Supplementary Information

Roll-to-Roll Printing of Perovskite Solar Cells

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Materials and Methods

Materials

Unless otherwise noted, all chemicals were from Sigma Aldrich and used without purification. PbI_2 (99.9985%), $PbBr_2$ (99.999%), $Sn(OCH(CH_3)_2)_4$ (98% (metals basis), 10% w/v in isopropanol)and SnO_2 (15% in H_2O colloidal dispersion) were purchased from Alfa Aesar. Spiro-OMeTAD(>99.5%) is from Lumtec. ITO glasses are from Colorado Concept Coatings. MAI, FAI, MABr, FABr were from Dyesol.

Perovskite film fabrication

1 M ACN/MA (10% w/w%) based $MAPbI_3$ solution is prepared from MAI and PbI_2, with MAI:PbI_2 (1:1.05), for blade coating, slot-die coating on rigid glass and roll-to-roll slot-die coating on flexible glass. Details of solution preparation can be seen S.I. (Solution and processing optimization for blade coating of $MAPbI_3$ and Fig. S2-S4). For blade-coated $MAPbI_3$ films, following coating parameters are applied: speed: 2.6 m min^{-1}; gap: 150 μm; coating stage temp: 25°C; solution volume: 10 μL $inch^{-2}$. After coating, the films were annealed at 130°C for 10 min. For slot-die coated $MAPbI_3$ films on rigid glass, following coating parameters are applied: speed: 1 m min^{-1}; flow rate: 1 mL min^{-1}; gap: 250 μm; coating stage temp: 25°C. For roll-to-roll slot-die coated films on flexible glass, following coating parameters are applied: coating speed: 0.7 m min^{-1}; flow rate: 0.7 mL min^{-1}; coating roll temp: 25°C, oven length and temperature: 2 m and 100°C. Due to the set-up differences, the slot-die coating on rigid glass is performed where slot-die head is vertical to the ground while in roll-to-roll slot-coating, the slot-die head is horizonal to the ground. The differences in coating speed and flow rate in slot-die coating on rigid substrate and roll-to-roll slot-die coating on flexible substrate is partially come

from such variations in slot-die head setup. FA alloyed solution were prepared by dissolving FAI, MAI and PbI_2 (FAI: MAI: PbI2 as 0.125: 0.875: 1.1) in ACN/MA with 1M concentration. This as-prepared solution is blade-coated with following parameters: speed: 1.6 m min^{-1}; gap: 150 μm; coating stage temp: 25°C; solution volume: 12 μL $inch^{-2}$. Br alloy solution were prepared by dissolving FABr, MABr and PbI_2 (FABr: MABr: PbI_2 as 0.125: 0.875: 1.1). This as-prepared solution is blade coated with following parameters: speed: 1.4 m min^{-1}; gap: 150 μm; coating stage temp: 25°C; solution volume: 12 μL $inch^{-2}$. For spin-coated films. 0.5 M solution of ACN/MA (10% w/w%) based $MAPbI_3$ is prepared from MAI and PbI_2, with MAI:PbI_2 (1:1.05) and spin-coated with following parameters: 2000 rpm for 45 min. All the films were annealed at 130 °C for 10 min after coating. All of the work were performed in ambient environment with relative humidity uncontrolled (typically 10% to 30%).

Solar Cell Fabrication

ITO glasses (Colorado Concept Coatings) were cleaned with deionized water and isopropanol (IPA), and then sonicated in IPA for 15 min, UV-ozone treated for 15 min. For active-layer blade coated or slot-die coated rigid devices, SnO_2 was blade coated (speed: 1 m min^{-1}; gap: 150 μm; coating stage temp: 100°C; solution volume: 15 μL $inch^{-2}$) from 3% (wt%) of aqueous SnO_2 nanoparticle solution. For R2R slot-die coated SnO_2, 5% (w/v%) of $Sn(OCH(CH_3)_2)_4$ in isopropanol solution is R2R slot-die coated (1 m min^{-1}) on IZO coated Corning® Willow® Glass with following parameters: speed: 1 m min^{-1}; gap: 100 μm; flow rate: 0.7 mL min^{-1}. An in-line plasma cleaner is applied right before coating $Sn(OCH(CH_3)_2)_4$. The as-coated $Sn(OCH(CH_3)_2)_4$ is rolled through two 1-meter long oven with a temperature of 220°C. Perovskite films are coated as described earlier. Spiro-MeOTAD is blade-coated Spiro-MeOTAD solution of 72 mg mL^{-1}

with chlorobenzene where 17. 7 μL of Li-TFSI solution (520 mg mL^{-1} in acetonitrile) and 28 μL of 4tBp is added as additives. The blade coating parameters for Spiro-MeOTAD is as follow: speed: 0.5 m min^{-1}; gap: 100 μm; solution volume: 15 μL $inch^{-2}$. 100 nm of gold (thermally evaporated) was chosen to be the top contact. For inverted devices, poly- (3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS, Clevios, HTL Solar) was deposited on the clean ITO glass substrate by spin-coating at 3000 rpm for 30 s and dried at 100 °C for 10 min. After blade-coating of perovskite layer, 30 nm of C_{60}, 10 nm of BCP, and 100 nm of Ag were thermally evaporated.

Material Characterization

The synchrotron *in situ* XRD experiments during blade coating were performed at beamline 7-2 at the Stanford Synchrotron Radiation Lightsource (SSRL).[1] To avoid beam damage, diffractograms are acquired at a frame rate of 18.2 Hz for the first 55 s (50 ms exposure time) and at 0.33 Hz for 30 min (100 ms exposure time), keeping the total exposure time under 4 min. A Dectris Pilatus 300K detector was used. XRD data was analyzed using pygix and pyFAI.[2, 3] After the 400 s, the blade stage temperature is set to 100°C to investigate whether the conversion to perovskite is complete and to monitor the effect of annealing on the film structure. The measurement were performed in heliumto prevent beam damage. Laboratory XRD spectra were taken using a Rigaku D-Max 2200 with Cu Kα radiation. 2D-XRD measurement were done with D-XRD was measured using a D8-Discover (Bruker) with GADDS four-circle detector (general area detector diffraction system). FEI Nova 630 NanoSEM was used to take the SEM images. Absorption measurements were taken on a Shimadzu UV–vis–NIR 3600 spectrometer at room temperature.

