

Electronic Supplementary Information

Low-Temperature Annealed Perovskite Films: A Trade-Off between 2 Fast and Retarded Crystallization via Solvent Engineering

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Experimental Section

Solar cell fabrications

F-doped SnO₂ (FTO, Pilkington, TEC15) glasses were scratched with aqueous HCl and Zn powder, then cleaned with a cleansing agent, de-ionized water and acetone sequentially and then sonicated for 20 min in ethanol. The compact TiO₂ blocking layer (bl-TiO₂) was deposited on the FTO substrate through spray pyrolysis at 460 °C and annealed for 30 min. Mesoporous TiO₂ (mp-TiO₂) layer was deposited on the bl-TiO₂ at room temperature by spin-coating of the TiO₂ solution (Dyesol, DSL 30NR-T) with ethanol (1:6, mass ratio), and then annealed at 500 °C for half an hour. 1.2 mol of PbI₂ (553 mg) and 1.17 mol of CH₃NH₃I (186 mg) were dissolved in a solvent system (1 mL) containing DMAC and NMP in 4:1 volume ratios respectively (Sigma-Aldrich), then the solution was stirred and heated at 65 °C for 12 hours. Change proportions of DMSO (%) as a fraction of NMP in the mixed DMAC/NMP solvents were added into the solution as 10%, 20%, 30% up to 50%. The prepared solution was filtered and deposited onto the mp-TiO₂ scaffold by spin coating in two stages as 1100 rpm for 10 s and 4200 rpm for 30 s at room temperature in a dry air environment. 100 µL chlorobenzene (CB) as an anti-solvent was dripped onto the as-deposited film at the last 12th second of the 2nd stage (4200 rpm for 30 s). Then, the prepared films were heated at 50 °C for 30 min. For traditional perovskite samples, precursors were dissolved in a mixed solvent system (1 mL) containing DMF and DMSO in 4:1 volume ratios, respectively (Sigma-Aldrich). Following deposition method as discussed above, prepared films were annealed at 100 °C for 1 hour. 25 µL of spiro-OMeTAD solution, which comprised of spiro-OMeTAD (73 mg), tert-butyl pyridine (28 µL) and 17.5 µL of lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI) solution (520 mg of Li-TFSI in 1 mL of acetonitrile) in 1 mL of CB, was spin-coated on the perovskite layer at 4000 rpm for 25 s (Sigma-Aldrich). In the end, gold electrodes with 60 nm of thickness were thermally evaporated onto the spiro-OMeTAD layer at a constant evaporation rate of 0.6 nm s⁻¹ under vacuum condition.

Characterization

The top and cross-sectional morphology of perovskite layers were examined by field emission scanning electron microscope (FEI Sirion 200, Netherlands). The crystal phase of the films was studied with X-ray diffraction (X'Pert Pro, Netherlands) using Cu K α beam ($\lambda = 1.54 \text{ \AA}$). The photocurrent density-voltage (J - V) curves were tested under one sun illumination (AM 1.5G, 100 mW/cm^2) with a solar simulator equipped with Keithley 2400 source meter (94043A, USA). When testing, a dark cover with 0.09 cm^2 aperture area was used to prevent light scattering through the edges and to define the active area of the cell. Ultraviolet-visible (UV-vis) absorption spectra were measured using the spectrophotometer (SOLID3700, Shimadzu Co. Ltd, Japan). Xenon lamp of 300 W rating with a spectral resolution of 5 nm equipped with order sorting filters (Newport/Oriel) was used to measure incident photon-to-electron conversion efficiency (IPCE) spectra. Photoluminescence intensity was measured by steady-state spectrometer (FLS980, Edinburgh Instruments, UK). The surface roughness of the prepared films was examined by atomic force microscope (AFM) (Bruker multimode 8, Bruker, USA). Fourier transform infrared spectroscopy (FTIR) (Tensor FTIR spectrophotometer, Bruker) was employed from 4000 cm^{-1} to 400 cm^{-1} . A Zahner electrochemical workstation was used for electrochemical impedance measurements (EIS) in the frequency range of 10 mHz to 1 MHz. Impedance data were analysed using Z-view equivalent circuit modelling software.

