Supporting Information

Rapid thermal annealing of $CH_3NH_3PbI_3$ perovskite thin films by intense pulsed light with aid of diiodomethane additive

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METHODS

All the materials were used as-received without any further purification. Dimethylformamide (DMF), dimethylsulfoxide (DMSO), titanium diisopropoxide bis(acetylacetonate) (TAA) and Bis(trifluoromethane)sulfonimide lithium salt were acquired from Sigma-Aldrich. Diiodomethane (DIM), and PbI_2 were acquired from Alfa-Aesar. The 2,20,7,70-Tetrakis(N,N-di-p-methoxyphenylamine)-9,90-spirobifluorene (Spiro-MeOTAD) was acquired from Merck. MAI and TiO_2 paste were acquired from Dyesol.

Etching and Cleaning

In the first step, the etching of FTO coated glasses (2 cm x 2 cm) was conducted using zinc powder and 2 M HCl. In the second step, cleaning of the FTO coated glass was initiated by dipping them in a Hellmanex soap solution diluted by DI water in 1:10 vol% and sonicated for 10 min. Successively, the glass slides were sonicated for 10 minutes in DI water, ethanol and in DI water. Finally, surface treatments were carried-out on the cleaned FTO glass slides by exposing to oxygen plasma for 10 minutes and successively, UV processing for 30 minutes prior to spin coating of TiO_2 layers.

TiO_2 Layer Deposition

The compact TiO_2 layer was deposited by spin coating a 0.15 M TAA solution dispersed in anhydrous 1-butanol with spin rates set at 700 rpm for 8 s, 1000 rpm at 10 s, and then 2000 rpm for 40 s without stopping in between. The spin coated slides were heated on a hot plate at 120 °C for 5 min to remove the remaining solvent after spin coating. In the next step, mesoporous TiO_2 (mp-TiO_2) layer was spin coated at 4000 rpm for 60s using a Dyesol 30NR-T TiO_2 paste diluted with ethanol in 1:4 (paste:ethanol) ratio by weight. The slides were heated on a hot plate at 120 °C for 5 min to remove the remaining solvent before placing them in a furnace to sinter at 500 °C for 60 min. Successively, slides with mp-TiO_2 layer were dipped in a 90 mM solution of $TiCl_4$ in 20% HCl diluted to 40 mM in DI water. The solution containing slides were heated in an oven at 70 °C for 30 min to fill the pores in mp-TiO2 layer. Finally, the slides were rinsed with water and heated at 500 °C for 30 min for the crystallization of TiO_2 from the $TiCl_4$ treatment.

Preparation of Perovskite Layer

The perovskite film deposition was carried-out in one-step method. In the first formulation, MAI-PbI2 precursor was mixed in DMF and DMSO with 1:1 molar ratio of MAI and PbI2 and total of 1.4M concentration of each precursor. In the second formulation, light sensitive diiodomethane additive was added to the first formulation with 0.125, 0.25 and 0.375 mL to DMF (1 mL) and DMSO (0.125 mL) solvent mix. The both perovskite precursor formulations were spin coated with 1000 rpm for 10 seconds and 4000 rpm for 30 seconds without stopping in between the different spin rates and poured 100 µl of chlorobenzene on the spin coating film before 15 seconds left for the end of the spin. The humidity inside the spin coater chamber was maintained below 10 %RH by introducing dry air to the spin coater. The film appeared completely transparent immediately after spin coating and then the glass slide with the film was placed on a hotplate at 75 ^{o}C for 2 min to evaporate the solvent and these films are considered as ‘As-deposited’ films from here onwards.

The humidity (60 %RH) was not controlled during solvent evaporation on the hot plate. The film was annealed with a Xenon Sinteron 2000 Intense Pulse Light (IPL) system. The capacitors were charged to 2.5 kV, which supplies approximately 25 J/cm^2 electrical energy to the lamp upon discharge. The duration of the flash was set to 2 ms. Unless otherwise stated, the perovskite films were prepared using 5 pulses at frequency of 1 Hertz. No effort was made to control the humidity during the IPL process. Here onwards, the perovskite films formed with the pure MAI and PbI2 are referred to as neat perovskite film whereas the perovskite films formed with CH_2I_2 additive mixed formulation are called CH_2I_2-perovskite films.

