Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information to

Understanding the rate-dependent *J-V* hysteresis, slow time component, and aging in $CH_3NH_3PbI_3$ perovskite solar cells: the role of a compensated electric field

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Device fabrication and characterization

Devices were prepared on clean fluorine-doped tin oxide coated glass (NSG 10). A hole blocking layer of compact TiO_2 was deposited by spray pyrolysis of a precursor solution of 0.6 ml titanium diisopropoxide bis(acetylacetonate) in 9 ml ethanol and 0.4 ml actylacetone, with oxygen as carrier gas at 450°C. The mesoporous TiO_2 was formed by spin coating of colloidal solutions of TiO_2 with particle size of 20 nm and at 5000 rpm for 20 sec. The films were then gradually heated to 500°C and sintered at that temperature for 15 min. 1.2 M lead iodide DMF solution was spin coated onto the mesoporous TiO_2 at 6500 rpm for 30 s and dried at 70°C. After drying, the deposition of lead iodide was repeated in order to ensure a better loading of the mesoporous structure with lead iodide. The perovskite layer was formed after dropcasting 0.2ml CH_3NH_3I solution in isopropanol (8 mg ml^{-1}) onto the substrate, waiting for 20 s, and then spinning for 20 s at 4000 rpm. The substrates were then dried at 70°C. For the hole transport layer formation, a solution of 72.3 g Spiro-MeOTAD in 1 ml chlorobenzene was prepared, containing 10 mol.% FK 209, 28.8 µl *tert*-butylpyridine and 17.5 µl solution of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI 520 mg/ml in acetonitrile). This solution was spin coated onto the perovskite surface 2000 rpm. The devices were completed with an 80 nm gold counter electrode, which was thermally evaporated on top of the device. The active area of the devices is approx. 0.56 cm^2.

Current-voltage curves and slow transients were recorded with a Bio-Logic SP300 potentiostat (1,000,000 samples/second), where the illumination was provided by white LEDs. The potentiostat was operated in CV mode, where the voltage sweep rate is set and the current is recorded. In detail the measurement works as follows: For rates <1,000 mV/s, voltage steps of 200 or 100 µV were applied. These numbers correspond to a time between voltage steps of 200 µs to 10 ms dependent on the voltage sweep rate. For each voltage point, the current was measured and averaged during the last 50 % of the time. To plot the JV curve, the current values of 50 points were averaged. This gives a point every 10 mV. For higher rates, the number of points to average was reduced to maintain a sufficient resolution in voltage as the potentiostat requires a 200 µs time to deliver one measurement point at a set voltage. In the case of 100,000 mV/s, we did note average and collected a measurement point at every 20 mV,

The electroluminescent photon flux is detected with a silicon photodiode.

The µs transients are recorded with an oscilloscope at 50 Ohm input impedance (Gould Classic 6000).

Figures

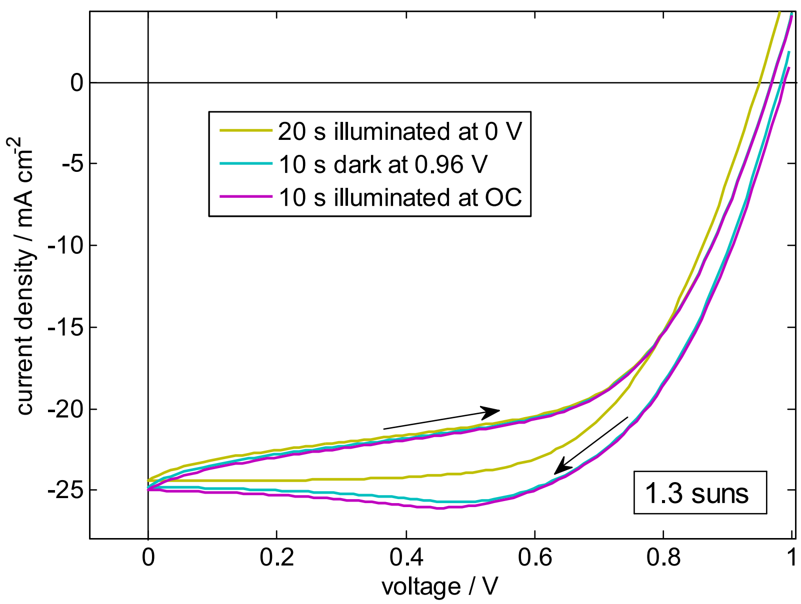

Fig. S1 Current-voltage scans with 50 mV/s for different pre-conditioning. The scan starts at 1 V to 0 V and back to 1 V. It is the voltage bias that dominates the strengths of the hysteresis independent of illumination. A forward bias increases the bump, whereas 0 V decrease the open-circuit voltage.