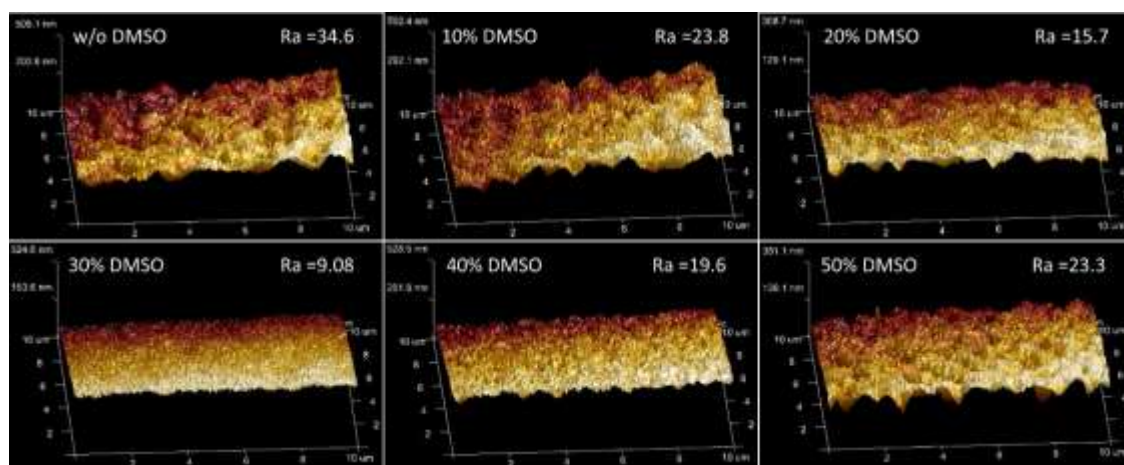


Figure S1. Atomic force microscopy (AFM) images of the perovskite films prepared by different proportions of DMSO (%) as a fraction of NMP.

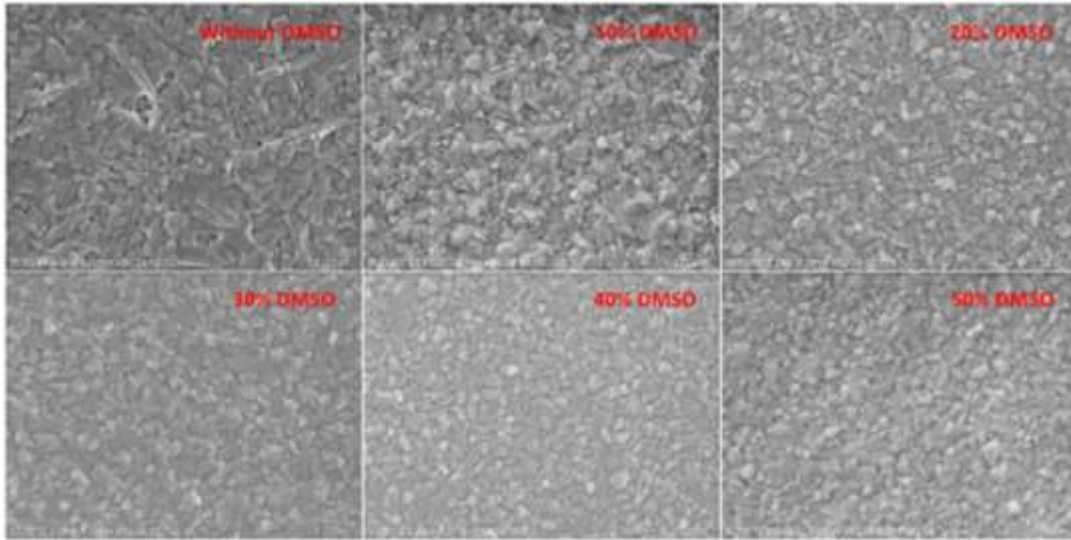


Figure S2. Top SEM images of the non-annealed films prepared by different proportions of DMSO (%) as a fraction of NMP.

