Temperature-assisted Rapid Nucleation: A Facile Method to Optimize the Film Morphology for Perovskite Solar Cells

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EXPERIMENTAL SECTION

Film Fabrication (diethyl ether)

461 mg of PbI_2, 159 mg of CH_3NH_3I, and 78 mg of DMSO (molar ratio 1:1:1) was mixed in 600 mg of DMF solution at room temperature with stirring for 1 h. The completely dissolved solution was spin-coated on the substrates at 4000 rpm for 25 s and 0.5 ml of diethyl ether was slowly dripped on the rotating substrate in 10 s before the surface changed to be turbid caused by rapid vaporization of DMF.

Film Fabrication (chlorobenzene)

The $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$ precursor solution was prepared in a glove box from a 1.35M PbX_2 (X = I, Br) in the mixed solvent of DMF and DMSO, with the molar ratios of DMSO/DMF= 1:4 and PbX_2/DMSO = 1:1. The completely dissolved solution was spin-coated onto the mp-TiO_2 layer at 1100 rpm for 20 s and 5000 rpm for 30 s and 0.75 mL of CBZ was quickly dripped on rotating substrate in the second step (5000 rpm for 30 s).

Solar Cell Fabrications

Fluorine-doped tin oxide (FTO) glasses (Pilkington, TEC15) were etched with 0.8 mol L^{-1} HCl aqueous and Zn powder. The etched glasses were cleaned with detergent, distilled water, ethanol and sonicated for 30 min. By means of spray pyrolysis, the blocking TiO_2 layers (bl-TiO_2) were deposited on the as-prepared FTO which was followed by heating at 510°C for 30 min. The mesoporous TiO_2 (mp-TiO_2) film was

deposited on cooling bl-TiO_2 by spin-coating of the TiO_2 paste (Dyesol 30NR-T) following by calcining at 510°C for 20 min.

The transparent perovskite film was heated at 100 °C for 20 min in order to obtain a dense film. Then, spiro-OMeTAD solution (25 μL), which consisted 73 mg of spiro-OMeTAD, 28 μL of 4-tert-butyl pyridine and 17.5 μL of lithium bis (trifl uoromethanesulfonyl) imide (Li-TFSI) solution (520 mg of Li-TSFI in 1 mL of acetonitrile) in 1mL of CBZ, was spin-coated on the perovskite film at 3000 rpm for 20 s. Finally, Au electrode with a thickness of 60 nm was deposited by using thermal evaporation under vacuum at a constant evaporation rate of 0.6 nm s^{-1}.

Characterization

The morphology of the perovskite film was studied by a field emission scanning electron microscope (FESEM, FEI Sirion 200, Netherland). The crystal phase was obtained with X-ray diffraction (X'Pert Pro, Netherland) using Cu Kα beam (λ=1.54 Å). The photocurrent density-voltage (*J-V*) curves were measured under one sun illumination (AM 1.5G, 100 mW cm^{-2}) with a solar simulator (94043A, USA) equipped with Keithley 2400 source meter. When measuring, a mask with 0.09 cm^2 aperture area was used to avoid light scattering through the sides and define the effective area of the device. Ultraviolet-visible (UV–vis) diffuse reflectance spectroscopy and absorption spectroscopy were measured using the UV–vis spectrophotometer (SOLID3700, Shimadzu Co. Ltd, Japan). (IPCE) spectra were measured with a spectral resolution of 5 nm, using a 300 W xenon lamp and a grating monochromator equipped with order sorting filters (Newport/Oriel). The

electrochemical impedance spectra (EIS) were carried out on a computer controlled potentiostat (Autolab 320, Metrohm, Switzer land) in a frequency range of 10 mHz~1000 kHz applied in the dark. The micrographs were obtained during cooling between crossed polarizers using a microscope (DM2500P, Leica, Germany) equipped with a hot-stage (LTSE-420, Linkam, UK) and a camera (Micropublisher 5.0 RTV, Qimaging, Canada).

