Supporting Information

Electric Field-Induced Degradation of Methylammonium Lead Iodide Perovskite Solar Cells

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Experimental

1. Preparation of materials

Titanium diisopropoxide bis (acetyleacetonate) (TTIP), 1-butanol (anhydrous, 99.8%), terpineol, ethyl alcohol (pure), chlorobenzene (anhydrous, 99.8%), N,N-dimethylformamide (anhydrous, 99.8%) (DMF), dimethyl surfoxide (anhydrous, 99.9%) (DMSO), 2-propanol (anhydrous, 99.5%), acetonitrile (anhydrous, 99.8%), 4-tert-butylpyridine (96%), and bis (trifluoromethane) sulfonamide lithium salt (LiTFSI) were purchased from Sigma-Aldrich. Lead (2) iodide (99.9958%) was purchased from Alfa Aesar. 18NR-T and MAI were purchased from Dyesol. 2,2', 7,7'-tetrakis (N,N-di-p-methoxyphenylamino) -9,9'-spirobifluorene (spiro-OMeTAD) was obtained by Lumtec.

2. Perovskite solar cell manufacture

7 ohm/sq patterned FTO glasses were cleaned by acetone, ethanol, and isopropanol for 10 min, in a bath using ultrasonication. For the formation of the TiO_2 compact layer (c- TiO_2), TiO_2 precursor solution (0.15 M TTIP in 1-butanol) was spun onto the FTO substrates and dried at 125 °C on a hot plate. The mesoporous TiO_2 (m- TiO_2) layer were deposited onto the c- TiO_2 substrates using spin coating of a mixed solution (18NR-T paste, terpineol, and ethyl alcohol). The substrate was dried at 100 °C on the hot plate and then annealed at 550 °C during 60 min in box furnace. We used the $MAPbI_3$ solution for one-step deposition (50 wt% of 1:1:1 MAI, PbI_2, and DMSO in DMF). The $MAPbI_3$ perovskite layers were deposited onto the m- TiO_2 substrates through the one-step deposition process by dripping of diethyl ether. The HTM solution was prepared by mixing 72.3 mg of spiro-OMeTAD in 1 ml chlorobenzene and 28.8 μl of 4-tert-butylpiridine and 17.5 μl of a LiTFSI solution (520 mg in 1 ml of acetonitrile) and coated using a

spin coater. Finally, 100 nm of Au was thermally evaporated in a vacuum chamber as contacts. Active area of device for operating was 0.075cm^2.

3. Aging condition

To minimize the effect of humidity, all the samples used in this study were capped by UV curable adhesive. (Optical Adhesive 88, NORLAND PRODUCTS, INC.) All tests were conducted in the temperature- and humidity-controlled chamber which had been used for the reliability test under the dark condition. At all temperature conditions from 25 ^{o}C to 55 ^{o}C, the humidity was set at 20 % RH. All measurements were started after 20 min of temperature saturation. Experiments of electric field aging were conducted at controlled 25 ^{o}C. To check the effect of ambient conditions during aging test, reference samples without biased were also observed. Although not shown here, we checked that reference samples were not affected by ambient conditions. Different solar cells that were made with the same sequence were used for each test to minimize the history of previous test.

4. Characterization

The light I–V characteristics were measured using a xenon lamp adjusted to AM 1.5 suns (the light source of a solar simulator, WACOM ELECTRIC Co., LTD.). Calibration was conducted before the measurement using the modulated reference silicon solar cell. The photo-generated current as a function of the voltage was measured using a source meter. (Keithley 2400) The delay time of each voltage step (0.01 V) was 200 ms and voltage was swept from 1.2 V to -0.1 V. calculated scan rate was about 65 mV/s. Scan direction was from open circuit to short circuit. The dark current decay with the temperature was measured using Keithley 2400 source meter. The samples were stored in the temperature- and humidity-controlled chamber during the measurement. The capacitance as a function of the frequency was measured using an LCR meter (HP 4284A), and the samples were kept in the dark during the measurement.