Device Characterizations.

J−*V* curves were taken in ambient environment with 100 mA cm^{-2} AM1.5G illumination. The solar simulator was calibrated with an encapsulated Si cell certified by the NREL Cell and Module Characterization group. The device areas are active areas are 0.15 cm^2, defined by a non-reflective shadow mask. The devices were scanned both forward (−0.3 to 1.2 V) and reverse (1.2 V to −0.3 V) scans, which were done at 100 mV s^{-1} without prior voltage bias or light soaking. EQE spectra were recorded with a Newport Oriel IQE 200 in ambient environment.

Thin Film Crystallization

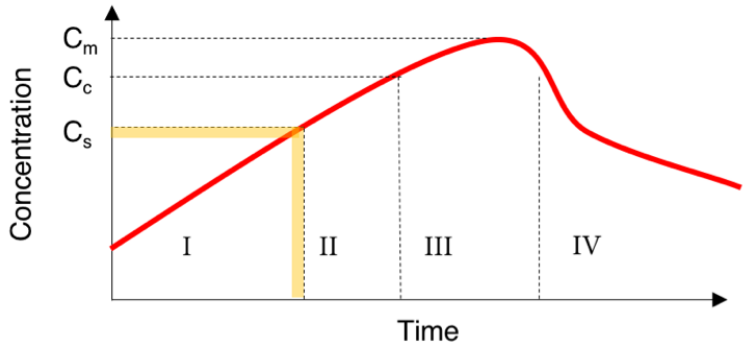

Fig. S1 LaMer Curve represents nucleation and crystal growth processes with concentration variations (solubility limit or C_s; critical concentration point or C_c; and maximum concentration point or C_m).

Solution and processing optimization for blade coating of $MAPbI_3$

MAI:PbI_2 (1:1.05) is dissolved in acetonitrile solution that is charged with methylamine gas (10 w/w%) to form a perovskite solution with a concentration of 1M. Further increasing the concentration will induce to form white precipitates on the bottom of solution vial. The as mixed solution is vortex mixed for 1 min and sonicated for another minute, until a clear yellow solution is formed which indicate a fully dissolved solution is formed.

Fabricating films from this as prepared solution has some major drawbacks. It is hard to control the exact volume of solution used for each of the deposition with this solution because the low boiling point (83 °C) of the solvents and low viscosity (0.25cP) of the solution. Often, before putting (i.e. pushing the pipette) the solution between the blade and substrate, a drop of solution will be dripping. Further, the low viscosity makes the control of the fluid dynamics challenging

as it will flow randomly before applying sheer stress from the blade. Last but not least, the solution evaporates in room temperature that brings inconsistency issues of solution.

To address these drawback, a method is developed to control the viscosity of solution and thus the quality of film coating is by manipulate the solution concentration to reach a highly concentrated solution. As illustrated in Fig. S2 (a-e), such process is achieved by five steps: (1) make a 1M $MAPbI_3$ solution; (2) flow the solution with N_2 gas until the white precipitates start to appear; (3) close the solution vial cap and vortex mix the solution which appears as cloudy; (4) heat the solution at 130 °C for 2 min; (5) cool the solution down to room temperature.

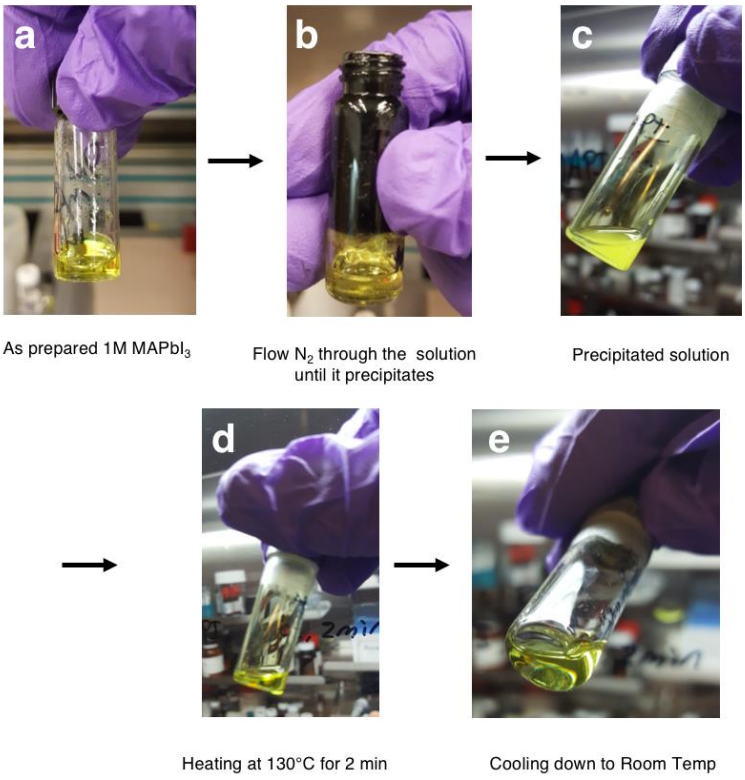

Fig. S2 Solution making process: (a) 1M $MAPbI_3$; (b) Flow N_2 through the solution until it precipitates; (c) precipitated solution; (d) Heat the solution at 130°C for 2 min; (e) Cool down the solution at room temperature

Among the five steps, step (d) is particularly important because if the heating profile is not well controlled, for instance, when heating longer time, then perovskite crystals start to precipitate (Fig. S3) and then hard to dissolve the crystals back to the solution.

