Electronic Supplementary Material (ESI) for Energy & Environmental Science.

SUPPORTING INFORMATION

Identifying and suppressing interfacial recombination to achieve high open-circuit voltage in perovskite solar cells

Juan-Pablo Correa-Baena,*[1] Wolfgang Tress,*[2] Konrad Domanski,[2] Elham Halvani Anaraki[1,5], Silver-Hamill Turren-Cruz,[1,6] Bart Roose,[3] Pablo P. Boix,[4] Michael Grätzel,[2] Michael Saliba,[2] Antonio Abate,[3] and Anders Hagfeldt[1]

[1]Laboratory of Photomolecular Science, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015-Lausanne, Switzerland.

[2]Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015-Lausanne, Switzerland.

[3]Adolphe Merkle Institute, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland

[4]Energy Research Institute at Nanyang Technological University (ERI@N), 50 Nanyang Drive Singapore 637553, Singapore

[5] Department of Materials Engineering, Isfahan university of Technology, Isfahan, 84156-83111, Iran.

[6]Benemérita Universidad Autónoma de Puebla, Puebla, 7200, México

*Corresponding author: JPCB juan.correa@epfl.ch; WT wolfgang.tress@epfl.ch

Keywords: Perovskite solar cell, photovoltaics, recombination, high open-circuit voltage, doping.

Experimental

Electron selective layer preparation

F:SnO_2 substrates were first wiped with acetone, and then cleaned for 10 min in piranha solution (H_2SO_4/H_2O_2 = 3:1) followed by 10 min in a plasma cleaner prior to ALD deposition.

SnO_2 was deposited at 118 °C using Tetrakis(dimethylamino)tin(IV) (TDMASn, 99.99%-Sn, Strem Chemicals INC) and ozone at a constant growth rate of 0.065 nm/cycle measured by ellipsometry. TDMASn was held at 65 °C. Ozone was produced by an ozone generator ((AC-2025, IN USA Incorporated) fed with oxygen gas (99.9995% pure, Carbagas) producing a concentration of 13% ozone in O_2. Nitrogen was used as a carrier gas (99.9999% pure, Carbagas) with a flow rate of 10 sccm.

Perovskite precursor solution and film preparation

Mixed-cation lead mixed-halide perovskite solution was prepared from a precursor solution made of FAI (1 M, Dyesol), PbI_2 (1.1 M, TCl), MABr (0.2 M, Dyesol) and $PbBr_2$ (0.22 M, TCl) in a 4:1 (v:v) mixture of anhydrous DMF:DMSO (Acros). A 1.5 M stock solution of CsI (abcr GmbH) in DMSO was added to above solution in 5:95 volume ratio. The triple cation perovskite solution was deposited through a two-step spin coating program (10 s at 1000 rpm and 20 sec at 6000 rpm) with dripping of chlorobenzene as anti-solvent[1, 2] during the second step, 5 s before the end. All the perovskite layers were annealed at 100°C for 45 min.

The spiro-OMeTAD (Merck) solution (70 mM in chlorobenzene) was spun at 4000 rpm for 20 s. The spiro-OMeTAD was doped at a molar ratio of 0.5, 0.03 and 3.3 with bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Sigma Aldrich), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)- cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (FK209, Dyenamo) and 4-tert-Butylpyridine (TBP, Sigma Aldrich), respectively.[3-5] For one experiment the Li concentration was varied from 0 to 1 molar ratio (0 to 100%). As a last step 70-80 nm of gold top electrode were thermally evaporated under high vacuum.

Solar cell characterization

A ZEISS Merlin HR-SEM was used to characterize the morphology of the device cross-section. The solar cells were measured using a 450 W xenon light source (Oriel). The spectral mismatch between AM 1.5G and the simulated illumination was reduced by the use of a Schott K113 Tempax filter (Präzisions Glas & Optik GmbH). The light intensity was calibrated with a Si photodiode equipped with an IR-cutoff filter (KG3, Schott) and it was recorded during each measurement. Current-voltage characteristics of the cells were obtained by applying an external voltage bias while measuring the current response with a digital source meter (Keithley 2400). The voltage scan rate was 10 mV s^{-1} and no device preconditioning was applied before starting the measurement, such as light soaking or forward voltage bias applied for long time. The starting voltage was determined as the potential at which the cells furnished 1 mA in forward bias, no equilibration time was used. The cells were masked with a black metal mask limiting the active area to 0.16 cm^2 and reducing the influence of the scattered light. It is important to note that the devices achieved the highest hysteresis-free efficiency after 1 week of preparation.

Light-intensity dependent and transient V_{oc} experiments

The illumination was provided by white, blue, or red LEDs, respectively. Intensities were adjusted to be equivalent to 1 sun. An aperture was not used in order to measure the real

V_{oc}. The electronic response of the device was measured by a Biologic potentiostat MPG 2. Using a silicon reference diode, it was verified that the PSC photocurrent at short circuit is linear in light intensity in the investigated range. Therefore, for best comparability, intensity dependent V_{oc} for illumination with different color is plotted vs the short circuit current. For experiments under N_2, a custom-made sample holder was flushed with N_2 during the measurements. Using Peltier cooling, the temperature was maintained at 20°C for the V_{oc} tracking experiments.

Electroluminescence

The EL spectra were recorded with an Ocean Optics CCD spectrometer (USB4000) during applying a constant current of approx. 1 mA with a Biologic Potentiostat SP300. The absolute EL was measured placing a large-area silicon photodiode (Hamamatsu) close to the sample and detecting its photocurrent while performing a voltage sweep on the PSC with a scan rate of 100 mV/s.

