Supporting Information

Hysteresis in current-voltage measurements of hybrid-perovskite absorber solar cells

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SI.1 Experimental details

Unless indicated otherwise, all chemicals were purchased from Sigma-Aldrich and used without further purification.

Methylammonium iodide was prepared as described elsewhere\textsuperscript{1} by slowly adding an aqueous solution of hydroiodic acid (HI, 57wt% in H\textsubscript{2}O,) to methylamine solution in ethanol at 0\degree C. The solution was stirred for 1 hour and excess solvent was removed by rotary-evaporation at 50\degree C.

Methylammonium iodide was isolated as a white precipitate which was thoroughly washed with ether, dried in a vacuum oven at 50\degree C over night and stored in a glove-box until further use.

For solar cell devices, fluorine-doped tin oxide (FTO) glass (Pilkington, 15 ohm/square) was used as substrates. Part of the FTO was etched away using 2M HCl and Zn powder.

The substrates were cleaned by consecutive sonication/rinsing in Extran (15 minutes sonication), deionized water (3 times rinsing), drying, acetone (15 minutes sonication), drying, isopropanol (15 minutes) and UV-ozone treatment (15 minutes). The substrates were coated with a compact titania layer by spray pyrolysis at 430\degree C using a commercial airbrush for vaporization and using air as a carrier gas. The layers were deposited in 6 spray cycles with a velocity of 10 cm/sec at a distance of ca 15 cm (that’s about 6 inches) giving compact titania layers of ca 50 nm thickness.

For meso-porous devices, a ca 350 nm thick layer of meso-porous titanium dioxide was deposited via spin-coating at 6500 rpm from a 1:3 diluted solution of titanium dioxide nanoparticles (dyesol NT18) with ethanol. The perovskite was deposited via 2-step sequential conversion as described by Burschka et al.\textsuperscript{2} A 1.3 M solution of lead iodide in N,N-dimethylformamide was prepared and spin-cast onto the meso-porous titania substrates at 4000 rpm followed by a drying step at 70\degree C.
The lead iodide covered substrates were immersed into a solution of 10 mg/ml methylammonium iodide in isopropanol for 1-15 minutes. The conversion process was monitored by in-situ UV-Vis measurements and stopped when the baseline started to dramatically increase indicating the formation of perovskite crystallites on top of the meso-porous titania film.

The thin film preparation was carried out as described elsewhere. Methylammonium iodide (2.64 M, 3 equivalents, preparation described above) and lead (II) chloride (0.88 M, 1 equivalent) in anhydrous N,N-dimethylformamide. Films were spin-cast from solution at 4000 rpm and annealed for 45 minutes.

The perovskite layers were contacted with a 60-90 mg solution of 2,2’,7,7’-tetrakis-(N,N-di-p-methoxyphenylamine)9,9’-spirobifluorene (spiro-OMeTAD, lumitech) in chlorobenzene containing 12 mol% of “pre-oxidized” spiro-OMeTAD\(^2\)(TFSI)\(_2\) compound synthesized as described elsewhere, \(^5\) LiTFSI and 4-tert-butylpyrididine. The spiro-solution was deposited by spin-casting at 2000 rpm for 60 seconds. Gold contacts were evaporated to form the back contact of the devices at a rate of 0.2A/sec (pressure ca. 1*10\(^{-6}\)) for the first 10 nm and 2 A/sec for consecutive 50 nm.

The current density–voltage (J-V) curves were measured using a source meter (Keithley, 2400 Series) under simulated AM 1.5 sunlight (Newport) at 1000 W m \(^{-2}\) calibrated with a reference diode. During characterization, the solar cells were masked with a black aperture to give an active area of 0.12 cm \(^{-2}\). External quantum efficiency measurements were carried out using monochromated light from a tungsten light source. The light intensity was constantly monitored by directing half of the incident light onto a reference diode via a beam splitter. The external quantum efficiency was calculated by comparison with the action spectrum of a calibration photodiode.

**SI.2 Relation between delay times and scan rates**

As hysteretic effects are caused by slow response times of devices to a change in voltage, it is not so much the scan-rate of an IV-measurements but rather the delay time after a voltage step before the device current is sampled. Delay times used in our laboratory and NPLC-settings (Number of Power Line Cycles) of the Keithley 2400 source meter are listed in Table S1. The NPLC sets how long the signal is read out after the delay time. The scan rate is estimated from the voltage step divided by the sum of delay time and NPLC/60.

**Table S1: Approximate IV scan-rates determined from delay times after voltage step**

<table>
<thead>
<tr>
<th>Delay time (s)</th>
<th>NPLC</th>
<th>Scan rate (V/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00E-03</td>
<td>0.1</td>
<td>18.8</td>
</tr>
<tr>
<td>1.00E-02</td>
<td>1</td>
<td>1.88</td>
</tr>
</tbody>
</table>
SI.3 Histograms and cyclic IV-measurement

Perovskite-absorber devices exhibit substantially different device performance depending on scan-rate. In Figure S1 the performance at a fast scan rate and negative scan direction is compared for mp-TiO\textsubscript{2} based and (right) and thin film devices (left). Thin film devices exhibit larger spread of device efficiencies and discrepancy between fast and slow scans.

