Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

A micron-scale laminar $MAPbBr_3$ single crystal for an efficient and stable perovskite solar cell

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Experimental Section

Chemicals and reagents. Lead bromide ($PbBr_2$, 98%), 4-*tert*-butylpyridine (*t*-BP, 96%), bis(trifluoromethane)sulfonimide lithium salt (Li-TFSi, 99.95%), dimethylformamide (DMF, anhydrous, 99.8%) and chlorobenzene (anhydrous, 99.8%) were purchased from Aldrich. 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD) was purchased from Zhuoxin Technology Co. Ltd (Wuhan). Methylamine (CH_3NH_2, 30-33 wt% in methanol) and hydrobromic acid (HBr, 40 wt% in water) were purchased from Aladdin. All chemicals were used as received without any further purification.

CH_3NH_3Br Synthesis. CH_3NH_3Br was synthesized by blending HBr and CH_3NH_2 solution with a molar ratio of 1.5:1 and stirring in ice-water bath for 2 h, then crystallized by reduced pressure distillation and purify by recrystallization with diethyl ether. It was dried in vacuum and stored in N_2 atmosphere.

Device Fabrication. FTO glass (8 Ω/square) was cleaned *via* ultrasonic process with deionized water, alcohol and acetone, successively. A compact TiO_2 electron transportation layer was formed by spin-coating of TiO_2 nanocolloidal solution at 4000 rpm for 40 s and annealing at 500 ℃ for 1 h in ambient air.[1,2] The TiO_2-coated FTO glass was soaking into 0.04 M $TiCl_4$ aqueous solution for 30 min at 70 ℃, and then sinter at 500 ℃ for 30 min. The $MAPbBr_3$ precursor solution prepared by dissolving 1.1 M $PbBr_2$ and MABr with molar ratio of 1:1 in DMF at 60 ℃, and then was injected to the module supplied local heating of 90 ℃. The 'cold' end of the substrate (FTO glass) in the module was exposed to the surroundings temperature, whose actual temperature was measured as 40 ℃. The thicknesses of polytetrafluoroethylene (PTFE) bounding box were 20, 35 and 50 μm, which were used to adjust thickness of laminar $MAPbBr_3$ SCs. The typical growing time is two days. Finally, the $CH_3NH_3PbBr_3$ crystal films grown on FTO or TiO_2 coated-FTO were separated and wiped with filter paper to remove residual solution carefully. Then a hole-transport material solution consisting of 72.3 mg spiro-MeOTAD, 28.8 uL *t*-BP, 9.1 mg Li-TFSi and 1 mL chlorobenzene was spin-coated onto the surface of perovskite at 5000 rpm for 60 s. Finally, an Au layer was deposited by magnetron sputtering.

Characterization. The morphologies, thicknesses and absorption spectra of the sample were examined by scanning electron microscope FE-SEM (Hitachi-SU8010), step profiler (Ambios XP-1) and Shimazu (UV-3600). The phase purity of the samples was characterized by powder X-ray diffraction (XRD) on a Rigaku MiniFlex 600 using Cu Kα radiation (λ=1.5418 Å). The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL, at 540 nm with excitation light of 472.0 nm) were measured *via* Edinburgh Instruments LTD (FLSP920). The photovoltaic performance of PSCs were recorded using a Keithley 2400 source meter under one sun AM 1.5 G (100 mW cm^{-2}) illumination with a solar light simulator (Oriel, Model: 91192) which calibrated with a NREL standard Si solar cell. The active areas of all solar cells were defined by graphics software. The incident photon-to-current conversion efficiency (IPCE) spectra were recorded on a Keithley 2000 multimeter as a function of wavelength on the basis of a Spectral Products DK240 monochromator.

SCLC measurement. The $MAPbBr_3$ SC (thickness of 16 μm) was grown on an insulated glass substrate. The sample was patterned with 120 nm thick Au electrodes, which structured a channel of 0.5 mm. Then, *I-V* characteristic was measured by Keithley 2400 under dark. The trap density (n_{trap}) and mobilty (μ) of sample was calculated by the equation:[3]

$$V_{\mathrm{TEF}} = \frac{e n_{\mathrm{trap}} L^2}{2\varepsilon_0 \varepsilon} \tag{1}$$

$$J = \frac{9\varepsilon_0 \varepsilon \mu V^2}{8L^3} \tag{2}$$

where e is the elementary charge, L is the channel width (0.5 mm), ε_0 is permittivity of vacuum and ε is dielectric constant of $MAPbBr_3$.[4,5] The trap-filled limit voltage (V_{TFL}) was obtained from

I-V curve and the V is the applied voltage in In the Child's regime (cyan).

