Supporting Information

Effects of Moisture Based Grain Boundary Passivation on Cell Performance and Ionic Migration in Organic-Inorganic Halide Perovskite Solar Cells

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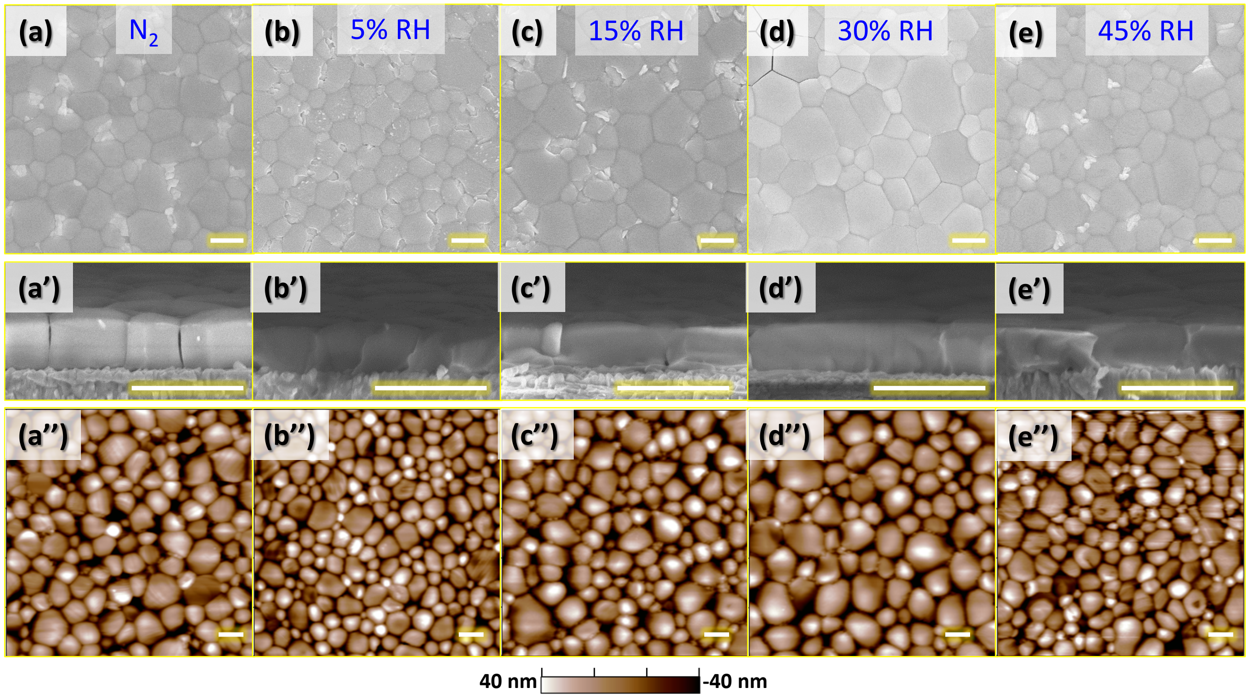

Figure S1. $MAPbI_3$ thin film fabricated at different conditions: (a-e) SEM surface images for samples S0, S1, S2, S3 and S4 respectively, (a'-e') SEM cross section images of the respective films, and (a''-e'') AFM topographic images for the corresponding films. All scale bars represent length of 1 µm.

