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1cm^2 $CH_3NH_3PbI_3$ mesoporous solar cells with 17.8% steady-state efficiency by tailoring front FTO electrodes

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Experimental Section

Deposition of FTO Thin Films

1.1 mm borosilicate glass substrates (Corning Eagle 2000) were cleaned with detergent, water, propan-2-ol, and dried in air prior to coatings. Films were deposited by atmospheric-pressure chemical vapor deposition at 600 °C using monobutyltin trichloride (MBTC) and aqueous trifluoroacetic acid (TFAA) delivered with a Sn precursor to H_2O molar ratio of 1:5. Precursors were vaporized using MBTC at 125 °C (0.6 L min^{-1} carrier gas) or flash evaporation (TFAA/water mix, 0.7 L min^{-1} carrier gas). N_2 was used as the carrier gas, with 15% oxygen at a total flow of 1.5 L min^{-1}. A single flow coating head was employed to simulate a production-type process configuration. A heated susceptor was translated under the static CVD head in an extracted, open atmosphere, enclosure. This allowed the deposition of films over 10 × 10 cm (± 2%) area with good uniformity. To deposit films of similar sheet resistance, the number of passes (8, 10 or 12) and TFAA concentration (0.3, 0.8, 1M) were adjusted under the CVD coating head. For the deposition of films with different thicknesses, TFAA concentration (0.6, 0.8 and 1M) and number of passes (4 or 6) were used.

Fabrication of Solar Cells

Blocking layers of TiO_{2-x} with 20 nm thickness have been deposited by RF sputtering (Oerlikon Systems Cluster Line cluster tool) at 60 °C in an Ar/oxygen atmosphere ($pO_2 = 7.5 \times 10^{-6}$ mbar). The mesoporous TiO_2 (m-TiO_2) layer was deposited on the TiO_{2-x} blocking layers/ FTO coated substrates by spin coating TiO_2 paste (Dyesol 18NRT) diluted in isopropanol (1 g in 5 g) at 4500 rpm for 30 s and annealed at 500 °C for 30 min. 461 mg of PbI_2, 159 mg of CH_3NH_3I, and 78 mg of DMSO (molar ratio 1:1:1) were mixed in 600 mg of dimethylformamide (DMF) solution at room temperature with stirring for 1 h in order to prepare the $CH_3NH_3PbI_3$ precursor solution. The precursor solution was spin coated on m-TiO_2 substrate in a two-stage sequence (1000 rpm for 10 s followed by 5000 rpm for 45 s) and 0.75 ml of diethyl ether was dripped on the substrate 12 s before the end of the procedure. The substrate was then heated at 50 °C for 2 min and 100 °C for 10 min. Spiro-OMeTAD solution was prepared by dissolving 72.3 mg spiro-OMeTAD (Merck), 28.8 μl 4-*tert*-butylpyridine (Sigma-Aldrich), 17.5 μl of a stock solution of 520 mg ml^{-1} lithium *bis*(trifluoromethylsulfonyl)imide (Sigma-Aldrich) in 1 ml chlorobenzene and spin coated on top of perovskite layer at 4000 rpm for 30 s. The cells were then finished with the evaporation of a 100nm thick gold electrode.

Characterisation of Thin Films

Transmission and reflection were measured using an Aquila nkd 8000 spectrophotometer between 400 and 1100 nm at an incident angle of 30° using s polarisation. The average film thickness was determined using a Dektak 3ST surface profiler by measuring at least five different points across the sample. The samples were step etched using zinc powder and hydrochloric acid prior to thickness measurements. Hall measurements to determine the carrier concentration and the electron mobility were carried out on a lab built system using an electromagnetic with a pole separation of 10 mm and current of 1 A to give a magnetic flux density of 0.66 T. A lab built spectrometer consisting of a 75 W xenon lamp and broadband filters centring on three wavelengths (650, 531, and 450 nm) was used to measure optical scattering i.e. haze. A silica sample was used to calibrate the throughput of the integrating sphere. The haze is determined using Equation 1.

$$\boxed{H_f(I_t) = \frac{[(H_f - z_o)\frac{T_t}{T_h} - T_r(Z_h - z_o)\frac{T_t}{T_z}]}{(I_t - z_o)}.}$$

where H_f is the forward haze, I_t is the transmitted intensity, Z_o is the is the zero reading when no light is present, Z_h is the residual light. T_o, T_h, T_t and T_z are the integrating sphere ‘through-puts’ (the ratio of light falling on the detector to the light entering the integrating sphere). T_r – represents one open port; T_h – one open port and one port with the sample over it and T_t one port with the sample over it and T_z – two open ports.

