Supplementary Information (SI) for EES Solar.

Supplementary Information

Nickel-Oxide Hole Transport Layers Prevent Abrupt Breakdown and Permanent Shorting of Perovskite Solar Cells Caused by Pinhole Defects

Materials & Experimental Methods:

Substrates:

Patterned tin-doped indium oxide (ITO) substrates with sheet resistances of 15-25 Ω/sq were purchased from Delta Technologies.

Precursors:

[4-(3,6-Dimethyl-9*H*-carbazol-9-yl)butyl]phosphonic acid ("Me-4PACz"), 1,6-hexylenediphosphonic acid (6dPA), lead (II) iodide (PbI_2), and bathocuproine (BCP) were purchased from TCI. Lead bromide ($PbBr_2$), lead chloride ($PbCl_2$), cesium iodide (CsI), methylammonium chloride (MACl), methanol, ethanol, *N, N*-dimethylformamide (DMF, anhydrous) and dimethylsulfoxide (DMSO, anhydrous), and anisole (anhydrous) were purchased from Sigma Aldrich. Formamidinium iodide (FAI), methylammonium iodide (MAI) and methylammonium bromide (MABr) were obtained from Greatcell Solar. Poly[(9,9-bis(30-((N, N-dimethyl)-N-ethylammonium)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] dibromide (PFN-Br) was purchased from Ossila.

Device fabrication:

ITO substrates were brushed with a nylon-bristle toothbrush soaked in detergent and deionized (DI) water for 2-3 minutes per substrate then rinsed with DI water. ITO substrates were then cleaned by sonication sequentially in DI water, acetone, and isopropanol for 15 minutes each. For ITO substrates without NiO_X, ITO was treated by UV-ozone for 20 minutes prior to deposition (spin casting) of organic HTLs and subsequent layers.

NiO_X was prepared by loading pre-patterned and cleaned ITO samples into a custom built Dielectics Sputter Chamber with Angstrom Engineering ONYX-2 sputter gun. Edges of the center ITO pad which are used as cell ground contacts were masked by Kapton tape prior to NiO_X deposition. The target of NiO_X was sourced from Heeger Materials. After achieving base pressure (5×10^{-6} Torr), pure Argon gas flow was adjusted to give a steady state pressure of 20 mTorr. Ar plasma is initiated after stabilizing at 20 mTorr. The NiO_X target was conditioned for 2 minutes priot to deposition. Sputtering was performed with 70 W RF power at 13.56 MHz. The sample shutter was opened and deposition was stabilized at a rate of about 0.5 Angstrom/second until the target thickness was achieved. The final thickness was confirmed by stylus profilometry. Before spin casting of subsequent layers, NiO_X-coated substrates were sonicated in IPA for 15 minutes to remove organic residues, then annealed in air at 250^{o} C for 30 minutes. This post-deposition anneal step in air is known to improve the hole-transport properties for perovskite cells by increasing the oxygen content and pushing the nickel oxidation state toward Ni^{3+} for improved hole conductivity.

All spin casting was done in a nitrogen-filled glovebox.

For Me-4PACz solutions, a 4:1 ratio of Me-4PACz (1 mg/mL in ethanol) and 6dPA (0.75 mg/mL in ethanol) was used. 6dPA was included to improve the wetting of the Me-4PACz to the underlying substrate. 1.25 M perovskite precursor was prepared by dissolving 0.3125 mmol CsI, 0.9375 mmol FAI, 0.2813 mmol $PbBr_2$, 0.9688 mmol PbI_2, 0.0625 mmol $PbCl_2$ and 0.0625 mmol MACl in a 4:1 volume ratio of DMF and DMSO.

The 4:1 Me-4PACz/6dPA mixture was dynamically cast onto the substrate at 5000 rpm for 20 s, annealed at 100° C for 10 minutes, and then allowed to cool to ambient temperature. The preparation and spin procedure were the same for the ITO/SAM and ITO/NiO_X/SAM combination. The perovskite was spun at 5000 rpm for 35 s and 500 uL of anisole was dropped onto the spinning film with 15 s remaining in the process. The films were annealed at 100° C for 30 minutes and allowed to cool before thermal evaporation.