Debye-Scherrer Formula

$$D_p = \frac{K\gamma}{B \cos \theta} \quad (\text{Eq. S1})$$

Where, D_p is the mean crystallite size, K is the Scherrer constant, β is the FWHM of (110) diffraction peak, θ is Bragg angle, and γ is X-ray with a wavelength of 0.15418 nm.

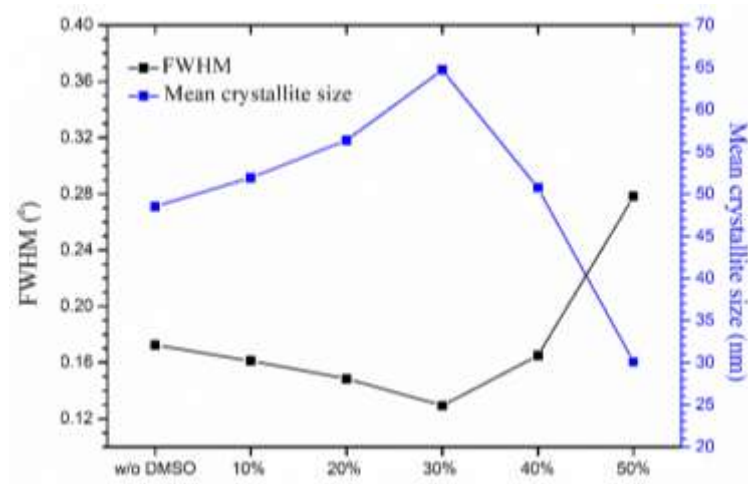


Figure S3. The full width at half maxima (FWHM) and mean crystallite size derived from (110) main peak of perovskite films prepared by different proportions of DMSO (%) as a fraction of NMP.

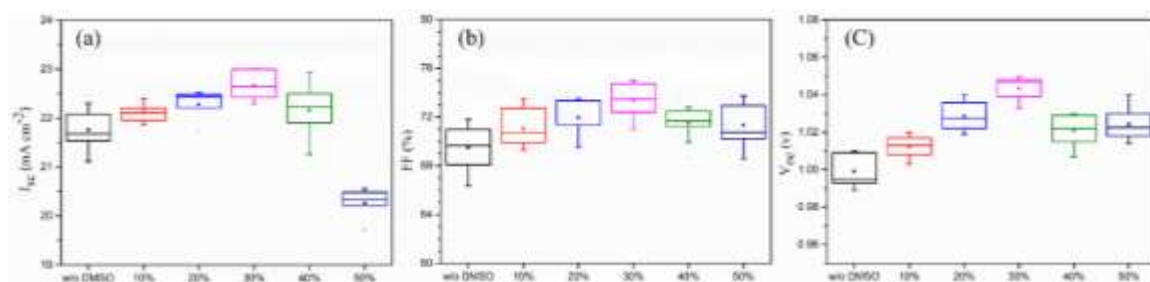


Figure S4. Statistical plot of (a) J_{sc} (b) FF and (c) V_{oc} of the PSCs prepared by different proportions of DMSO (%) as a fraction of NMP.