Intensity modulated photocurrent spectroscopy was performed using Autolab PGSTAT302N according to procedures previously reported.[6]

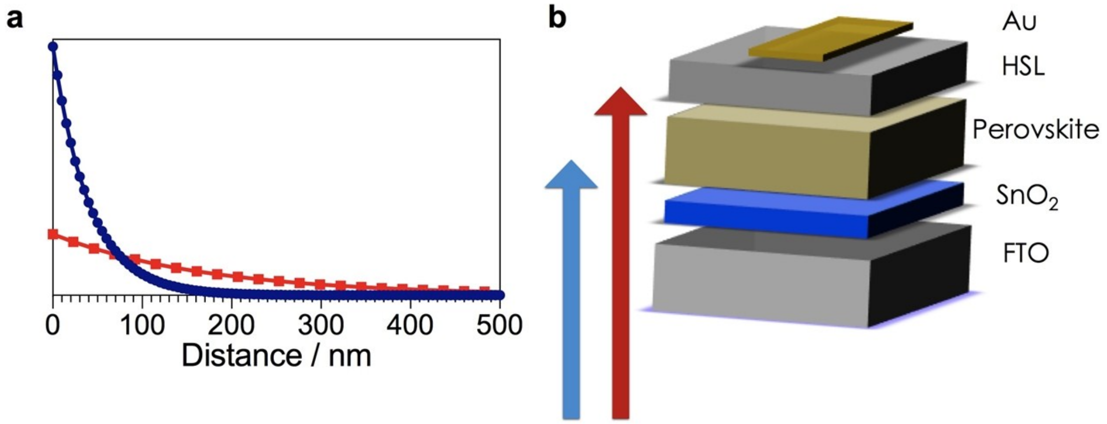

Figure S1. Estimated light absorption of the perovskite film for different light wavelengths. a. An estimatate of the light absorption by the perovskite film for LED of 460 (blue) and 630 nm (red) wavelengths, as a function of distance of the incoming light. The estimation is based on calculations using measured absorption coefficients and the Beer-Lambert law. **b.** A schematic showing a device stack being illuminated by blue and red light from the glass/SnO2 side. Using a blue light, almost all light is absorbed within the first 150 nm.

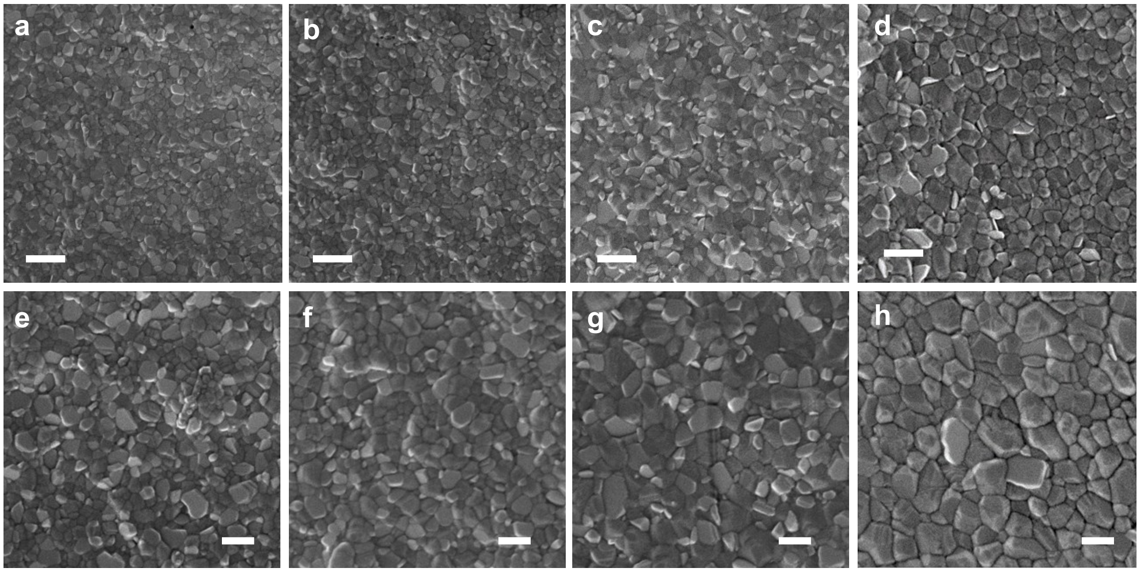

Figure S2. Modification of grain boundary density. a-d scale bar 400 nm. **e-h** scale bar 200 nm.

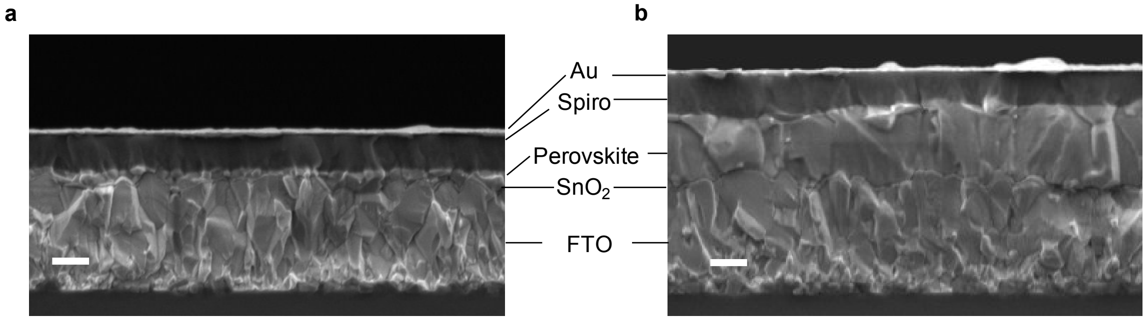

Figure S3. Cross-sectional SEM Imaging. a. Device with smallest grains and thinnest perovskite layer. **b.** Device with largest grains and thickest perovskite layer. Scale bars are 200 nm.

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