30 nm of C_{60} fullerene was deposited on top of the perovskite film by thermal evaporation with a rate of 0.1 Å/s for the first 5 nm and 0.3 Å/s for the remaining 25 nm. Bathocuproine (BCP) was thermally evaporated at a rate of 0.1 Å/s for the entire 6 nm thickness. 200 nm of Ag was thermally evaporated at a rate of 0.1 Å/s for the first 10 nm, then at 0.5 Å/s for the next 40 nm, and then at a rate of 1.5 Å/s for the remaining 150 nm. Ag top contacts are **0.119 cm^2** in area.

Perovskite Solar Cell Architectures with BCP:

- ITO / 30 nm NiO_X / 400 nm (1.67 eV) $Cs_{0.25}FA_{0.75}MAPb(I_{0.85}Br_{0.15})_3$ / 30 nm C_{60} / 6 nm BCP / 200 nm Ag
- ITO / Me-4PACz / 400 nm (1.67 eV) $Cs_{0.25}FA_{0.75}MAPb(I_{0.85}Br_{0.15})_3$ / 30 nm C_{60} / 6 nm BCP / 200 nm Ag
- ITO / 30 nm NiO_X / SAM / 400 nm (1.67 eV) $Cs_{0.25}FA_{0.75}MAPb(I_{0.85}Br_{0.15})_3$ / 30 nm C_{60} / 6 nm BCP / 200 nm Ag

Transport Layer Diode (TLD) Architectures with BCP:

- ITO / 30 nm NiO_X / 30 nm C_{60} / 6 nm BCP / 200 nm Ag
- ITO / SAM / 30 nm C_{60} / 6 nm BCP / 200 nm Ag
- ITO / 30 nm NiO_X / SAM / 30 nm C_{60} / 6 nm BCP / 200 nm Ag

For samples with SnO_X included in the ETL, 20 nm of SnO_X was deposited in place of BCP. SnO_X was deposited via atomic-layer deposition (ALD) using a Beneq TF-200 using TDMA-Sn and H_2O precursors with a reactor temperature of 87° C. 167 cycles were used to achieve about 20 nm of SnO_X.

Electrical characterization of cells:

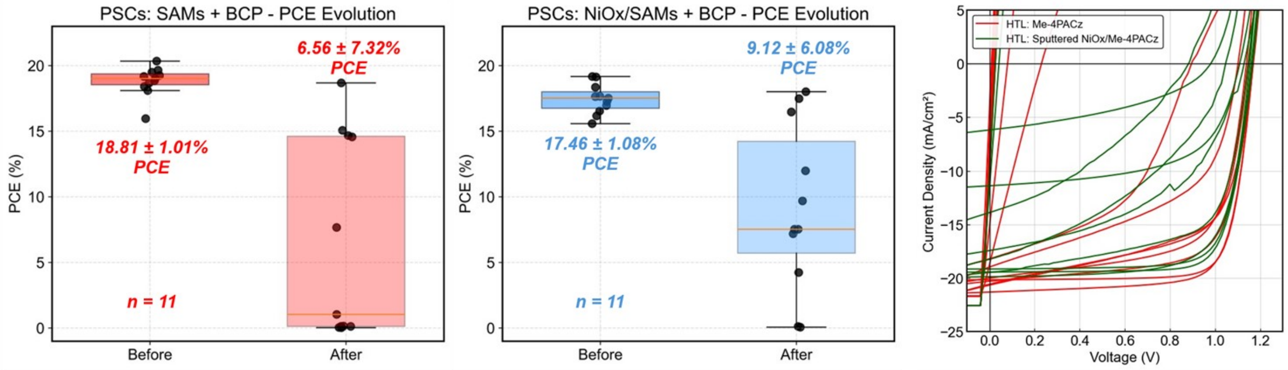
All current-voltage measurements were performed in a nitrogen-filled glovebox using a Keithley 2400 and home-built control software at a temperature of ~20°C (no intentional heating or cooling). Constant-voltage measurements used the Keithley's source voltage and measure current modes. Constant-current measurements used the Keithley's source current and measure voltages modes. Reverse current-voltage measurements were performed with a scan rate of about 100 mV/second. Similarly, forward current-voltage measurements were performed with a scan rate of about 125 mV/second. A current compliance of 2.4 mA (20 mA/cm^2) was used for all electrical measurements. Samples were illuminated using an LED array from G2V (calibrated to 1-Sun intensity using a Si photodiode). Electro-/photo-luminescence (EL/PL) images were captured by using a Nikon DSLR camera modified by BrightSpot Automation, a 532 nm green LED, and a Keithley 2400 power supply, which were controlled by custom software from BrightSpot Automation. All EL/PL measurements were performed in a nitrogen-filled glovebox.

