

Supporting Information

Two-Step Sequential Blade-Coating of High Quality Perovskite Layers for Efficient Solar Cells and Modules

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Experimental Section

Materials: SnCl₂·2H₂O, 4-tert-Butylpyridine (TBP) pyridine and GBL were purchased from Aladdin, urea was purchased from Alfa Aesar, Lead iodide (PbI₂) and methylammonium chloride (MAcI) were purchased from Xi'an Polymer Light Technology Corp, Formamidinium iodide (FAI) and methylammonium bromide (MABr) were purchased from Lumtec, Taiwan. N, N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich, Spiro-OMeTAD was purchased from Shenzhen Feiming Science and Technology Co., Ltd.

Precursor preparation: The 0.6 M PbI₂ solution was prepared by dissolving 276.7 mg PbI₂ powder in 1 mL DMF or mixed solvents (DMF: additives) with different ratio. The perovskite seeds solution was prepared by dissolving 548.7 mg PbI₂, 77.5 mg PbBr₂, 204.7 mg FAI and 23.5 mg MABr in mixed solvent (DMF: DMSO=4:1 volume ratio) to prepare 1.4 M (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} solution.

Device Fabrication: F-doped SnO₂ glass substrates (FTO) were etched by femtosecond laser, and followed by ultrasonic cleaning through detergent, deionized water and ethanol for 15 min, respectively. Then they were dried and treated by

ultraviolet (UV) light for 15 min before deposition of SnO₂ ETL. The compact SnO₂ film was achieved by chemical bath deposition (CBD) according to previous report. [1] After UV treated for 15 min, the perovskite films were deposited onto the achieved SnO₂ substrates via the two-step blade-coating sequential process in ambient environment. Firstly, a certain amount of PbI₂ precursor solution (generally 75 μL for 5×5 cm² substrate and 150 μL for 10×10 cm²) was dripped into the gap (about 0.3 mm) between the blade coater and substrate, the horizontal movement of blade coater was controlled by the computer with the speed of 15 mm/s. The wet films were dried immediately by a hot air blowing and then annealed at 100 °C for 10 min to remove solvent completely. After the substrate cooled down to room temperature, the mixture solution of FAI: MABr: MACl (60 mg: 6 mg: 6 mg in 1 mL IPA) was bladed onto the PbI₂ films (generally 100 μL for 5×5 cm² substrate and 200 μL for 10×10 cm²), then annealed at 150 °C for 15 min for perovskite crystallization. After cooling down, a 5 mg/mL tBAI/IPA solution was spun onto the small size blade-coated perovskite films and followed by annealing at 100 °C for 10 min. The Spiro-OMeTAD solution was prepared by dissolving 73 mg Spiro-OMeTAD and 18 μL Li-TFSI (from 520 mg/mL stock acetonitrile solution) and 29 μL FK209 (300 mg/mL stock acetonitrile solution) and 30 μL 4-tert-butylpyridine in 1 mL chlorobenzene (CBZ). After stirring adequately, the desired solution was spun onto perovskite films by 3000 rpm for 30s. Finally, 80 nm Au was evaporated to finish the complete device. All the blade-coating process was implemented in ambient air with humidity around 20 % RH.

Characterizations: The *J-V* curves of these PSCs were measured in room environment using a Keithley 2400 source meter and a solar simulator (Oriel 94023 A, 300 W) match AM 1.5 G. The intensity of the light was 100mW/cm² calibrated by a standard silicon reference solar cell (Oriel, VLSI standards). The 0.16 cm² devices were tested using a scan rate of 10 mV/s, 5×5 cm² module used a metal mask with an aperture area of 10 cm² using a scan rate of 50 mV/s, 10×10 cm² module used a metal mask with an aperture area of 53.6 cm² using a scan rate of 100 mV/s. All the surface morphologies and microstructures were characterized by a field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus) and an atomic force microscope (AFM,

SPM9700, Shimadzu, Japan). The crystallinity of perovskite films was characterized by an X-ray diffractometer (XRD, D8 Advance). The UV-Vis spectra of the different perovskite films were measured by a UV-Vis spectrometer (lambda 750S, PerkinElmer). The steady-state photoluminescence (PL) spectra were characterized by a PL microscopic spectrometer (Flex One, Zolix, China).

