Cover sheet-Supporting Information

Manuscript title: "Preparation of Perovskite Films under Liquid Nitrogen Atmosphere for High Efficiency Perovskite Solar Cells"

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Electronic Supplementary Information for

Preparation of Perovskite Films under Liquid Nitrogen Atmosphere for High Efficiency Perovskite Solar Cells

Experimental Section

Materials. Unless specified otherwise, all materials were purchased from either Wako or TCI and used as received.

Device fabrication.

Substrate preparation: Firstly, fluorine doped tin oxide substrates (FTO-coated glass) (Nippon Sheet Glass Co. Ltd.) were cut into squares with dimensions of 20 × 20 mm^2 and etched with Zn powder and HCl aqueous (6 M). Then the substrates were washed by ultrasonication with diluted detergent, (10% in water), isopropanol, acetone and deionized water for 20 min, respectively. A 30~50 nm-thick compact layer of TiO_2 (c-TiO_2) was then coated on the substrates by spin coating of a 0.15 mM bis(isopropoxide)bis(acetylacetonato)titanium(IV) solution (75% in 2-propanol, Sigma-Aldrich) in 1-butanol at 2000 rpm for 20 s and then baked on the hotplate at 125 °C for 5 min (thickness of the c-TiO_2 is about 40 nm in this work, see Fig. S1 in supporting information). After cooling down to room temperature, the diluted-TiO_2 paste (30 NRD/ethanol = 1/ 4, weight ratio) was spin-coated on the c-TiO_2 layer at 5000 rpm for 30 s, followed by drying on a hotplate at 125 °C for 10 min, then annealing at 500 °C for 1 h to provide a 150~200 nm-thick mesoporous TiO_2 (m-TiO_2) (in this work thickness of the m-TiO_2 is about 174 nm, see Fig. S2).

Perovskite precursor solution and film deposition: Perovskite layer, $CH_3NH_3PbI_3$, was formed using one-step anti-solvent method. Perovskite precursor solutions with a concentrations of 1.5 M were prepared by dissolving Methylammonium iodide (MAI) and lead iodide (PbI_2) (MAI/PbI_2 = 1:1.05, molar ratio) in a mixture solution of N, N-dimethylformide (DMF) and dimethyl sulfoxide (DMSO) (DMF/DMSO = 4/1, volume ratio) and stirring at room temperature for 1 hour. To prepare light harvesting layer, the perovskite solution (50 μL) was first dropped onto a TiO_2/FTO substrate. The substrate was then spun at 4000 rpm for 25 s, and during the 10^{th} seconds 500 μL of anhydrous ethyl acetate was quickly dropped on the spinning substrate. The obtained films were then annealed at 100 °C for 10 min in air environment. For the preparation of perovskite film by LN method, as shown in Fig. S3 b, two stainless steel petri dishes (5cm in diameter and 1.5cm in depth) filled with liquid nitrogen (～20 mL) were placed under the spinner before spin coating.

Hole transporting layer and Au electrode: A 50 μL of Spiro-OMeTAD solution was spin-coated on the top of perovskite layer at 4000 rpm for 30 s. The Spiro-OMeTAD solution was prepared by dissolving 72.3 mg of Spiro-OMeTAD in 1 mL of chlorobenzene, to which 28.8 μL of 4-tert-butyl pyridine (4-tBP) and 17.5 μL of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) (520 mg LI-TSFI in 1 mL acetonitrile) were added. Finally, an 80-nm-thick of Au was thermally evaporated

on the Spiro-OMeTAD-coated film. Note that the samples were left in a desiccator overnight before the gold electrode was prepared.