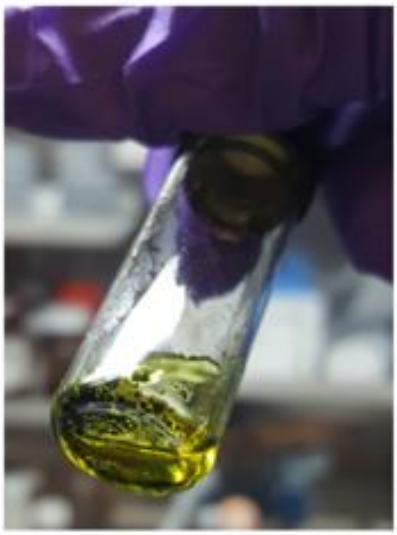

Fig. S3 Over-heated solution

Blade coating speed can be a big factor in determining the morphology of the resulted perovskite films. Depends on the blade coating speed, the film morphology can be categorized into five group (Fig. S4): rough, whitish films (Fig. S4a); uniform smooth films (Fig. S4b); films with whitish lines (Fig. S4c); films with cracks (Fig. S4d); and rough thick (1 μm) films. The morphology in Fig. S4b is what targeted to achieve. The best film morphology (Fig. S4b) is abstained at 2.5 ~ 3 m min^{-1} for the choice of solution.

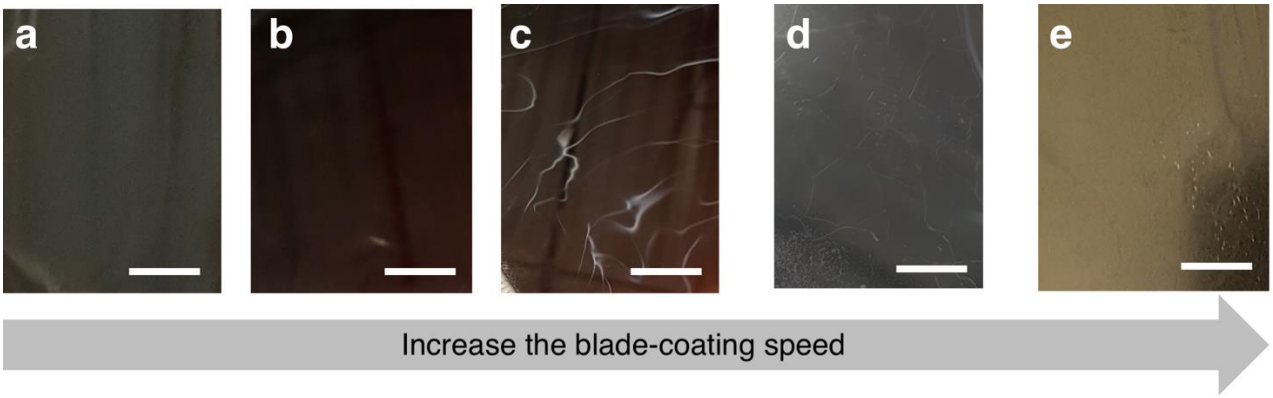

Fig. S4 Representative film morphology evolution at different speeds. (a-e) Coating speed from low to high as 0.8 m min^{-1} in a, 2.6 m min^{-1} in b, 3.2 m min^{-1} in c, 3.5 m min^{-1} in d, 4 m min^{-1} in e. The scale bar is 1 cm.