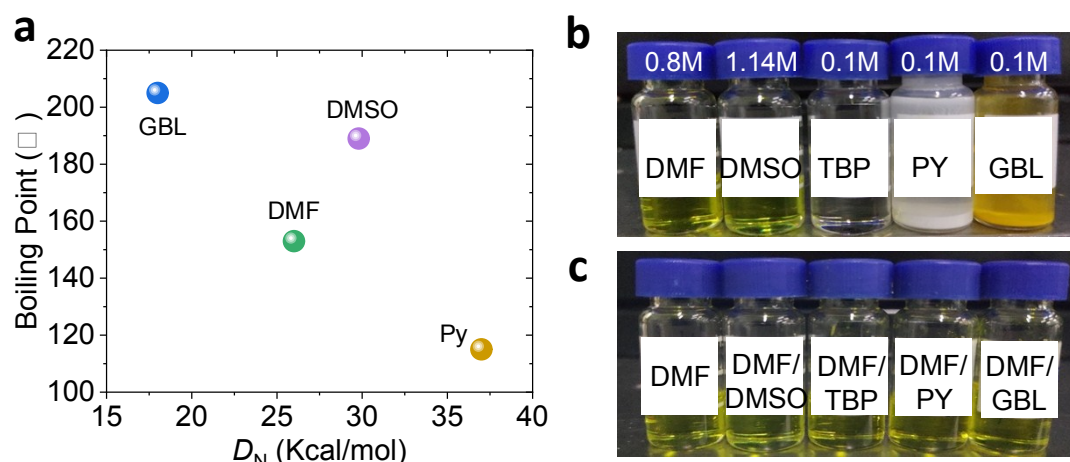


Figure S1. (a) Boiling point versus Donor number of different solvents. (b) The presentation of PbI_2 solubility in different solvents. (c) The solubility of 0.6 mol PbI_2 powder dissolved in 1 mL DMF with 5 vol.% different solvent additives.

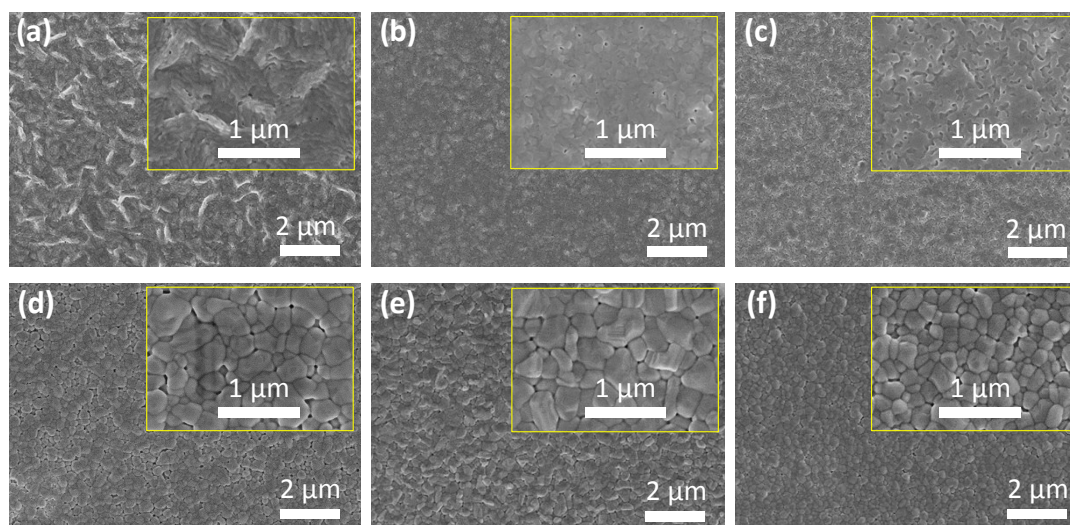


Figure S2. The SEM images of blade coated PbI_2 films from DMF solution with different solvents additives: (a) GBL, (b) DMSO, (c) PY. The corresponding SEM images of the achieved perovskite films via blade-coating after annealing at 150 °C for 15 min: (d) GBL, (e) DMSO, (f) PY.