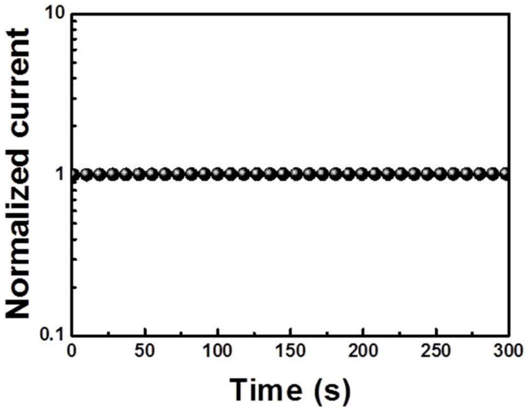

Figure S1. Dark current of conventional crystalline silicon solar cells (at 0.6 V)

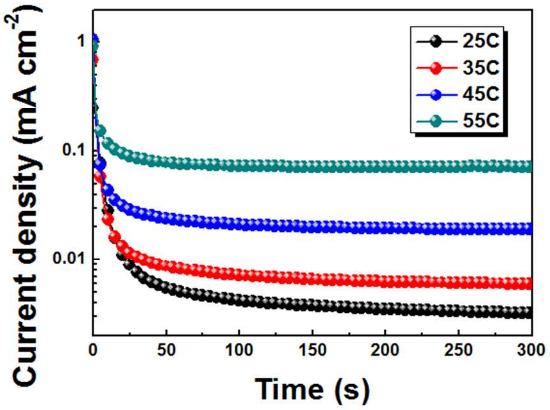

Figure S2. Dark current density with different temperatures. Voltage is constantly applied to the device at 0.6 V during measurement.