Film and device characterization

The thickness of the TiO_2 layer were measured using a Veeco Dektak 150 surface profilometer. A field-emission scanning electron microscope (FE-SEM, Jeol JSM 6700F) was used to investigate the morphology of the perovskite film top view and the device cross section. Absorption spectral measurements were recorded using Shimadzu UV-2550 UV-visible spectrophotometer. A solar simulator (KHP-1, Bunko-Keiki, Japan) fitted with a filtered 1000 W xenon lamp was used to provide simulated solar irradiation (AM1.5, 100 $mW \cdot cm^{-2}$). Illumination intensity of the solar simulator was confirmed by a standard silicon reference cell (BS-520 S/N 007, Bunko-Keiki, Japan). Current-voltage (J-V) characteristics were measured using a Keithley 2400 source meter. The solar cells were masked with a non-reflective metal aperture of 0.1 cm^2 to define the working area of the device and avoid light scattering through the edges. Incident photon to current efficiency (IPCE) spectra were recorded using a 150 W xenon lamp (KHP-1, Bunko-Keiki, Japan) fitted with a monochromator (Cornerstone 260) as a monochromatic light source. IPCE photocurrents were recorded under short-circuit conditions using the Keithley 2400 source meter.

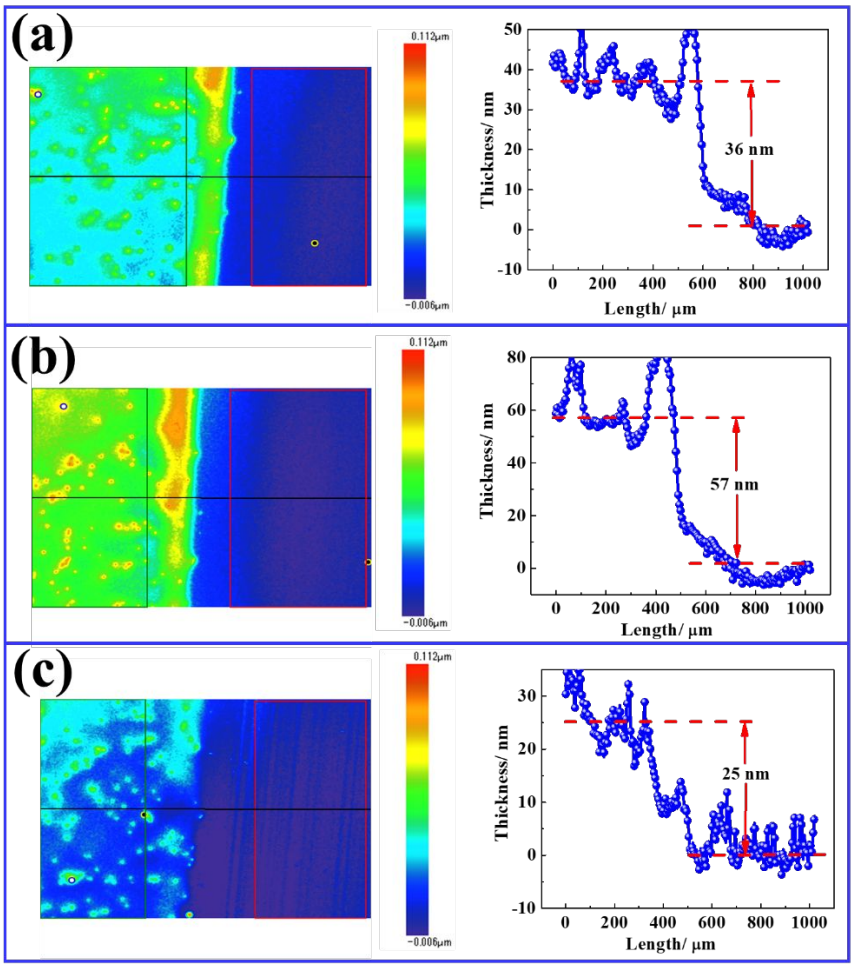

Fig. S1 Thickness of TiO_2 compact layer (c-TiO_2) on FTO glass. (a) 36 nm, (b) 57 nm, (c) 25 nm. The c-TiO_2 were prepared by spin-coating method, in detail 0.15 M titanium diisopropoxide bis (acetylacetonate) (75 wt% in isopropanol, Sigma-Aldrich) in 1-butanol (99.8%, Sigma-Aldrich) solution was spin-coated on an FTO substrate at 2000 rpm for 20 s, which was followed by heating on a hotplate at 125 °C for 5 min. Three samples were randomly selected with an average thickness of 39 nm ((36+57+25)/3=39 nm).