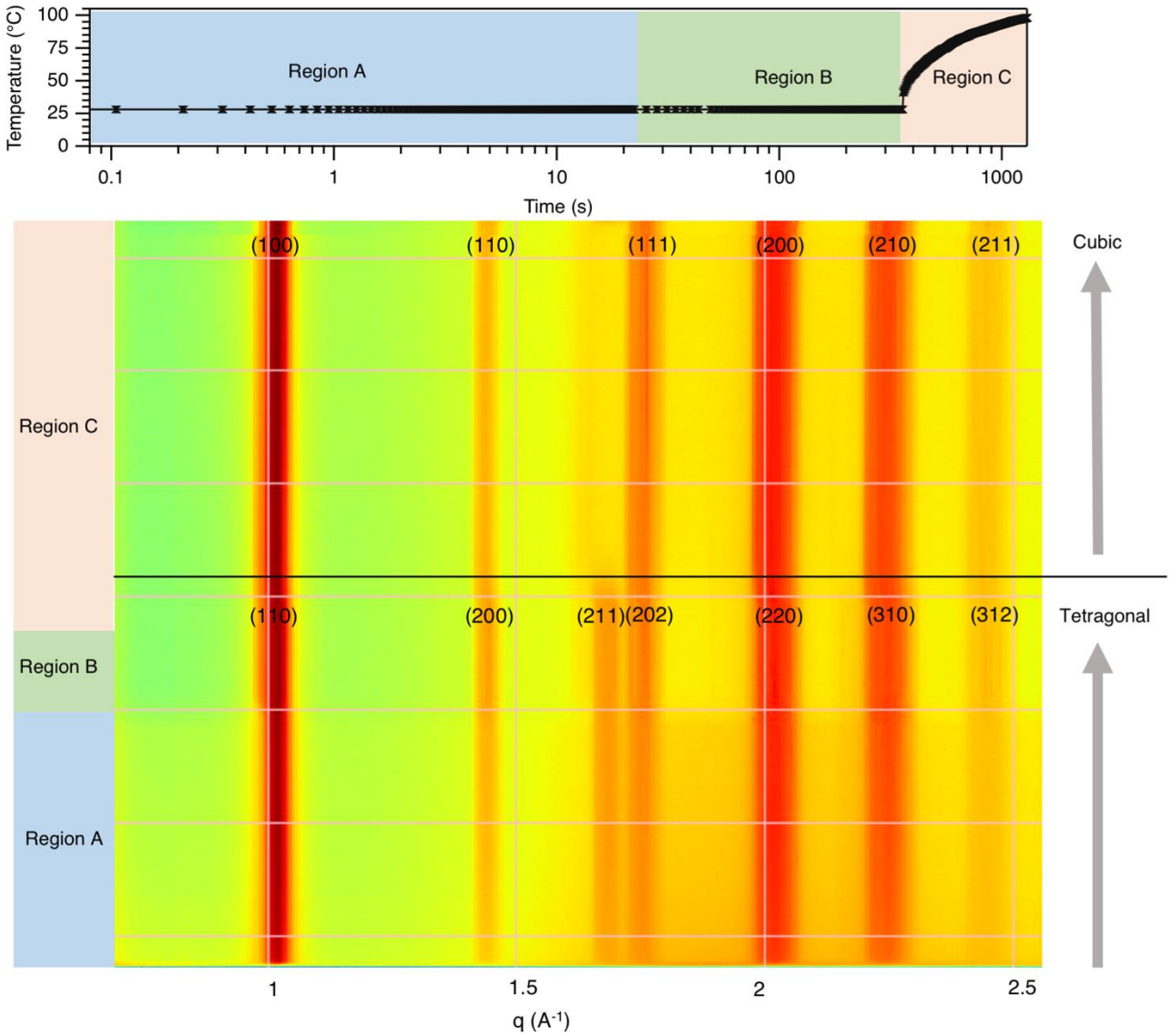

Fig. S5 in situ XRD study temperature profile (top) and resulted data (bottom) for blade coating of $MAPbI_3$. Points on the temperature profile represent X-ray scans where for the first 22s (Region A), the scan interval is 100 ms per scan, and for the rest 1300 s, 3 s per scan. At 360 s (Region B and Region C boundary), the blade stage temperature is increased to 100°C. Phase transition of $MAPbI_3$ can be seen as the tetragonal $MAPbI_3$ (211) at q = 1.66 A^{-1} disappears.

Orientation distribution fit

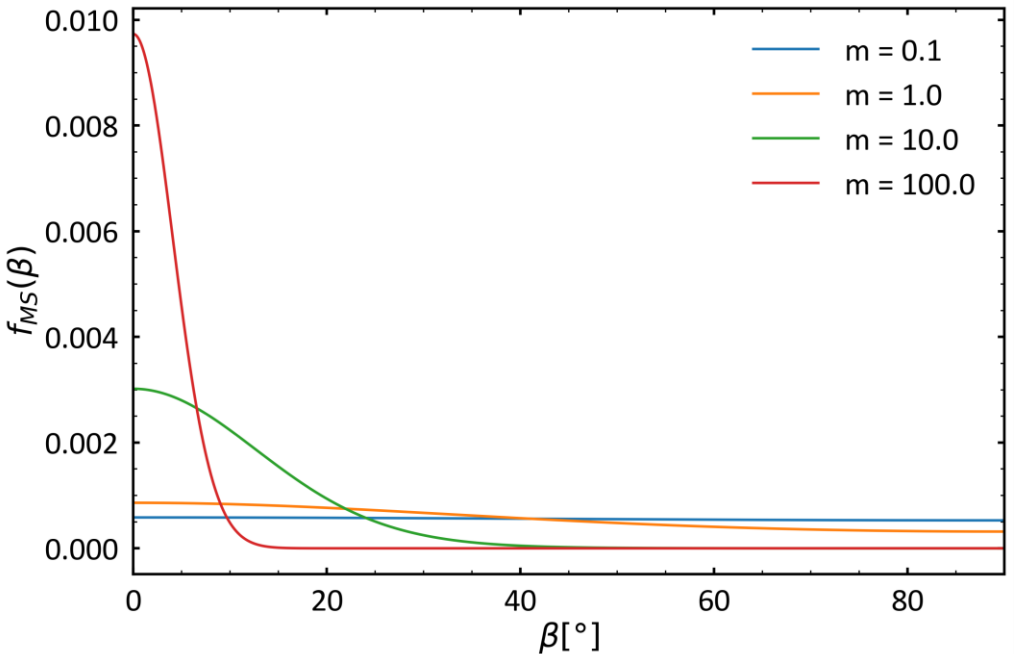

Fig. S6 Implication of Maier-Saupe orientation distribution parameter on crystal orientation distribution function.

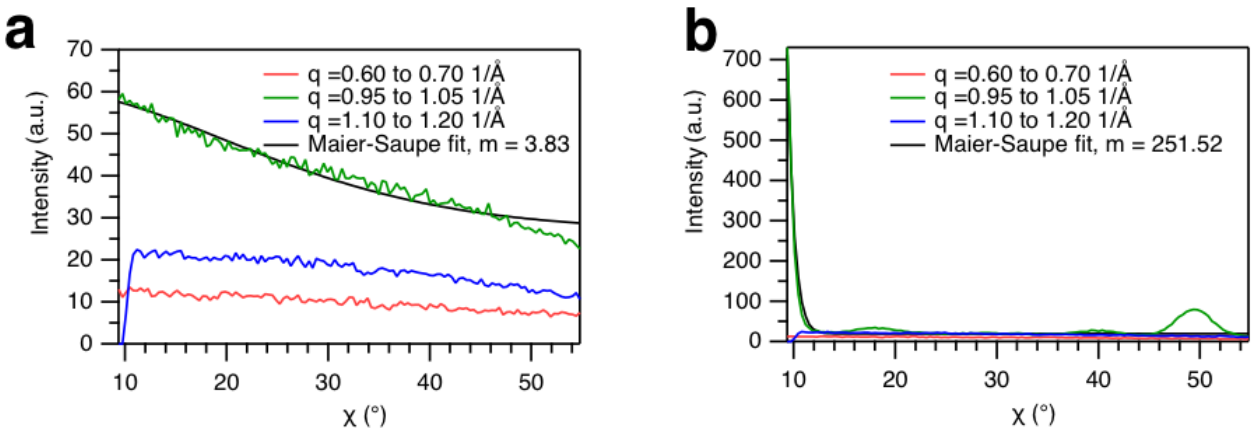

Fig. S7 Maier-Saupe orientation distribution parameter fitting (from ex-situ XRD data) of films from spin – (a) and blade- (b) coating.

