Electronic Supplementary Information

Intercalation Crystallization of Phase-Pure α-HC(NH$_2$)$_2$PbI$_3$ upon Microstructurally Engineered PbI$_2$ Thin Films for Planar Perovskite Solar Cells

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Experimental Procedure

**Film Fabrication.** These four different types PbI$_2$ thin films were fabricated: (i) compact (dense) PbI$_2$ film with low crystallinity (PbI$_2$-CL), (ii) porous PbI$_2$ film with low crystallinity (PbI$_2$-PL), (iii) porous PbI$_2$ film with high crystallinity (PbI$_2$-HP), and (iv) compact PbI$_2$ film with high crystallinity (PbI$_2$-CH). PbI$_2$-CL film was a freshly spin-coated (4000 rpm, 40s) film using 40 wt% PbI$_2$ precursor solution in dimethyl formamide (DMF). The PbI$_2$-LP and PbI$_2$-HP films are obtained by aging the PbI$_2$-CL films at room temperature for 2 h and 48 h, respectively. The PbI$_2$-CH film is processed by heat-treating the PbI$_2$-CL film at 150 °C for 1 h. After the deposition of the PbI$_2$ thin films, fresh HC(NH$_2$)$_2$I solution of 20 mg.ml$^{-1}$ in anhydrous isopropanol (IPA) was spin-coated onto the as-prepared PbI$_2$ thin films, and they were then annealed at 170 °C for 1 min, which constitutes the first spin-coating/annealing (SSCA) cycle. This SSCA cycle was then repeated for three times. The excess MAI was washed away using IPA, and the final thin films were annealed at 170 °C for 15 min to obtain a dark-colored α-HC(NH$_2$)$_2$PbI$_3$ (α-FAPbI$_3$) perovskite film with thickness of ~280 nm. The thickness of α-FAPbI$_3$ thin films can be controlled via spinning/annealing conditions.

**Materials characterization.** X-ray diffraction (XRD) was performed on a diffractometer (D8-Advance, Bruker, Germany) using Cu Kα$_1$ radiation (λ=1.5406 Å) at step size/time 0.02° conditions. Surface and cross-sections (fractured) morphology of the films were observed in a scanning electron microscope (SEM; LEO 1530VP, Carl Zeiss, Germany). The optical absorption spectroscopy was conducted on a spectral response measurement system (QEXL, PV Measurements, Boulder, CO).

**Device fabrication and characterization.** For the fabrication of the PSCs, a compact TiO$_2$ electron-transporting layer (ETL) was first deposited on pre-patterned FTO-coated glass by spray pyrolysis at 450 °C. The perovskite layer was then deposited using the procedure described above. This was followed by spin-coating a hole-transporting material (HTM) solution, which consisted of 80 mg 2,2',7,7'-tetrakis(N,N-dip-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD), 30 μl bis(trifluoromethane) lithium salt stock solution (500 mg Li-TFSI in 1 ml acetonitrile), and 30 μl 4-tert-butylpyridine (TBP), and 1 ml chlorobenzene solvent. The HTM spin-coating process was performed in a dry-air atmosphere with humidity <10%. Finally a 150 nm Ag layer was deposited using thermal evaporator and a shadow mask. The external quantum efficiency (EQE) spectra were recorded at a chopping frequency of 5 Hz in AC mode on a solar cell quantum efficiency measurement system (QEX10, PV Measurements, Boulder, CO). The current density (J) - voltage (V) characteristics of the cells were obtained using a 2400 SourceMeter (Keithley, Cleveland, OH) under simulated one-sun AM 1.5G illumination (100 mW.cm$^{-2}$) (Oriel Sol3A Class AAA Solar Simulator, Newport Corporation, Irvine, California).
Typical $J-V$ scan started from short-circuit to open circuit and then back to short-circuit at the rate of 20 mV.s$^{-1}$. The maximum-power output stability of the solar cells was measured by monitoring $J$ output at the maximum-power $V$ bias using a VersaSTAT MC potentiostat (Princeton Applied Research, Acton, MA). A shutter was used to control the one-sun illumination on the PSC. A typical active area of 0.12 cm$^2$ was defined using a non-reflective mask for the $J-V$ measurements.