

Supplementary Information

Sec-butyl alcohol assisted pinhole-free perovskite film growth for high-performance solar cells

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Experimental

Material synthesis and purification

The CH₃NH₃I crystal was synthesized using the method described by Lee et al.¹ A concentrated aqueous solution of hydroiodic acid (HI) (15.0 ml, 57 wt% in water, Aldrich) was reacted with methylamine (CH₃NH₂) (13.5 ml, 40 wt% in aqueous solution, Aldrich) at 0 °C for 2 h with constant stirring under nitrogen atmosphere. The precipitate was recovered by evaporation at 70 °C for 1 h. MAI was dissolved in ethanol at 80 °C, recrystallized from the supersaturated solution at room temperature, and dried at 60 °C in a vacuum oven for 12 h. PbI₂ (Aladdin, 98%) was dissolved in DMF (Aldrich, 99.9%) at low concentration (0.5 M). After filtrating and concentrating, the PbI₂ crystal recrystallized from the supersaturated solution. Then, the PbI₂ crystal was filtered and dried at 80 °C in a vacuum oven for 24 h.

Solar cell fabrication

After cleaning the indium tin oxide (ITO) substrate, a poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT: PSS) layer was spun on ITO at 2000 rounds per minute (rpm).

For the traditional fast crystallization process, the PbI₂ and MAI precursors with a 1:1 molar ratio (PbI₂ 461 mg and MAI 159mg) were dissolved in 1 mL of DMF and 100 μL of N,N-dimethyl sulfoxide (DMSO). The mixture solution was then spin coated on the PEDOT: PSS layer at 6,000 rpm; after 5s delay time, the wet films were selectively washed with 300 μL of toluene, chlorobenzene, or sec-butyl alcohol. The films were then annealed in ambient air at 100 °C for 5 min.

For the modified 270 nm thick film, a mixture solution with a 1:2 optimal PbI₂:MAI molar ratio (461mg: 318 mg) was used as example. The mixture solution was spin coated on the PEDOT: PSS layer at 6,000 rpm, the wet film was selectively washed with 300 μL of sec-butyl alcohol after 7s delay time. At this step, the film change from yellow to light brown. After 30s spin-coating stopped, 200 μL sec-butyl alcohol were dipped onto perovskite film. 10 s is an optimal time at this step. After sec-butyl alcohol soaking step, the films were spun on the perovskite layer at 6,000 rpm for 30 s, and then annealed in ambient air at 100 °C for 30 min. In this study, the optimal soaking time for different PbI₂:MAI molar ratio was investigated.

The devices with different precursor ratios were optimized in terms of the thickness, 110 nm (PbI₂ 230.5 mg and MAI 159mg), 190nm (PbI₂ 322.7 mg and MAI 222.6 mg), 270 nm (PbI₂ 461 mg and MAI 318 mg), 450 nm (PbI₂ 691.5 mg and MAI 357.75 m), 610 nm (PbI₂ 922 mg and MAI 477 mg). In addition, they were dissolved in 1 mL of DMF and 100 μL of DMSO.

The spin coating process is typically conducted in the glove box under nitrogen atmosphere and with a real-time humidity of 15%. The films were then annealed in ambient air at 100 °C for 30 min.

Subsequently, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) was dissolved in chlorobenzene at a concentration of 20 mg/ml and spun on the perovskite layer at 2,500 rpm. The devices were completed by evaporating a 100-nm-thick aluminium film as the electrode with an active area of 0.09 cm².

Characterization

Ultraviolet-visible (UV) light absorption spectra were analyzed to assess the absorption properties of the perovskite film with a UV-VIS spectrophotometer (UV-2600). Scanning electron microscopy (SEM) images and X-ray diffraction (XRD) patterns of the films were obtained with a Zeiss Supra 55 microscope and a Bruker QUANTAX 200 diffractometer, respectively. A sun simulator (Zolix Sirius-SS) was used to provide simulated solar irradiation (AM 1.5, 100 mW/cm²). Current-voltage characteristics were measured using a Keithley 2400 source meter. The output of the light source was adjusted using a calibrated silicon photodiode (ABET technology). The J-V curves were measured by backward—forward bias (1.5 V) → negative bias (-0.5 V)—or forward—negative bias (-0.5 V) → forward bias (1.5 V)—scan. The step voltage was fixed at 10 mV and the delay time, which is a set delay at each voltage step before the current is measured, was modulated. The internal PCE (IPCE) was measured using a power source (Zolix Sirius-SS) with a monochromator (Zolix Omni-λ) and a source meter (Keithley 2400).