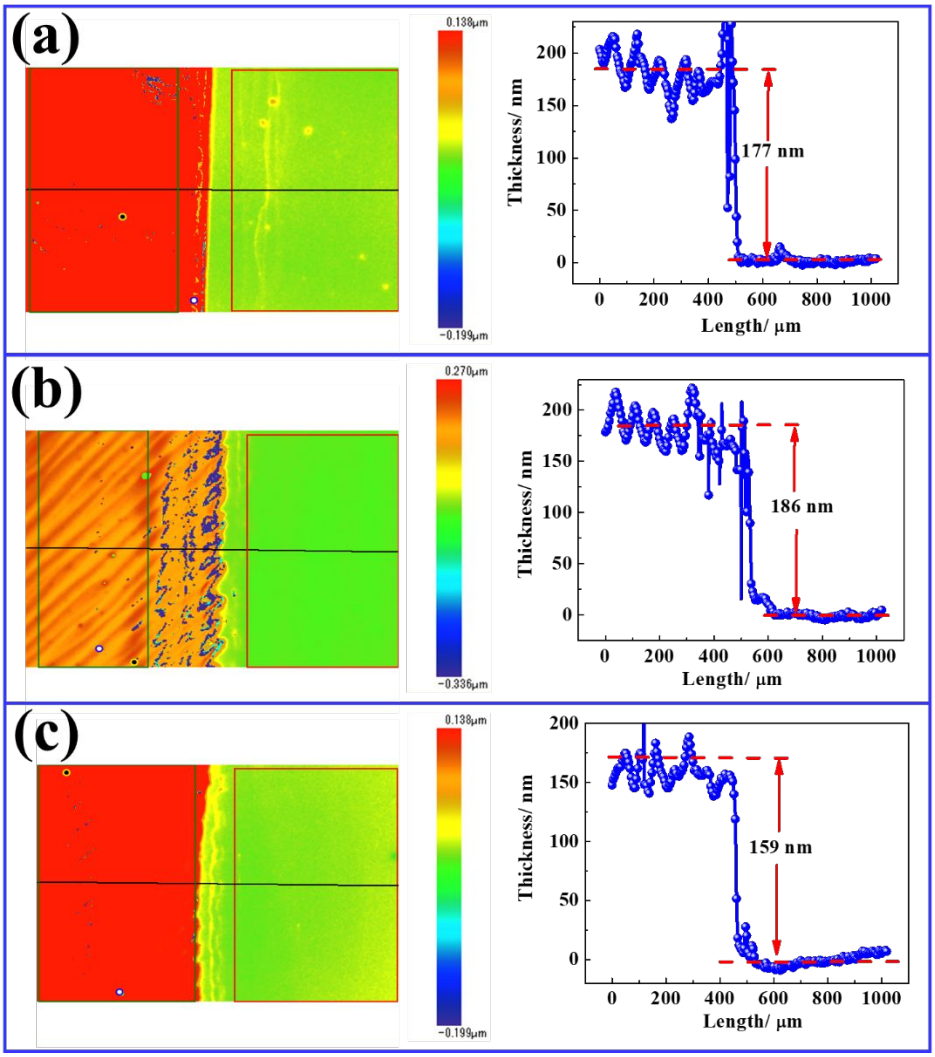

Fig. S2 Thickness of mesopourousTiO_2 layer (m-TiO_2) on FTO/c-TiO_2. (a) 177 nm, (b) 186 nm, (c) 159 nm. In detail the diluted-TiO_2 paste was spin-coated on the c-TiO_2 layer at 5000 rpm for 30 s, where the paste (Dyesol, 30 NR-D) was diluted in ethanol (TiO_2 paste/ethanol = 1/ 4, weight ratio). After drying on a hotplate at 125 °C for 5 min, the film was annealed at 500 °C for 1 h, providing m-TiO_2 with thickness of about 174 nm. Three samples were randomly selected. ((177+186+159)/3=174 nm).

