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Supporting Information

Annealing-free perovskite films by instant crystallization for efficient solar cells

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Experiments

1. Materials and reagents

PbI_2 (99%), dimethyl sulfoxide (DMSO), chlorobenzene, and nickel acetylacetonate (95%) were all purchased from Sigma Aldrich. Toluene and methanol were purchased from Wako Co., Japan. MAI (98%) and γ -Butyrolactone (GBL) were purchased from TCI. $PC_{61}BM$ (99.5%) was purchased from Lumtec Co., Taiwan. Ethyl acetate was purchased from Sinopharm. Other commonly used solvents and reagents were used as received without further purification.

2. Solar Cell Fabrication

Fluorine-doped tin oxide (FTO) coated glass substrates were etched with zinc powder and 2 M HCl to obtain the electrode pattern. The etched substrates were then washed with soap, deionized water, acetone and ethanol in an ultrasonic cleaner for 30 minutes. After dried by the N_2 flow, the substrates were put under UV plasma for 20 minutes to remove any organic residues. The washed FTO glasses were heated to 560 °C on a hotplate. 100 ml 0.005 M nickel acetylacetonate in acetonitrile/ethanol (95:5/v:v) solution was sprayed on the FTO glass within 20 minutes at 560 °C. After that, the sprayed substrates were kept at 560 °C for half an hour to promote NiO crystallization; a thickness of about 20nm was obtained. After cooling, the substrates were transferred quickly into a N_2 protected glovebox. The perovskite solution was composed of 1.45 M PbI_2 and CH_3NH_3I (1:1/n:n) in GBL and DMSO (7:3/v:v). The perovskite precursor solution was placed on a hotplate at 60 °C and stirred overnight in N_2 protected glovebox. 80 μl perovskite solution was spread on the warm NiO/FTO substrate and the spin-coating process is composed of two stages: first rotating 1000 rpm for 12 seconds and then 4000 rpm for 30 seconds. 800 ul toluene or ethyl acetate was dripped quickly 10 seconds after the second stage. When the spin-coating process finished, the substrates were transferred to a hotplate to anneal at 100 °C for 10 minutes. To make perovskite solar cells with the annealing-free $CH_3NH_3PbI_3$ film, we use the same film deposition method as demonstrated above, but do not anneal the

perovskite films after the spin-coating procedure. After the perovskite film deposition, 50nm PCBM film and 10nm bathocuproine (BCP) layer were sequentially deposited by spin-coating 20 mg ml^{-1} PCBM/chlorobenzene solution and saturated BCP/methanol solution. All of these procedures were processed in the N_2 protected glovebox with O_2 and H_2O of less than 0.5 ppm. Finally, a Ag layer of 120 nm was thermally evaporated on top of the devices under high vacuum (2×10^{-4} Pa). The perovskite solar cells were measured using a black metal mask with an aperture area of 0.09 cm^2.

3. Solar Cell Characterization

Current density-voltage (*J-V*) characteristics were taken by a digital source meter (Keithely model 2400). The light source was 100 mW cm^{-2} (AM 1.5G simulated irradiation) determined by a standard silicon reference cell (Wacom, Japan). Forward sweep was scanning from -0.2 to +1.2 V, and reverse sweep was from +1.2 to -0.2 V. The voltage step and delay time are 10 mv and 50 ms, respectively. The scanning electron microscope morphologies of films and devices were characterized by a JEOL JSM-7800F Prime. Monochromatic incident photo-to-current conversion efficiency (IPCE) spectra measurements were carried out using a monochromatic incident light in direct current mode. X-ray diffraction patterns were recorded by a D8 ADVANCE DA VINCI X-ray diffractometer with a Cu Ka radiation source. UV-Vis absorption spectra of film samples were measured by a Shimadzu UV 2450 spectrophotometer. Attenuated total reflectance Fourier transform IR (ATR-FTIR) measurement was taken by a Nicolet iN10 MX Fourier transform microscopic infrared spectrometer. The photoluminescence decay was measured by Horiba Fluorolog-3 Time Correlated Single Photon Counting (TCSPC) system with excitation wavelength at 460 nm.

