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Supporting Information

Retarding the crystallization of PbI_2 for highly reproducible planar-structured perovskite solar cells via sequential deposition

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1. Experiments

1. 1 Materials and reagents

PbI_2, 4-tert-butylpyridine (TBP), lithium bis(trifluoromethane-sulfony)imide (Li-TFSI), spiro-OMeTAD and Au were purchased from sigma Aldrich. CH_3NH_3I was synthesized according to literature. N,N-dimethylmethanamide (DMF), dimethyl sulfoxide (DMSO), 2-propanol, ethanol, *n*-butanol, titanium tetraisopropanolate, HCl (35% aqueous solution), chlorobenzene, acetonitrile were purchased from commercial and used without purification.

1. 2 Equipments

Thin films such as c-TiO_2, PbI_2, spiro-OMeTAD, were fabricated by using spin coater (Oshine spin-coater SC-150). Film heating and/or annealing were conducted on hot plate (IKA C-MAG, HP7). Film thickness of PbI_2 was measured by a profile-system. Au electrodes were deposited in (Vacuum Deive Inc, VE-2030). XRD patterns were recorded by using an X-ray diffractometer (Rigaku, RINT-2500) with a CuKa radiation source. The surface morphology of PbI_2 and perovskite films as well as cross-section of solar cell device was analyzed by using a JEM-6500F field-emission scanning electron microscope (SEM). Absorption spectra of the film samples were recorded by using a Shimadzu UV/Vis 3600 spectrophotometer.

1.3 Fabrication of PbI_2 films

PbI_2 films were usually prepared by spin-coating a concentrated PbI_2-DMF solution, and drying at 70-100 °C for removing the solvent and crystallization of the PbI_2, resulting in a polycrystalline precursor (***pc***-precursor) for sequential deposition. Actually, even without drying process at 70-100 °C, PbI_2 in the resultant films is also crystallized easily due to the high volatile solvent of DMF. In order to inhibit the crystallization of PbI_2, we chose a low volatile solvent of DMSO to dissolve the PbI_2 and fabricate the desired ***α***-precursor films. The concentration of the DMSO solution and conditions for film spin-coating are the same with that of DMF one as shown below.

1. 4 Weighting experiment

In order to determine the molar ratio between PbI_2 and solvent in the DMSO based films, we fabricated PbI_2 films on larger area FTO glass substrates (6.0x6.0cm). Prior to film deposition, the mass of the substrate were measured, using an accurate balance. Subsequent to film deposition and vacuum-heating (120 °C for 2 h), the samples were re-weighed, and the difference in mass before and after vacuum-heating treatment was used to determine the molar ratio of PbI_2 and DMSO in the film.

1. 5 Perovskite thin film and solar cell fabrication

For common measurement, such as absorption, XRD and SEM experiments, the compact TiO_2 was prepared by spin coating a 0.7 M Titanium tetraisopropanolate in *n*-butanol solution (containing 0.2 M HCl) and sintering at 500 °C for 30 min. For fabrication solar cells, we used ALD produced TiO_2 compact layer, which we have proved to be benefit to device performance and reproducibility. The preparation method is the same as reference. Planar-strucutred devices are made as follows: several drops of PbI_2 (1.0 M in DMF or DMSO) solution were placed on the compact TiO_2 substrate and spin coated at 4000 rpm for 30 s to obtain PbI_2 films with thickness around 200 nm. The PbI_2 films were immersed into a solution of CH_3NH_3I in 2-propanol (10 mg/mL) for 10 min, washed with 2-propanol and dried with N_2 flow, then spiro-OMeTAD based hole-transfer layer (180 mg spiro-OMeTAD, 18 μL tBP and 40 μL Li-TFSI solution (170 mg Li-TFSI in 1 mL acetonitrile) all dissolved in 1 mL chlorobenzene) was deposited on perovskite layer by spin-coating at 4000 rpm for 30 s. Finally, a 100 nm thick Au layer was deposited by thermal evaporation at a base pressure of 2×10^{-6} mbar.

1. 6 Solar cell characterization

The current-voltage curves of solar cells were measured in ambient using a Keithely 2400 source-measure unit. The cells were illuminated by a 500 W Class AAAAA solar simulator equipped with an AM 1.5G filter (WXS-90L2, Wacom) at a calibrated intensity of 100 mV cm^{-2}, as determined by a standard silicon reference cell. The effective area of the cell was defined as 0.09 cm^2 using a non reflective metal mask.