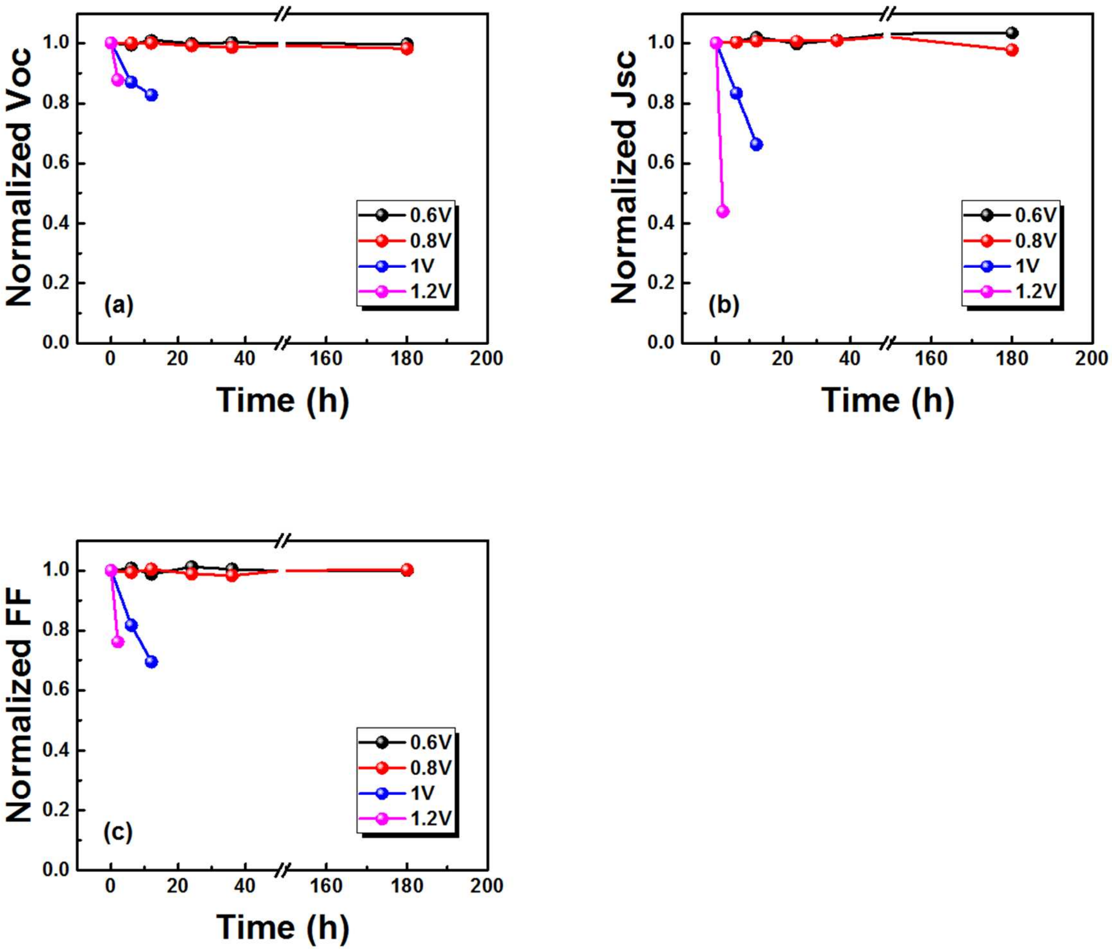

Figure S3. Changes in the properties of the perovskite solar cells with the applied bias (a) Voc, (b) Jsc, and (c) FF

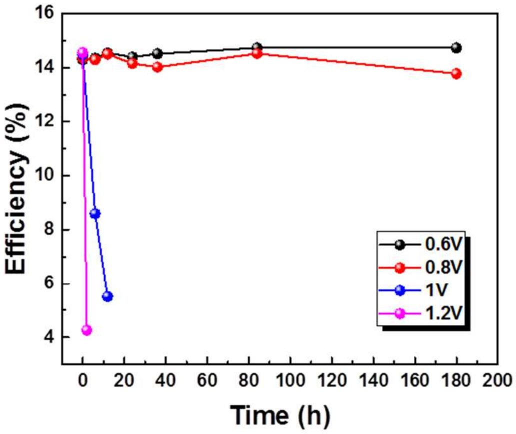

Figure S4. Efficiency changes of the perovskite solar cells for different applied voltages

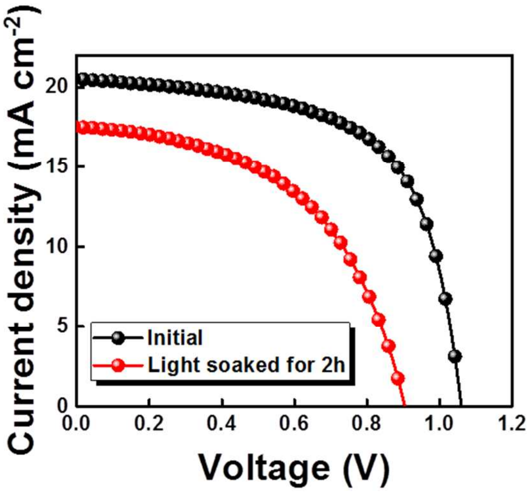

Figure S5. Changes in the light I–V curve with the light soaking time. The circuits of the solar cells are opened during light soaking.