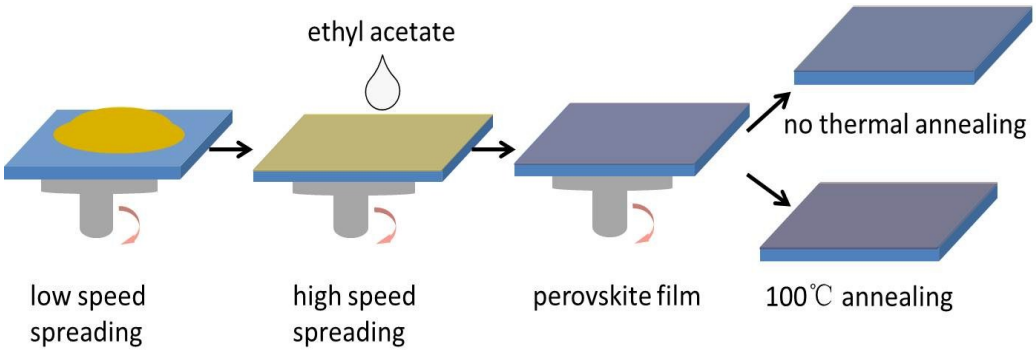

Fig. S1 Fabricating procedure of perovskite films prepared with ethyl acetate.

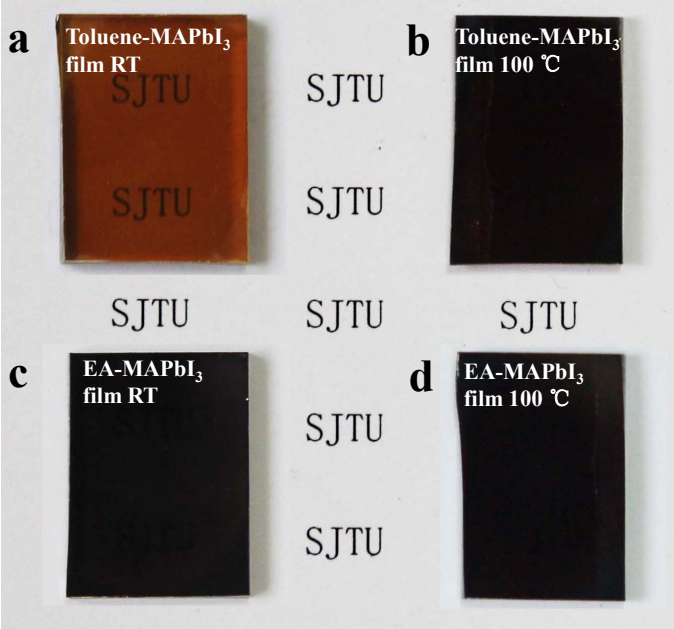

Fig. S2 A comparison of $CH_3NH_3PbI_3$ perovskite films prepared with (a) Toluene at room temperature without annealing (RT), (b) Toluene with annealing at 100 °C for 10 minutes, (c) EA at room temperature without annealing (RT), and (d) EA with annealing at 100 °C for 10 minutes.