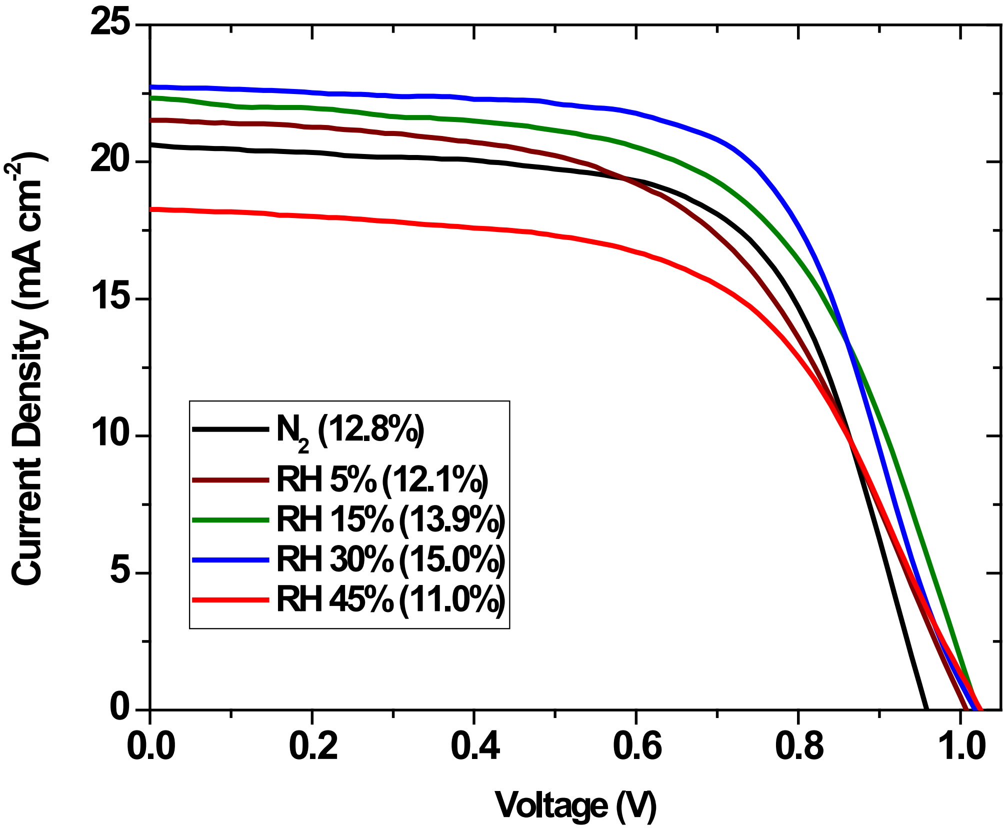

Figure S2. J-V curve comparison of the samples fabricated at different conditions under 1-sun with the indication of the PCE for champion devices in parenthesis.

Table S1. PSC Performance Comparison for Samples Prepared at Different Moisture Contents.

	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE_{MAX} (%)	R_S (Ω-cm^2)	R_{SH} (Ω-cm^2)
S0	20.62	0.95	65	12.8	10.3	769
S1	21.53	1.00	56	12.1	14.5	833
S2	22.34	1.016	61	13.9	11.1	606
S3	22.74	1.02	65	15.0	10.1	994
S4	18.27	1.02	59	11.0	17.0	749