Transient photovoltage (TPV) and transient photocurrent (TPC) measurement. Steady and transient light intensity were offered by a white LED and laser (455 nm), respectively. For TPV measurement, the transient voltage decay was directly monitored by an oscilloscope with high impedance (1MΩ, Tektronix TDS2014C). The pulse intensity was adjusted to maintain a transient photovoltage signal with an amplitude of about 20 mV. For TPC measurement, a resistor (50 ohms) was load on device forming circuit. The photocurrent signal on the resistor was monitored *via* signal amplifier and oscilloscope.

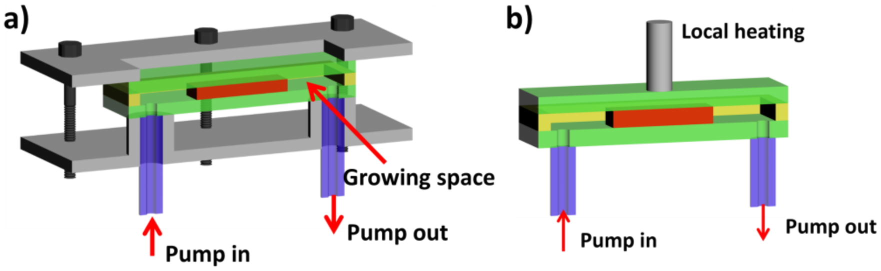

Fig. S1. Schematic diagram of growth module (a) and local heating with homothermal aluminium block (b) for the laminar $MAPbBr_3$ SCs.

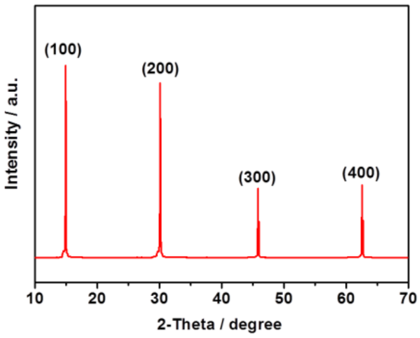

Fig. S2. XRD pattern of the flat $MAPbBr_3$ SC on TiO_2-coated FTO glass.

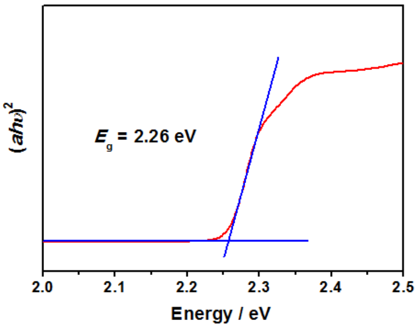

Fig. S3. Calculation of the optical bandgap (2.26 eV) *via* corresponding Tauc plots for the laminar MAPbBr$_3$ SC on TiO$_2$-coated FTO glass.

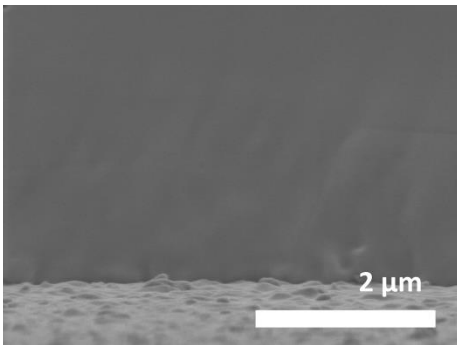

Fig. S4. High magnification SEM the interface of TiO$_2$ coated FTO glass/MAPbBr$_3$ SC.

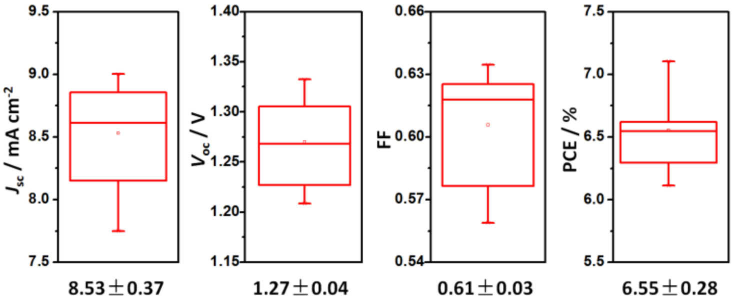

Fig. S5. The box-chart images of photovoltaic parameters for 20 devices which extracted from measuring *I-V* curves at simulated one sun illumination (100 mW cm^{-2}, AM 1.5G).