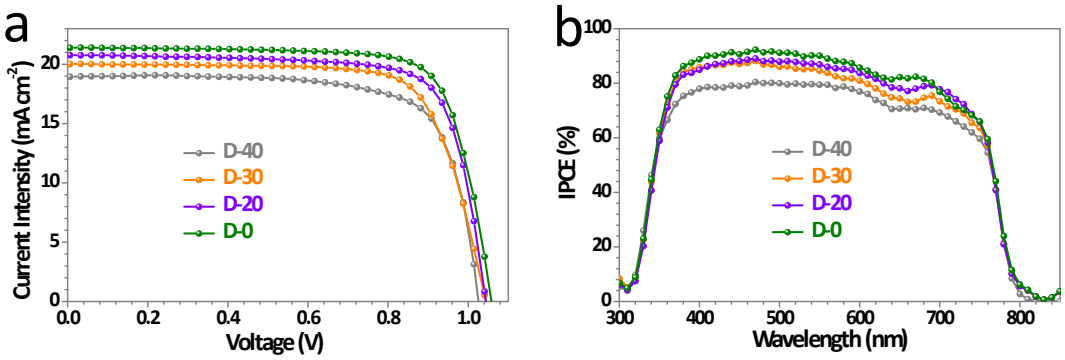

Figure S1 (a) The current density–voltage curves of PSCs dripping with DE at different temperatures. (b) Internal photo-to-current efficiency measurement for the corresponding devices.

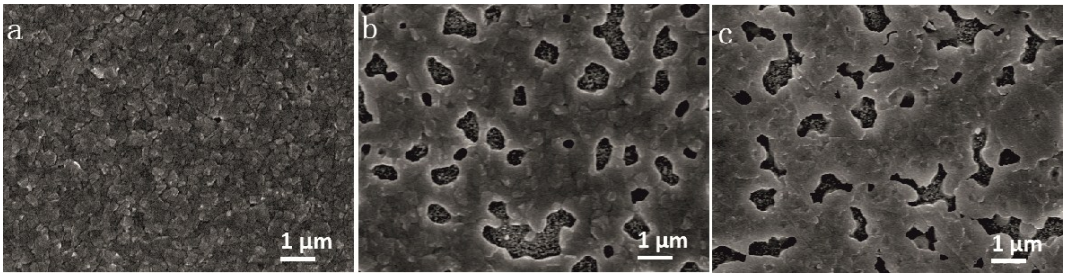

Figure S2 Top-view SEM images of perovskite films washed with different temperature of toluene at (a) 0, (b) 15 and (c) 30 °C, respectively.

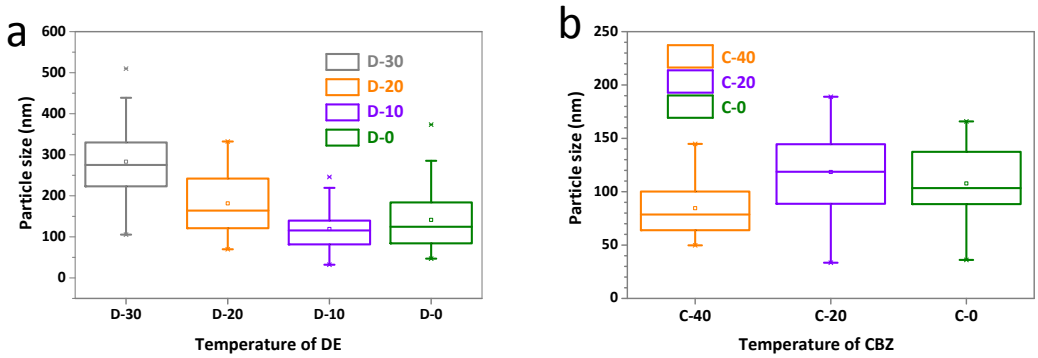

Figure S3 The statistical distribution of the particle size for perovskite films base on (a) different temperature of DE and (b) CBZ.

Table S1 Parameters of current density–voltage curves of PSCs dripping with DE at different temperatures.

PSCs	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF (%)	PCE (%)	Average PCE (%)
D-40	1.03	18.7	74.2	14.3	12.8
D-30	1.04	19.7	74.3	15.2	14.7
D-20	1.04	20.5	76.2	16.2	15.6
D-0	1.06	21.1	76.9	17.2	16.8

Table S2 Parameters obtained by fitting the EIS

PSCs	R_s (Ω)	R_{rec} (KΩ)	n
C-40	28.5	3.24	1.00
C-20	36.4	10.4	0.98
C-0	40.9	17.6	0.99