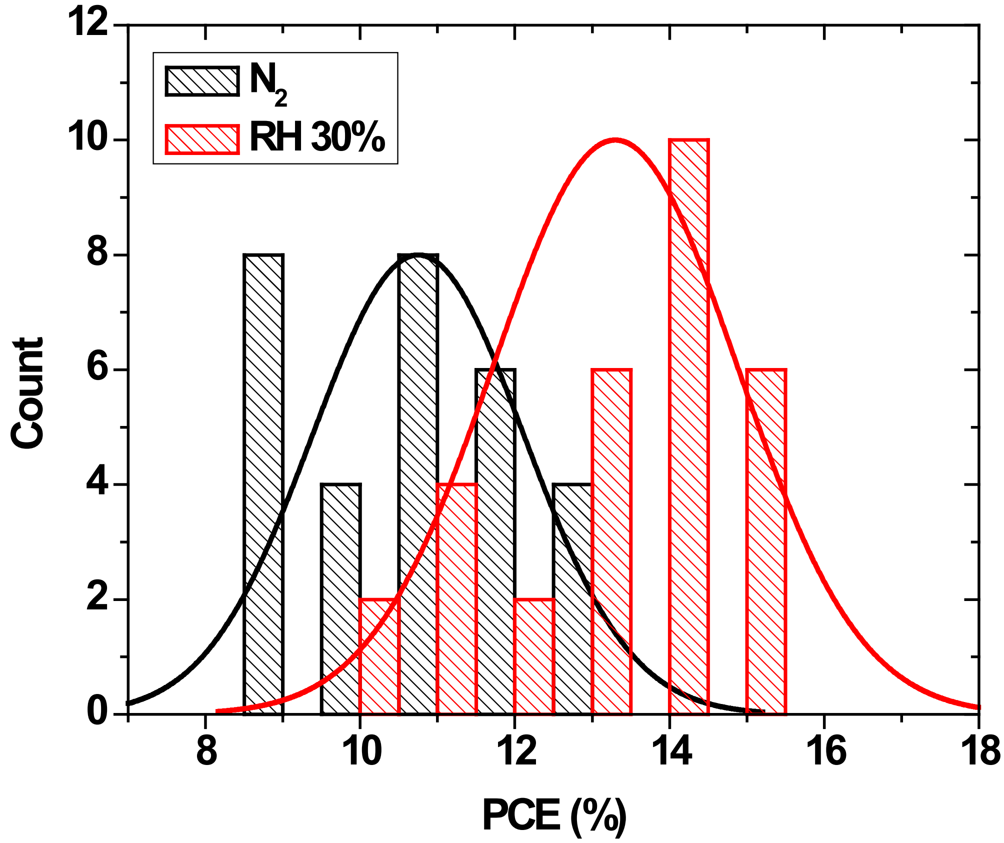

Figure S3. The PCE distribution histograms for samples prepared in N_2 and at 30% RH.

SKPM Measurement:

As shown in Figure S4, SKPM measured contact potential difference (V_{CPD}) or surface potential between the sample and the conductive tip, which can be calculated using the following formula,

$$V_{CPD} = \frac{q\varphi_{tip} - q\varphi_s}{-q} = \varphi_s - \varphi_{tip}$$

Where $q\varphi_{tip}$ is the work function of the tip and $q\varphi_s$ is the work function of the sample. For the SKPM experiment, ASYELEC.01-R2 conductive probes (Si coated with Ti/Ir (5nm/20nm)) from Asylum Research were used, which have a work function of 4.9 eV.

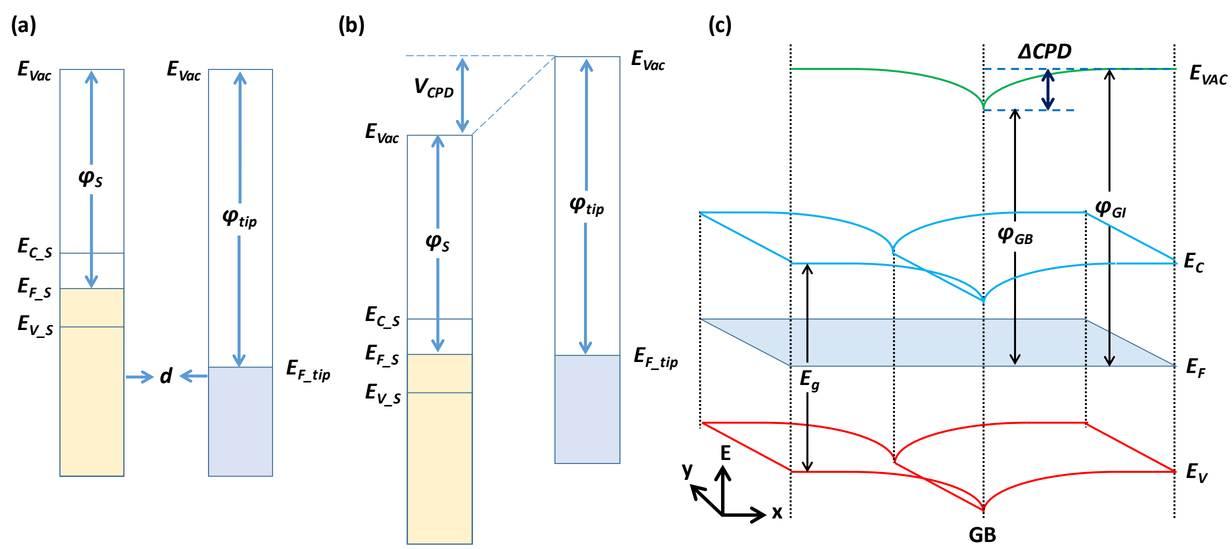

Figure S4. Band energy diagram of SKPM measurement between the sample and the tip. (a) With no electrical contact and being separated by distance d, sample and tip have different Fermi levels. (b) While in contact, the two Fermi levels will be aligned causing a potential difference called a contact potential difference (V_{CPD}). This amount of potential is applied during SKPM measurement to nullify the potential difference. (c) Electronic band diagram in two-dimensional space near a grain boundary (GB) area.

