### **Electronic Supplementary Information**

# Nanoarchitectonics in fully printed perovskite solar cells with carbon-based electrodes

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# **Experimental Methods**

## **1. Sample preparation**

### 1.1. Polystyrene (PS) nanoparticle suspension for spin-coating thin film

The colloidal suspension for spin-coating PS nanoparticles was prepared by combining the dispersion of PS nanoparticles (200 nm) with a diluted surfactant solution in a 2:3 volumetric ratio. The latter consisted of methanol and surfactant Triton X-100 with a volume ratio of 400:1. After all the components of the spin-coating PS suspension were added together in a vial, it was vigorously shaken for 1 minute and then sonicated for 10 mins. To produce a homogeneous layer of PS nanoparticles, a volume of  $100\mu$ L of the synthesized suspension was spin-coated on  $2.5 \times 2.5 \text{ cm}^2$  FTO substrates. The spinning procedure roughly resembled an approach reported by Hörantner et al.<sup>1</sup> The spin-coating was carried out in 3 step processes, (i) 600 rpm for 10 seconds (ii) 1000 rpm for 60 seconds (iii) 2000 rpm for 60 seconds. With this ink optimization step, a well-ordered arrangement of PS-nanoparticles was obtained (Figure S1a).

#### 1.2. Polystyrene (PS) nanoparticle suspension for inkjet-printing thin film

The low boiling point of methanol causes fast solvent evaporation from the PS suspension (one that was optimized for spin-coating), leading to particle coagulation and clogging in the inkjet nozzles (since their diameter is in µm-range). Moreover, the concentration of PS nanoparticles had to be also lower to reduce the rapid clogging of the nozzles. In addition, methanol was replaced with a 1:1 mixture of isopropanol and 1-pentanol, and combined with Triton X-100 in the same ratio as in the diluted surfactant solution needed for the spin-coating PS-suspension. Next, the pristine PS suspension was added in a 1:10 ratio. After that, formamide was added to this solution in a 1:5.6 volumetric ratio to limit the ink droplet diameter and to increase the evaporation rate, which was found particularly useful for inkjet-printing silica and PS nanoparticles by Sowade et al.<sup>2</sup> The resulting ink was sonicated for 10 minutes and deposited by an inkjet printer using a Dimatix printing head with 16 nozzles. The layers were deposited using 800x800 droplets per inch with 10 pL volume each. With this ink optimization step, a well-ordered arrangement of PS nanoparticles was obtained (Figure S1b).

#### 1.3. Fabrication of ZrO<sub>2</sub> on FTO and Glass substrates

 $ZrO_2$  layer was screen-printed using Zr Nanoxide ZT/SP paste from Solaronix SA with a 90–48 mesh stencil on a glass-substrate. After dwelling for 10 min at room temperature, the samples were dried at 120°C for 10 min more, and then transferred to a hotplate for firing at 500°C for 30 min with a 30 min ramp time.

The methylammonium lead iodide perovskite precursor solution containing 5-ammonium valeric acid additive (5-AVAI) was provided by Solaronix SA. This solution was deposited selectively on the area of interest by inkjet with a 10 pL droplet volume and a spatial resolution of 650 x 650 dpi. The freshly printed samples were subsequently annealed for 10 min on a hot plate set to 50°C, thus forming the perovskite crystals in the porous electrode structure.

### 1.4. Fabrication of perovskite solar cells with carbon-based electrodes

Perovskite solar cells with carbon-based electrodes were fabricated on 10x10 cm<sup>2</sup> plates of FTO-coated glass (TCO22-7/LI, sheet resistance – 7  $\Omega$ /sq.). First, a laser pattern defined cathode and anode areas with an automated fiber laser. After that, the substrate was subjected to sequential cleaning steps in 1% aqueous solution of Hellmanex (Sigma-Aldrich), acetone (Carl-Roth), and isopropanol (Sigma-Aldrich) respectively (20 min each) in an ultrasonic bath and subsequently dried in air. The thin compact titania layer (c-TiO<sub>2</sub>) was grown by spraypyrolysis on a hot plate set to 450°C, using a glass mask to protect the contact areas. A volume of 20 mL of titanium diisopropoxide bis (acetylacetonate) (Sigma-Aldrich) diluted in absolute ethanol (Alcosuisse) (1:160) was sprayed with oxygen as a carrier gas, and warming was prolonged for 30 min before allowing the sample to cool down. An array of 18 electrodes was subsequently defined by screen-printing silver contacts (silver paste Elcosil SG/SP), m-TiO<sub>2</sub> (titania paste Ti Nanoxide T165/SP), ZrO<sub>2</sub> (zirconia paste Zr Nanoxide ZT/SP) and carbon layers (carbon-graphite paste Elcocarb B/SP) using a 100-40, 165-30, 90-48, and 43-80 mesh stencil, respectively (the number of strands is per cm). All the pastes mentioned above come from Solaronix SA. After printing the wet film, each screen-printed layer was allowed to dwell for 10 min before drying at 120°C for 10 min, followed by a firing step at 500°C (or 400°C for carbon) for 30 min, after a 30 min ramp.

