Supplementary Information for
Efficient, High Yield Perovskite Photovoltaic Devices Grown by Interdiffusion of Solution-Processed Precursor Stacking Layers

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1. Experimental details:

CH_3NH_3I precursor synthesis: Methylammonium iodide (CH_3NH_3I, MAI) was synthesized using the method described by Michael M. Lee, *et. al*. A concentrated aqueous solution of hydroiodic acid (HI) (15.0 mL, 57 wt% in water, Alfa Aesar) was reacted with methylamine (CH_3NH_2) (13.5 mL, 40 wt% in aqueous solution, Alfa Aesar) at 0 °C for 2 h with constant stirring under nitrogen atmosphere. Methylammonium was crystalized through removing the solvent by a rotary evaporator. The generated white powder was washed with diethyl ether (Alfa Aesar) three times and dried in vacuum overnight.

Precursor solution preparing and PbI_2 and MAI layer deposition: PbI_2 and MAI were dissolved in DMF and 2-propanol with different concentrations from 130 mg/ml to 450 mg/ml for PbI_2, and from 17.5 mg/ml to 50 mg/ml for MAI, respectively. Both solutions were heated at 100 °C for around 10 min before use to make sure both MAI and PbI_2 can be fully dissolved. The PbI_2 solution was spun on PEDOT:PSS substrate at 70 °C at 6,000 round per second (rpm) for 35 s. Then the PbI_2 film was transferred onto a hot plate quickly and dried at 70 °C. The MAI solution was spun on top of dried PbI_2 film at 6,000 rpm for 35 s at room temperature to get films with thickness ranging from 70-320 nm. The thickness of MAI was obtained by subtract PbI_2 thickness from the total thickness. It is surprise that the MAI layer thickness depends on not only the precursor solution concentration but also the thickness of the underneath PbI_2 layer, which might be caused by the immediate reaction of the precursor upon their contacting. A thicker MAI layer is generally found on thicker PbI_2 layer even using MAI solutions of the same concentration. The spin coated PbI_2/MAI stacking films were dried at 100 °C from 15 min to two hours.

Film characterization: XRD measurements were performed with a Rigaku D/Max-B X-ray diffractometer with Bragg-Brentano parafocusing geometry, a diffracted beam monochromator, and a conventional cobalt target X-ray tube set to 40 KV and 30 mA. The single path absorption was measured using an Evolution 201 UV-Visible spectrometer (thermo Scientific). A Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM) using a field-emission gun (FEG) electron source was used to scan the surface and cross-sectional film morphology. The films were first covered with a thin layer of gold coated using a Cressington 108 Auto Sputter

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Coater before the SEM measurement. The XPS studies were performed by a MgK_α X-ray source (1253.6 eV).

Device fabrication and characterization: PEDOT:PSS (Baytron-P 4083) was spin coated on clean ITO substrate at a speed of 3000 rpm. The film was then annealed at 105 °C for 30 min. PbI_2 (dissolved in DMF) and MAI (dissolved in 2-propanol) with various concentrations were spun on top of PEDOT:PSS substrate subsequently and then annealed at 100 °C for various durations. Then, the PCBM (dissolved in DCB, 2% wt) was spin coated on top of the perovskite layer at 6000 rpm for 35 s. then the films was annealed at 100 °C for 60 min. The device was finished by thermal evaporating C_{60} (20 nm), BCP (8 nm) and Al (100 nm). The device area is defined to be the overlap of the ITO and Aluminum electrodes to be 9.6 mm^2

The steady-state photocurrent curves were measured under simulated AM 1.5G irradiation (100 mW/cm^2) using a Xenon-lamp-based solar simulator (Oriel 67005, 150 W Solar Simulator). For each measurement, the lamp was turned on and the testing started 30 mins later. A Schott visible-colour glass-filtered (KG5 colour-filtered) Si diode (Hamamatsu S1133) was used to calibrate the light intensity before photocurrent measurement. In order to exclude the overestimation of the photocurrent density, an aperture size of 8 mm^2 was used to define the light absorbing area. We used Keithley 2400 Source-Meter for the I-V measurement. For the transient photocurrent measurement, a chopper was used to provide the light pulse with duration of 4-10 seconds, and the photocurrent was recorded using a Keithley 2400 Source-Meter at a bias of +0.8 V. For the light intensity dependent photocurrent, the light intensity change was realized by using neutral density filters of different optical densities.

2. Controlling the thickness of the perovskite layers

Table S1: The thickness of perovskite layers fabricated by the interdiffusion method using precursor solutions with different PbI_2 and MAI concentrations.