The morphology and surface roughness of the samples was obtained by atomic force microscopy (NanoScope IIIa, Digital Inst. Ltd). X-ray diffraction measurements were recorded on a Bruker D8 using a Cu Kα source. Crystallite size was calculated by Scherrer Equation (2) and texture coefficients using Equation (3). Scanning electron microscope (SEM) images were recorded on a Quanta 250 ESEM. Samples were carbon coated before SEM analysis.

$$D = \frac{0.94\lambda}{\beta cos\theta} \tag{2}$$

where D is the size of the crystallites, β is the broadening of diffraction line measured at half its maximum intensity and λ is the wavelength of X-rays (1.54056 Å).

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{\frac{1}{n}\sum I(hkl)/I_0(hkl)} \tag{3}$$

where I (hkl) and I_o (hkl) are the measured intensity and standard integrated intensity (from JCPDS No. 021-1250) for (hkl) reflection, respectively, and n is the number of reflections observed.

Cell Characterization

All cells were characterized under a two-lamp class AAA WACOM sun simulator with an AM1.5g irradiance spectrum at 1000 W/m^2. The cell area was defined using a metal mask. The I-V characteristics of the cells were obtained under both reverse (from V_{OC} to J_{SC}) and forward (from J_{SC} to V_{OC}) bias. A Maximum Power Point (MPP) tracking was usually performed to extract the steady state power output. External Quantum Efficiency (EQE) spectra were acquired on a custom-made spectral response setup equipped with a xenon lamp, a grating monochromator and lock-in amplifiers.

Table S1. Grain sizes and texture coefficients (TC) of selected films

Sample No	Crystal Size (nm)	TC (110)	TC (200)	TC (211)
S1	36	0.11	3.72	0.17
S7	37	0.14	3.56	0.30
TEC22-15	26	0.29	3.39	0.32

