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The Interface between FTO and the TiO_2 Compact Layer Can Be One of the Origins to Hysteresis in Planar Heterojunction Perovskite Solar Cells

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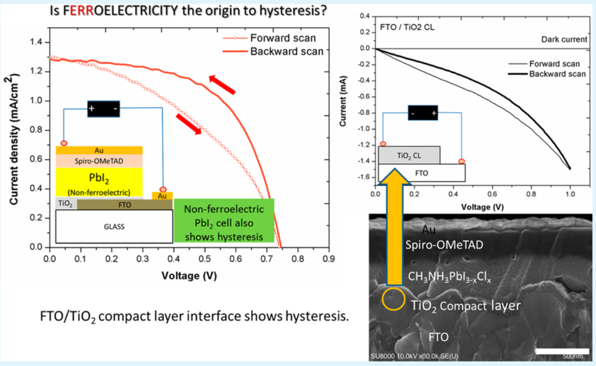
Supporting Information

ABSTRACT: Organometal halide perovskite solar cells have shown rapid rise in power conversion efficiency, and therefore, they have gained enormous attention in the past few years. However, hysteretic photovoltaic characteristics, found in these solid-state devices, have been a major problem. Although it is being proposed that the ferroelectric property of perovskite causes hysteresis in the device, we observed hysteresis in a device made of nonferroelectric PbI_2 as a light absorber. This result evidently supports the fact that ferroelectric property cannot be the sole reason for hysteresis. The present study investigates the roles of some key interfaces in a planar heterojunction perovskite ($CH_3NH_3PbI_{3-x}Cl_x$) solar cell that can potentially cause hysteresis. The results confirm that the interface between fluorine doped tin oxide (FTO) substrate and the TiO_2 compact layer has a definite contribution to hysteresis. Although this interface is one of the origins to hysteresis, we think that other interfaces, especially the interface of the TiO_2 compact layer with perovskite, can also play major roles. Nevertheless, the results indicate that hysteresis in such devices can be reduced/eliminated by changing the interlayer between FTO and perovskite.



FTO/TiO_2 compact layer interface shows hysteresis.

KEYWORDS: *perovskite solar cell, planar heterojunction, hysteresis, interface, PbI_2, TiO_2 compact layer*

1. INTRODUCTION

The rapid and continuous rise in performance of organometal halide perovskite solar cells[1−4] has attracted huge attention in the past few years. This new photovoltaic technology shows promising potential as an alternative to conventional solar cells because of high power conversion efficiency (PCE) supported by high voltage, which has reached up to 20%[5] in the laboratory, and easy fabrication through simple solution processes. However, there are several major issues with these devices which need to be addressed before realizing the technology in real use. The challenges are (i) difficulty in reproducibility and/or wide variation in performance for the devices prepared under the same conditions, (ii) hysteresis in photovoltaic characteristics, (iii) change in performance with prebiasing and light soaking conditions, and (iv) short-lived performance. We believe that these issues need serious attention and necessary actions for making this emerging organic−inorganic hybrid solar cell a commercially successful technology.

Unlike other kinds of solid-state solar cells, perovskite cells exhibit hysteresis in their current−voltage (I−V) characteristics, resulting in an appreciable difference in the PCEs calculated from forward scan (from short circuit to open circuit) and backward scan (from open circuit to short circuit) of applied voltage. Such hysteretic behavior of these solid-state perovskite cells breeds ambiguity about the working mechanism of the device and remains as a core challenge to achieving stable and reliable performance. Indeed, such anomalous hysteretic I−V characteristics of these cells have created doubts about the cell performance, which is being suspected to have been overestimated.[6−8] Although it has been found that hysteresis in perovskite cells depends strongly on the device structure and the methods by which they are fabricated,[9] the origin to such behavior is not yet completely understood. In the recent past, it has been proposed that either ferroelectric polarization,[9−11] ion migration,[9,12] or deeper trap states[9] might be responsible for the emergence of hysteresis in $CH_3NH_3PbI_3$-based perovskite solar cells. However, there was no direct and discrete evidence that could support these proposed mechanisms of the origin to hysteresis. Although it is known that $CH_3NH_3PbI_3$ perovskite shows ferroelectric property,[13] determination of its effect on the cell performance distinctively is not easy because of the

