

Supporting Information

for

Planar heterojunction perovskite solar cells via vapor assisted solution process

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Experimental section:

CH₃NH₃I Synthesis. CH₃NH₃I was synthesized by reacting 24 mL of methylamine (33 wt. % in absolute ethanol, Sigma) and 10 mL of hydroiodic acid (57 wt% in water, Aldrich) in a 250 mL round-bottom flask at 0 °C for 2 h with stirring. The precipitate was recovered by putting the solution on a rotary evaporator and carefully removing the solvents at 50 °C. The yellowish raw product CH₃NH₃I was re-dissolved in 80 mL absolute ethanol and precipitate with the addition of 300 mL diethyl ether. After filtration, the step was repeated again. And the solid was collected and dried at 60 °C in a vacuum oven for 24 h.

Thin Film and Solar Cell Fabrication. Substrate preparation was carried out under ambient conditions. FTO-coated glass (13 Ω/sq, Aldrich) was patterned by etching with Zn powder and 2 M HCl diluted in deionized water. The substrates were then cleaned with detergent diluted in deionized water, rinsed with deionized water, acetone and ethanol, and dried with clean dry air. After oxygen plasma treatment, the clean substrates was spin-coated with 0.15 M and 0.3 M titanium diisopropoxide bis(acetylacetonate) (Aldrich) at 3,000 r.p.m. for 30 s subsequently. After drying at 125 °C for 10 min, they were sintering at 550 °C for 15 min in air. The substrate was immersed in 50 mM TiCl₄ (Aldrich) aqueous solutions for 30 min at 70 °C and washed with distilled water and ethanol, followed by annealing at 550 °C for 30 min in air to form a compact n-type layer of TiO₂(c-TiO₂). The solution of 400 mg/mL PbI₂ (Sigma) in DMF were spin coated on the FTO/c-TiO₂ substrates at 2,000 r.p.m. for 30s, and dried at 110 °C for 15 min. CH₃NH₃I powder was spread out around the PbI₂ coated substrates with a petridish covering on the top ,

and heated at 150 °C for desired time. Both the deposition of PbI₂ film and vapor treatment of PbI₂ film are carried out in glovebox. After cooling down, the as-prepared substrates was washed with isopropanol, dried and annealed. The FTO/c-TiO₂/Perovskite substrates was deposited by spin coating a hole transport layer (HTL) solution at 2000 r.p.m for 30s, where a spiro-OMeTAD (Lumtec)/chlorobenzene (180 mg/1 mL) solution was employed with addition of 50 μL Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI, Sigma)/acetonitrile (170 mg/ 1 mL) and 20 μL tert-butylpyridine (tBP, Sigma). Finally, the counter electrode was deposited by thermal evaporation of silver under a pressure of 5×10^{-5} Torr. The active area was 0.12 cm².

Characterizations. X-ray diffraction pattern (2θ scans) were obtained from samples of perovskite deposited on the FTO/c-TiO₂ substrates using an X-ray diffractometer (Panalytical X'Pert Pro), using Cu-Kα radiation ($\lambda=1.54050\text{\AA}$). An emission SEM (The Nova 230 NanoSEM) was used for collecting the SEM images. The instrument uses an electron beam accelerated at 500V to 30 kV, enabling operation at a variety of currents. Atomic force microscope (AFM) was performed using Bruker Dimension 5000 Scanning Probe Microscope (SPM) in "tapping" mode. The photovoltaic performance was characterized in air without any encapsulation under an AM 1.5G filter at 100 mW/cm² using a Newport Oriel 92192 Solar Simulator, as calibrated using a certified silicon photodiode. The solar devices were masked with a metal aperture to define the active area of about 0.11 cm², and measured in a sample holder to minimize any edge effects. The external quantum efficiency (EQE) was measured using a system designed by Enli Tech.