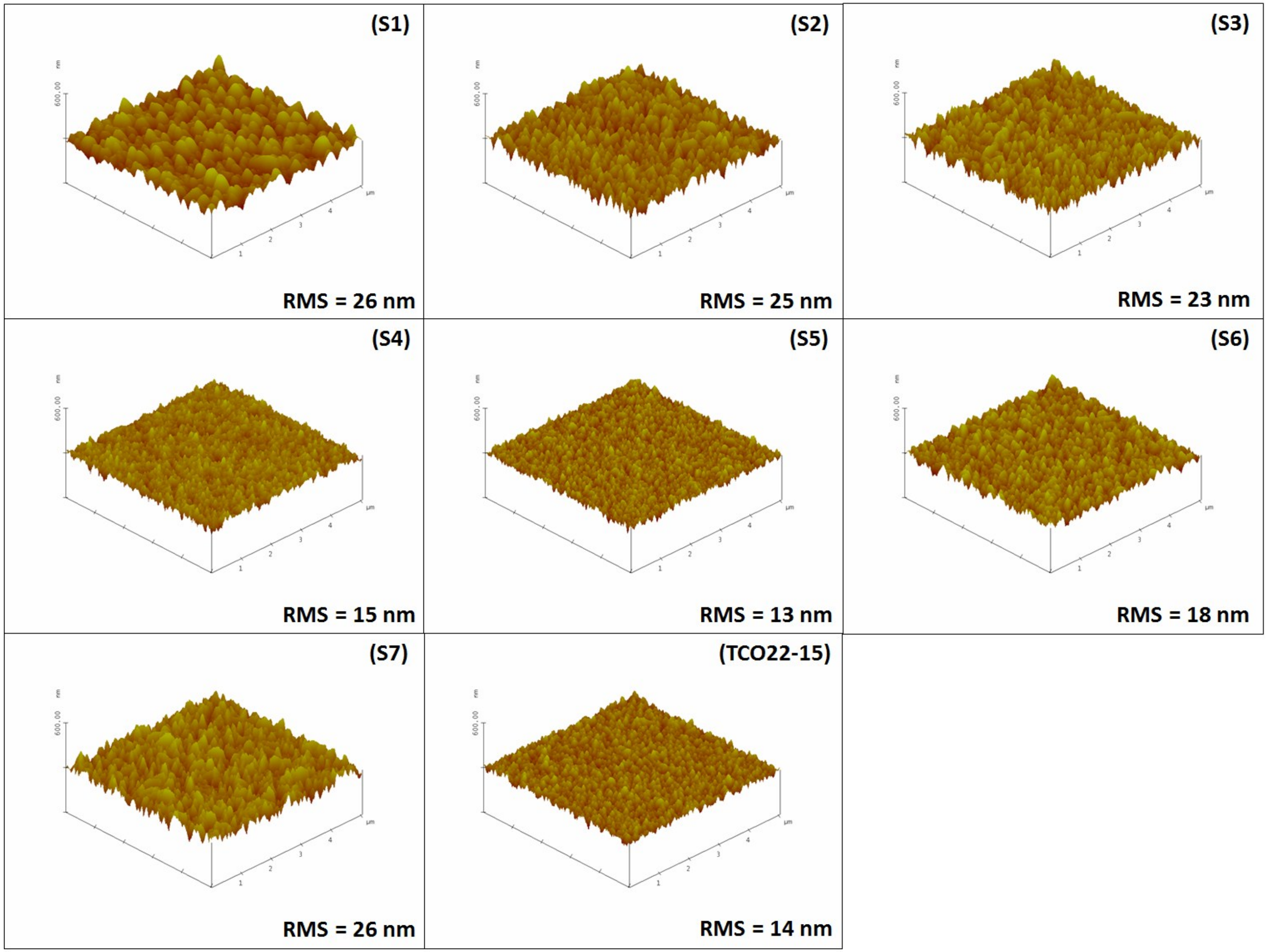

Fig. S1 AFM images of FTOs.