X-ray Photoemission Spectroscopy:
XPS measurements were conducted using a Kratos Analytical Axis Supra with a monochromatic Al Kα source with an emission current of 20mA and a total power of 300 W. Elemental scans were acquired using a pass energy of 40 eV with a 0.1 eV energy step used for all scans. All scans were collected with an incident x-ray angle of 45° and a takeoff angle of 0°.

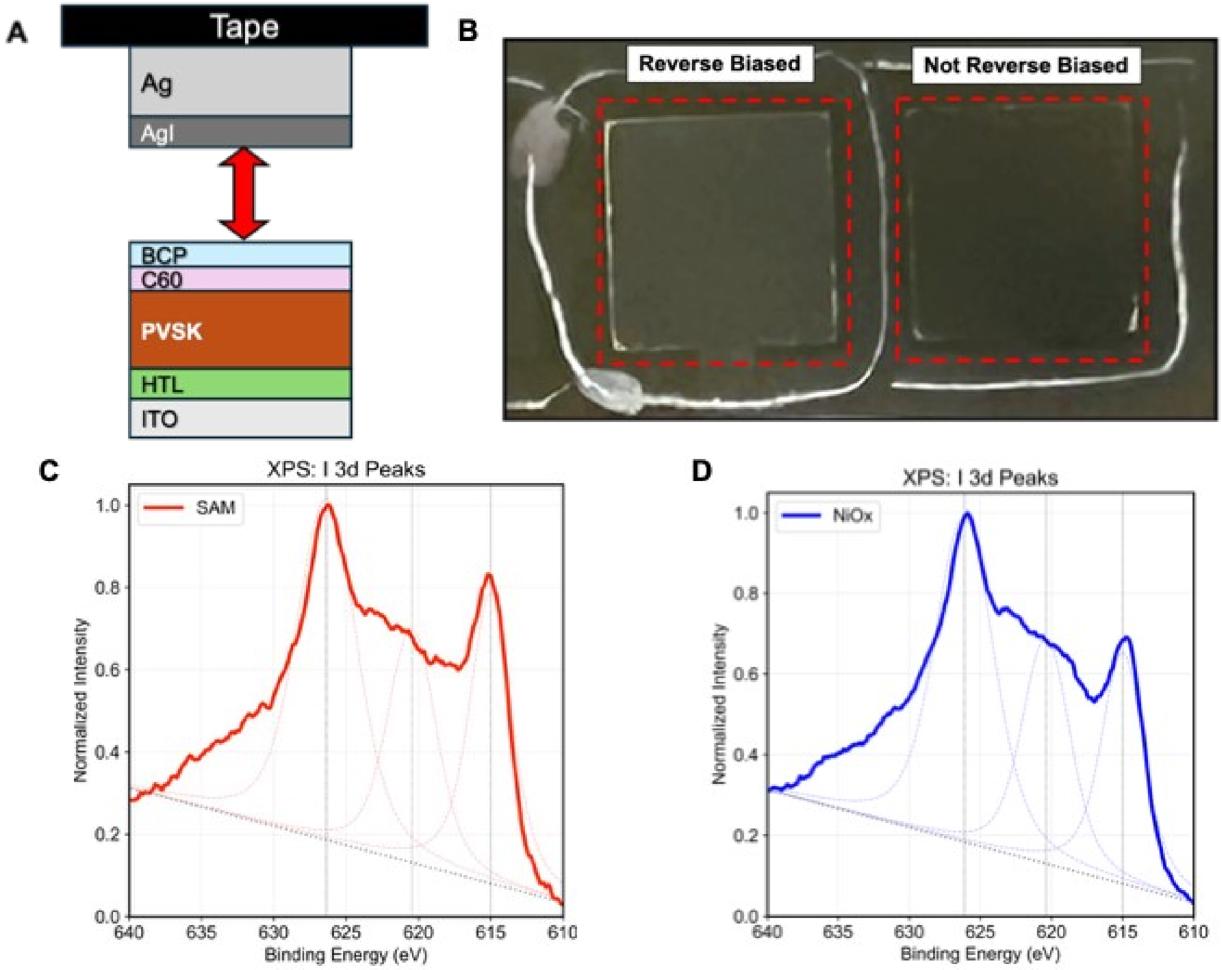
Estimating pinhole densities:
We estimate the areal density of pinholes that lead to abrupt breakdown in our cells ("killer defects"). Electroluminescence imaging (e.g., Figs. 2d,f) frequently reveals about 3 pinholes in our cells with area 0.12 cm^2. This suggests an average pinhole density of 25 cm^{-2} (3/0.12 cm^2). Statistically, finding N randomly distributed pinholes in a given area is a Poisson sampling problem. If there is an average defect density of X cm^{-2} and a device area of A cm^2, the expected number of defects in the device is $<n>=XA$. The "yield" is the probability of finding *zero* killer defects in a device with area A. It is given by $P(0)=\exp(-XA)$. We assume that a solar cell will show *gradual* breakdown only if it has zero killer defects. (A cell with ≥1 defect will show abrupt breakdown.) So, $P(0)$ is the probability that a cell shows gradual breakdown; we take $P(0)$ from breakdown statistics from our cells (e.g., Fig. 1e). We solve for X. From those statistics, $P(0)=1/11$ (the number of cells showing gradual breakdown), and we conclude X=20 cm^{-2}. Interestingly, if we do this same analysis with NiOx HTLs, the density of "killer defects" is reduced to <1 cm^{-2}. So thick NiO_x can be thought of as a way to "passivate" defects that lead to abrupt breakdown. These results are summarized in the table below:

