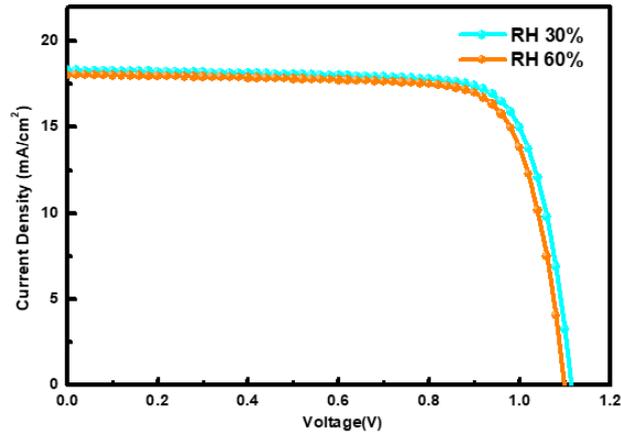
- [1] H. Wang, H. Bian, Z. Jin, H. Zhang, L. Liang, J. Wen, Q. Wang, L. Ding, S. F. Liu, *Chem. Mater.* **2019**, *31*, 6231-6238.



**Figure S1.** J-V curves of the CsPbI<sub>3</sub> PSCs fabricated by Anti-hot method in Air and N<sub>2</sub>.

**Table S1.** Comparison of the J-V characteristics of CsPbI<sub>3</sub> PSCs based on Anti-hot method in open air and N<sub>2</sub> (extracted from **Figure S1**).

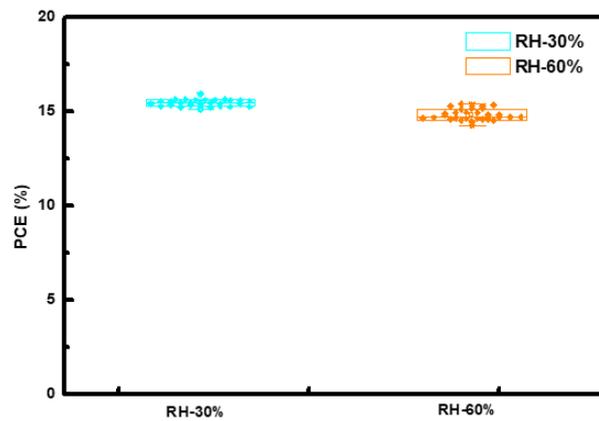
	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF (%)	PCE (%)
<b>Air</b>	18.31	1.11	77.97	15.91
<b>N<sub>2</sub></b>	19.14	1.09	76.61	16.05



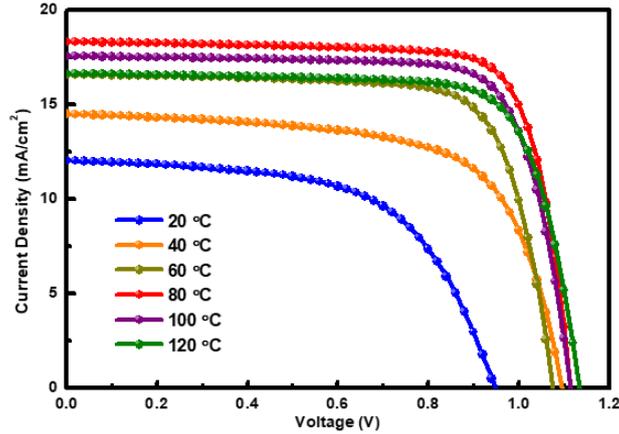
**Figure S2.** J-V curves of the CsPbI<sub>3</sub> PSCs fabricated by Anti-hot method in low (RH~30%) and high (RH~30%) humidity environment.

**Table S2.** Comparison of the J-V curves of CsPbI<sub>3</sub> PSCs based on Anti-hot method in open air under different relative humidity environment (extracted from **Figure S2**).

	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)
<b>RH~30%</b>	18.31	1.11	77.97	15.91
<b>RH~60%</b>	18.03	1.09	77.98	15.39



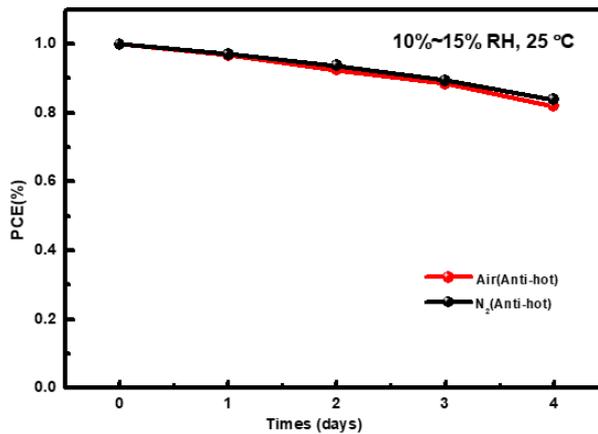
**Figure S3.** PCEs statistics of 30 individuals fabricated by Anti-hot method in air under different ambient moisture (RH~30% and RH~60%).



**Figure S4.** J-V curves of the CsPbI<sub>3</sub> PSCs fabricated by Anti-hot method in air with different substrate temperatures (20 °C, 40 °C, 60 °C, 80 °C, 100 °C and 120 °C).

**Table S3.** Comparison of the J-V characteristics of the CsPbI<sub>3</sub> PSCs based on Anti-hot method in open air with different substrate temperatures (extracted from **Figure S4**).

	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)
20 °C	12.03	0.94	59.13	6.74
40 °C	14.49	1.09	66.20	10.51
60 °C	16.57	1.07	75.12	13.37
80 °C	18.31	1.11	77.97	15.91
100 °C	17.56	1.11	76.78	15.03
120 °C	16.62	1.13	75.99	14.34



**Figure S5.** Long-term stability of the devices fabricated by Anti-hot method in Air and N<sub>2</sub> stored and measured in the open air (10%~15%RH, 25 °C).