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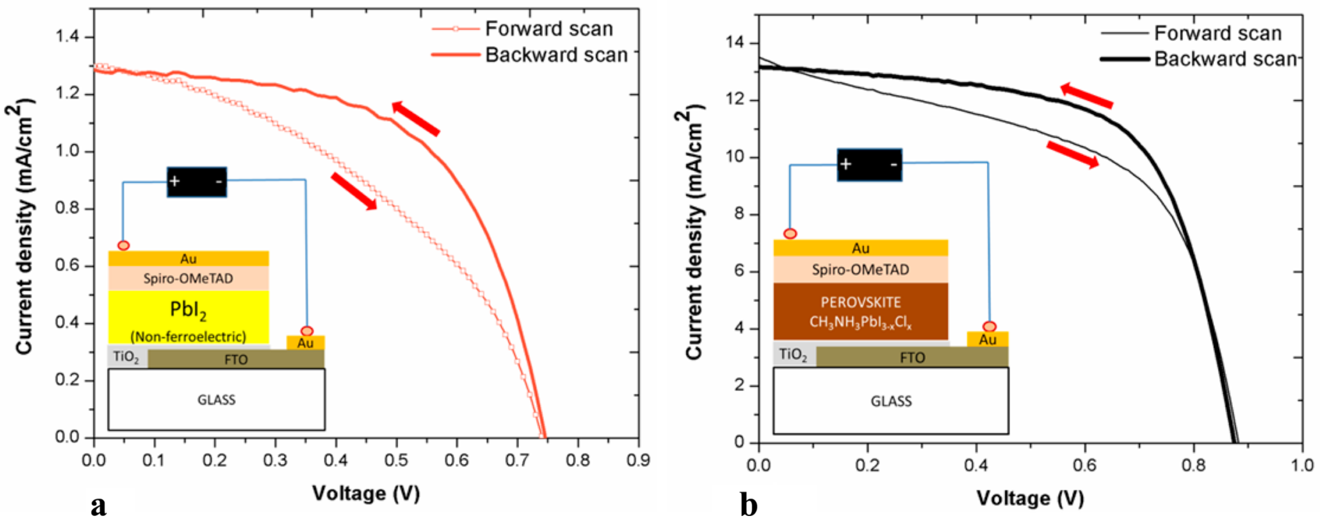

Figure 1. *J*−*V* characteristics of (a) planar heterojunction PbI_2 and (b) $CH_3NH_3PbI_{3-x}Cl_x$ perovskite solar cells. The measurements were taken under 1 sun illumination (100 mW/cm^2) and at a voltage scan speed of 200 mV/s. Insets represent corresponding structures of the devices.

complex thin film junction structures of the device. It had been suggested by Sanchez et al.[14] that slow dynamic processes observed in perovskite could be due to the polarizability of perovskite, which can be also related to hysteresis. Having observed an extremely slow photoconductivity response in $CH_3NH_3PbI_3$ perovskites, Gottesman et al.[15] proposed that structural changes in the perovskite under the working conditions of the solar cell might be the reason for the hysteresis. Recently, Kutes et al. observed ferroelectric domains in $CH_3NH_3PbI_3$ ($MAPbI_3$)[16] by using piezoforce microscopy. Unfortunately, there was no detailed discussion about how ferroelectric polarization, which is believed to depend on grain size and morphology, could cause hysteresis in a perovskite-based solar cell. Wei et al. proposed a ferroelectric diode model to explain the origin of hysteresis.[17] In their report, they confirmed the ferroelectric behavior from electric field−polarization (*E*−*P*) that showed an S-shape curve for a perovskite-loaded device as the only difference to the *E*−*P* curve obtained for a controlled sample without perovskite. This was a little unconvincing for us. Moreover, very recently, Fan et al.[18] reported that $MAPbI_3$ is not ferroelectric at room temperature. Therefore, ferroelectric property and proposed mechanisms of hysteresis based on ferroelectric behavior or trap states are still controversial with no direct and convincing evidence.

The present study gives a very different insight about hysteresis. Interestingly, some findings from the present study, which are discussed in the following sections, reveal the existence of a different origin to hysteresis. The present work basically investigates the role of different interfaces in a planar heterojunction perovskite solar cell in causing hysteresis, and the results show that the FTO/TiO_2 interface has a definite contribution to hysteresis. In addition, there are indications that the anomalous hysteresis in perovskite cells may be enhanced by ferroelectric or ion migration phenomena taking place in the bulk of perovskite, but it might not be solely originated from these phenomena.

