## Supporting Information

## Formation of High-quality Perovskite Thin Film for Planar Heterojunction Solar Cells

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**Figure S1.** SEM image of the as-synthesized  $PbI_2$  crystals with the hexagonal geometries (scale bar is  $5\mu m$ ).



**Figure S3.** SEM images of crystal surface of the products after sequential reaction for 10 min with different solvents.



Figure S3. Histogram of surface CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> crystal size synthesized with different solvents.



**Figure S4.** XRD pattern of  $PbI_2$  and  $CH_3NH_3PbI_3$  mixture as a standard sample for the quantitative analysis. The weight ratio between  $PbI_2$  and  $CH_3NH_3PbI_3$  is 7:10.



**Figure S5.** SEM images of the as-prepared  $PbI_2$  films. Scale bars are 2  $\mu$ m and 500 nm, respectively.



**Figure S6.** AFM image of the as-prepared  $PbI_2$  films. Scale bar is 500 nm. Inset is the height profiles of the green lines in the figure.



**Figure S7.** SEM image of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film prepared by a 10 mg/mL CH<sub>3</sub>NH<sub>3</sub>I TBA slution.



**Figure S8.** *J-V* characteristics of a solar cell device by sweeping the voltage from forward to reverse and from reverse to forward bias (scan rate:  $0.15 \text{ V s}^{-1}$ ).



**Figure S9.** *J*–*V* curves for a best-performing cell measured at a simulated AM1.5G solar irradiation under the reverse voltage scan with a scan rate of  $0.15 \text{ V s}^{-1}$ .



**Figure S9.** SEM image of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film prepared in a CH<sub>3</sub>NH<sub>3</sub>I IPA slution. Spiro-OMeTAD was coated to illustrate the foramtion of (A) metal-semiconductor contact region (pinhole through spiro-OMeTAD layer) and (B) large pinhole through perovskite layer.



**Figure S10.** J–V curves in the reverse bias measured under dark condition. The shift from the linear Ohmic shunt current indicates the presence of an additional shunt pathway of non-Ohmic shunt currents. Non-linear dark current in reverse bias may also be an effect of diode breakdown, but this rarely occurs in the voltage range that is typically used for solar cell measurements (up to 1 V).

Cell	V <sub>oc</sub>	J <sub>sc</sub>	FF	PCE
	mV	mA cm <sup>-2</sup>		%
1	965	19.3	0.66	12.32
2	949	19.1	0.66	11.96
3	946	18.9	0.62	11.03
4	952	19.5	0.67	12.44
5	959	19.9	0.64	12.14
6	982	20.3	0.63	12.56
7	967	19.7	0.61	11.70
8	975	20.1	0.66	13.06
9	969	19.2	0.69	12.85
10	985	20.2	0.63	12.56
Average	964.9±13.5	19.63±0.49	0.647±0.025	12.26±0.59

**Table S1.** Photovoltaic parameters of a batch of ten devices measured under 100 mW cm<sup>-2</sup> simulated AM1.5G illumination.