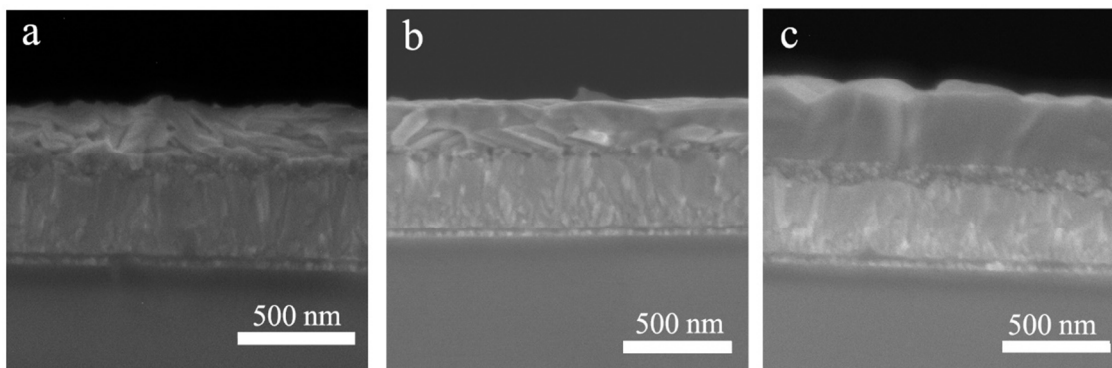


Figure S1 Cross-sectional SEM images of the PbI₂ film annealed at 150 °C for (a) 0 h, (b) 0.5 h and (c) 4 h in the presence of CH₃NH₃I.

Figure S1 depicts the cross-sectional SEM images of the PbI₂ film annealed at 150 °C for 0 h, 0.5 h and 4 h, respectively. As indicated in Figure S1a, the thickness of PbI₂ film is ~ 200 nm, which is composed of several “platelets” in the vertical direction. With the reaction time prolonged to 0.5 h, the “platelets” at the top enlarged and formed well-defined grains, while those at the bottom remained the same. The film thickness increased to ~300 nm consequently. This is in the agreement of the possible growth of perovskite on top of the PbI₂ grains, as indicated in the manuscript. The film at post stage, where the reaction time further increase to 4 h, didn’t show obvious difference to that of completed stage (2h), in terms of the grain morphology and the film thickness. The film kept the undulation characteristic of the surface, suggests the absence of distinctive ripening and coarsening process thereafter.

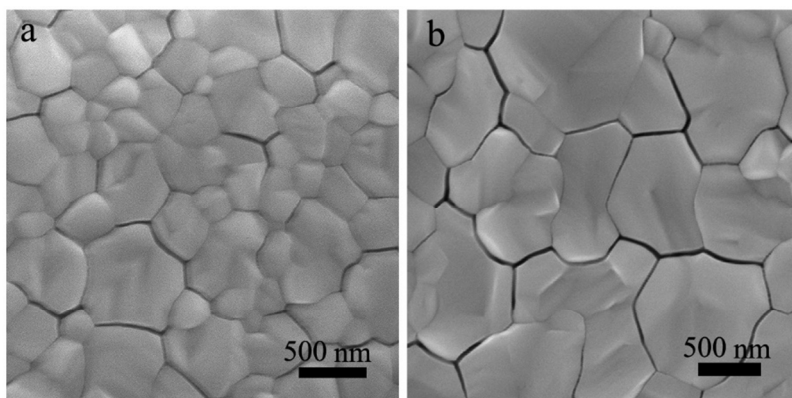


Figure S2 SEM images of the PbI_2 film annealed at 150 °C for (a) 1 h and (b) 3 h in the presence of $\text{CH}_3\text{NH}_3\text{I}$.

Figure S2 shows the top-view SEM image of the PbI_2 film annealed at 1 h and 3 h in the presence of $\text{CH}_3\text{NH}_3\text{I}$, respectively. It is clearly that certain amount of small grains of ~ 150 nm coexisted with the large grains of over 500 nm, when the annealing time is 1 h (Figure S2a). Compared with the complete stage (2h), the existence of the relatively smaller grains indicates the grain growth is underway at this stage. At the post stage (3h, Figure S2b), it shows similar morphology as that of the reaction at 2 and 4 h. This further confirms the reaction between PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ completed within 2 hour without obvious film progression further.

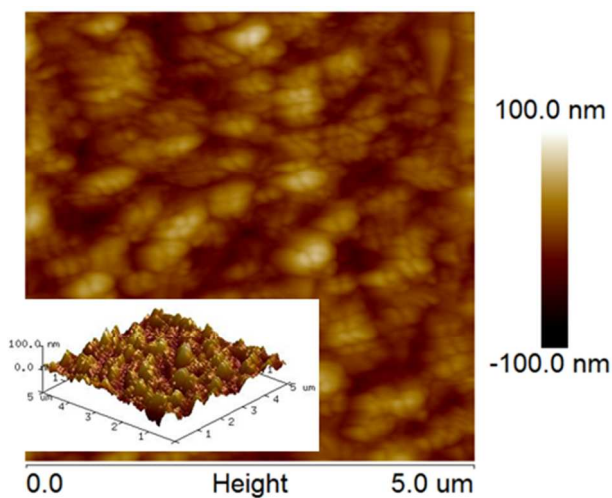


Figure S3 Tapping-mode AFM height images ($5 \times 5 \mu\text{m}$) of the as-prepared PbI_2 films (Inset: the corresponding 3D topographic image).