2. EXPERIMENTAL SECTION

All of the planar heterojunction perovskitesolar cells used in the present study were fabricated by a one-step solution method in dry (relative humidity is almost 0%) atmospheric conditions. For all of the devices, the TiO_2 thin compact layer (CL), which is a prerequisite to obtain sufficiently high photocurrent density and open circuit voltage, was prepared by spray-pyrolysis method. Titanium diisopropoxide bis(acetylacetonate) solution (75 wt %, Aldrich) diluted in ethanol (100 μL of Ti(acac) + 1 mL of EtOH) was sprayed on the cleaned FTO substrate that was heated at 450 °C. The compact layer of Ti(acac) was kept at 450 °C for 45 min on the hot plate and then further annealed at 500 °C in a muffle furnace. The thickness of the CL, as measured from the cross-sectional view of scanning electron micrographs, was found to vary between 120 and 130 nm (Supporting Information (SI) Figure S1). $CH_3NH_3PbI_{3-x}Cl_x$ was prepared by a mixed halide (chlorine−iodide) route of synthesis and used for forming the perovskite layer, as described previously.[2,11] In short, a 40 wt % mixed solution of $PbCl_2$ (Aldrich) and CH_3NH_3I (synthesized in the laboratory) in *N*,*N*-dimethylformamide ($PbCl_2$:MAI = 1:3) was spin-coated on substrates. The spin-coating conditions followed for formation of perovskite layer were 3000 rpm for 60 s after dropping 100 μL of the mixture solution onto a 25 mm × 25 mm $FTO-TiO_2$ CL substrate and holding it for 30 s before spinning. This perovskite precursor-coated substrate was then heated at 100 °C for 45 min on a hot plate for crystallization of perovskite. The dark brown color perovskite film was then cooled to room temperature before coating 2,2′,7,7′-tetrakis(*N*,*N*-di-4-methoxyphenylamino)-9,9′-spirobifluorene (spiro-OMeTAD, from Merck) as the hole transporting material (HTM). A 12 wt % solution of spiro-OMeTAD in cholobenzene was prepared using lithium bis(trifluoromethylsyfonyl)imide salt (Li-TFSI) and *tert*-butylpyridine (*t*-BP) as dopant and additive, respectively. The spiro-OMeTAD solution was then coated on perovskite film by spinning at 4000 rpm for 60 s. The devices were then stored in a desiccator in the dark overnight before checking the performance. Au back contact was deposited on spiro-OMeTAD by vacuum and thermal evaporation technique.

The PbI_2 planar cell was prepared by spin-coating (3000 rpm for 30 s) a 40 wt % PbI_2 solution in DMF and then heating the film at 100 °C for 45 min. Spiro-OMeTAD was then coated on PbI_2 at the same conditions followed for the planar perovskite cells. For the devices with no CL, the cleaned and dried FTO substrate was directly used for coating perovskite. In order to characterize the FTO/TiO_2 interface, the specimens of FTO/TiO_2 CL structures were prepared by spray-coating the CL in the same way as that followed for the active devices of perovskite or PbI_2. In these FTO/TiO_2 CL structures, a part of the FTO substrate was masked while spraying the Ti(acac) solution for obtaining a bare FTO portion that was used as one of the contacts across the interface. Current−voltage measurements on the devices and FTO/TiO_2 interface structure were taken with a Keithly source meter (Model 2400). For all of the devices, the bias voltage was

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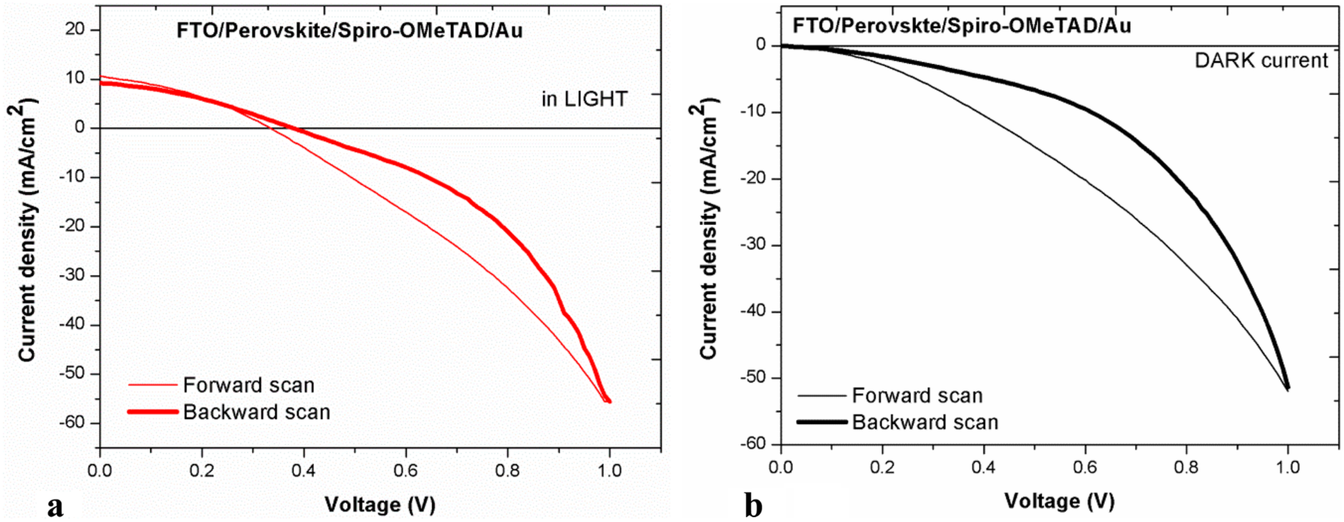

Figure 2. *J*−*V* characteristics of a planar perovskite cell made without a TiO_2 compact layer (FTO/$CH_3NH_3PbI_{3-x}Cl_x$ /spiro-OMeTAD/Au) measured in (a) light and (b) dark.

scanned from 0 to 1 V and vice versa at a speed of 200 mV/s. A solar simulator (Peccell Technologies) was used for the light source (AM 1.5, 100 mW/cm^2) for all photovoltaic measurements. The active area (illumination area) of all of the devices was 0.09 cm^2.

