

## Supplementary Information

### Spontaneous Configurational Evolution Induced by an in-situ Self-formed p-type CuI Interface Layer in Perovskite Solar Cells

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#### Experimental details:

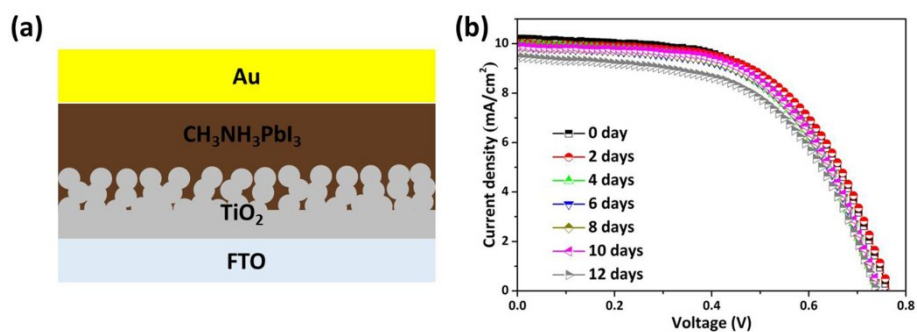
*Synthesis of CH<sub>3</sub>NH<sub>3</sub>I.* The CH<sub>3</sub>NH<sub>3</sub>I was synthesized by reaction of CH<sub>3</sub>NH<sub>2</sub> (27.8 mL, 40 wt% in methanol, Aldrich) and HI (20 mL, 57 wt% in water, Aldrich) at 0 °C for 2 h with stirring. The precipitate was collected by rotary evaporation at 50 °C for 1 h and then washed by diethyl ether for three times. After that, the final CH<sub>3</sub>NH<sub>3</sub>I was collected and dried in vacuum oven for 24 h.

*Fabrication of solar cells.* First of all, FTO glass substrates were in turn cleaned in dilute NaOH hydrous solution, deionized water, acetone, and absolute alcohol by ultrasonic washing for 30 min. Second, the as-cleaned substrates were treated with ultraviolet and ozone for 30 min. The as-treated substrates were coated with a thin compact layer of TiO<sub>2</sub> by spin coating a TiO<sub>2</sub> sol at 5000 rpm for 30 s, followed by annealing at 500 °C for 30 min. Then, a porous layer of TiO<sub>2</sub> was coated by spin coating an ethanol solution of TiO<sub>2</sub> paste at 6000 rpm for 30 s, followed by annealing at 500 °C for 60 min. After that, a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer was deposited by one-step spin

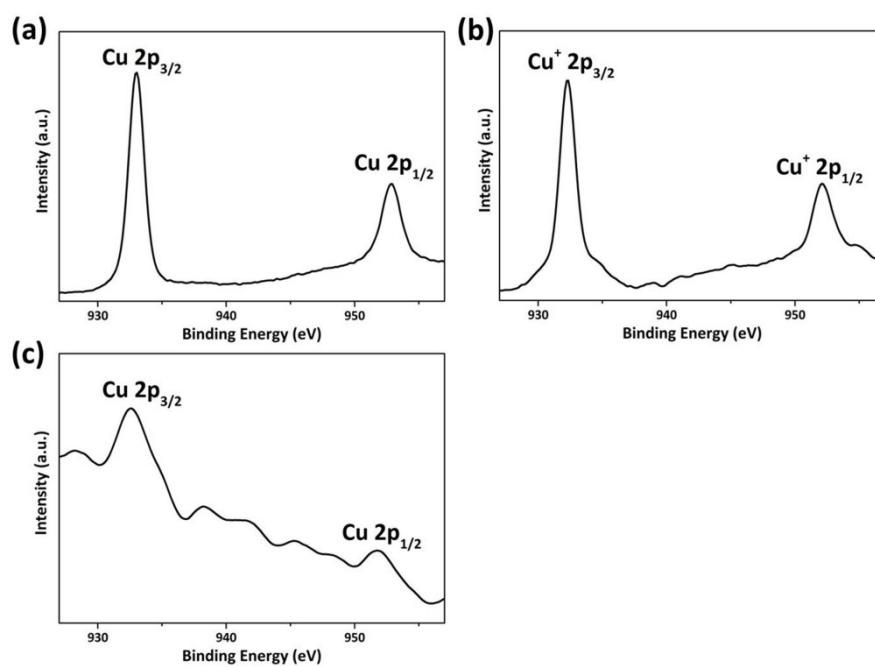
coating a precursor of  $\text{PbI}_2$  (461 mg, 99.999%, Aldrich) and  $\text{CH}_3\text{NH}_3\text{I}$  (159 mg, as-synthesized) in DMF (600 mg, 99.5%, Aladdin) solution and then heated at 60 °C for 2 min and 120 °C for 10 min. Finally, a cathode of copper was deposited on top of perovskite layer by thermal evaporation.