As an example, an arbitrary grain boundary band energy diagram is shown in Figure S4c. If the V_{CPD} value at grain boundary (GB) is - 0.2 V, it implies the work function, $q\varphi_{GB}$ value is 4.7 eV, while a V_{CPD} value of - 0.17 V at neighboring grain interior (GI) implies the work function, $q\varphi_{GI}$ value is 4.73 eV. This implies a downward band bending of 30 meV at the GB. It is noteworthy here that the $q\varphi_s$ value ~ 4.7 eV is almost in the middle of the conduction (3.9 eV) and valence (5.43 eV) bands of $MAPbI_3$ being an intrinsic semiconductor material.

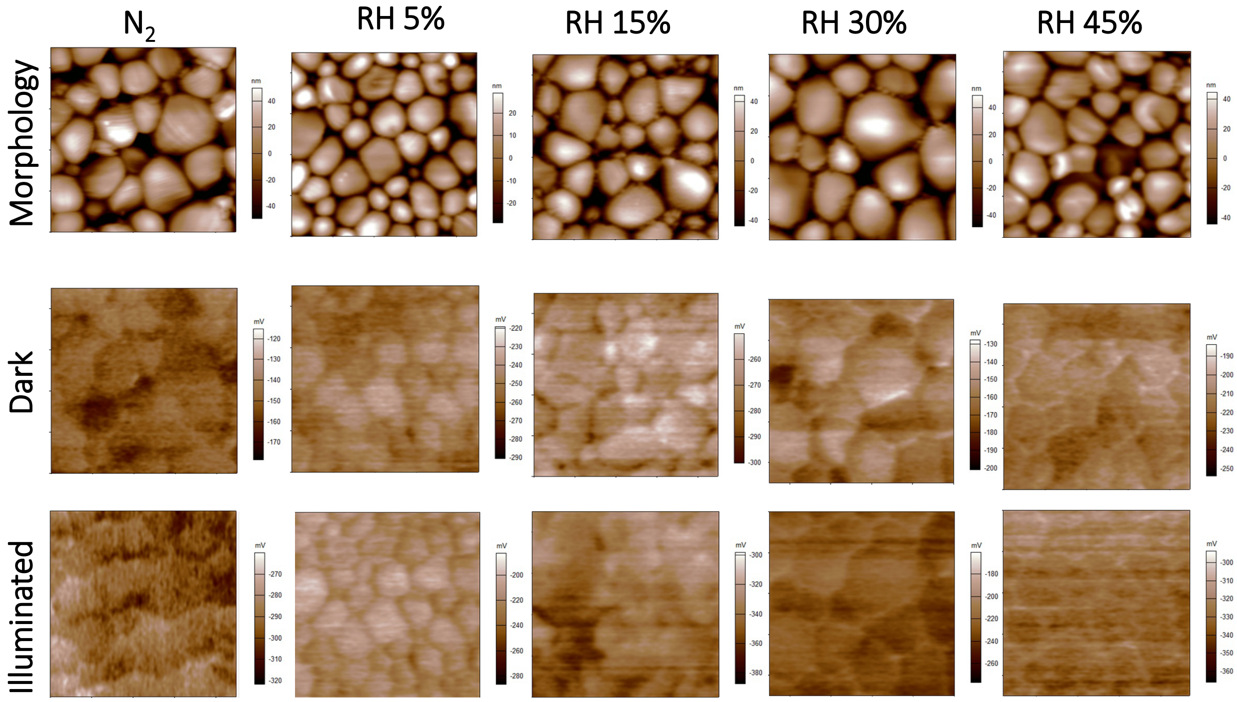

Figure S5. AFM surface and SKPM images of $MAPbI_3$/FTO samples prepared at different atmosphere under dark and light conditions.