3. RESULTS AND DISCUSSION

Although there has been much talk about the ferroelectric property of the perovskite being responsible for hysteresis, to our surprise, we found that a planar heterojunction cell (FTO/TiO_2 CL/PbI_2/spiro-OMeTAD; inset in Figure 1a) made of PbI_2, which is a nonferroelectric semiconductor (P-type, E_g = 2.5 eV) for sure, shows hysteretic photocurrent density−voltage (*J*−*V*) characteristics (Figure 1a). Being a wide band gap semiconductor (2.5 eV), PbI_2 absorbs up to ∼495 nm and, thus, generates photocurrent density much lower than that generated by the narrow band gap (∼1.5 eV) $CH_3NH_3PbI_{3-x}Cl_x$ perovskite. The trend in hysteresis observed for the PbI_2 cell was exactly the same as that observed for any planar heterojunction perovskite ($CH_3NH_3PbI_{3-x}Cl_x$) solar cell (FTO/TiO_2 CL/$CH_3NH_3PbI_{3-x}Cl_x$/spiro-OMeTAD; Figure 1b). For both cells, the backward scan shows higher current collected at all voltages.

Hysteresis observed in the PbI_2 cell was remarkable, exhibiting efficiencies of 0.4% and 0.6% for forward (short circuit to open circuit) and backward (open circuit to short circuit) scans, respectively. Since the photocurrent of the PbI_2 cell (∼1 mA/cm^2) was significantly low compared to that of a planar perovskite cell (∼13 mA/cm^2), the dark *J*−*V* characteristics (SI Figure S2) of both cells were checked for fairer comparison. It was found that hysteretic behavior of the PbI_2 cell was consistent with that of a perovskite cell both in the dark and the light. Both PbI_2 and $CH_3NH_3PbI_{3-x}Cl_x$ cells show higher current during the backward scan in the light (Figure 1a,b) and the dark (SI Figure S2a,b). Furthermore, hysteresis in both cells gets magnified with an increase in the voltage scan range (0 to 1, 2, and 3 V) in the dark (Supporting Information Figures S3 and S4). An increase in hysteresis magnitude with voltage scan range indicates that hysteresis can be proportionately related to the amount of current allowed to pass through the device. Such behavior was more clear and prominent in a planar perovskite cell measured under varying light intensity (SI Figure S5). The photocurrent of the cell increases with illumination intensity and so does hysteresis. Such dependence of hysteresis on light intensity or photocarrier density may provide a deeper insight into the mechanism of carrier transport and, also, hysteresis. However, a detailed analysis and thorough discussion of this property of the device is beyond this report.

For PbI_2 generating low current density, the influence of internal resistance (IR) of the device on voltage is smaller than that for the $CH_3NH_3PbI_{3-x}Cl_x$ cell. Instead, at a given RC constant, photocurrent response tends to be slowed down when photocurrent density decreases. These relations can also influence hysteresis, which needs to be proved. Regardless, hysteresis in a nonferroelectric PbI_2 cell, observed with a close resemblance to that of a perovskite cell, confirms that the origin to hysteresis cannot be solely a ferroelectric property of the perovskite. There must be some other origin to hysteresis in addition to ferroelectric polarization. Another presumption is ion migration. Unger et al. proposed that ion migration in the bulk of perovskite under illumination may cause hysteresis.[12] According to them, photoexcitation of $MAPbI_3$ (or PbI_2) enhances photoconductivity of the material and, thus, results in transient currents, which leads to hysteresis. It is known that ion diffusion in ionic crystals such as $PbBr_2$, $PbCl_2$ and PbI_2 can take place in the dark through the existing defects (halide ion vacancies).[19] Hence, it is possible that ion migration causes hysteresis in the PbI_2 cell. This might be the reason why the PbI_2 cell showing significantly lower photocurrent (Figure 1a) exhibits obvious hysteresis, comparable to perovskite solar cells producing current more than 10 times of that seen for the PbI_2 cell. The phenomenon of ion migration may also happen in perovskite cells by diffusion of highly mobile $CH_3NH_3^+$ and I^-ions. Such ion diffusion in the bulk of perovskite (or PbI_2) is expected to depend on the external bias conditions and must not be affected by any change in the interfaces formed on either side of the perovskite (or PbI_2) film. In contrast, we found that hysteresis can be changed by changing the interfaces. A perovskite cell made without TiO_2 CL (FTO/$CH_3NH_3PbI_{3-x}Cl_x$/spiro-OMeTAD/Au) showed hysteresis with a reversed trend to that found for cells having TiO_2 CL between FTO and perovskite (FTO/TiO_2 CL/$CH_3NH_3PbI_{3-x}Cl_x$/spiro-OMeTAD/Au). Figure 2 shows the