Device data, additional SEM images and photograph of coated films

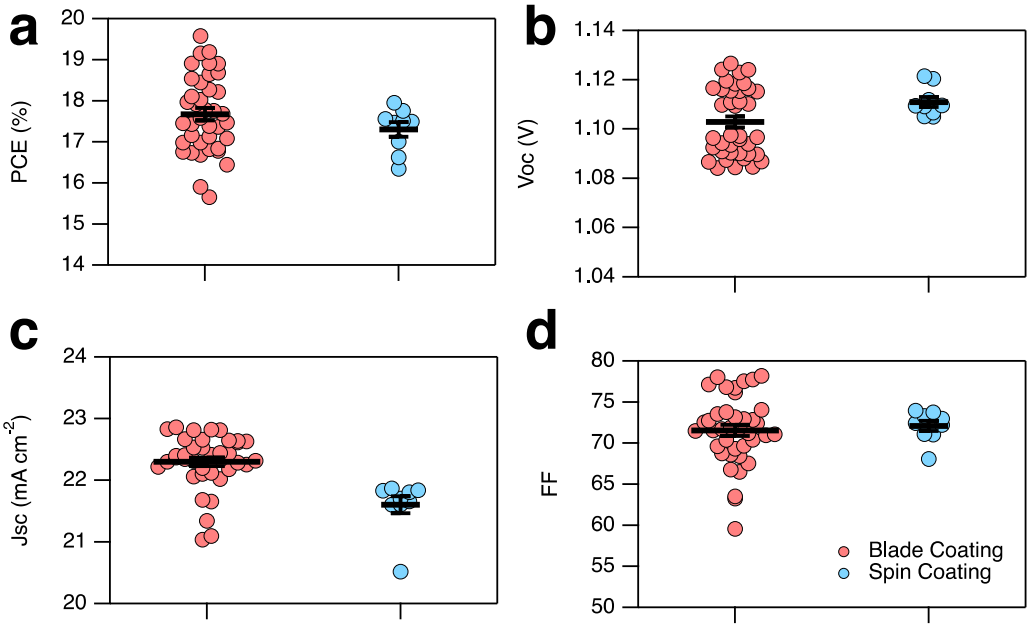

Fig. S8 Device Statistics for blade and spin coating. (a) PCE, (b) Voc, (c) J_{SC}, and (d) FF. Lines represents average values and standard deviations.

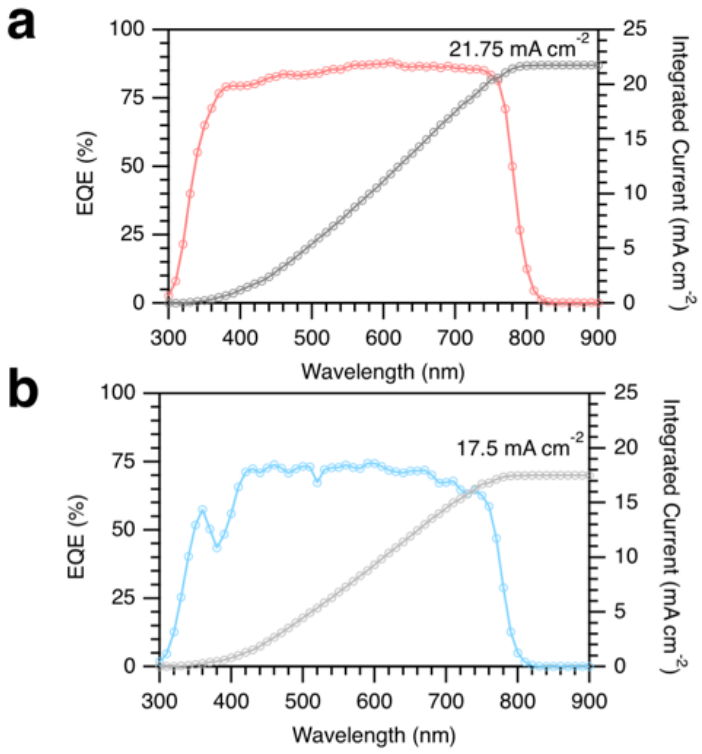

Fig. S9 EQE of champion device for (a) all-blade-coated device and (b)active layer spin coated.