Method	Cell area (cm^2)	$P(0)$	X (cm^{-2})
$P(0)=\exp(-XA)$ (No NiO_x)	0.12	1/11	20
Electroluminescence imaging	0.12	NA	25
$P(0)=\exp(-XA)$ (30 nm NiO_x)	0.12	10/11	<1

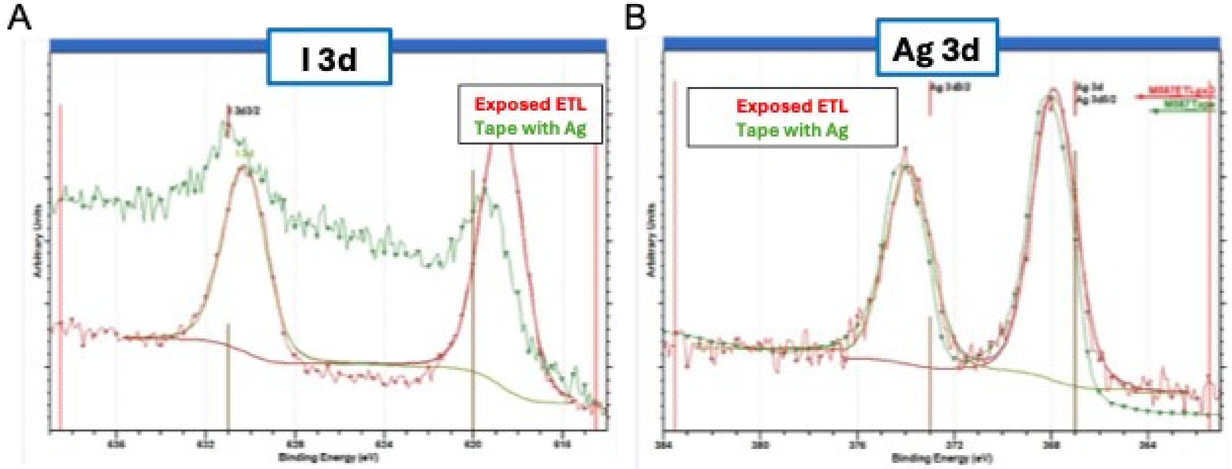
Supplementary Figures:



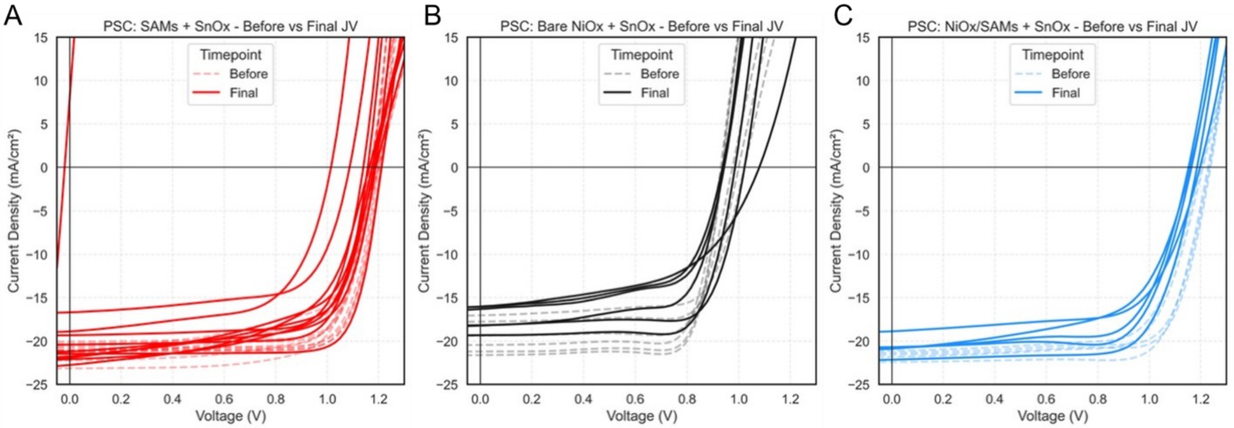
SI Figure 1: (left) *The PCEs (%) of the solar cells with the SAM-only HTLs before and after reverse bias.* ***(center)*** *The PCEs of the solar cells with* NiO_X*/SAMs at the HTL before and after reverse bias.* ***(right)*** *Forward-bias JV curves measured immediately after reverse-bias stressing (no recovery) solar cells using* NiO_X *only (red curves) and* NiO_X*/SAM (green curves). All cells shown here used a* C_{60}*/BCP ETL.*