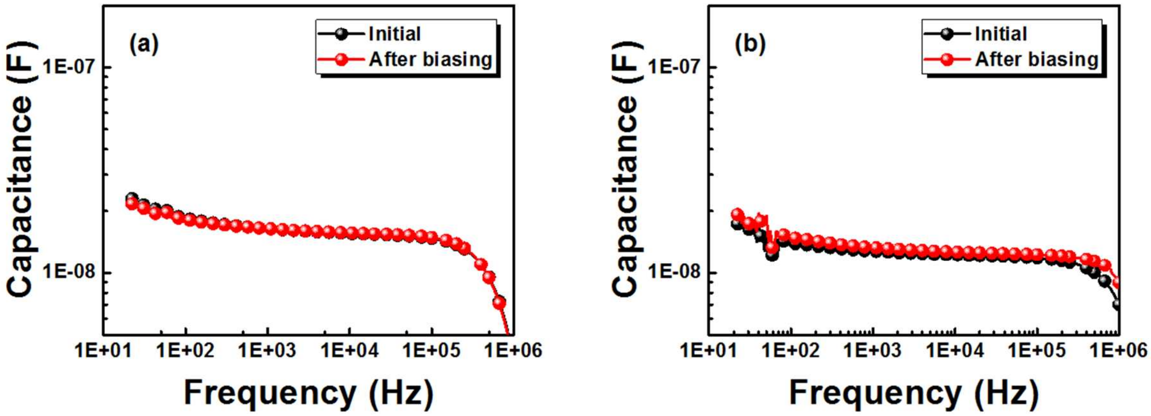

Figure S6. Capacitance–frequency curves (a) biased at 0.6 V and (b) 0.8 V

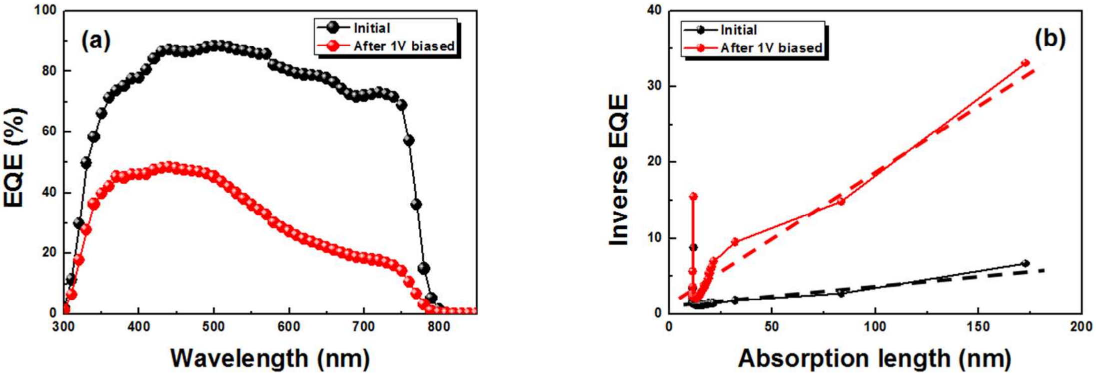

Figure S7. (a) External quantum efficiency (EQE) results before and after biasing test at 1 V (b) inverse EQE with absorption length calculated from EQE data. Diffusion length can be obtained from QE measurements by calculating the slope of inverse internal quantum efficiency (IQE) with absorption length.[1] $\mathrm{IQE}^{-1} = 1 + L_{\alpha}/L_{eff}$ (L_{α} : absorption length, L_{eff} : diffusion length)

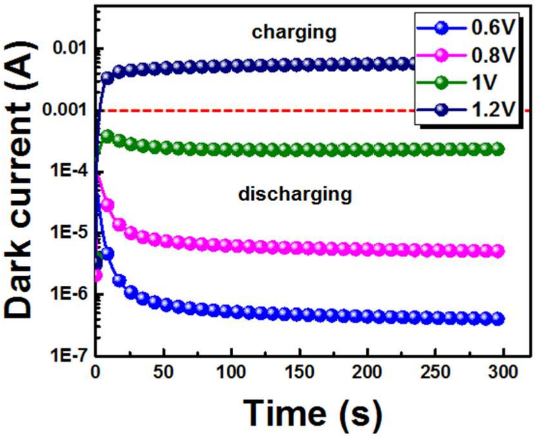

Figure S8. Dark current decay with biasing voltage at 25 ^{o}C. Dark current shows discharging property under 1 V.