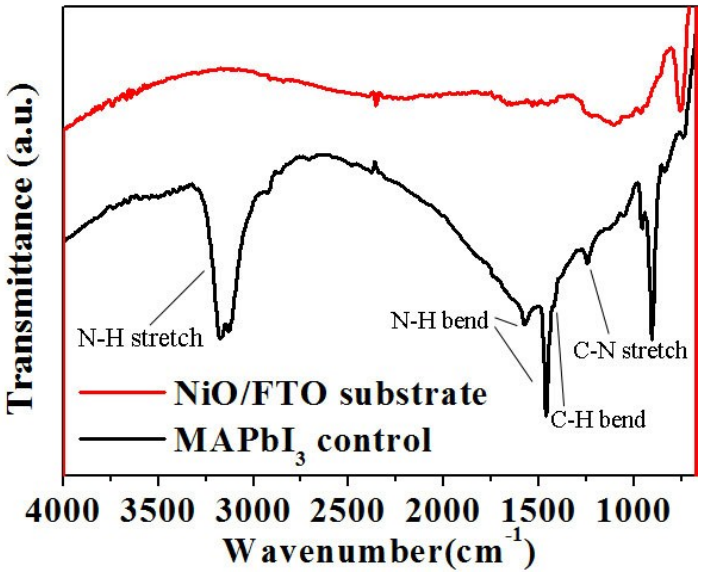

Fig. S3 ATR-FTIR spectra of control $MAPbI_3$ film without drop-casting (black line) and NiO/FTO film (red line). Perovskite film is deposited on NiO/FTO substrates using a conventional solution-processed one-step method.[1] The perovskite film was annealed at 100 °C for 10 minutes.

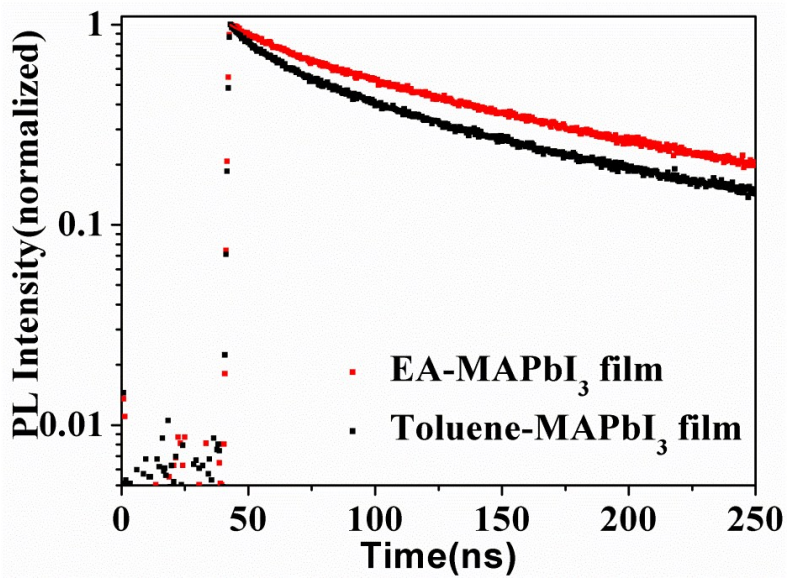

Fig. S4 Normalized time-resolved photoluminescence spectra after excitation at 460 nm for $MAPbI_3$ film prepared with EA (red square) and toluene (black square). The corresponding solid lines are the bi-exponential fit curves of the two PL decay spectra. $MAPbI_3$ films were deposited on glass substrates and annealed at 100 °C for 10 minutes.

