Electronic Supplementary Information

Intercalation Crystallization of Phase-Pure α-$HC(NH_2)_2PbI_3$ 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 $HC(NH_2)_2I$ 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-$HC(NH_2)_2PbI_3$ (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 $K\alpha_1$ 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) sulfonimide 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, CA). 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.