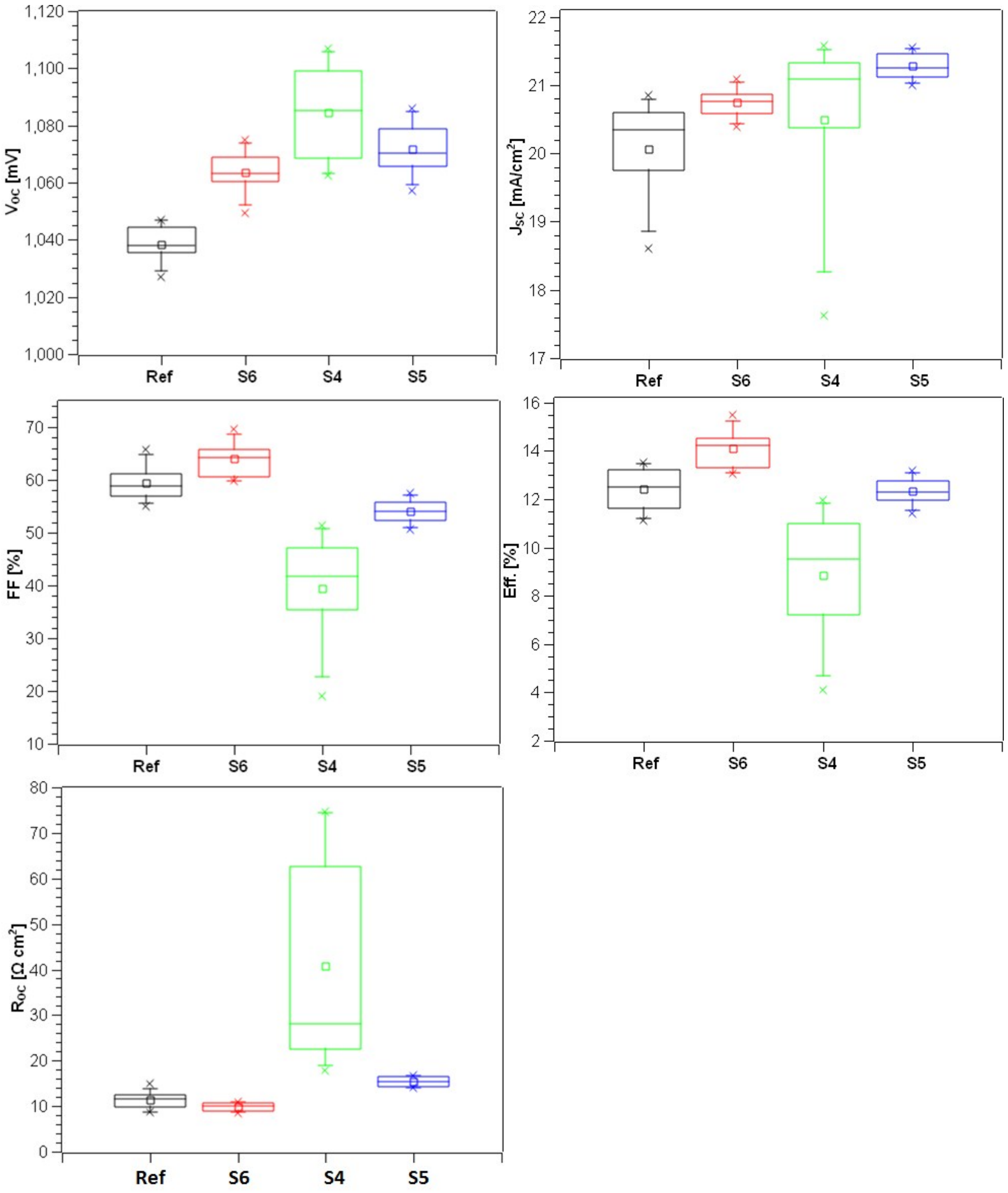

Fig. S2 Statistical analysis of the photovoltaic parameters of the solar cells processed with commercial and batch 2 FTOs.

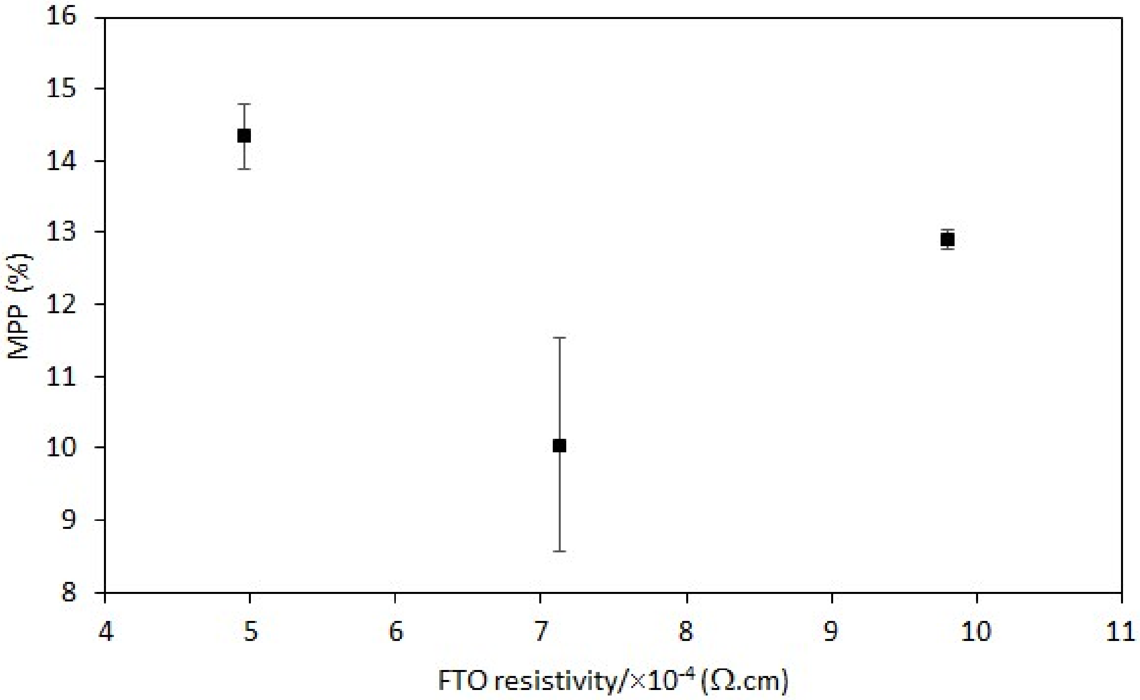

Fig. S3 Maximum power point tracking (MPPT) values as a function of FTO resistivities for Batch 2.