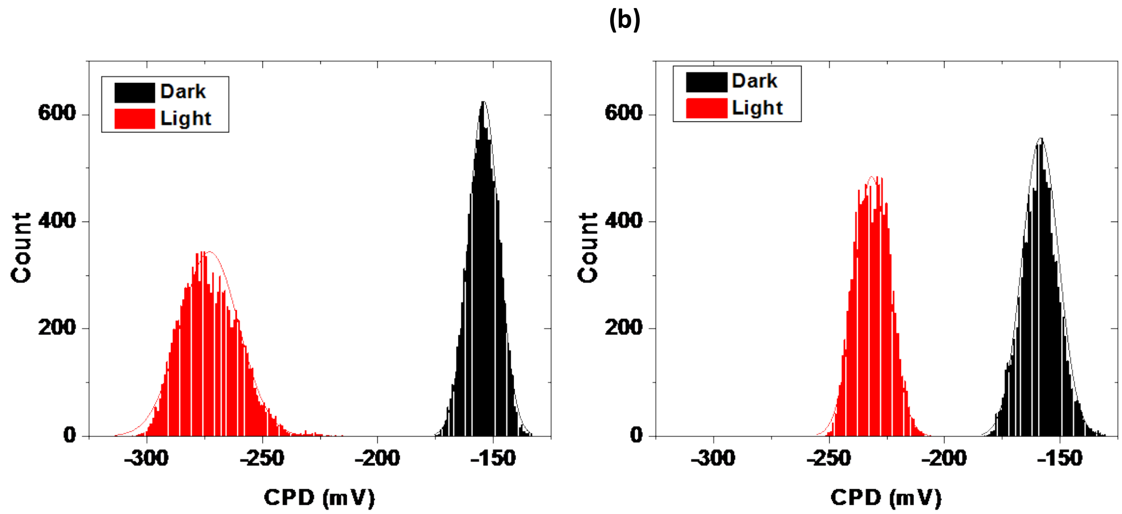

Figure S6. Histogram distributions of CPD for samples fabricated (a) in N_2 ambient, and (b) at 30% RH, under dark and light conditions.

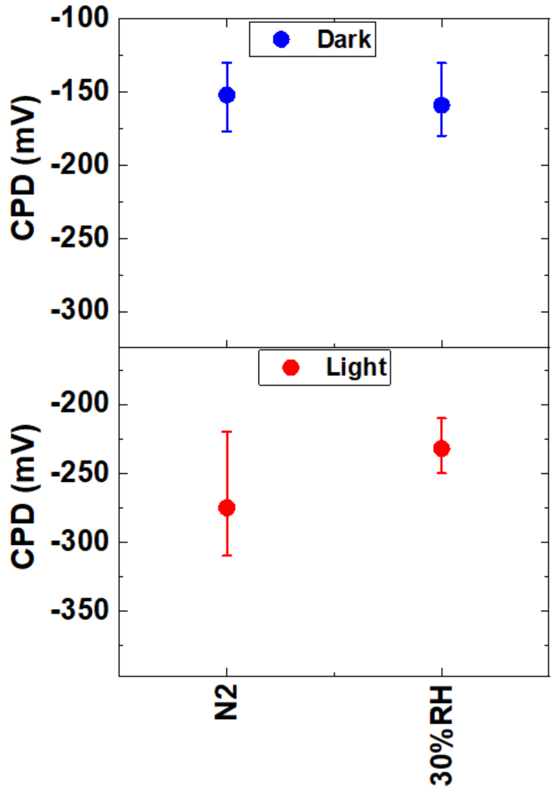

Figure S7. Contact potential difference (CPD) for samples fabricated in N_2, and at 30% RH, under dark and light conditions. The average data have been obtained from Gaussian distribution, while the error bars represent the width of the distribution. Essentially, the length of the error bar represents average difference of CPD between grain boundary and grain interior.