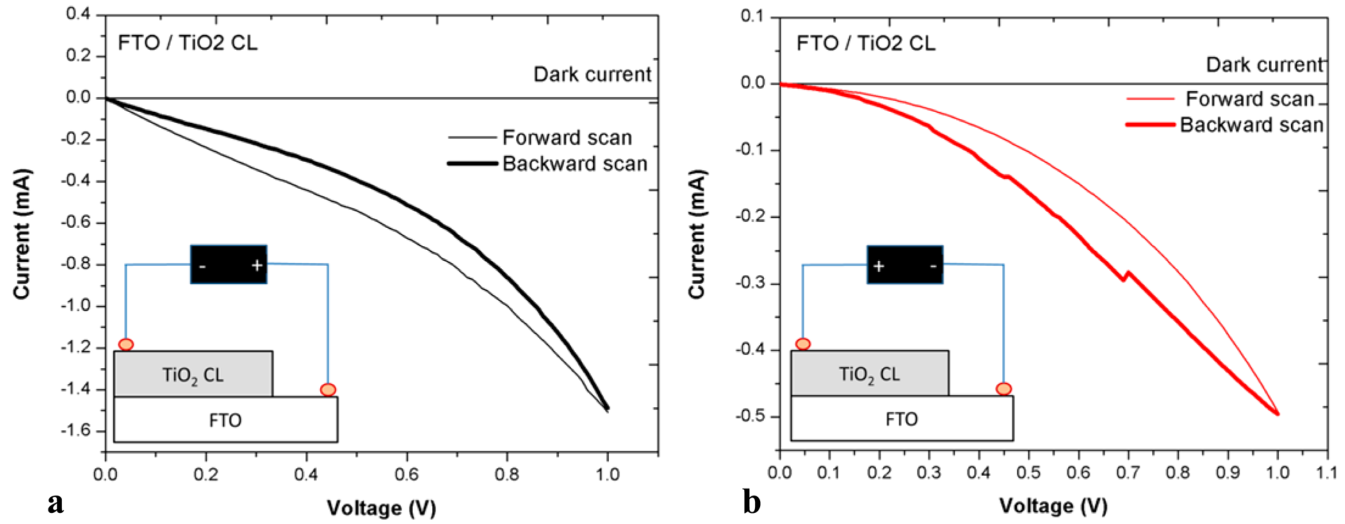

Figure 3. Dark $I-V$ characteristics of the FTO/TiO_2 CL interface with positive voltage applied to (a) FTO and (b) the TiO_2 compact layer. Inset schematics show the conditions of voltage applied across the interface.

light $J-V$ curves of a perovskite cell without TiO_2 CL. Cells without the compact layer show reasonable J_{sc} (10−15 mA/cm^2) but extremely lower V_{oc} (0.1−0.4 V) because of no blocking TiO_2 CL layer against charge recombination. It can be seen from Figure 3a that hysteresis in this device was insignificant in the voltage range less than the V_{oc} (photocurrent) while it was significantly large for all of the bias voltages beyond V_{oc}, where the current direction is opposite to photocurrent (i.e., dark current direction). Moreover, if the scan was made up to the V_{oc}, the hysteresis observed for the cell was found to be less (SI Figure S6). This suggests that hysteresis found in the cell (without TiO_2 CL) in the photocurrent direction (first quadrant) might be an effect of the behavior seen in the dark current direction (fourth quadrant). Therefore, we rather compared the hysteresis behavior of both cells in the dark. Interesting, it was found that the cells (with and without TiO_2 CL) exhibited just opposite trends in hysteresis. The structure with no TiO_2 CL showed lower current (i.e., smaller negative current) during backward scan (from 1 to 0 V; Figure 2b) while the standard planar perovskite cells using TiO_2 CL showed higher current (i.e., greater negative current) during the scan from 1 to 0 V (Figure 1b). This indicated that hysteresis in a perovskite cell is rather influenced by interface properties than bulk of the perovskite. If any bulk property (e.g., ferroelectric, ion migration, and so on) of perovskite was the only reason for hysteresis, then both cells, with and without CL, would have shown the same trend of hysteresis (backward scan showing higher current), irrespective of the change in interface.

We believed that carrier transfer dynamics at different interfaces in the device must play important roles in causing hysteresis. The key interfaces in a planar heterojunction cell that can potentially cause hysteresis are (i) FTO/TiO_2, (ii) TiO_2/perovskite, and (iii) perovskite/spiro-OMeTAD. With results like those reported by others, we also found that a planar perovskite device without spiro-OMeTAD (FTO/TiO_2 CL/$CH_3NH_3PbI_{3-x}Cl_x$/Au) also shows hysteresis (SI Figure S7). This suggests that the perovskite/spiro-OMeTAD interface might not play an essential role in hysteresis. Perovskite cells of mesoporous TiO_2 (meso-TiO_2) structure (FTO/TiO_2 CL/meso-TiO_2/$CH_3NH_3PbI_{3-x}Cl_x$/spiro-OMeTAD/Au) having a large TiO_2/perovskite interface area was found to exhibit the least or almost no hysteresis (SI Figure S8) as compared to planar cells (FTO/TiO_2 CL/$CH_3NH_3PbI_{3-x}Cl_x$/spiro-OMeTAD/Au). This result makes us think that the TiO_2/perovskite interface may not cause hysteresis. However, it is expected that the TiO_2/perovskite interface in a planar cell can differ from that of a meso-TiO_2 structure cell in terms of physical structure or defects, which can change the behavior completely. Therefore, it is not easy to reject the possibility of the origin of hysteresis from the TiO_2/perovskite interface in a planar cell.