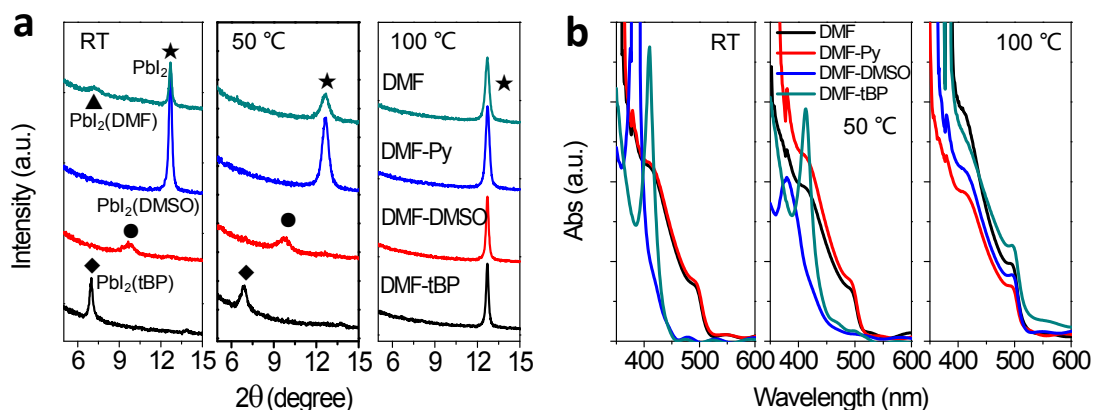


Figure S3. XRD patterns and UV-Vis spectra of blade-coated PbI_2 films from DMF solution with 5 vol. % different solvent additives treated at different temperature.

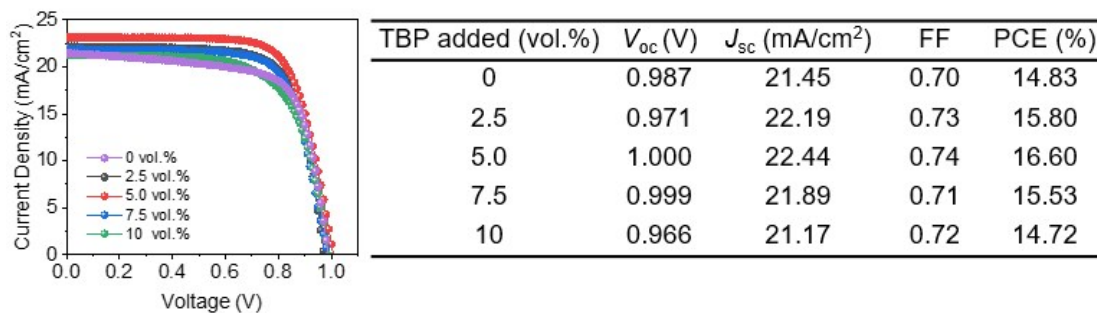


Figure S4. The J - V curves of PSCs based on different volume of TBP in the pristine PbI_2 films via the sequential blade-coating process. The corresponding parameters derived from J - V curves are listed in the right table.