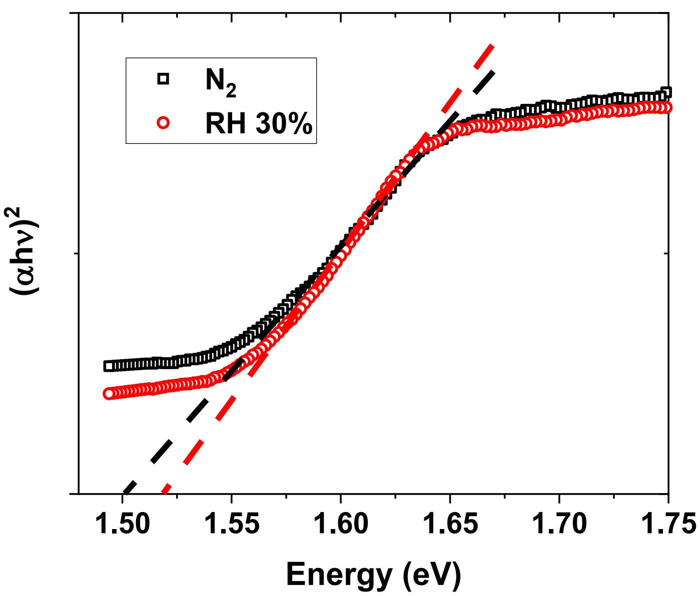

Figure S8. Tauc plot showing measured bandgap from absorbance spectra for samples prepared in N_2 and at 30% RH.

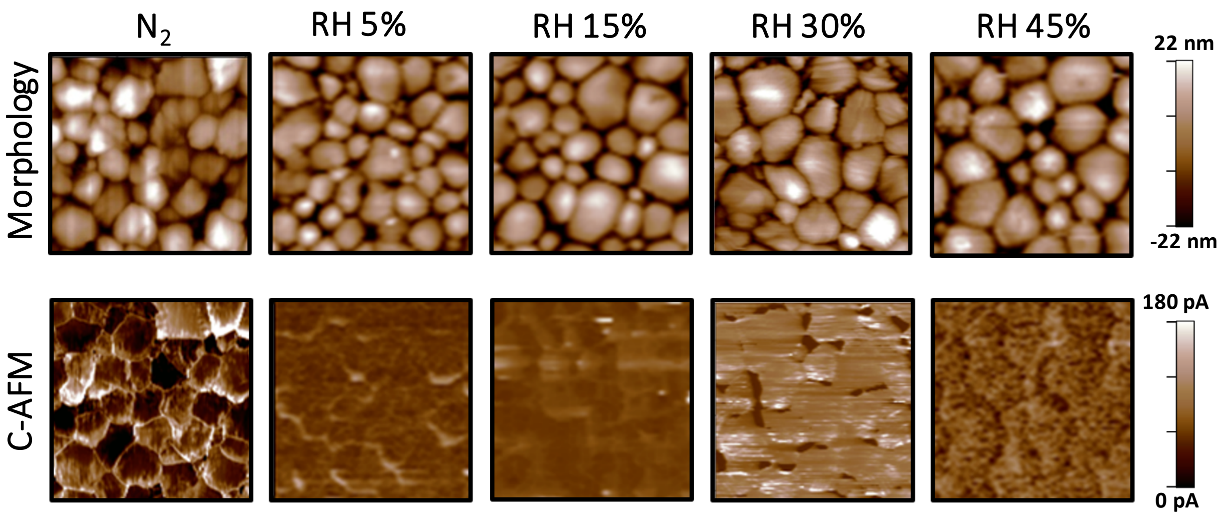

Figure S9. AFM surface and c-AFM images of $MAPbI_3$/FTO samples prepared at different atmosphere, measured under dark condition.