## **Characterizations**

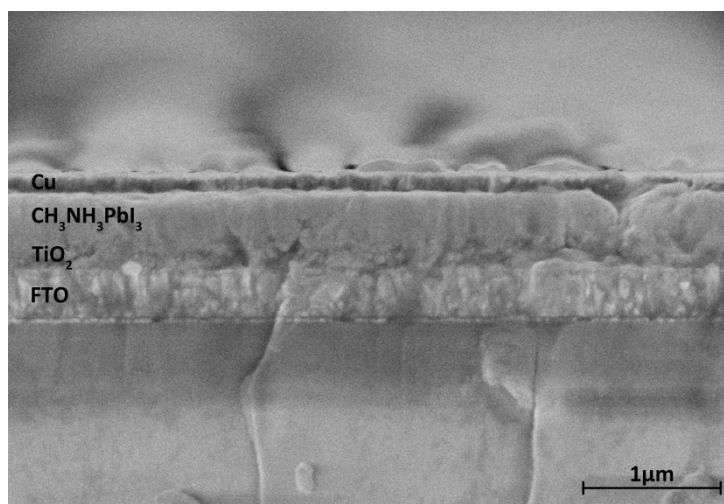
The J-V curves of PSCs were tested with a Keithley 2400 source meter under AM 1.5 illumination using an Oriel 92251A-1000 solar simulator. X-ray diffraction (XRD) patterns were obtained by a Rigaku Ultima III X-ray diffractometer ( $\text{Cu K}\alpha$ ) with the range from 10° to 40°. X-ray photoelectron spectroscopy (XPS) measurement of all samples was performed by PHI-5000 Versaprobe with  $\text{Al K}\alpha$  radiation. Raman spectra were recorded on a Jobin Yvon LabRam with an excitation laser wavelength of 532 nm. A FEI NOVA NanoSEM230 scanning electron microscopy (SEM) was used to obtain the cross-section views of PSCs.



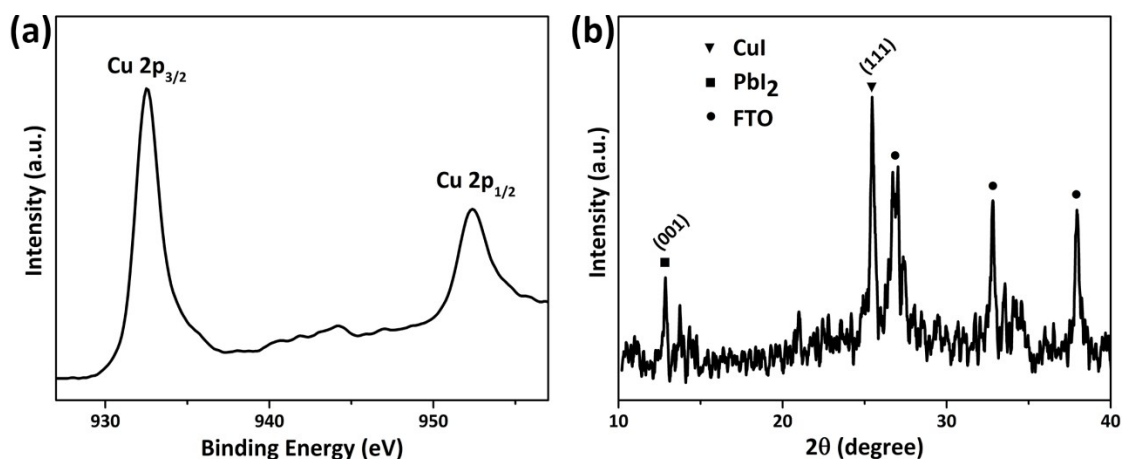
**Fig. S1** (a) Schematic configuration of Au-PSCs. (b) J-V curves of Au-PSCs after different storage days.



**Fig. S2** (a) XPS spectrum of Cu film deposited by thermal evaporation. (b) XPS spectrum of CuI powder. (c) XPS spectrum of Cu cathode peeled off from the Cu-PSCs aged for one week.