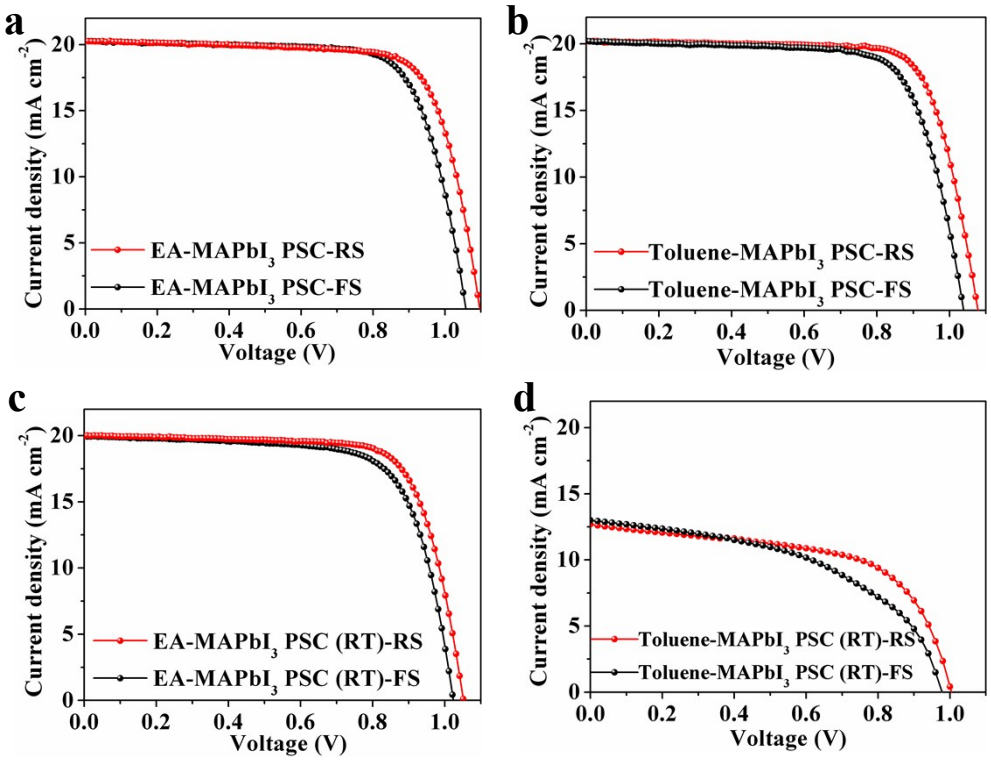

Fig. S5 Forward and reverse sweep (FS and RS) *J-V* curves of FTO/NiO/$MAPbI_3$/PCBM/BCP/Ag PSCs based on films prepared with (a) ethyl acetate, (b) toluene with thermal annealing, and PSCs based on films prepared with (c) ethyl acetate, (d) toluene without annealing (RT).

Table S1 Photovoltaic parameters for forward- and reverse-swept inverted perovskite solar cells fabricated with ethyl acetate (EA)- and toluene-perovskite films either with annealing at 100 °C or without annealing.

Drip solvent	Sweep direction	Perovskite film treatment	V_{OC} [V]	J_{SC} [mA cm^{-2}]	*FF* [%]	Efficiency [%]
EA	Forward	Annealing	1.058	20.265	73.81	15.83
		Annealing free	1.024	19.957	71.30	14.57
Toluene	Forward	Annealing	1.039	20.221	73.26	15.39
		Annealing free	0.977	12.975	49.15	6.23
EA	Reverse	Annealing	1.096	20.263	74.89	16.64
		Annealing free	1.052	19.968	74.22	15.58
Toluene	Reverse	Annealing	1.078	20.168	76.49	16.63
		Annealing free	1.003	12.759	58.99	7.55

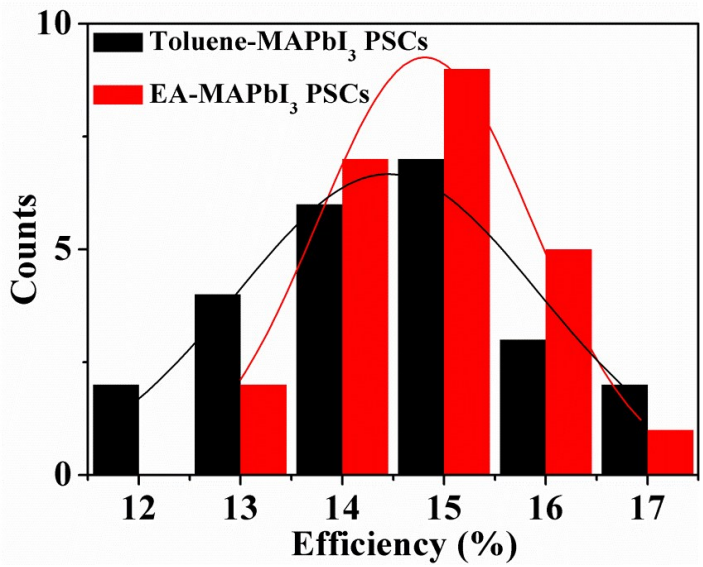

Fig. S6 Histogram of PSC devices efficiency distribution based on perovskite films prepared with toluene and ethyl acetate with annealing. A batch of 48 solar cells was tested. The cells were unsealed and the humidity of ambient air was controlled between 30% and 50%.