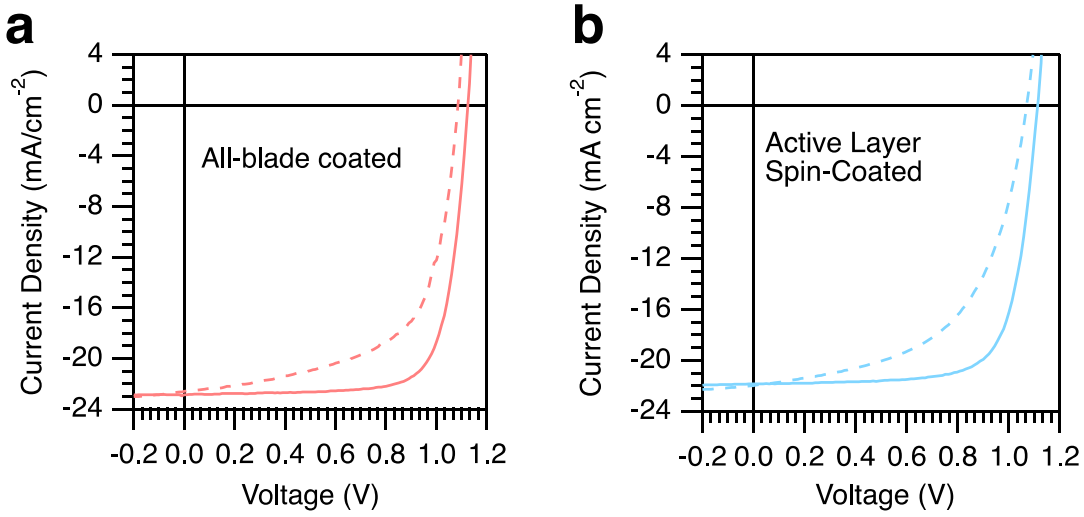

Fig. S10 *J-V* curves of champion device for (a) all-blade-coated device and (b) active layer spin coated.

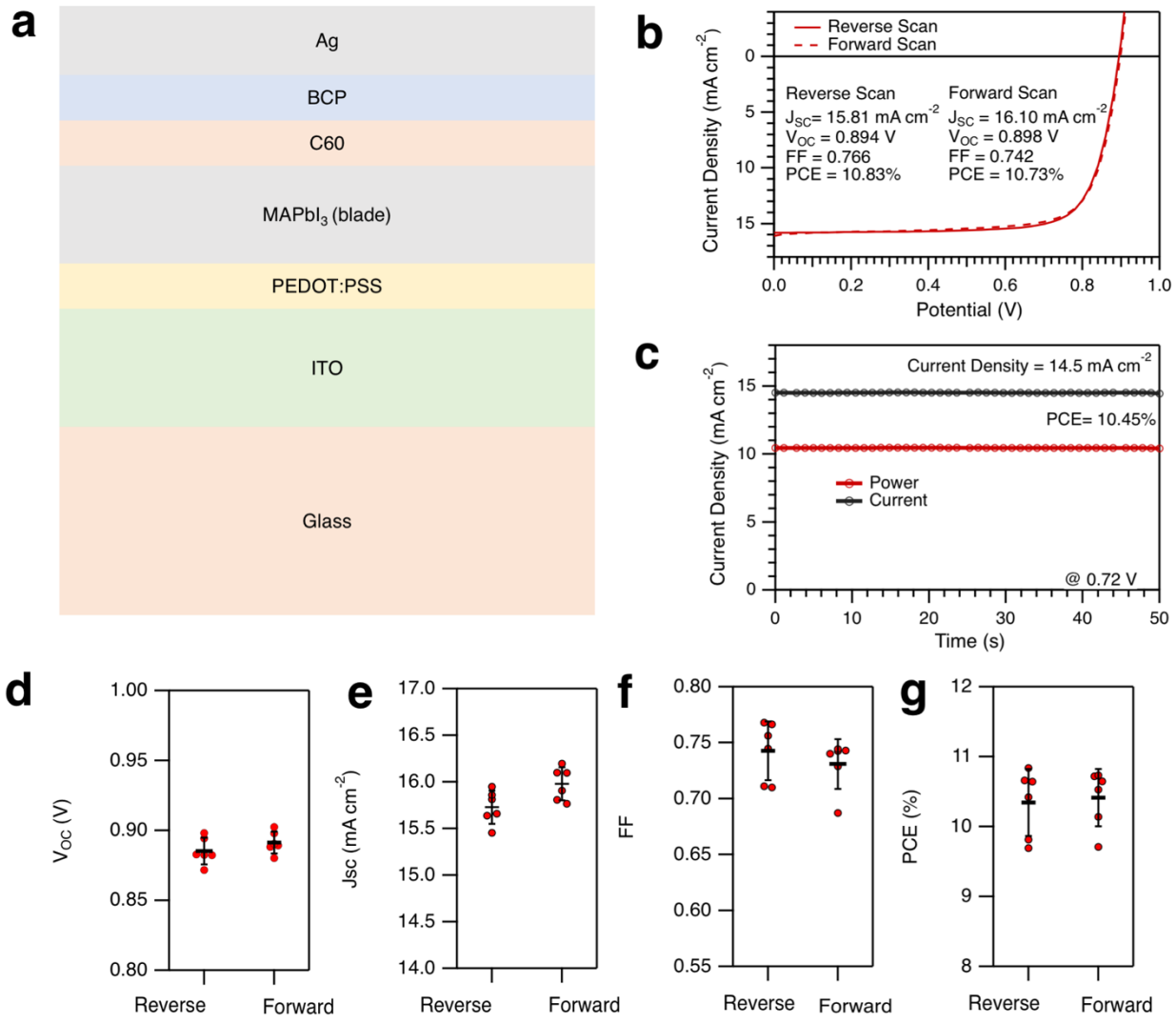

Fig. S11 Inverted Devices. (a) Device Structure. (b) J-V curves. (c) SPO. Device statistics from 10 devices where (d), (e), (f), (g) respectively represent V_{OC}, J_{SC}, FF and PCE.

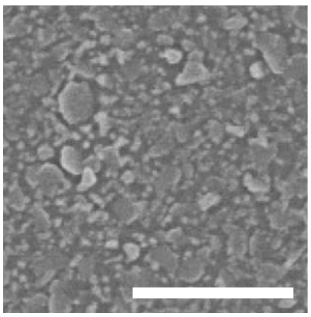

Fig. S12 Top view SEM image of a slot-die coated film (scale bar as 500nm).