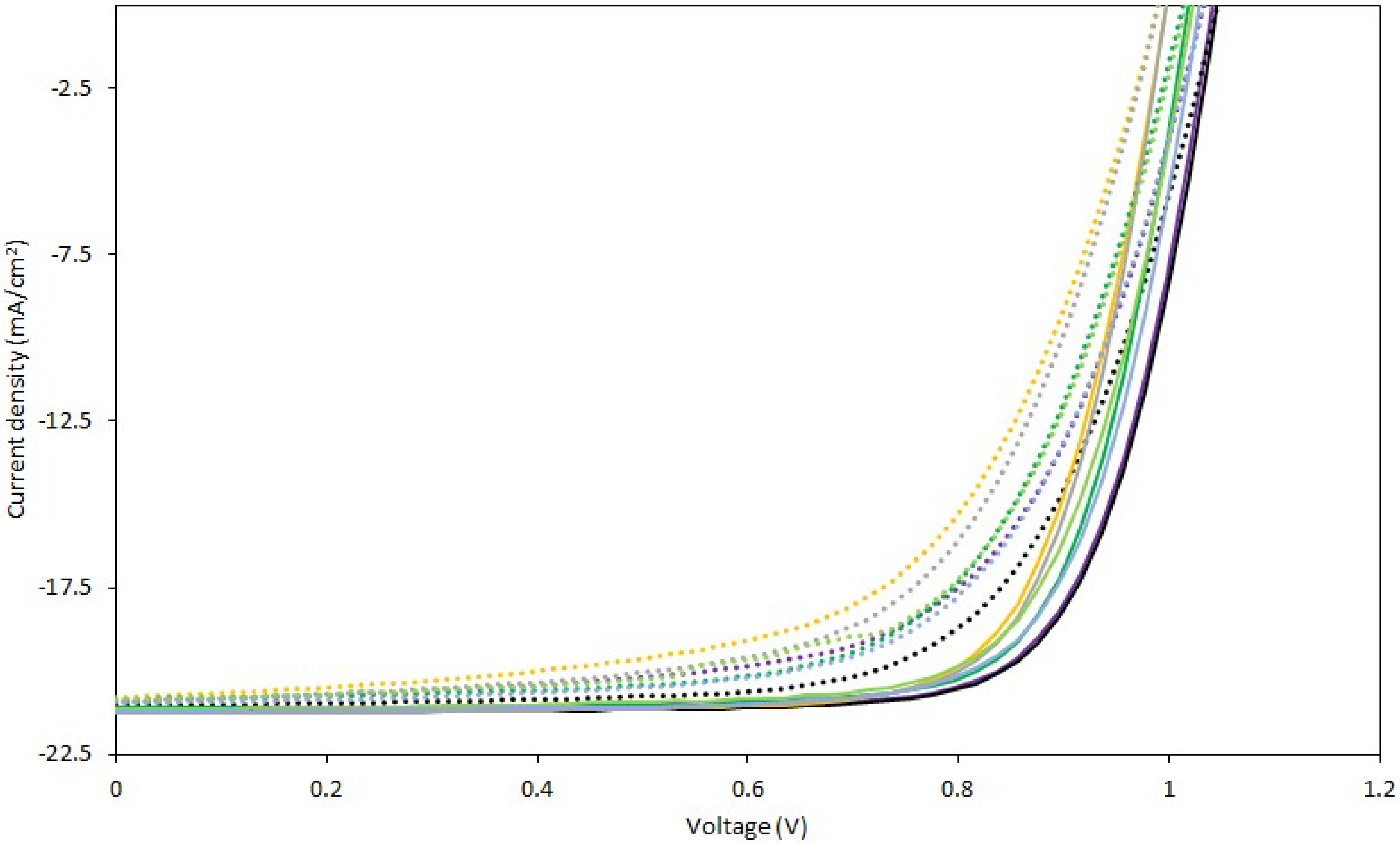

Fig. S4 Photocurrent-voltage curves under forward (dotted) and reverse (solid) scan direction for batch 3 FTOs measured at a simulated AM1.5 sun illumination.