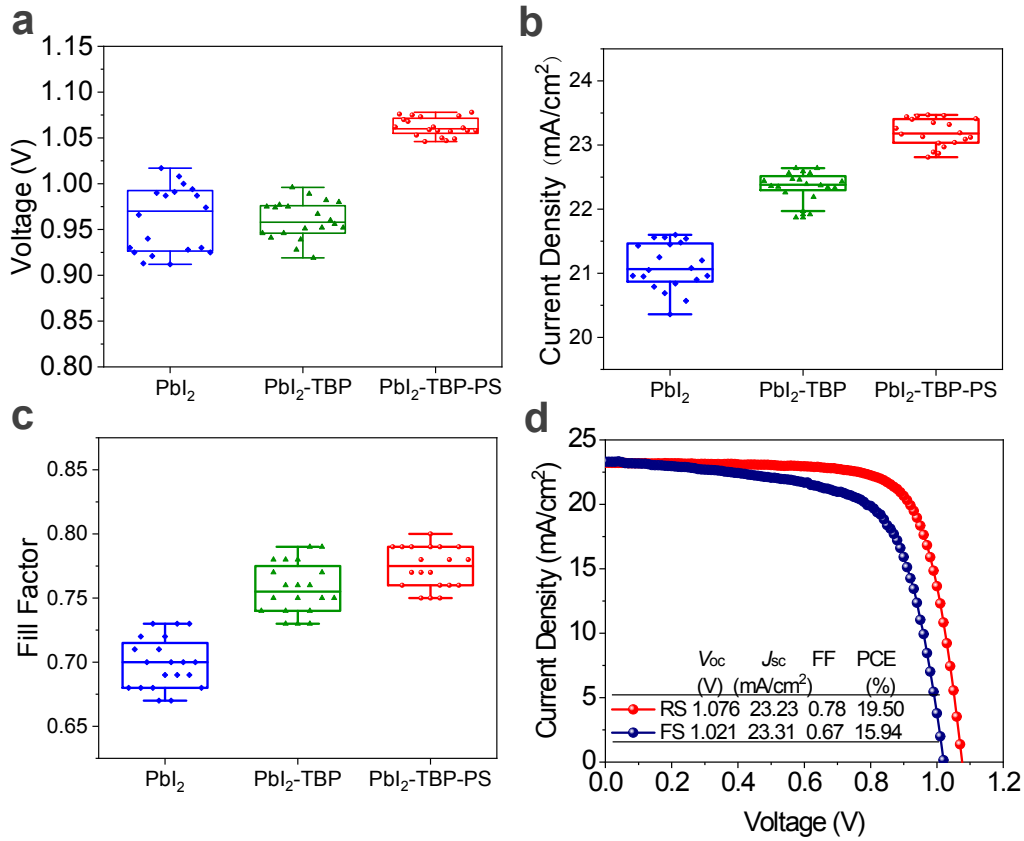


Figure S5. The distribution of (a) V_{oc} , (b) J_{sc} , (c) FF and the champion J - V curve of PbI_2 -TBP-PS based devices. The TBP and PS contents are 5 vol.% and 15 vol.% in PbI_2 -TBP-PS samples.

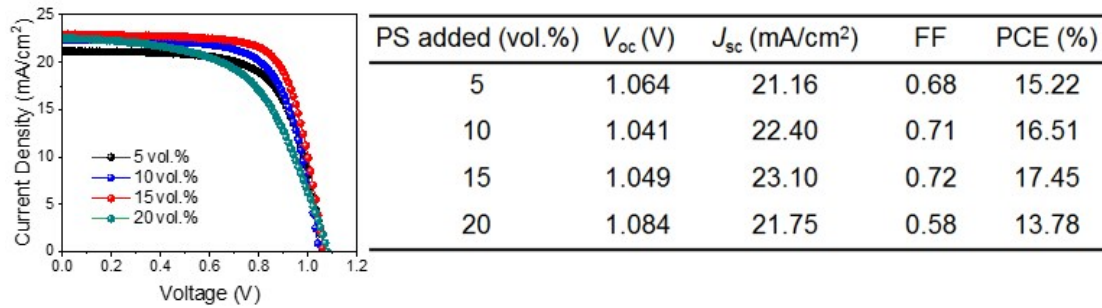


Figure S6. The J - V curves of PSCs based on different additional volume of perovskite seed in the pristine PbI_2 films via the sequential blade-coating process. The corresponding parameters derived from J - V curves are showed in the right table.