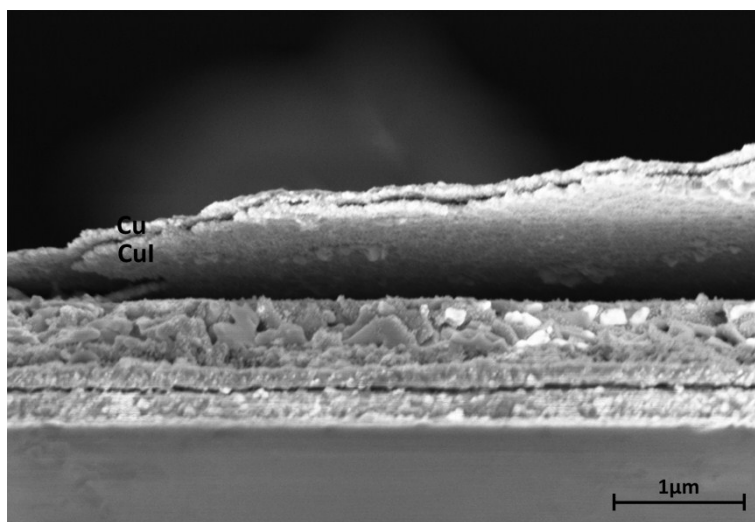
**Fig. S3** Cross-sectional SEM photograph of the pristine Cu-PSCs.



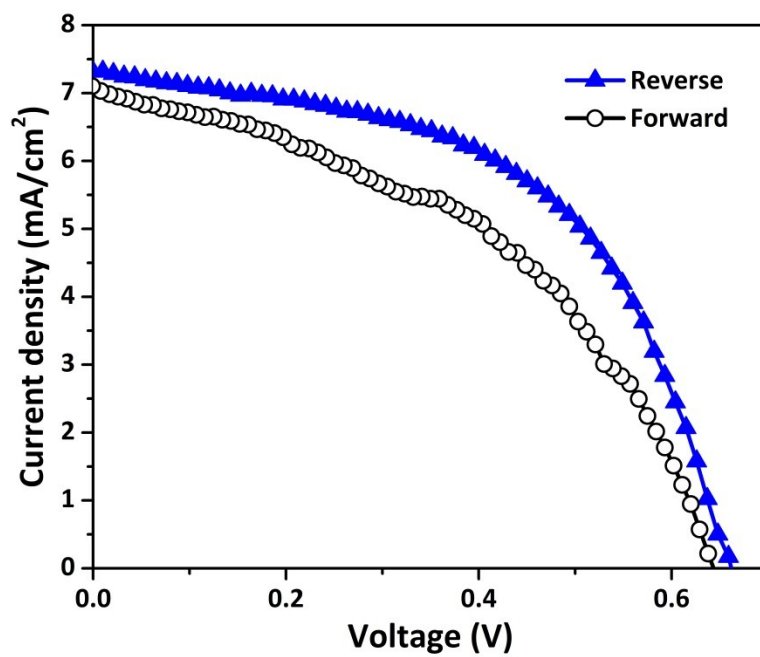
**Fig. S4** (a) XPS spectrum of 8-day aged Cu-PSCs stored in dry nitrogen-filled glovebox. (b) XRD pattern of 8-day aged Cu-PSCs stored in ambient conditions with 60% humidity.

About the mechanism of spontaneous formation of CuI, humidity may play a very important role. We also stored the Cu-PSCs in dry nitrogen-filled glovebox as well as ambient conditions with 60% humidity. XPS measurement was performed to check whether CuI layer was in-situ formed when the cells was stored in glovebox for 8 days. As shown in Fig. S4(a), The two main peaks show symmetric shapes and the binding energy of them were at 932.6 and 954.4 eV respectively, corresponding to the binding energy of Cu  $2p_{3/2}$  and  $2p_{1/2}$  peaks. So, CuI was not formed when the Cu-

PSCs were stored in extremely dry environment. As a contrast, the Cu-PSCs were aged for 8 days in ambient conditions with 60% humidity. XRD measurements of the 8-day aged cells in this condition were performed. As shown in Fig. S4(b), the peaks of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  in XRD pattern were too weak to recognize.  $\text{CH}_3\text{NH}_3\text{PbI}_3$  may be thoroughly degraded because of high humidity. The peak located at  $12.9^\circ$  was clear, which was assigned to the (001) lattice planes of  $\text{PbI}_2$ . This demonstrated the degradation of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . The peak located at  $25.5^\circ$  was assigned to the (111) lattice planes of  $\text{CuI}$ . So,  $\text{CuI}$  could be formed when the cells was stored in high humidity.



**Fig. S5** Cross-sectional SEM image of 30-day aged Cu-PSCs.



**Fig. S6** J-V curves with forward and reverse scans of 10-day aged Cu-PSCs.