Supporting Information

Improved Morphology Control using Modified Two-Step Method for Efficient Perovskite Solar Cells

Dongqin Bi,[a] Ahmed M. El-Zohry,[a] Anders Hagfeldt,[a,b] Gerrit Boschloo [a] *

Characterization Methods:

Scanning electron microscope measurements SEM-images were recorded by Zeiss LEO1550. The acceleration voltage (EHT) was 10 kV and the working distance (WD) ranged as required.

X-ray diffraction measurements For XRD measurements, $CH_3NH_3PbI_3$ samples were deposited onto the TiO_2-ITO (tin-doped indium oxide) substrate. The samples were measured using Siemens D5000 equipped with Kristallo-Flex 710D X-ray generator, and CuKα1 (0.1540562 nm long, fine focus sealed tube source with Gobel mirror). A step size of 0.01 degree was chosen and a baseline correction was applied to all X-ray patterns.

Current-voltage (J-V) characteristics were measured using a Keithley 2400 source/meter and a Newport solar simulator (model 91160) giving light with AM 1.5 G spectral distribution, which was calibrated using a certified reference solar cell (Fraunhofer ISE) to an intensity 1000 W/m^2. A black mask of 0.127 cm^2 was applied on top of the cell to avoid additional contribution from light falling on the device outside the active area. The J-V scan was made from V_{oc} to short J_{sc} with a time delay at V_{oc} of 20 s and a scan rate of 50mV/s. No significant hysteresis effect was observed in J-V scans.

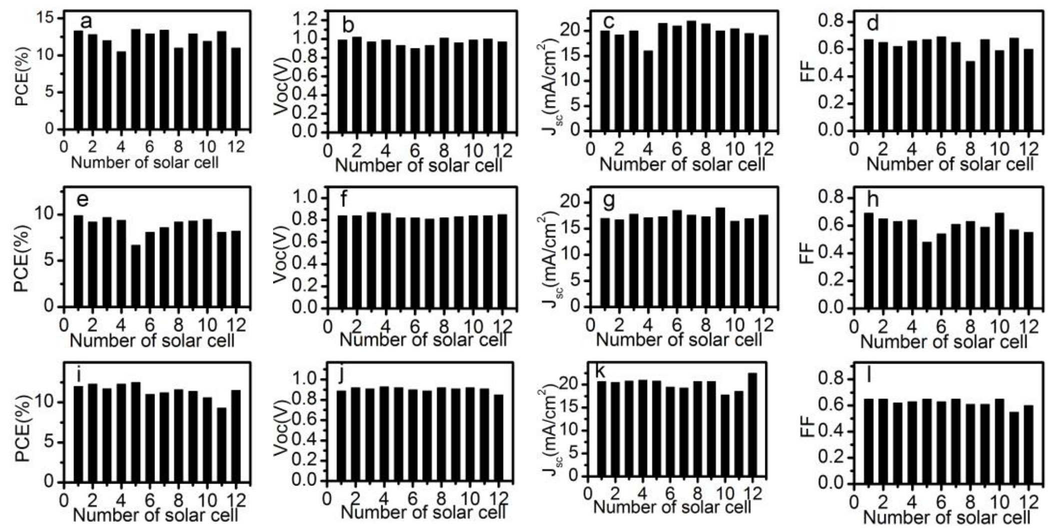
Incident photon to current conversion efficiency (IPCE) spectra were recorded using a computer-controlled setup consisting of a xenon light source (Spectral Products ASBXE-175), a monochromator (Spectral Products CM110), and a Keithley 2700 multimeter, calibrated using a certified reference solar cell (Fraunhofer ISE).

Electron lifetime and transport times were performed using a white LED (Luxeon Star 1W) as the light source. Voltage and current traces were recorded with a 16-bit resolution digital acquisition board (National Instruments) in combination with a current amplifier (Stanford Research Systems SR570) and a custom-made system using electromagnetic switches. Transport time and lifetimes were determined by monitoring photocurrent and photovoltage transients at different light intensities upon applying a small square wave modulation to the base light intensity. The electron lifetime measured with transient photovoltage was calculated using the following equation: $V_{oc}=V_{oc,0}+ \Delta V \exp(-t/\tau)$, where ΔV is the change in open-circuit voltage (V_{oc}) due to the modulated small change in light intensity, $V_{oc,0}$ is the open-circuit voltage before the change in light intensity, and τ is the electron lifetime. The photocurrent and photovoltaic responses were fitted using first-order kinetics to obtain time constants.

Time Correlated Single Photon Counting (TCSPC) The emission decay of the perovskite samples have been examined by Time Correlated Single Photon Counting (TCSPC). An excitation laser source of 404 nm with 15 pJ/pulse at maximum has been used (picosecond diode laser Edinburgh Instruments, EPL405). An attenuator filter was used before the sample to obtain reasonable emission intensity that match with the principle of detecting only one photon per pulse at maximum.[1] A yellow filter (GG475) was put after sample to prohibit the arrival of the excitation laser pulses to the detection system. Two time ranges, 50 ns (IRF ≈ 77.1 ps) and 5μs (IRF ≈ 200 ps), were used depending on the observed kinetics from the samples. More detailed information about the instrument, and the fitting procedures have been reported before.[2]

[1] D. V. O'Connor, Phillips, D. Time-correlated Single Photon Counting, Academic Press ***1984.***

[2] A. El-Zohry, A. Orthaber, B. Zietz, Isomerization and Aggregation of the Solar Cell Dye D149 *J Phys Chem C* **2012**, 116, 26144-26153.



S1 Photovoltaic parameters of FTO/TiO_2/$CH_3NH_3PbI_3$/spiro-OMeTAD/Ag solar cells(a,b,c,d: DCM, e,f,g,h: ND, i,j,k,l: HT). There are 12 solar cells in each series, identified by numbers 1 to 12.

S2 Fitting lifetimes for the emission decays of perovskite samples. Lifetimes are in ns with amplitudes in percent.

Sample No.	ND				HT				DCM			
	τ_1	τ_2	τ_3	τ_4	τ_1	τ_2	τ_3	τ_4	τ_1	τ_2	τ_3	τ_4
On Glass	0.2 (77)	1.5 (14)	15.3 (4)	175 (5)	0.16 (74)	1.5 (17)	15.5 (5)	172 (5)	0.67 (65)	4.7 (21)	27 (14)	
On ZrO2	0.16 (64)	0.91 (31)	5.15 (5)		0.15 (64)	0.98 (29)	8.05 (4)	144 (3)	0.24 (65)	1.8 (24)	10.3 (8)	141 (3)
On TiO2	0.13 (80)	1.06 (17)	6.0 (3)		0.17 (74)	1.3 (22)	6.2 (4)		0.089 (82)	0.7 (15)	5.8 (3)	
On ZrO2/Spiro	0.083 (68)	0.44 (24)	2.3 (8)		0.06 (57)	0.25 (33)	1.0 (10)		0.044 (61)	0.22 (31)	1.1 (8)	
On TiO2/Spiro	0.06 (73)	0.41 (20)	2.84 (7)		0.093 (72)	0.45 (23)	2.84 (5)		0.06 (82)	0.38 (13)	1.8 (2)	