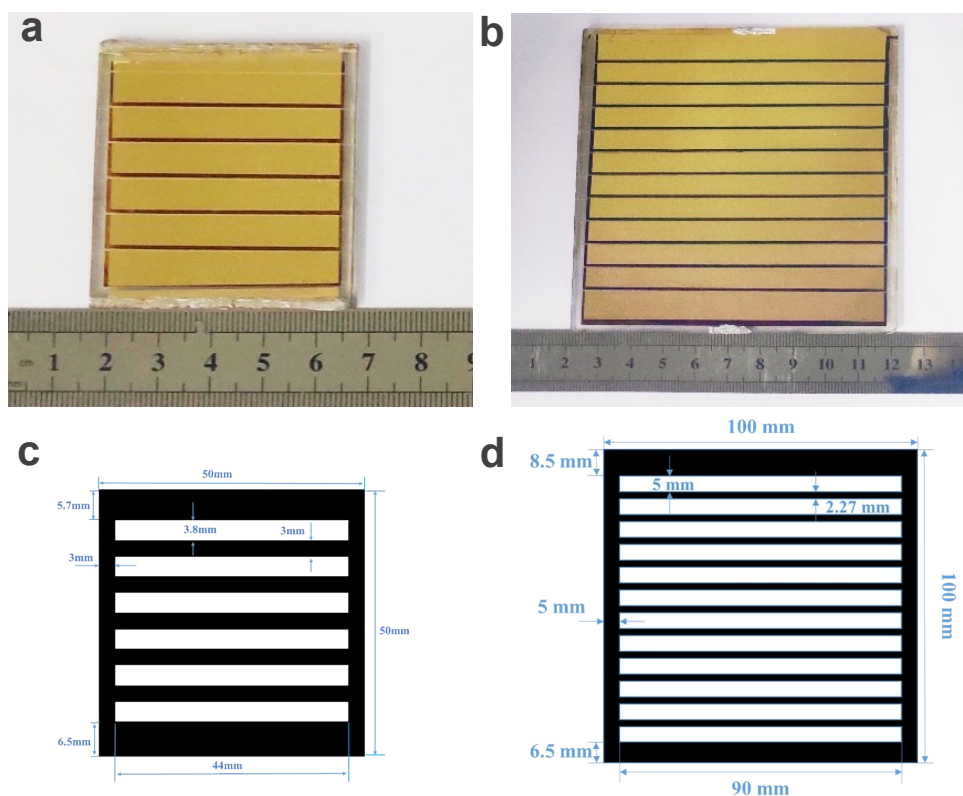


Figure S7. Photographs of optimized modules: (a) $5 \times 5 \text{ cm}^2$ and (b) $10 \times 10 \text{ cm}^2$ fabricated by the sequential blade-coating process. The corresponding diagram of these two metal masks are used to test the different modules: (c) $5 \times 5 \text{ cm}^2$ mask with aperture area of 10 cm^2 and (d) $10 \times 10 \text{ cm}^2$ mask with aperture area of 53.64 cm^2 .