![Figure S1: Histogram of device efficiencies determined from IV-measurements in negative scan direction at fast (10 ms delay) and slow (5 s delay) scan-rates for mp-TiO\textsubscript{2} (left) and thin film (right) devices.](image)

**SI.4 IV-curve shapes**

IV-measurements discussed in the main article, section 2.2 were recorded in single sweeps. Before each sweep, devices were held at open circuit and illumination for a period of ca 3 seconds. This gives rise to the discrepancy between the single and cyclic scan in the positive scan direction in Figure S2 as the single scan is over-layed by a transient photocurrent induced during illumination under open-circuit conditions.
**Figure S2:** Comparison of IV-measurements performed as single scans vs in a cyclic manner from $V_{OC}$ towards $V=0$ V and back to $V_{OC}$.

In Figure S3, the resulting IV-curves are shown, if the long-delay time data shown in Figure 3 in the main document is overlayed by a transiently decaying photocurrent with a time-constant of 2.4 s measured for the same device when switching the device from open-circuit to short-circuit. Figure S4 illustrates that also thin film devices can be measured “hysteresis-free” at both slow and fast scan-rates.

**Figure S3:** Example of meso-porous titania-based devices that exhibits no hysteresis between the positive and negative IV-scan direction both at fast and slow scan-rates. The figure on the right shows resulting IV-curves for this data, if the slow-scan would be overlayed with an exponentially decaying current with a time constant of 3 s.

**Figure S4:** Example of meso-porous titania-based devices that exhibits no hysteresis between the positive and negative IV-scan direction both at fast and slow scan-rates. The figure on the right shows resulting IV-curves for this data, if the slow-scan would be overlayed with an exponentially decaying current with a time constant of 3 s.
SI.5 Slow photocurrent transients under steady and on/off illumination

When held at steady bias, thin film devices exhibit a decrease in photocurrent. This is not the case, when the illumination source is switched on and off. This effect complicates the comparison of integrated EQE values with $J_{SC}$ further. These effects are probably related to the photo-induced polarization effects discussed in section 2.4 and 2.5.

![Figure S5: Photocurrent of thin film device decreasing with time under continuous 1-sun illumination but constant when light source is switched on and off.](image)

SI.6 Effect of photocurrent decrease on EQE measurements

It was found to be difficult to correlate the EQE-measurements with steady-state $J_{SC}$ data for thin film devices investigated herein. This is related to the slow transient decrease in current observed under steady illumination shown in Figure S5. This steady decline will also affect the spectral shape of the EQE spectrum. Note that to achieve EQE spectra matching the $J_{SC}$, devices were subjected to a light-soaking treatment at forward bias prior to the measurement.

![Figure S6: Effect of photocurrent decrease on spectral shape of EQE spectrum](image)
SI.7 Step-IV in the dark and transient photocurrent measurements

Step-IV measurements in the dark did not exhibit current transients with the same order of magnitude as the transients observed during step-IV measurements under illumination.

![Figure S7](image1.png)

**Figure S7**: Step-IV measurements in the dark for thin film device.

Transient photocurrent measurements to investigate the response to a 500 us light pulse with and without bias illumination. We find that the response time is markedly slower for 1 sun light bias indicating that slow processes in the device are induced by illumination.

![Figure S8](image2.png)

**Figure S8**: Transient photocurrent response to a 500us light pulse with and without a 1 sun bias light.

SI.8 Effect of light soaking on meso-porous titania devices

We also investigated the effect of light-soaking at reverse bias on meso-porous titania-based devices. After 5 minutes, a minor effect on the IV-curve was observed but the effect is far less dramatic as observed for thin film devices.
Figure S9: Comparison of IV-curves of a meso-porous titania-based device measured prior and after light-soaking at reverse bias (-1.2 V) for 5 minutes.

SI.9 Inverted devices and devices contacted without hole transporter

With regard to hysteresis in perovskite-absorber devices, claims have been made that hysteresis is not observed in MAPbI₃ devices using other selective contacts such as PEDOT:PSS and PC₆₀BM as described elsewhere.⁶ For this architecture we still observe a hysteretic effect in current-voltage measurements at fast scan rates but unlike in the architecture using TiO₂ and spiro-OMeTAD, we observed a lower rather than higher photocurrent at fast scan rates. This is consistent with dynamic changes in polarization of MAPbI₃ during IV-scans but associated differences in the photocurrent seem to be strongly dependent on specific properties at selective contacts.

Devices without the hole-transporter layer exhibited a similar hysteretic behavior to full devices. The dependence of the photocurrent on scan rate may thus be caused by titania or the interface between titania and the perovskite and is not solely induced by the spiro-OMeTAD interface or ions such as Li⁺ introduced to the device with the hole transporting medium. However, such small ions could give rise to additional effects such as ionic currents or interfacial alignment that would have to be careful investigated.
Figure S10: (left) IV-measurements at different scan velocities and directions for inverted devices
ITO/PEDOT:PSS/perovskite/PC$_{60}$BM/Al (right) Thin film device contacted directly with gold of the structure
FTO/compact TiO$_2$/perovskite/spiro-OMeTAD/Au

References