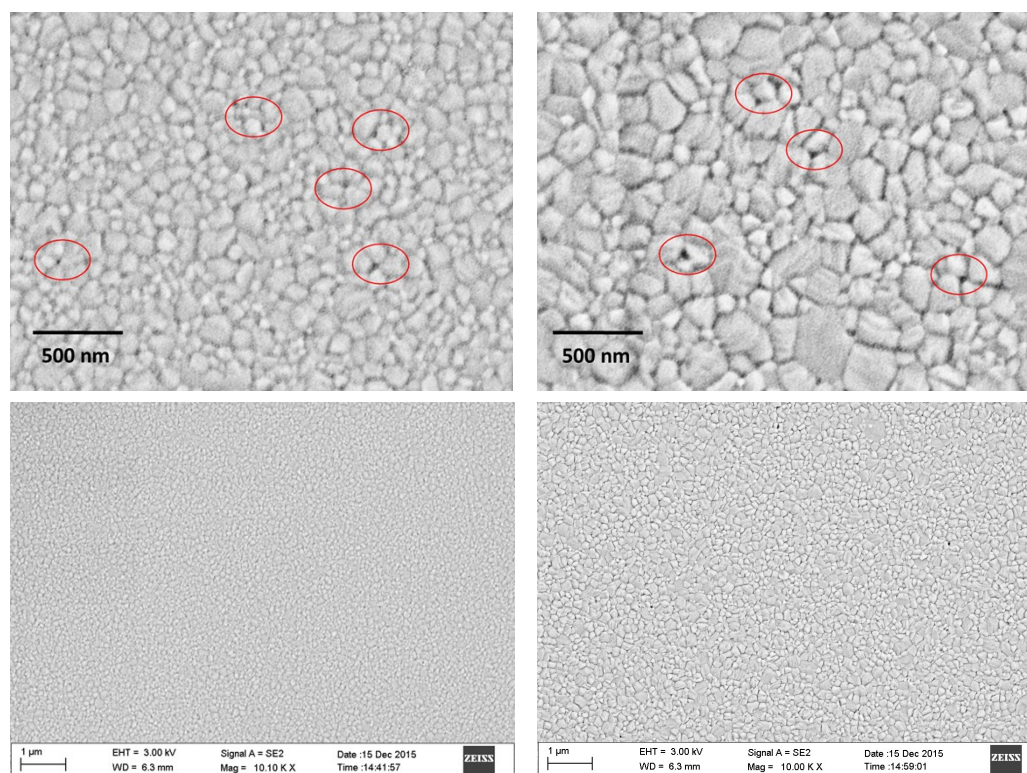


Fig. S1 Plane-view scanning electron microscopy images for the CH₃NH₃PbI₃ perovskite films, the wet films were washed with (a, c) toluene, (b, d) chlorobenzene. The films were produced in N₂ glove box (H₂O < 1 ppm). It is obviously that less pinholes were present in the film.

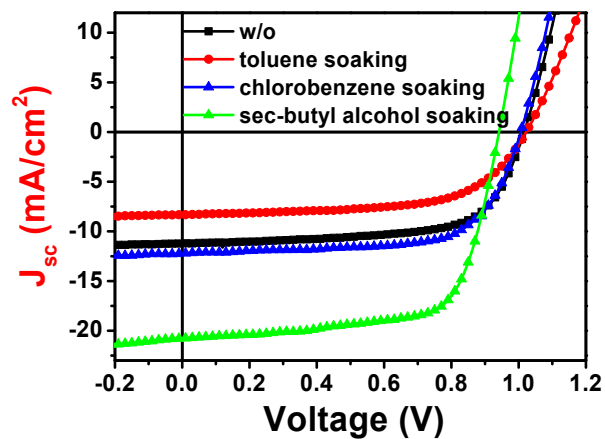


Fig. S2 The photocurrent curves of the devices with different soaking solvent toluene (red), chlorobenzene (blue), and sec-butyl alcohol (green). Toluene and chlorobenzene as nonpolar solvent are difficult to dissolve MAI and unable to remove the excess of MAI in the films.

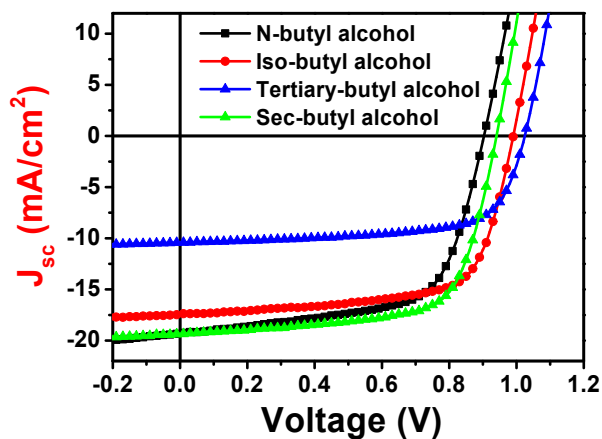


Fig. S3 The photocurrent curves of the devices with different soaking solvents: n-butyl alcohol (black), iso-butyl alcohol (red), ter-butyl alcohol (blue) and sec-butyl alcohol (green).

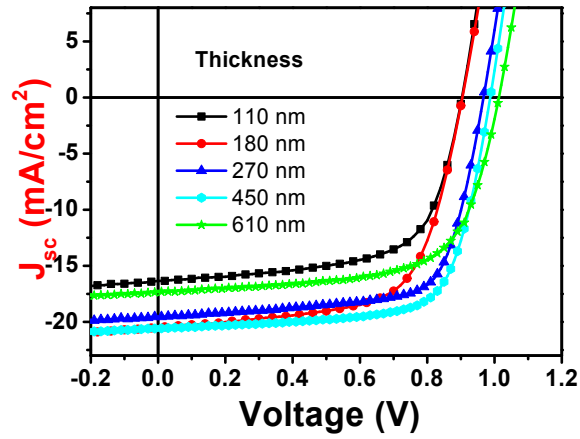


Fig. S4 The photocurrent curves of the devices with different film thickness.

Table S1 Photovoltaic performance of perovskite solar cells based on different film thickness.

Thickness (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE
110	16.35	0.90	66.6	9.8
190	20.5	0.904	65.1	12.07
270	19.54	0.967	70.6	13.35
450	20.6	0.99	71.0	14.4
610	17.3	1.01	65.8	11.6

Notes

1 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, 338, 643.