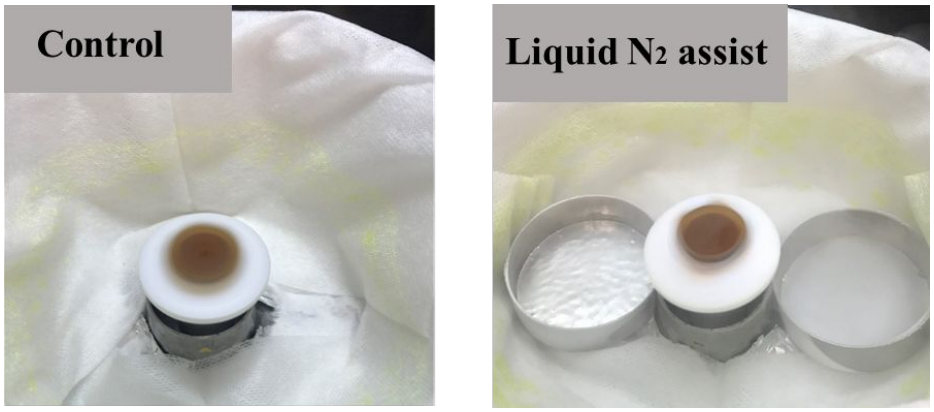

Fig. S3 One-step anti-solvent method for preparing perovskite films. (a) Conventional process and (b) liquid nitrogen assist process, the ambient temperature is about 23 ℃ and the temperature during spin-coating was about 4 ℃.

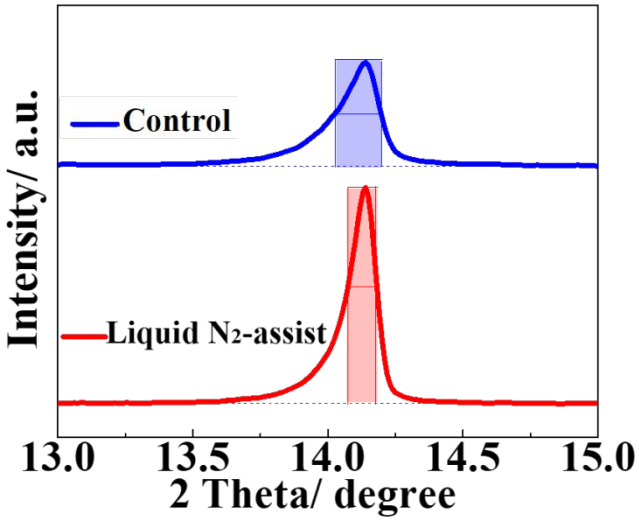

Fig. S4 X-ray diffraction spectra of $CH_3NH_3PbI_3$ perovskite films prepared by conventral process and liquid nitrogen assisted process. The full width at half maximum (FWHM) of peak at 14.17°。