MAI / PbI_2	1.75%	2.25%	2.5%	3.0%	3.5%	4.0%	4.5%	5.0%
13%	60-70 nm	80-90 nm	_____	_____	_____	_____	_____	_____
20%	_____	130-140 nm	135-145 nm	_____	_____	_____	_____	_____
25%	_____	_____	160-180 nm	180-190 nm	190-200 nm	_____	_____	_____
30%	_____	_____	180-190 nm	190-200 nm	200-215 nm	_____	_____	_____
35%	_____	_____	_____	205-215 nm	225-240 nm	250-270 nm	_____	_____
40%	_____	_____	_____	_____	250-260 nm	270-300 nm	280-300 nm	_____
45%		_____	_____	_____	_____	280-300 nm	300-320 nm	320-340 nm

3. XPS/UPS characterization of the perovskite film formed by interdiffusion

The perovskite film for XPS and UPS study started from a PbI_2/MAI stacking layer with thickness of 140 nm/190 nm respectively. It was fabricated on ITO/PEDOT:PSS substrate, and was annealed for two hours.

Table S2 Element composition percentage of the peroskite film formed by interdiffusion

	C 1s(%)	O 1s(%)	N 1s(%)	I 3d(%)	Pb 4f(%)
Pristine	22.05	4.6	7.58	52.06	13.7
Annealed	18.08	4.1	6.97	55.17	15.7

4. Film morphology and device performance using the dipping method.

The 140 nm PbI_2 thick film was dipped into MAI solution (10 mg/ml dissolved in 2-propanol). The obtained films are very non-uniform, rough perovskite films, as shown in Fig. S1a. The efficiency of the devices based on these films only reached 3.2%, as shown in Fig. S1b

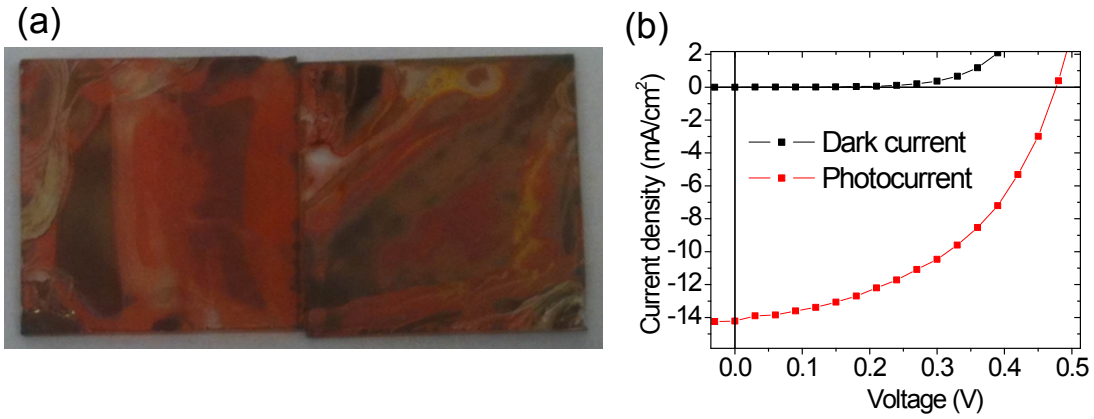

Figure S1. (a) Photo image of the perovskite films deposited by dipping 140 nm PbI_2 film into MAI. The MAI concentration is 10 mg/ml dissolved in 2-propanol. (b) The performance of the devices based on the as-fabricated perovskite film.

5. SEM images of the as-prepared PbI_2 and MAI stacking layer without annealing

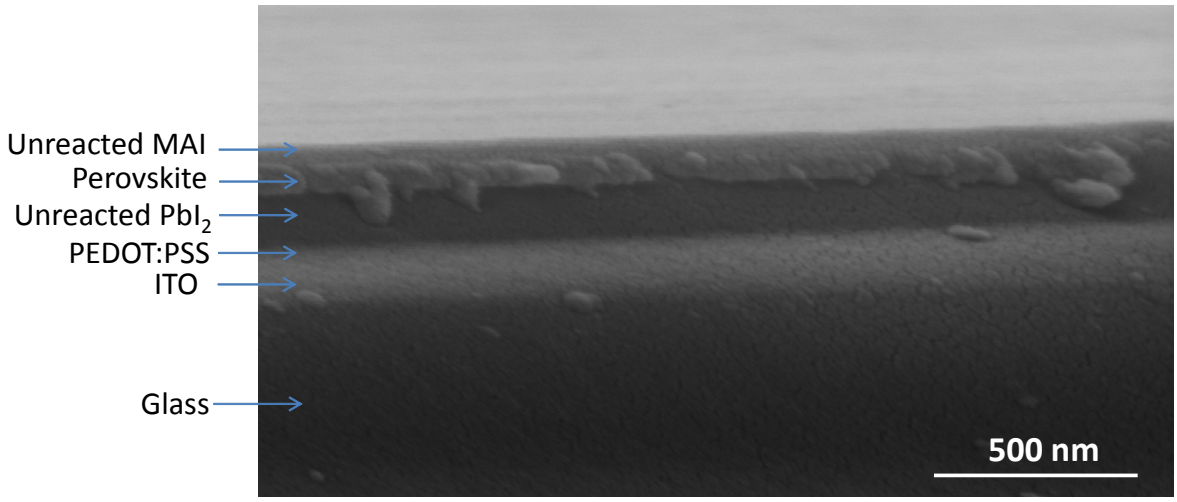

Figure S2 SEM image of as prepared PbI_2 and MAI stacking layer without annealing