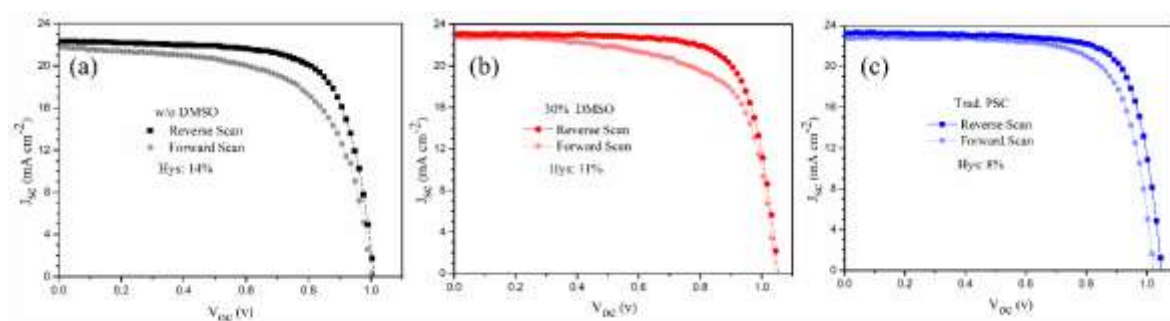


Figure S5. J - V characteristics of PSCs fabricated from (a) without (b) with 30% DMSO and (c) traditionally high-temperature annealed PSC.

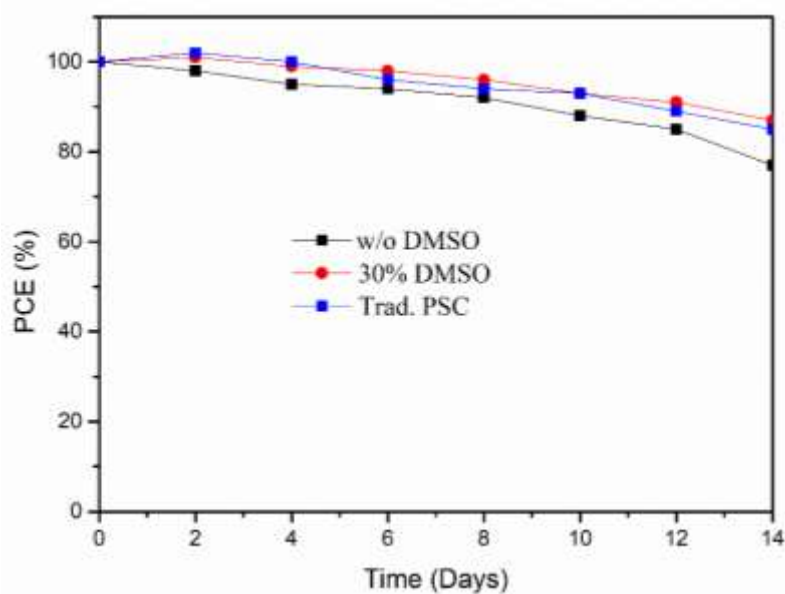


Figure S6. Efficiency evolution of the prepared devices kept in 40% humid environment for 2 weeks.

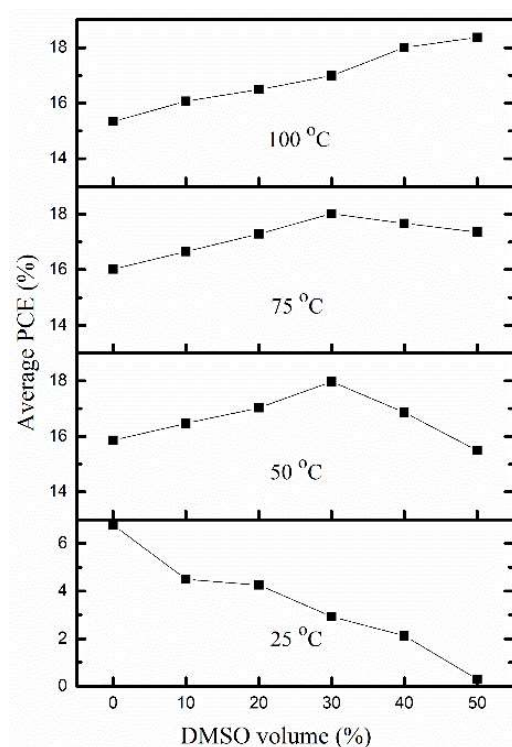


Figure S7. Average performance statistics for the devices based on each case annealed at varied temperature from room to traditional high temperature (25 °C, 50 °C, 75 °C and 100 °C) for 30 min. A total of 16 devices based on each case of samples heat treated at 50 °C and total of 12 devices based on the each case of samples heat treated at 25 °C, 75 °C and 100 °C were tested.