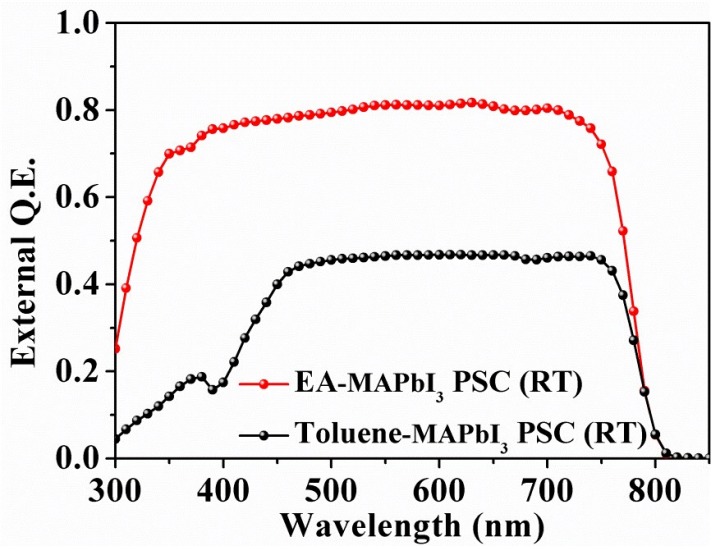

Fig. S7 Incident photo-to-current conversion efficiency spectra of PSCs based on annealing free perovskite films (RT) prepared with ethyl acetate and toluene.

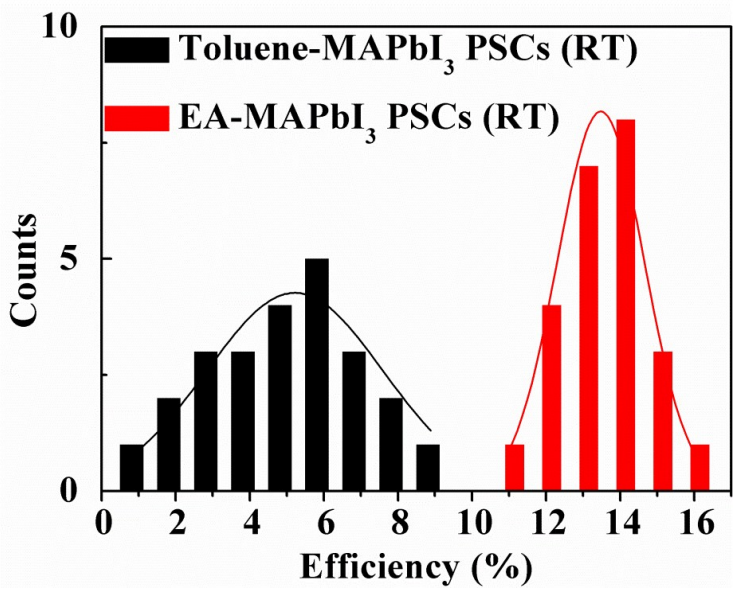

Fig. S8 Histogram of PSC devices efficiency distribution based on perovskite films prepared with toluene and ethyl acetate without annealing (RT). A batch of 48 solar cells was tested. The cells were unsealed and the humidity of ambient air was controlled between 30% and 50%.

References

1. J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-j. Kim, A. Sarkar and M. K. Nazeeruddin, *Nature Photonics*, 2013, **7**, 486-491.