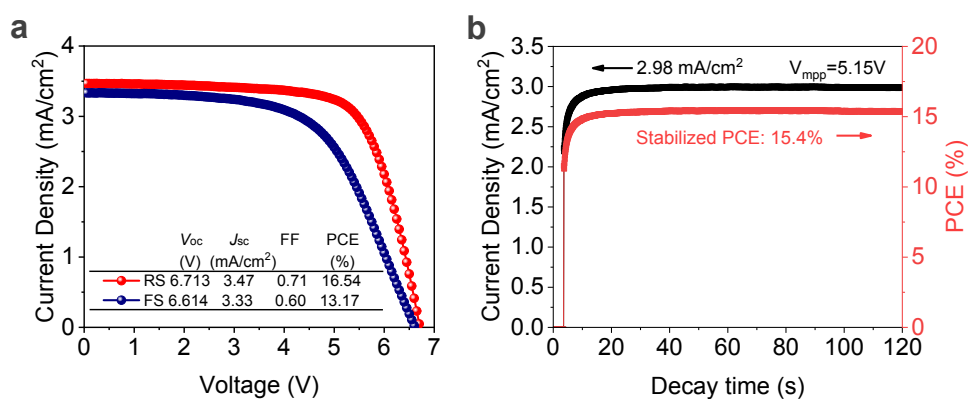


Figure S8. (a) The J - V curve of $5 \times 5 \text{ cm}^2$ module and (b) the steady state output current density under maximum power point tracking.

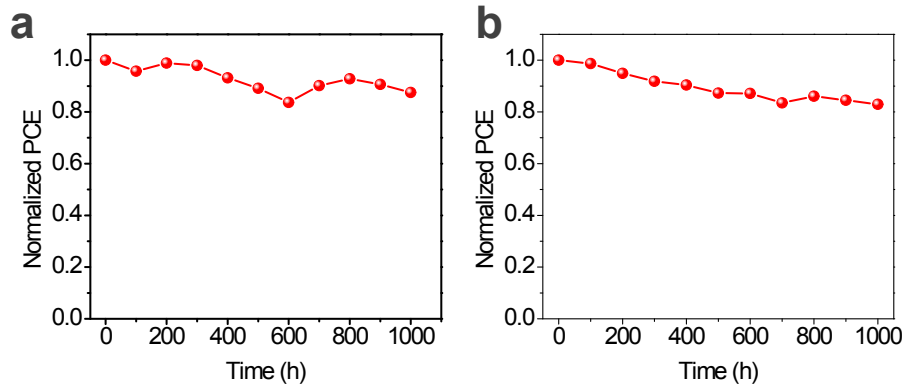


Figure S9. The stability measurements of 5×5 cm² and 10×10 cm² module performed at the indoor environment with the relative humidity of 20±5% at room temperature (~25 °C).

Table S1. The average J - V performance parameters of different blade-coated devices.

Device	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
PbI ₂ -TBP-PS	1.062±0.01	23.19±0.21	0.77±0.02	19.00±0.39
PbI ₂ -TBP	0.960±0.02	22.36±0.22	0.76±0.02	16.36±0.30
PbI ₂	0.961±0.03	21.11±0.36	0.70±0.02	14.54±0.33

Table S2. Champion PCEs of the reported devices via two-step sequential deposited scalable printing methods in different area so far.

Methods	Structure	Area (cm ²)	η (%)	Ref.
Blading PbI ₂ , dipping MAI	FTO/TiO ₂ /MaPbI ₃ /P ₃ HT/Au	0.1(cell area)	13.3	42
		10.1(active area)	10.4	
		100 (module area)	4.3	
Blade-coating	ITO/NiO _x /MAPbI ₃ /PCBM/B CP/Ag	0.09 (active area)	16.71	25
		1(active area)	10.91	
Blade-coating	FTO/m-TiO ₂ /MAPbI ₃ /Spiro- OMeTAD/Au	13.6 (active area)	13.2	43
		49.8(active area)	11.03	
Blade-coating	FTO/c-TiO ₂ /m-TiO ₂ / (FA _{1-x-y} MA _x Cs _y)Pb(I _{1-x} Br _x) ₃ / Spiro-OMeTAD/Au	1(active area) 50(active area)	17.77 11.59	45
Slot die	ITO/ZnO/ MAPbI ₃ /P ₃ HT/Ag	0.1(active area)	11.96	28
Slot die	ITO/ZnO/ MAPbI ₃ /Bifluo- OMeTAD/Ag	0.1(active area)	14.7	44

References:

- [1] T. Bu, X. Liu, Y. Zhou, J. Yi, X. Huang, L. Luo, J. Xiao, Z. Ku, Y. Peng, F. Huang, Y.-B. Cheng and J. Zhong, *Energy Environ. Sci.*, 2017, **10**, 2509-2515