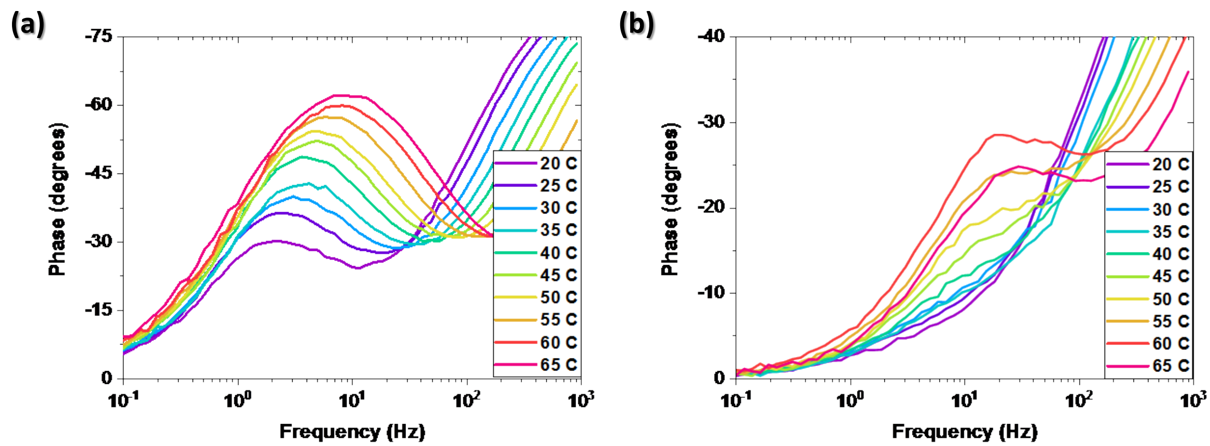

Figure S10. The Bode plots obtained from impedance spectroscopy data at different temperatures ranging from 20 to 65 °C to measure the ion hopping rate constant for (a) sample prepared in N_2, and (b) sample prepared at 30% RH.

The low frequency peaks from the Bode plot are result of ionic migration that happens at a much slower rate (on the order of several hundreds of ms) than electronic conduction. This low frequency peak (f_0), also known as relaxation frequency of ion hopping transportation, can be used to determine the relaxation time constant, τ, following the formula:

$$\tau = \frac{1}{2\pi f_0}$$

Finally, ion hopping rate constant, k can be determined by the following formula:

$$k = \frac{1}{\tau}$$

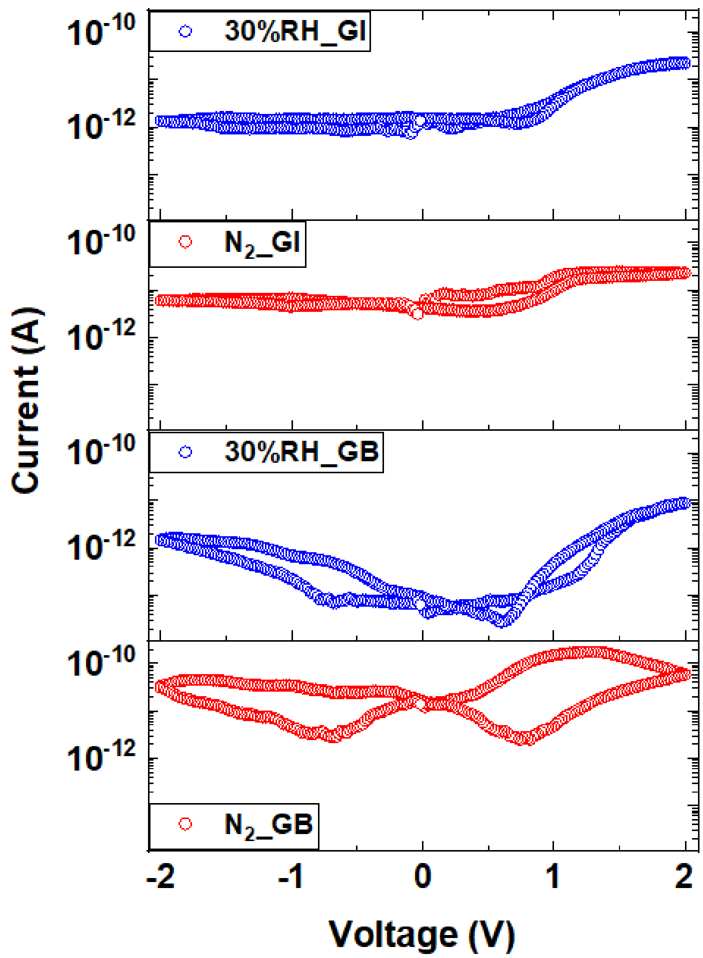

Figure S11. c-AFM based local dark current measured at the GI and the GB for samples S0 and S3 on surface of $MAPbI_3$/FTO.