

Supporting Information

A Unified Description of the Electrical Properties with Complex Dynamical Patterns in Metal Halide Perovskite Photovoltaics

Experimental Methods

Fabrication. Fluorine-doped tin oxide (FTO) glass sheets were etched with Zn powder and diluted HCl. Then, the etched substrates were cleaned in an ultrasonic bath with Hellmanex®, acetone, and ethanol for 15 min, before immediately drying with dry air. Compact TiO₂ (c-TiO₂) solution was prepared with titanium diisopropoxide bis(acetylacetonate), acetylacetone, and ethanol (0.6:0.4:9 v/v) and then sprayed onto FTO substrates at 450 °C. Mesoporous TiO₂ (m-TiO₂) paste was prepared with titanium paste and ethanol (1:6 w/w), and then spin-coated onto c-TiO₂ substrates at 5000 rpm for 20 s before annealing at 450 °C for 30 min. After that, the as-prepared FTO/c-TiO₂/m-TiO₂ substrates were quickly transferred to a N₂-filled glove box for perovskite and spiro-OMeTAD deposition. The triple-cation halide perovskite Cs_{0.05}MA_{0.15}FA_{0.80}Pb_{1.05}(Br_{0.15}I_{0.85})₃ was prepared as follows: briefly, a 1.5 M stock solution of (1) CsI (DMSO), (2) PbBr₂ (DMSO:DMF = 1:4), and (3) PbI₂ (DMSO:DMF = 1:4) were first prepared. Then, 1.5 M (4) (MABr)(PbBr₂) (DMSO:DMF = 1:4) and (5) (FAI)(PbI₂) (DMSO:DMF=1:4) were freshly prepared by dissolving MABr or FAI power in solutions (2) and (3), respectively. After that, the solutions were mixed at a ratio of (4):(5):(1):(3) = 150:800:50:100 (v/v) in sequence. The perovskite spin-coating process was carried out at 2000 rpm for 10 s, and then 6000 rpm for 30 s. Initially, 50 µL of perovskite solution was dropped on a 1.5 × 2.5 cm² FTO/c-TiO₂/m-TiO₂ substrate. During the second step of spin coating, 100 µL of chlorobenzene was dropped for 15 s before ending. The samples were annealed at 100 °C for 1 h on a hot plate for crystallization.

The hole transporting layer was prepared by dissolving 0.12 g of spiro-OMeTAD in 1130 μL of chlorobenzene and then doping with 47.3 μL of TBP and 23.5 μL of Li-TFSI (1.8 M in acetonitrile). The spin coating was conducted at 4000 rpm for 20 s with 50 μL solution. The finished devices were placed inside a dry air box for 12 h to fully oxidize the spiro-OMeTAD. Finally, 80 nm Au was deposited as the front electrode via thermal evaporation. The evaporation rate was controlled in different stages to limit the damage to the spiro-OMeTAD layer.

Characterization. Electrical measurements were carried out using an AutoLab potentiostat/galvanostat model PGSTAT204 (Eco-Chemie), equipped with the FRA32M impedance module. The instrument was controlled by a computer and driven by the NOVA software. Dark current–voltage curves were obtained by performing a cyclic voltammetry test, in order to check hysteresis behavior, with a 10 mV step at different scan rates (ranging from 1 down to 0.005 V/s) from -0.25 V to 1 V. On the other hand, illuminated current–voltage characteristics were measured from -0.2 to 1.2 V, under AM1.5 100 mW/cm^2 simulated sunlight (Newport VeraSol-2 light-emitting diode, LED, class AAA) previously calibrated with an NIST-certified KG3 filtered Si reference cell. The obtained solar cell parameters, using a 0.16 cm^2 mask, were $V_{\text{OC}} = 1.09$ V, $J_{\text{SC}} = 23.14$ mA/cm^2 , $\text{FF} = 72.53\%$, and $\text{PCE} = 18.29\%$, assessed under a slow voltage sweep velocity (25 mV/s). Impedance measurements were carried out immediately after current–voltage experiments, by configuring the AutoLab to apply sinusoidal signals of 10 mV amplitude from 1 MHz to 1 Hz at different bias voltages. Fitting of all of the impedance spectra was performed using Scribner's ZView software. The reproducibility of experimental data was checked and assured by conducting current–voltage measurements and impedance spectroscopy in 12 cells. Figures in the manuscript show illustrative examples of the obtained results and respective simulated data.