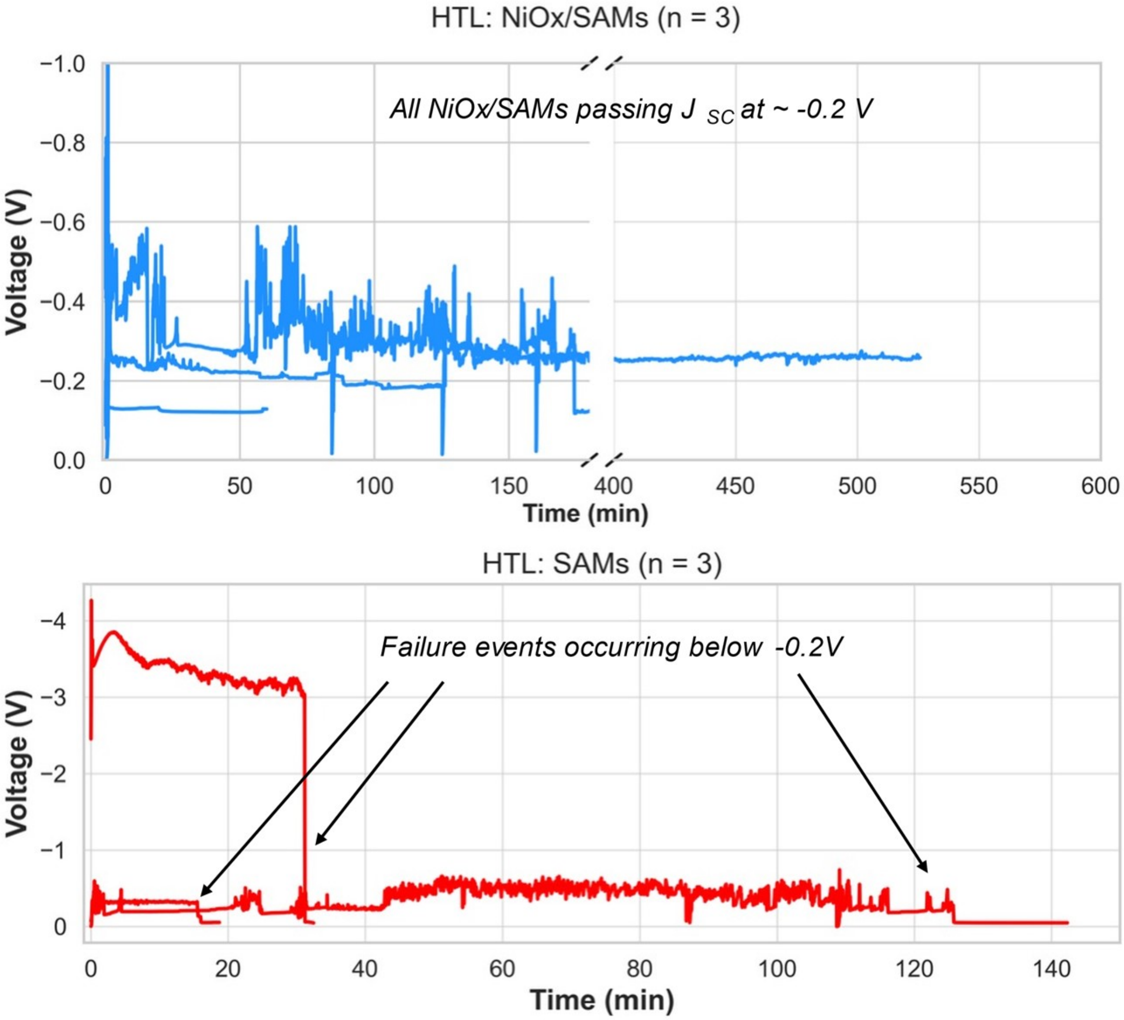
SI Figure 2: (A) *Schematic of removing the Ag electrodes with tape for XPS measurements.* ***(B)*** *Optical images of the top of two perovskite cells after delaminating the top metal contacts, imaged under white-light illumination. Left pixel: reverse bias stress. Right pixel: unstressed. A light-gray hue in reverse-biased cell arises from some type of surface corrosion, seemingly related to AgI, and texture. These cells did not exhibit abrupt breakdown or hot-spot type failure.* ***(C)*** *XPS I 3d signals on delaminated Ag electrodes/electrical tape for a solar cell with a SAM HTL (red), peaks are highlighted at 615 eV, 620.45 eV, and 626.35 eV.* ***(D)*** *XPS I 3d signals on delaminated Ag electrodes/electrical tape for a solar cell with a* NiO_X *HTL (blue), peaks are highlighted at 615 eV, 620.38 eV, and 626.16 eV.*



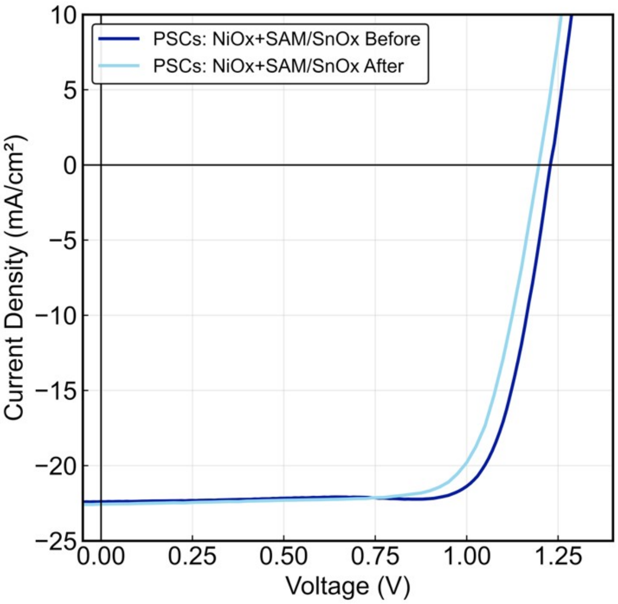
SI Figure 3: ***(A)*** *I 3d XPS spectra on solar cells after reverse bias with SAM HTLs on the delaminated tape (green) and the exposed ETLs (red), highlighting the presence of* I^- *on both interfaces,* ***(B)*** *Ag 3d XPS spectra on solar cells with SAM HTLs on both the delaminated tape (green) and the exposed ETLs (red), highlighting the presence of* Ag^+ *on both interfaces after reverse bias.*