In order to determine which interface is responsible for the phenomenon, we pursued electrical characterization of simplified structures with minimum interfaces. A simplified device without a perovskite layer (spiro-OMeTAD sandwiched between TiO_2 CL and Au-FTO/TiO_2 CL/spiro-OMeTAD/Au) was found to exhibit hysteresis (SI Figure S9), indicating that either one or both of the interfaces, FTO/TiO_2 CL and TiO_2 CL/spiro-OMeTAD, play a role. The electrical property of the FTO/TiO_2 CL interface was first investigated by taking $I-V$ measurements across this interface in a simple FTO/TiO_2 structure. We found that $I-V$ measured across an FTO/TiO_2 interface exhibits hysteresis. Figure 3 shows the $I-V$ curves of an FTO/TiO_2 interface. Although the magnitude of hysteresis is not large, it was interesting to see that the trend of hysteresis caused by this interface resembled the behavior of a perovskite cell. The trend of hysteresis (i.e., backward scan showing greater positive current in light and greater negative current in dark) depends on the direction of current in the device. In the same way, the hysteretic behavior of the FTO/TiO_2 CL interface changed with the direction of current across the interface. When the positive end is connected to FTO (i.e., positive bias is applied to FTO/scan and is performed from 0 to 1 V), the electron moves from TiO_2 to FTO, as in the case of a perovskite cell measured in light. In this case, a backward scan curve comes above the forward scan (Figure 3a). The trend matched that of the perovskite cell in the light (Figure 1b). On the other hand, when the negative end is connected to FTO (i.e., negative bias is applied to FTO/scan and is performed from 0 to −1 V), the electron moves from FTO to TiO_2, as in the case of perovskite cell measured in the dark. Here, the backward scan curve falls below that of the forward scan (Figure 3b), which is exactly the same trend observed when a perovskite cell is measured in the dark (SI Figure S2b).

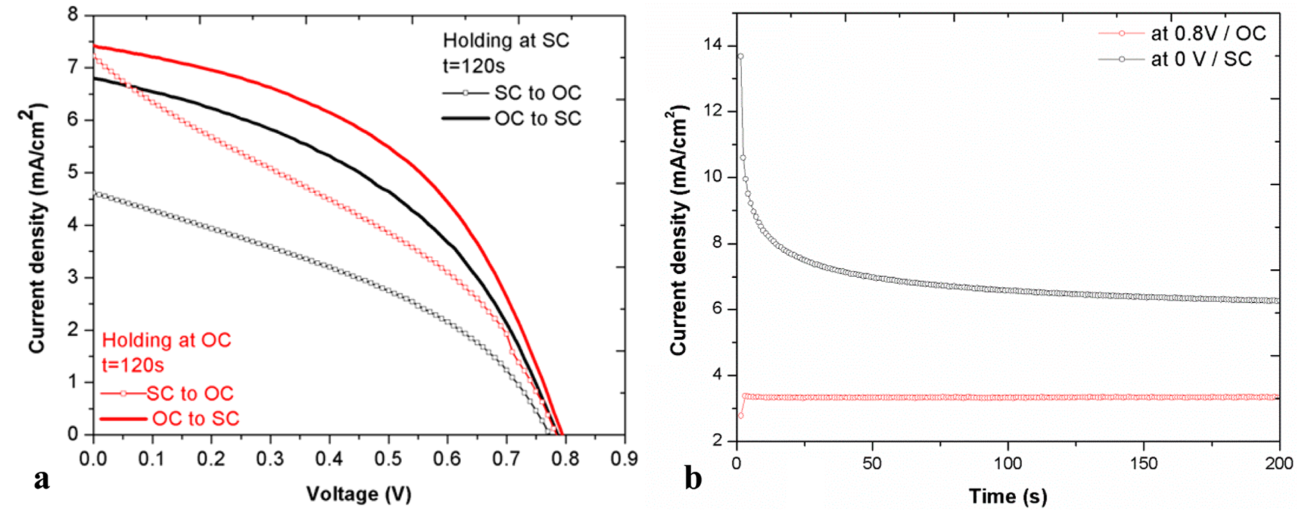

Figure 4. (a) *J*−*V* characteristics of a planar perovskite cell measured by holding the cell at short circuit (SC) or open circuit (OC) for 120 s and (b) photocurrent of a planar perovskite cell measured over time at SC (0 V bias) or near to OC (0.8 V).