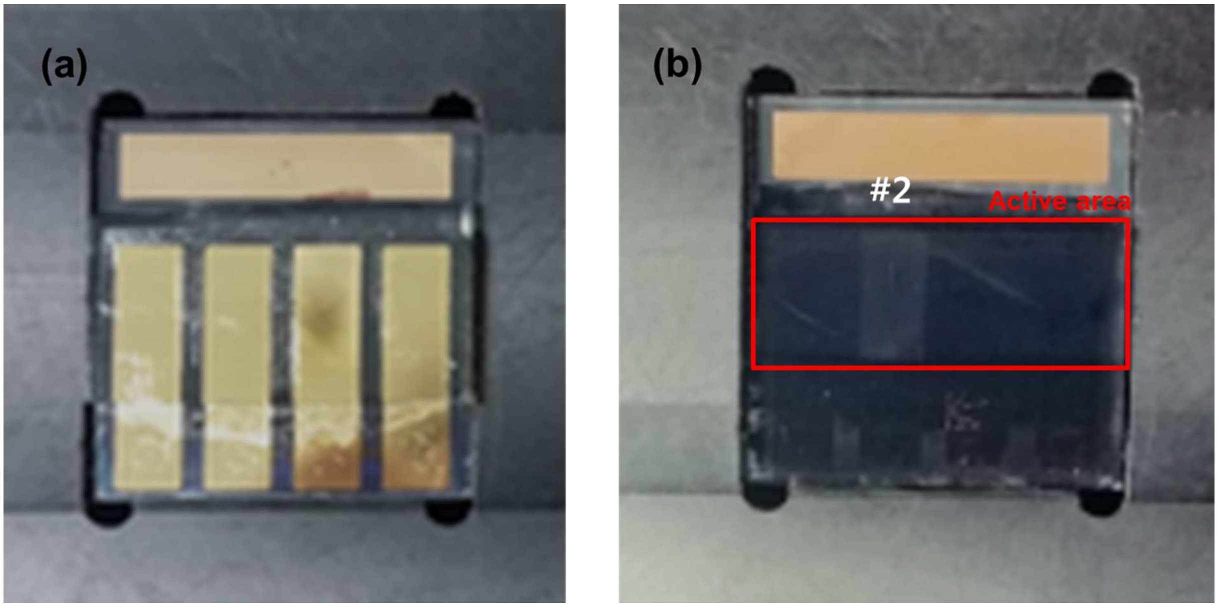

Figure S9. (a) Solar cell image used in this study. Four active area are on the substrate. (b) Sunny side view of image for degraded samples biased only to the #2 area at 1.2 V for 4 hours. Color was changed after biasing test compared to other perovskite layers.

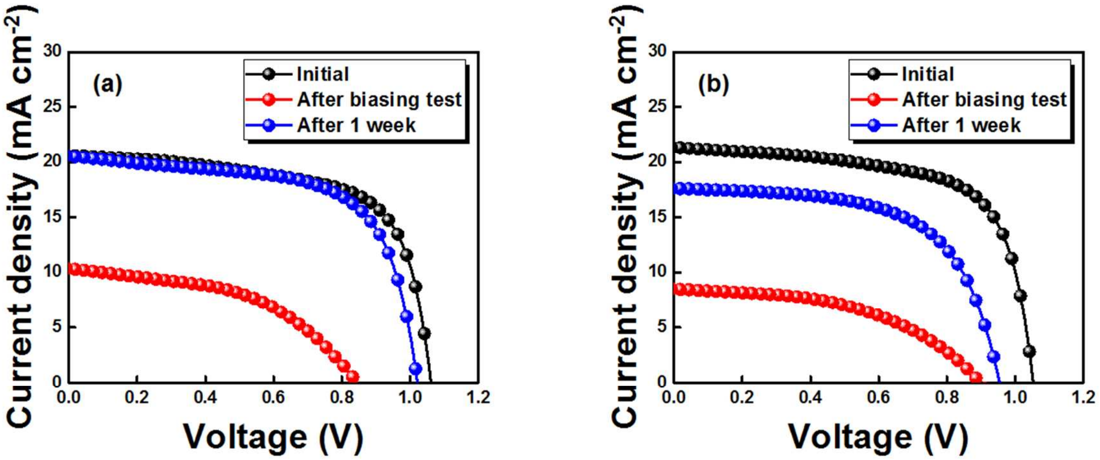

Figure S10. Light I–V curves of the tested solar cells were re-measured after 1 week for (a) 1 V biased sample and (b) 1.2 V biased sample stored in the dark.

REFERENCES

1. Basore. P. A. Extended Spectral Analysis of Internal Quantum Efficiency. *Photovoltaic Specialists Conference* **1993,** *Conference Record of the Twenty Third IEEE,* 147–152.