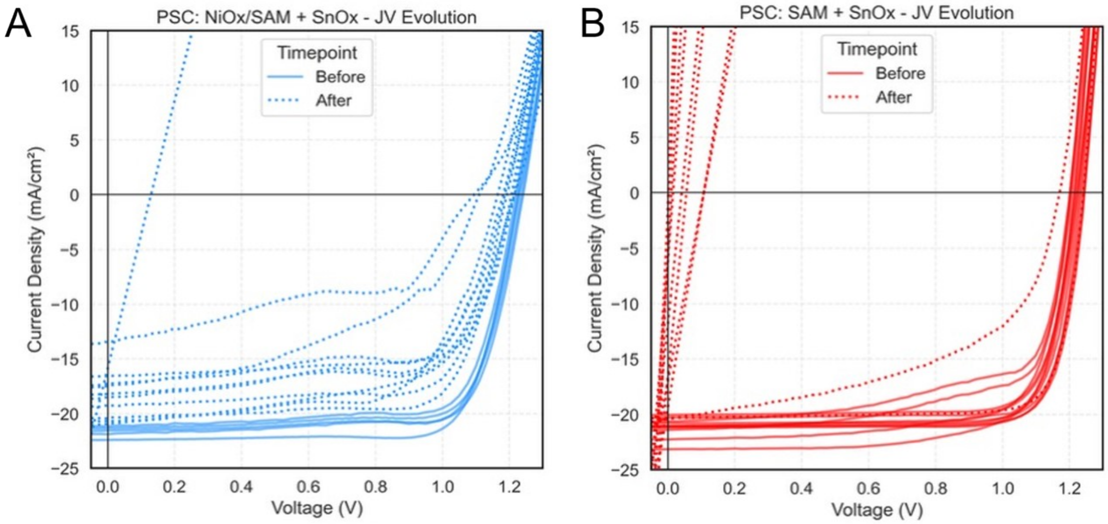
SI Figure 4: *JV curves before (dashed) and after (solid lines) reverse-JV sweeps on solar cells with ALD* SnO_X *ETLs using* ***(A)*** *SAM HTL,* ***(B)*** *bare* NiO_X *HTL,* ***(C)*** NiO_X*/SAM combination HTL.*



SI Figure 5: (Top; blue) *Fixed current hold measurements for* NiO_X*/SAM HTL devices. This shows the voltage required to maintain -20* mA/cm^2 *average current density (~*J_{SC}*), or -2.4 mA. Measurements are shown for devices that were held for at least 20 minutes. The longest hold time was 525 minutes.* ***(Bottom; red)*** *Fixed current holds for SAM-only devices. The longest hold time was 140 minutes.*



***SI Figure 6: Dark blue**: Initial JV curves of a NiO_X + SAM device with ALD SnO_X. **Light blue**: JV curves for the same NiO_X + SAM device after being held at -2.4 mA (-20 mA/cm^2) for 8.75 hours (525 minutes) in the dark and allowed to rest overnight in the dark.*



***SI Figure 7: (A)** JV curves for PSCs using NiO_X/SAMs before (solid blue curves) and after (dashed blue curves) being held at -20 mA/cm^2 in the dark for 5 minutes. **(B)** Boxplots for the PSCs using NiO_X/SAMs PCEs before (left) and after (right) being held at -20 mA/cm^2 in the dark for 5 minutes. **(C)** JV curves for PSCs using SAMs before (solid red curves) and after (dashed red curves) being held at -20 mA/cm^2 in the dark for 5 minutes. Ohmic shunts can be seen going through J = 0 mA/cm^2 voltages less than about 0.12 V. **(D)** Boxplots for the PSCs using NiO_X/SAMs PCEs before (left) and after (right) being held at -20 mA/cm^2 in the dark for 5 minutes.*