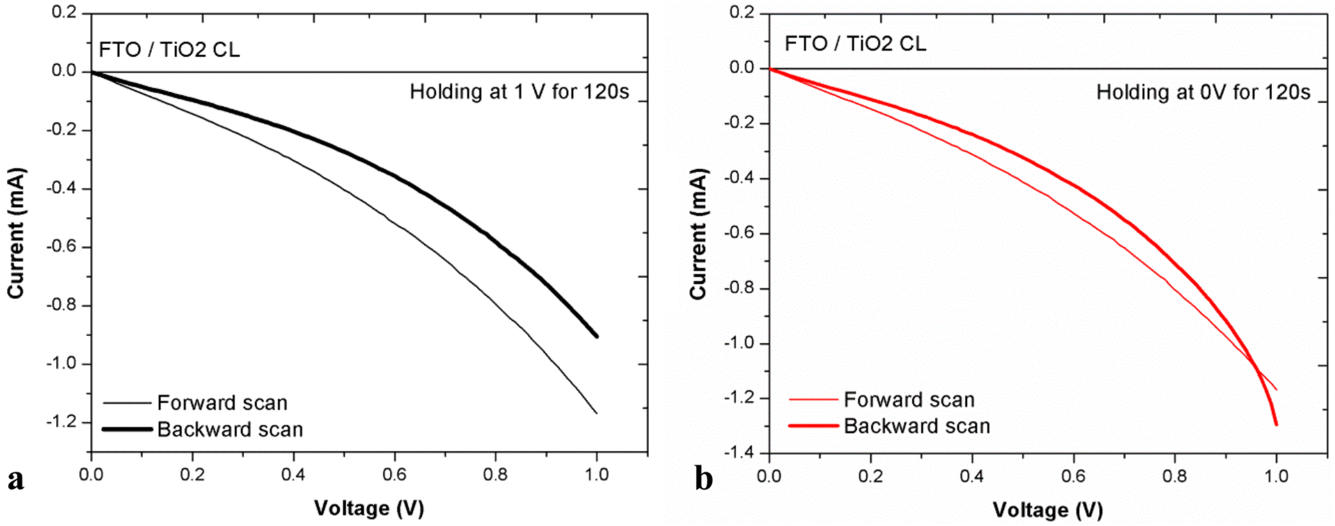

Figure 5. *J*−*V* characteristics of the FTO/TiO_2 interface measured by holding the cell at (a) 1 and (b) 0 V for 120 s between the forward and backward scans.

It was found that the photocurrent of the perovskite cell is affected by holding the device at short circuit (SC) or open circuit (OC) for different time durations between the scans. Holding the cell at 1 V after the forward scan (from 0 to 1 V) for 2 min and then scanning back (from 1 to 0 V) does not bring any change in the J_{sc} measured during both scans (Figure 4a). On the contrary, holding the cell at SC (0 V) after BS (from 1 to 0 V) and then scanning in the forward direction (from 0 to 1 V) shows a large difference in J_{sc} measured for both scans (Figure 4a). This difference in J_{sc}, observed when the cell was held at SC, was due to a continuous decrease in current measured for the cell at SC over time (Figure 4b). Hence, it is inferred that photocurrent drops significantly when the current is collected continuously from the device over time (at 0 bias/at SC). On the other hand, if the device is held near to perfectly forward bias condition (biasing 1 V or ideally at OC), where no current is allowed to pass through it, J_{sc} does not change. Interestingly, the same differential behavior of current was observed for the FTO/TiO_2 interface. When current was allowed to pass across the interface for 2 min (when the interface was biased at 1 V for 2 min), current decreased (Figure 5a), showing a large difference between the current at the starting points. In the other case, where there was no current passing through the structure (i.e., 0 bias conditions), no difference in current (start point) collected on both scans was observed (Figure 5b). This is similar to the case where the perovskite cell is held at OC, allowing no current through the device.

The preceding results are evidence that hysteresis in a planar perovskite solar cell includes the hysteresis caused by the interface at FTO and the TiO_2 compact layer. We can think of several possible processes that may be responsible for creating hysteresis at this interface. It is probable that electrical capacitance generated by small defects at the FTO/TiO_2 CL interface causes hysteresis, which might be further enhanced by dipole polarization of the perovskite material. Recently, Yuan et al.[20] found that a planar device using a TiO_x compact layer embedded with Au nanoparticles showed lesser hysteresis than the cells using a pristine TiO_x layer. Here, the Au nanoparticles inject electron to fill the trap states in TiO_x and thus help in better carrier extraction, which might have reduced hysteresis. Thus, it is possible that the TiO_2 compact layer used in our study has a lot of trap states, and filling and emptying of these trap states lead to hysteresis. However, we need to understand how filling and emptying of these trap states take place during the forward and backward scans such that the backward scan always shows higher current. We also believe that hysteresis at the FTO/TiO_2 interface can be related to band alignment at the interface. Any change in TiO_2 band bending during forward and backward scans may result in a difference in carrier collections during the scans, showing hysteresis. Having disclosed about the preceding possible processes that can create hysteresis, we like note here that the mechanism would be valid only when the dynamics of changes corresponding to the preceding processes are consistent with hysteresis. Hence, further deeper and extensive investigation is needed to understand the mechanism of hysteresis at the FTO/TiO_2 interface as well as in the perovskite solar cells.