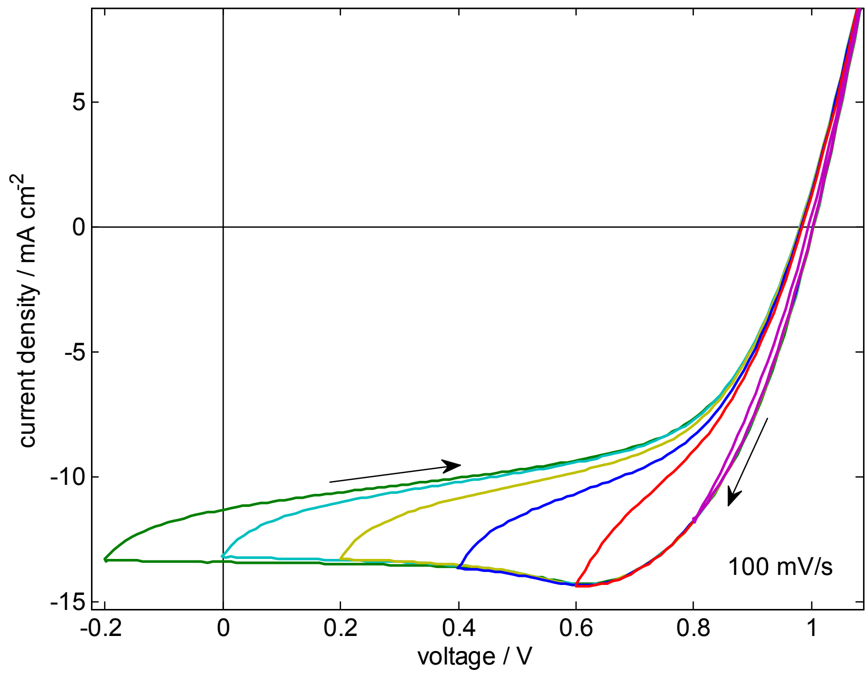

Fig. S2 Current-voltage scans with varied turning points. The backward scan depends strongly on the voltage at the turning point.

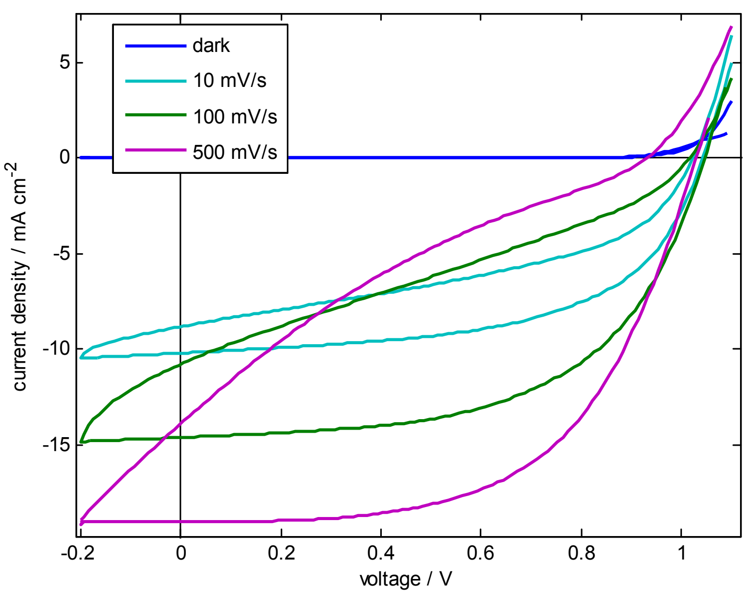

Fig. S3 Current-voltage scans of a device containing an Al_2O_3 scaffold measured with varied voltage sweep rate. The qualitative behavior is the same as for TiO_2 based devices.

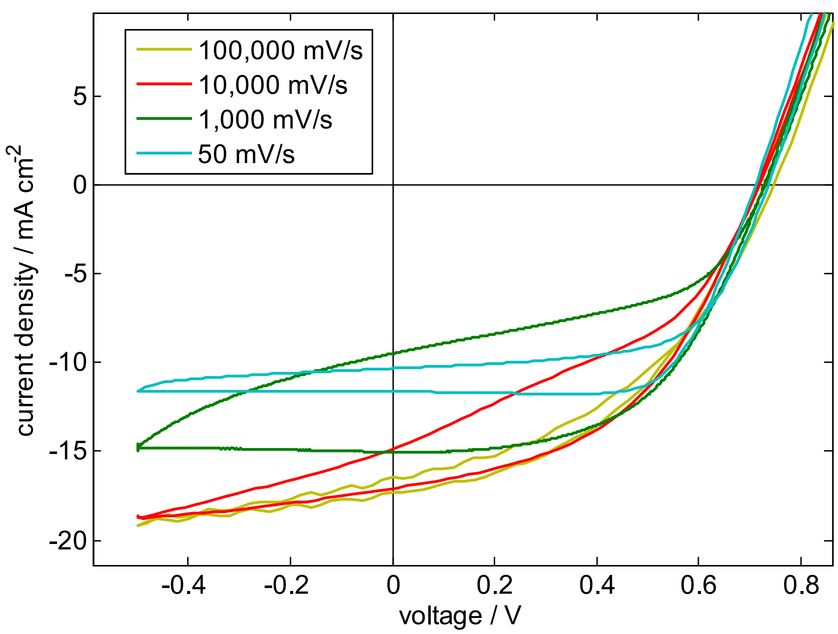

Fig. S4 Current-voltage scans of a device without hole-transport layer measured with varied voltage sweep rate. There is hysteresis also without hole-transport layer.