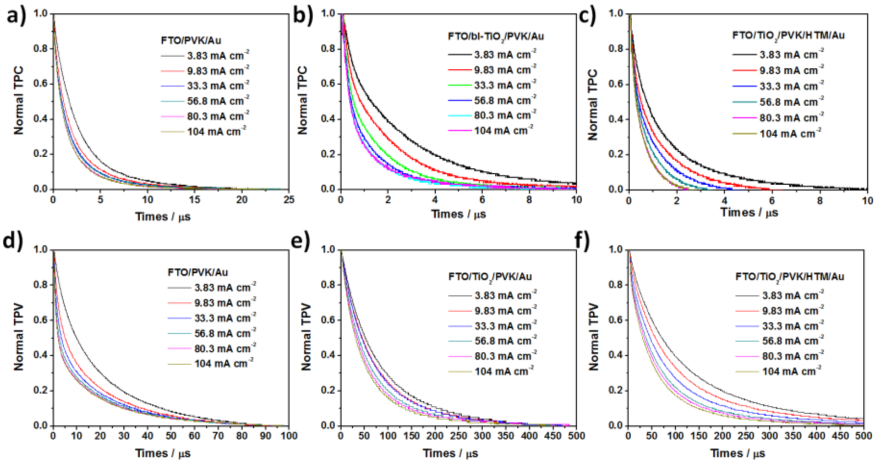

Fig. S6. TPC (a-c) and TPV (d-f) curves of cell (I) FTO/PVK/Au, (II) FTO/TiO_2/PVK/Au and (III) FTO/TiO_2/PVK/HTM/Au.

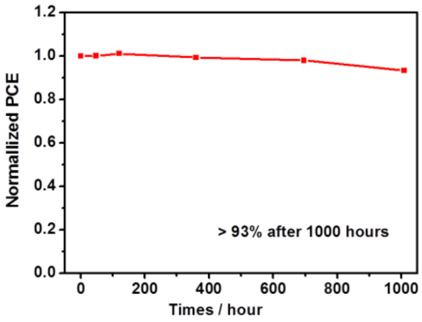

Fig. S7. The stability test of the cell (III) as a function of storage time in dry air without encapsulation.

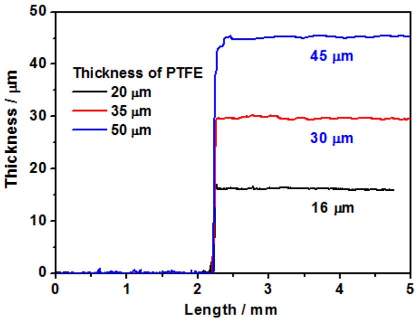

Fig. S8. Thickness curves of laminar $MAPbBr_3$ SCs with different PTFE thin membrane of 20, 35 and 50 µm *via* step profiler.

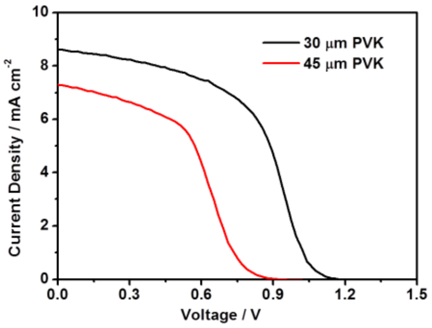

Fig. S9. The *J*-*V* curves of cell (III) with 30 and 45 μm thick $MAPbBr_3$ SC at one sun illumination (100 mW cm^{-2}, AM 1.5G).

Table S1. The values of photovoltaic parameters for cells (I), (II) and (III) extracted from the *J*-*V* curves of Fig. 2c under simulated one sun illumination (100 mW cm^{-2}, AM 1.5G).

Cells	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	PCE/%
(I)	7.77	0.65	0.39	1.98
(II)	8.35	0.91	0.53	4.08
(III)	8.77	1.31	0.62	7.11

Table S2. The detailed parameters bi-exponential fitted from the TRPL at 545 nm with the excitation laser of 472 nm.

Samples	**FTO side**					**PVK side**				
	τ_1 / ns	ratio/%	τ_2 / ns	ratio/%	Avg/ns	τ_1 / ns	ratio/%	τ_2 / ns	ratio/%	Avg/ns
(i)	13.70	8	131.8	92	122.4	90.26	39	373.7	61	262.1
(ii)	7.94	53	42.17	47	23.89	10.00	2	111.4	98	109.2
(iii)	0.28	99	13.39	1	0.42	0.27	99	8.60	1	0.39

Table S3. The values of photovoltaic parameters for cell (III) based on 30 and 45 μm thick laminar $MAPbBr_3$ SC extracted from the *J-V* curves of Fig. S9 under simulated one sun illumination (100 mW cm^{-2}, AM 1.5G).

Cells	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	PCE/%
30 μm	8.62	1.17	0.51	5.10
45 μm	7.62	1.12	0.48	4.10

Refrences

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