2. Characterization of DMSO based PbI_2 films before and after heat treatment

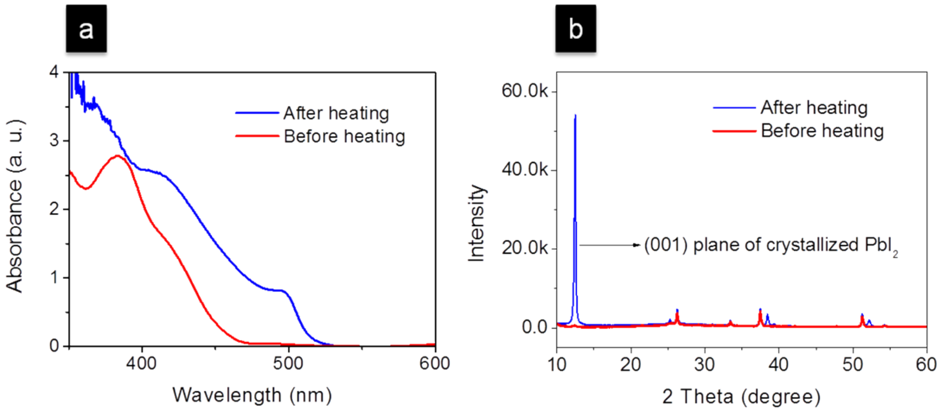

Fig. S1 (a) absorption spectra and (b) XRD pattern of DMSO based PbI_2 film before (red) and after (blue) heating at 120 °C in vacuum for 2 h. DMSO based PbI_2 films are transparent and show different color to DMF based PbI_2 films. This should be caused by strong interaction between DMSO molecules and PbI2 in the film, retarding the crystallization process of PbI_2. After heating at 120 °C in vacuum for 2 h, DMSO based PbI_2 films become yellow with the same absorption spectra to DMF based PbI_2 films, indicating PbI_2 crystallized after the DMSO was removed. This could be certified by the variation of XRD pattern as shown above.

3. Reaction of crystallized PbI_2 with CH_3NH_3I

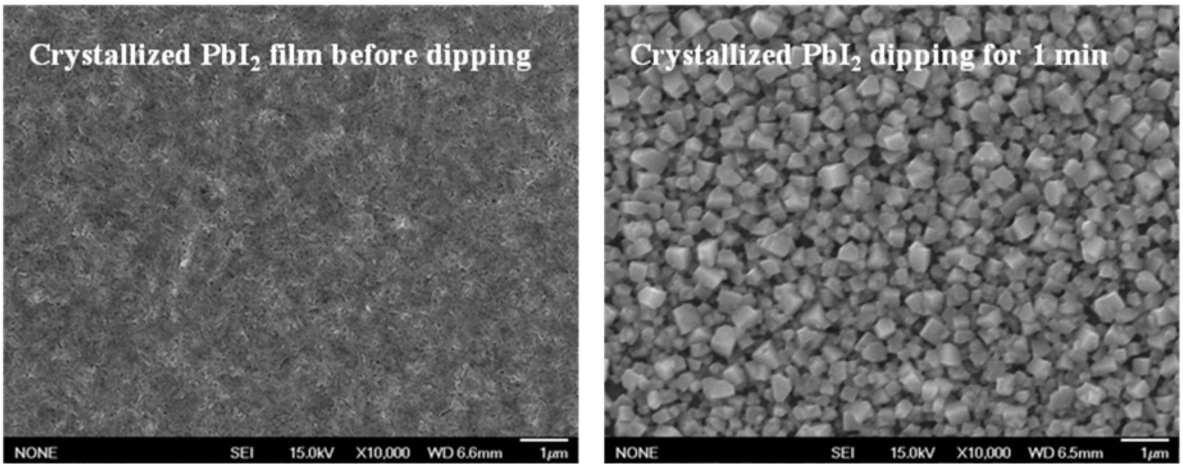

Fig. S2 SEM images of crystallized PbI_2 film before (left) and after (right) dipping for 1 min in CH_3NH_3I solution. We can see that almost all the PbI_2 at the crystal surface have been converted to perovsktie after dipping for only 1 min. The surface morphology showed a large difference as plate-shaped PbI2 turned to cuboids structure particles. It should be noted that in the large cuboids particles, there are a lot of remaining PbI_2 i. e., it is composed of perovkite-PbI_2 mixtures.

4. Evolution of XRD patterns upon dipping DMSO based PbI_2 films in CH_3NH_3I solution.

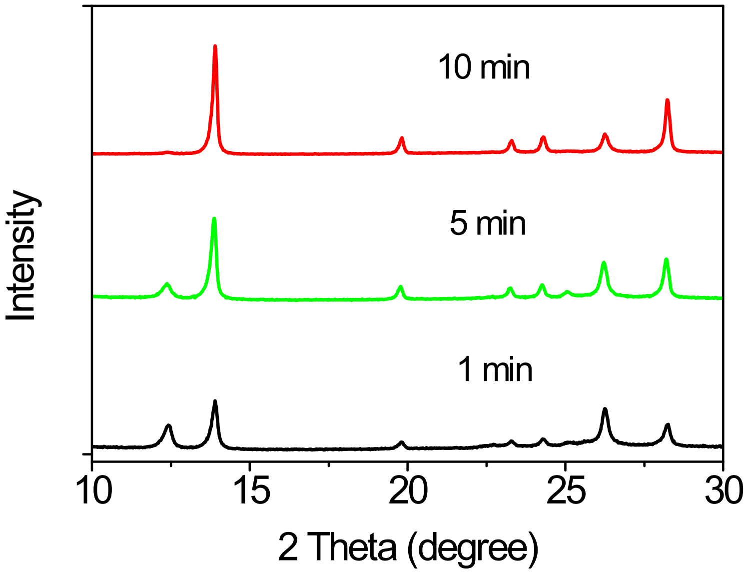

Fig. S3 XRD patterns of DMSO based PbI_2 films after dipping in CH_3NH_3I solutions for 1, 5 and 10 min. As we knew that before dipping in CH_3NH_3I solutions, PbI2 in DMSO based films is uncrystallized and does not show diffraction peak in XRD. However, after dipping 1 or 5 min the PbI_2 peak at 12.6 recovered. This means that washing and heating treatment could remove the DMSO molecules in the film, which results the unreacted PbI_2 crystallized again.