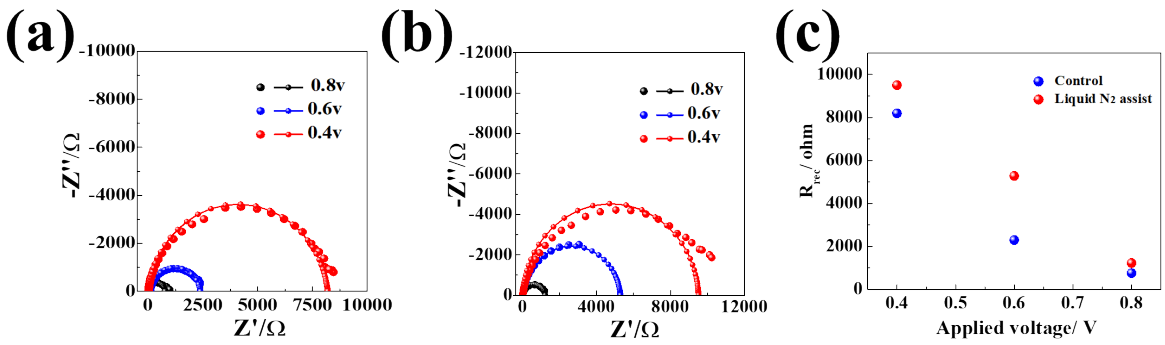

Fig. S5 Nyquist plots of perovskite solar cells based on $CH_3NH_3PbI_3$ measured in dark condition with different applied bias (0.4, 0.6 and 0.8 V). (a) Control group and (b) liquid nitrogen assisted group. (c) Charge recombination (Rrec) resistance extracted from EIS measurements at different applied bias.

Tab. S1. Photovoltaic parameters for thirty perovskite solar cells of control group.

Device #	J_{sc} /mAcm^{-2}	V_{oc} /V	FF	PCE /%
1	21.549	1.028	0.655	14.506
2	21.62	1.016	0.643	14.13
3	20.4	1.019	0.706	14.68
4	21.687	1.031	0.699	15.632
5	21.322	1.047	0.638	14.247
6	21.429	1.042	0.647	14.453
7	21.269	1.055	0.683	15.328
8	18.781	1.055	0.738	14.626
9	21.491	1.024	0.667	14.695
10	21.775	1.05	0.674	15.45
11	21.682	1.008	0.699	15.292
12	21.59	1.007	0.676	14.72
13	20.799	1.043	0.653	14.175
14	20.391	1.049	0.658	14.077
15	18.861	1.055	0.736	14.659
16	21.231	1.034	0.653	14.32
17	21.079	1.021	0.68	14.641
18	21.39	1.014	0.656	14.23
19	19.587	1.055	0.652	13.482
20	21.674	0.98	0.685	14.539
21	21.1	1.002	0.668	14.12
22	19.807	1.033	0.698	14.277
23	20.99	1.006	0.66	13.93
24	18.941	1.021	0.733	14.686
25	20.761	1.041	0.659	14.252
26	21.346	1.023	0.668	14.6
27	21.194	1.043	0.647	14.299
28	21.113	1.055	0.657	14.64
29	20.168	1.007	0.663	13.478
30	21.294	1.051	0.663	14.835
Average	20.877± 0.863	1.030± 0.019	0.673± 0.027	14.499± 0.488

Tab. S2. Photovoltaic parameters for thirty perovskite solar cells prepared by LN method.

Device #	J_{sc} /mAcm^{-2}	V_{oc} /V	FF	PCE /%
1	20.284	1.062	0.731	15.745
2	19.679	1.038	0.738	15.077
3	22.127	1.059	0.692	16.216
4	19.814	1.057	0.737	15.426
5	21.599	1.055	0.719	16.38
6	20.235	1.067	0.695	15.007
7	21.503	1.052	0.719	16.277
8	21.594	1.054	0.684	15.566
9	20.13	1.062	0.735	15.698
10	22.29	1.024	0.639	14.6
11	22.194	1.058	0.704	16.532
12	19.907	1.056	0.735	15.454
13	20.373	1.064	0.723	15.664
14	21.989	1.048	0.663	15.28
15	21.73	1.058	0.679	15.619
16	21.793	1.057	0.717	16.523
17	21.278	1.05	0.722	16.139
18	22.545	0.985	0.633	14.051
19	22.603	1.018	0.656	15.098
20	21.186	1.049	0.723	16.071
21	19.947	1.058	0.736	15.546
22	20.482	1.038	0.673	14.311
23	19.987	1.058	0.731	15.467
24	21.992	1.061	0.678	15.826
25	21.515	1.056	0.674	15.3
26	19.713	1.056	0.725	15.102
27	20.549	1.069	0.722	15.852
28	21.148	1.087	0.692	15.911
29	22.752	1.037	0.648	15.288
30	21.816	1.039	0.665	15.071
Average	21.158± 0.959	1.051± 0.018	0.700± 0.032	15.536± 0.595