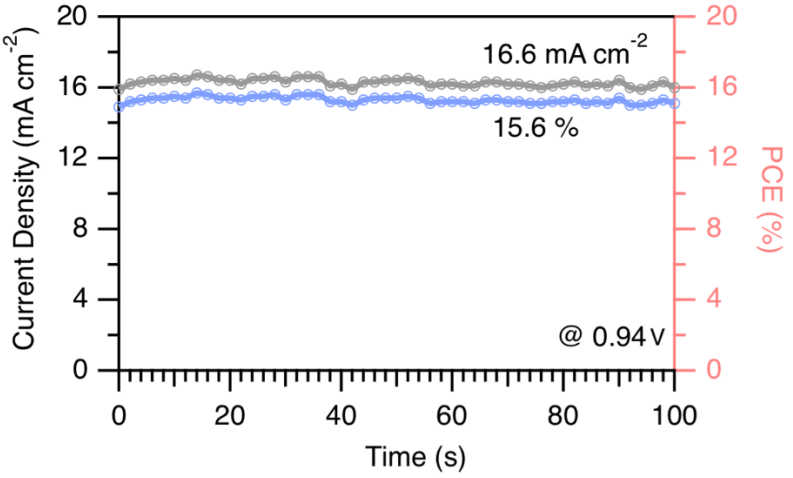

Fig. S13 SPO of the champion slot-die coated device at V = 0.94 V.

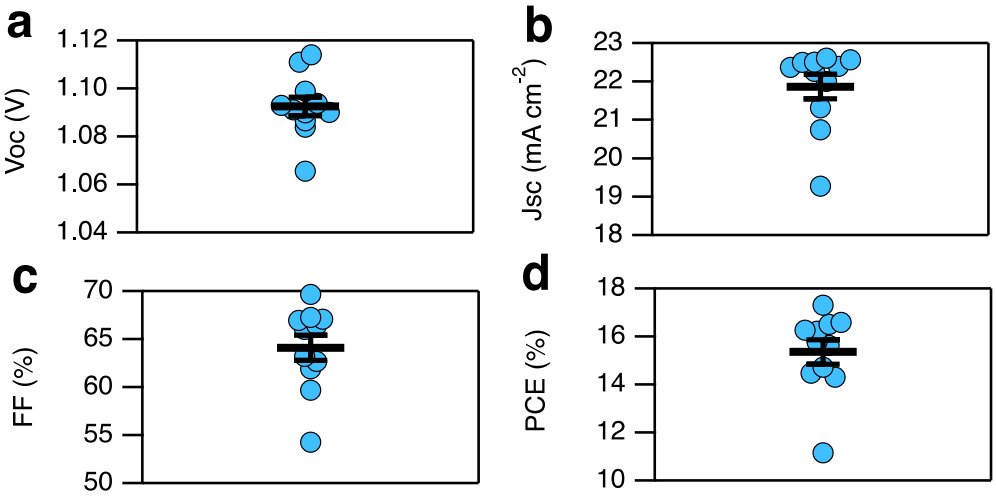

Fig. S14 Slot-die coated device statistics. (a) Voc, (b) Jsc, (c) FF, and (d) PCE, Lines represents average values and standard deviations.

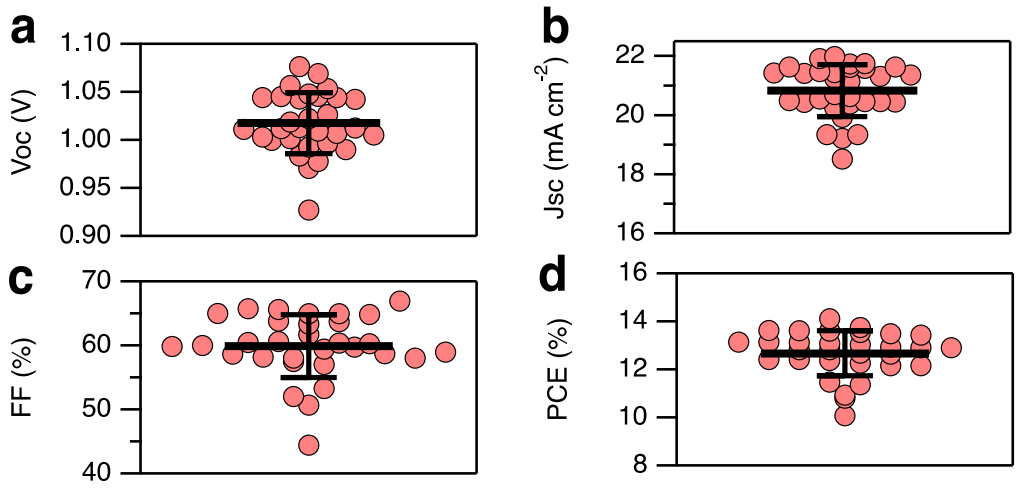

Fig. S15 Device Statistics for devices with R2R coated $MAPbI_3$ films and R2R coated SnO_2 films. Samples were taken from multiple spots all over the 20-meter-long length. (a) Voc, (b) Jsc, (c) FF, and (d) PCE, Lines represents average values and standard deviations.