As indicated in Figure S3, the PbI_2 film exhibits a calculated roughness of ~ 17 nm. The smooth film serves as a superior platform for the further growth of perovskites.

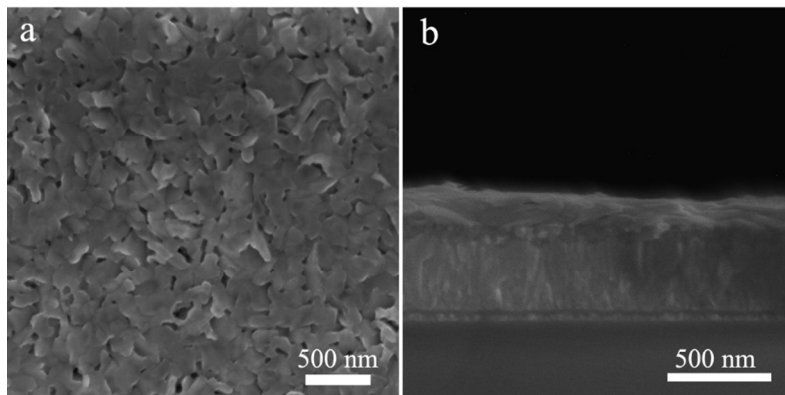


Figure S4 (a) Top-view SEM image and (b) cross-sectional SEM image of the PbI_2 film annealed at $150\text{ }^\circ\text{C}$ for 2 h.

As shown in Figure S4, the PbI_2 film annealed without the involvement of $\text{CH}_3\text{NH}_3\text{I}$, exhibits the similar grain size and morphology as that of the initial PbI_2 film. It indicates that no obvious grain growth driven by diffusion occurred within the sole PbI_2 film at current temperature. In contrast, grain growth is observed within the PbI_2 in the presence of $\text{CH}_3\text{NH}_3\text{I}$, which is ascribed to 1) the intercalation induced volume expansion, or possibly 2) re-arrangement of PbI_2 .

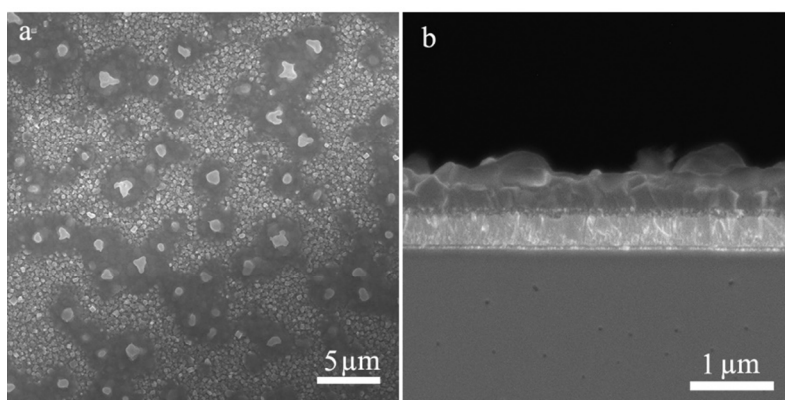


Figure S5 (a) Top-view SEM image and (b) cross-sectional SEM image of the PbI_2 film after dipping in the $\text{CH}_3\text{NH}_3\text{I}$ IPA solution (10mg/ml) for 30 min.

Two-step process, by dipping the PbI_2 film in $\text{CH}_3\text{NH}_3\text{I}$ solution (10 mg/mL), is also studied in the current work. Both top-view and cross-sectional SEM images indicate a rough surface of the film. As suggested by the reported results, a rather long reaction time is required to construct the 3D structured $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, since there is no kinetically favorable van der Waals gap in the interface of $\text{PbI}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ where the transformation occurs. It thus results in the film with strikingly enhanced surface roughness, or ultimately film peel-off from the substrate, which hampers its application in PVs.