From the preceding findings, although it is evident that the FTO/TiO_2 CL interface plays a contributory role to hysteresis in perovskite cells, we believe that the interface of CL and perovskite can play an even bigger role in causing hysteresis. There are reasons to support this in our study conducted here. First, although the FTO/TiO_2 CL interface gives hysteresis, we see less hysteresis in the TiO_2 meso-structure cell that uses the same TiO_2 CL (see SI Figure S8), where TiO_2 CL is almost perfectly covered with a composite of meso-TiO_2 and perovskite. In both structures, with and without a mesoposrous layer, we have a TiO_2/perovskite interface but they can vary significantly in morphology. This indicates that the structure of the interface between perovskite and TiO_2 can also be an important player in hysteresis. The interface of TiO_2 CL and perovskite might have structural defects and voids which can produce electrical capacitance. Second, the cell without TiO_2 CL does not essentially generate hysteresis in the photovoltaic effect (positive current region) while the structure exhibits large hysteresis in the negative current region, with an opposite trend in the dark, which also suggests that the TiO_2/perovskite interface may play an important role. Third, in addition to our TiO_2 CL-free example, many of the perovskite-based devices with structures using an organic electron-accepting layer that replaces TiO_2 CL[21−23] show little or no hysteresis. Recently, Wojciechowski et al.[24] also reported that modification of TiO_2 CL with fullerene reduced hysteresis. All of these observations suggest that the interface of TiO_2 CL and perovskite can be a major origin to hysteresis. In any case, changing the interlayer between FTO and perovskite will change both the FTO/interlayer and interlayer/perovskite interfaces, which will eventually affect the hysteresis significantly.

In addition to hysteresis, the problems, such as wide distribution of performance of the cells prepared under the same conditions, change in performance of a cell with prebias, and voltage scan conditions, are suspected to be closely related to the interface of FTO and the TiO_2 compact layer. Although it has not yet been thoroughly and systematically investigated, preliminary observations on the change in magnitude of hysteresis coming from the FTO/TiO_2 interface with contact points over the area of the same substrate (12 mm × 12 mm) and prebiasing conditions is indicative that this interface might be also responsible for several other fundamental issues with a perovskite solar cell. However, this discussion is beyond the scope of the present work, and we will report the relevant results soon.

4. CONCLUSIONS

Although there have been several studies that proposed the ferroelectric property of perovskite to be responsible for emergence of hysteresis in perovskite cells, hysteresis found in planar PbI_2 (nonferroelectric) cells (FTO/TiO_2 CL/PbI_2/spiro-OMeTAD/Au) in the present study confirms that ferroelectric polarization of perovskite cannot be the only reason for hysteresis. A reversed trend in hysteresis observed in a perovskite cell not using a TiO_2 blocking layer (FTO/$CH_3NH_3PbI_{3-x}Cl_x$/spiro-OMeTAD/Au) is evident that hysteresis is much influenced by interfaces. *I*−*V* characterization of the interface between FTO and the TiO_2 compact layer shows that the FTO/TiO_2 interface exhibits hysteresis that closely resembles the behavior observed for a planar perovskite ($CH_3NH_3PbI_{3-x}Cl_x$) cell, confirming a contributory role of this interface in causing hysteresis. We think that hysteresis at this interface can be related to either (i) macrodefects at the interface that can create capacitive components in the device, (ii) trap states in the TiO_2 compact layer that are filled and emptied at different rates during backward and forward scans, or (iii) band alignment at the interface that changes with the scan. However, further investigation is needed to understand the mechanism correctly and completely. Besides the direct evidence that confirms the FTO/TiO_2 interface as an origin to hysteresis, there are indications that the interface between TiO_2 CL and perovskite can play even a greater role in enhancing hysteresis in the perovskite devices, either by direct contribution or by influencing the behavior of the FTO/TiO_2 interface. A systematic and thorough investigation is required to find out the precise role of this interface in hysteresis shown by the perovskite solar cells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cross-sectional SEM image of planar perovskite cell showing the TiO_2 compact layer, dark *J*−*V* characteristics of planar heterojunction PbI_2 and $CH_3NH_3PbI_{3-x}Cl_x$ perovskite solar cell, dark *J*−*V* curves of a planar PbI_2 cell obtained over voltage scan ranges, dark *J*−*V* curves of a planar perovskite cell obtained over voltage scan ranges, *J*−*V* curves of a planar perovskite cell measured under different light intensities, *J*−*V* curves of a perovskite cell using no TiO_2 CL (voltage scan is just above the V_{oc} = −0.25 V), dark *J*−*V* curves of a planar perovskite cell free of HTM, *J*−*V* curves of a TiO_2 mesostructure perovskite cell, and dark *J*− *V* curves of a simple structure without perovskite. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01789.

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Notes

The authors declare no competing financial interest.

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