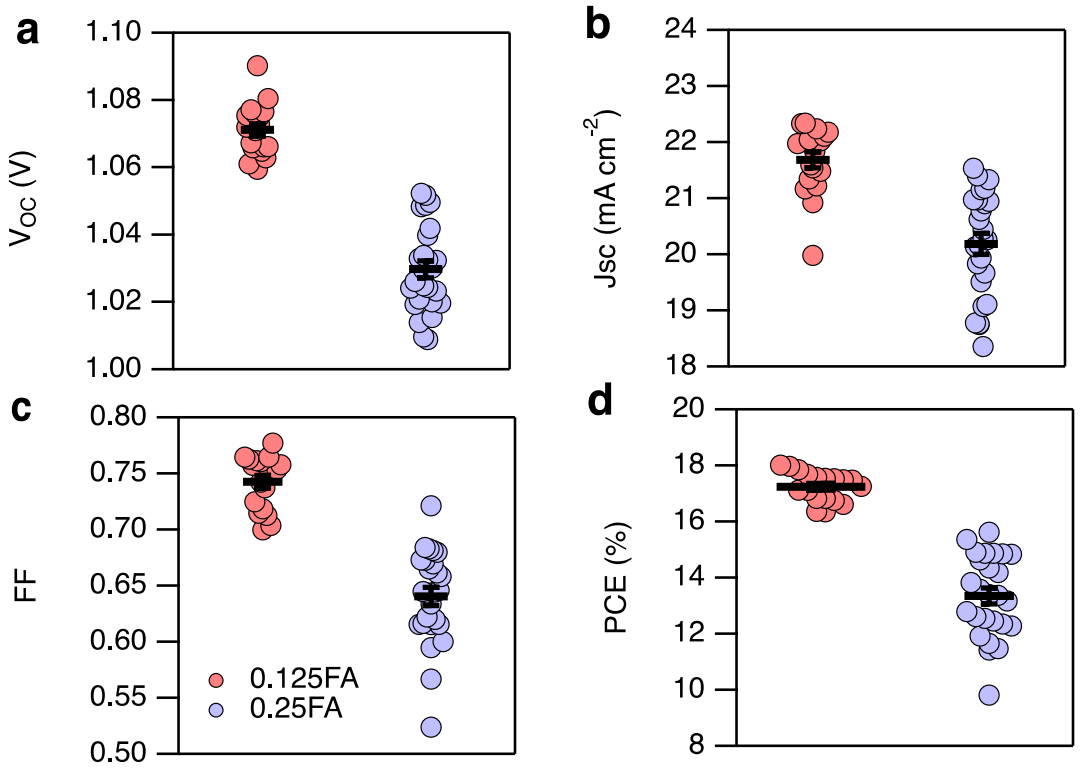

Fig. S16 Device Statistics for $FA_{0.125}MA_{0.875}PbI_3$ and $FA_{0.25}MA_{0.75}PbI_3$ based devices. (a) Voc, (b) Jsc, (c) FF, and (d) PCE, Lines represents average values and standard deviations.

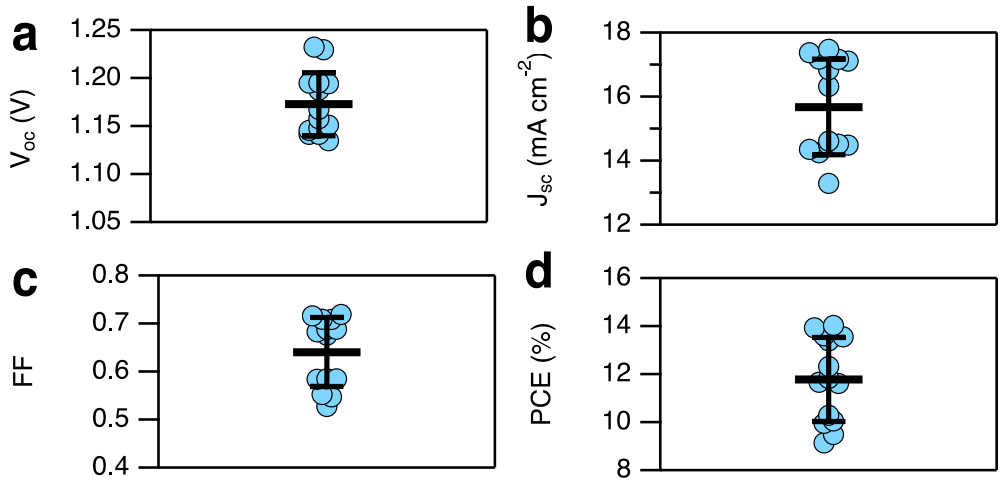

Fig. S17 Device Statistics for $FA_{0.125}MA_{0.875}Pb(I_{0.67}Br_{0.33})_3$based devices. (a) Voc, (b) Jsc, (c) FF, and (d) PCE, Lines represents average values and standard deviations.

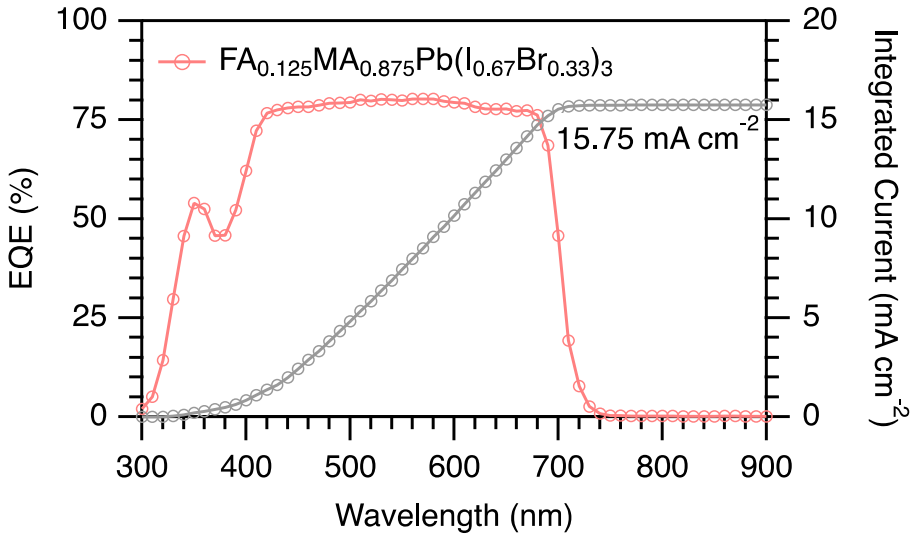

Fig. S18 EQE of $FA_{0.125}MA_{0.875}Pb(I_{0.67}Br_{0.33})_3$based device.

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