Device Fabrication

After depositing and annealing the perovskite films on the $TiCl_4$ treated mesoporous TiO_2 layer, spiro-MeOTAD layer was spin coated. The spiro-MeOTAD layer was prepared by spin-coating at 1700 rpm for 30 min inside a nitrogen filled glovebox. The solution was prepared by dissolving a 72.3 mg of spiro-MeOTAD in 1 mL of chlorobenzene along with a 28.8 μL 4-tert-butyl-pyridine, a 17.5 μL portion of stock solution of 520 mg/mL lithium bis(trifluoromethylsulfonyl) imide in anhydrous acetonitrile and a 29 μL of Dyesol cobalt dopant FK209 TFSI salt with concentration of 300 mg/mL in anhydrous acetonitrile. Finally, 100 nm thick Au electrode was deposited via thermal evaporation.

Characterization

X-Ray diffraction (XRD) studies were carried out using a Bruker AXS D8 X-ray di□ractometer with a scan rate of 1 s/step and a step size of 0.02°. Microstructure of the films was characterized using an FEI Nova NanoSEM 600 with an accelerating voltage of 5 kV and a working distance of 5 mm. The J-V characteristics of the devices and Electroimpedance spectroscopy were performed using an AM 1.5 simulated light from a Newport LCS-100 system

and a Metrohm Autolab potentiostat. The neat and CH_2I_2-perovskite cells were held at a bias voltage of 0.6 V under one sun illumination during impedance spectroscopic analysis.

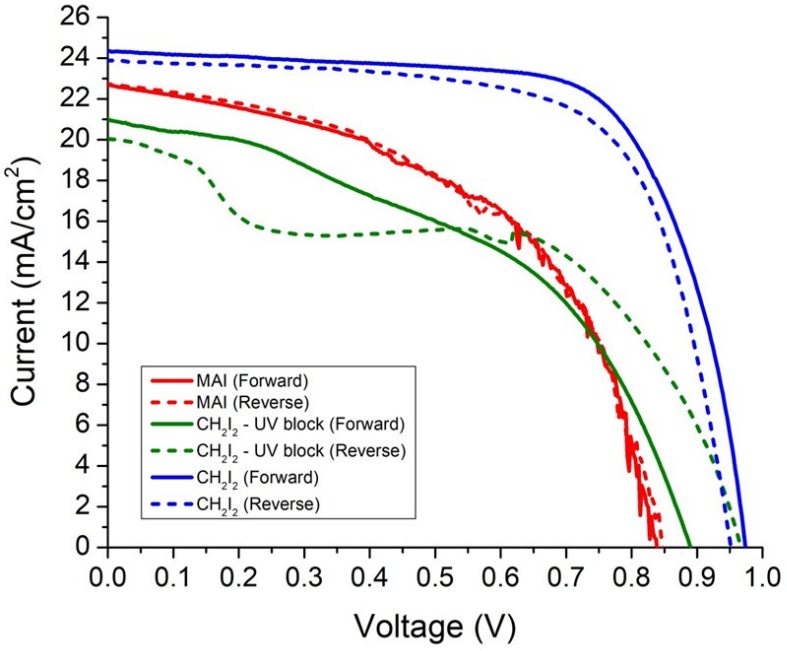

Fig. S1 Impact of the addition of the CH_2I_2 on the performance of photovoltaic devices built with the IPL processed perovskite layers. Forward and reverse scans are shown to illustrate the hysteresis. The neat cells are shown in red (two lower scans) and have an efficiency 10%. The cells with CH_2I_2 added but processed in the IPL with a UV filter are shown in green (two middle scans) and have an efficiency of 10% with large hysteresis. The cells with CH_2I_2 and processed with IPL are shown in blue (top two scans) and have an efficiency of 16.5%.