The same perovskite solution was deposited selectively on the area of interest by inkjet similarly to the manufacturing procedure of filling perovskite in  $ZrO_2$  layer, mentioned above. The only

difference was the optimal resolution, which was determined to be 1200 x 1200 dpi. The freshly printed samples were subsequently annealed for 10 min on a hot plate set to 50°C, thus forming the perovskite crystals in the porous electrode structure. The resulting devices were submitted to heat and damp treatment at 40°C and 75%r.h. for 150 h. according to the previously reported method by Hashmi et al.<sup>3</sup>

## 2. Characterization techniques

Scanning Electron Microscopy (SEM) images of the PS layers were obtained with a Zeiss EVO 10 electron microscope, but for a 3D-nanotomography, Zeiss Auriga 60 equipped with an inlens secondary electron detector and FIB-gun (with Ga<sup>+</sup> ion source) was utilized. TRPL measurements were conducted using externally triggered CW laser (Coherent Orbis) of 660nm wavelength with 10 mW power on a spot-sized widened to ca. 1 cm<sup>2</sup>, with a fall and rise time (10% and 90 %) below 2 ns. The laser was triggered to produce rectangular-shaped signals at 7 Hz frequency. The PL images were obtained by OLYMPUS BX50 stereomicroscope and sCMOS camera ("Zyla 5.5 sCMOS" by Andor) with a long-pass filter while the partial illumination of the sample at an intensity equivalent to approximately 1 sun was provided by a 623 nm LED (Thorlabs, SOLIS-623C). The current-density and voltage curves of fabricated devices were measured with a source meter (Keithley 2400) at a scan rate of 40 mV/s using a class A solar simulator providing 100 mW/cm<sup>2</sup>, AM1.5G illumination. The light intensity-dependent measurements of  $^{Jsc}$  and  $^{Voc}$  were obtained from  $^{JV}$ -measurements performed under incident irradiation, varied by polymeric optical density filters to reduce light intensity incident on the cell.

## 3. Simulation

Simulation was carried out using SCAPS software and all the simulation parameters and further details are described in more details in our previous work.<sup>4</sup> SCAPS is an open-source 1D driftdiffusion simulation tool, that can be obtained from https://users.elis.ugent.be/ELISgroups/solar/projects/scaps upon the request from the developers Marc Burgelman et al.



Spin-coated

Inkjet-printed

Figure S1: Top-View SEM images of (a) spin-coated and (b) inkjet-printed polystyrene (PS) nanoparticles. Cross-section SEM images of (c) spin-coated and (d) inkjet-printed layer of PS nanoparticles. Scale bar – 500 nm.



Figure S2: Incident photon-to-electron conversion efficiency (IPCE) measurement of a reference and a nanoarchitectured CPSCs along with the  $J_{SC}$  obtained from the integration of product of IPCE and incident (AM 1.5G) light spectrum.



Figure S3: Nyquist plots obtained from the electrochemical impedance spectroscopy (EIS) measurements of reference and nano-architectured cells under a bias of 0.6V and under (a) no illumination, as well as (b) under illumination. Both measurements were fitted (blue and grey lines for nanoarchitectured and reference cells, respectively) to the equivalent circuits shown below each graph. The inset in (b) demonstrates the ohmic series resistance  $R_S$  of a reference and nanoarchitectured cells, which are very similar in value. However, the resistance of the charge-transfer ( $R_{CT}$ ) process is reduced in the nanoarchitectured cell. The resistance of the low-frequency semicircle ( $R_{LF}$ ) is slightly reduced as well.

### **Supplementary Note 1**

Since photoluminescence quantum yield (PLQY) is defined as:

$$PLQY = \frac{J_{rad}}{J_{rad} + J_{nrad}} = \frac{J_{rad}}{J_{tot}}$$
(1)

at the open-circuit condition (when no charge carriers are extracted), it can also be described by the photocurrent density  $J_{ph}$ , which is equivalent to the total recombination current density  $J_{tot}$ , since all the charge carriers recombine radiatively or non-radiatively:

$$J_{rad} = J_{ph} PLQY \tag{2}$$

From the Shockley-Queisser expression<sup>5</sup> for radiative recombination current density  $J_{rad}$  we know that it depends on the radiative current density under thermal equilibrium in the dark ( $J_{0,rad}$ ) and quasi-Fermi level splitting  $\Delta E_F$  via:

$$J_{rad} = J_{0,rad} \exp\left(\frac{\Delta E_F}{k_B T}\right)$$
(3)

meaning that using Equation (2)  $\Delta E_F$  can be written as:

$$\Delta E_F = k_B T \ln\left(\frac{J_{rad}}{J_{0,rad}}\right) = k_B T \ln\left(\frac{J_{ph}}{J_{0,rad}} P L Q Y\right)$$
(4)

When all the recombination processes are radiative, according to Equation (1) PLQY=1, meaning:

$$J_{rad} = J_{tot} = J_{ph} \tag{5}$$

and we can express QFLS at the radiative limit as:

$$\Delta E_F^{rad} = k_B T \ln \left( \frac{J_{ph}}{J_{0,rad}} \right) \tag{6}$$

Combining Equations 4 and 6 we can describe the QFLS of the sample using  $\Delta E_{F}^{rad}$  (which is constant for specific material) and measured PLQY:

$$\Delta E_F = k_B T \left( \ln \left( \frac{J_{ph}}{J_{0,rad}} \right) + \ln PLQY \right) = \Delta E_F^{rad} + k_B T \ln \left( PLQY \right)$$
(7)

And in case of a solar cell, its implied open-circuit voltage can be described as:

$$V_{OC} = \frac{\Delta E_F}{q} = V_{OC}^{rad} + \frac{k_B T}{q} \ln \left( PLQY \right) = V_{OC}^{rad} + \frac{k_B T}{q} \ln \left( \frac{j_{rad}}{j_{tot}} \right)$$
(8)

where  $V_{OC}$  is expressed as a function of PLQY, the  $V_{OC}^{rad}$  denotes the potential difference between quasi-Fermi levels at the radiative limit.



Figure S4: QFLS and implied  $V_{OC}$  (i $V_{OC}$ =QFLS/q) of the simulated MAPbI<sub>3</sub> photoabsorbers (Eg=1.61 eV) with different grain sizes: 25 nm, 50 nm, 80 nm, 133 nm and 400 nm (single grain along a 400 nm thick perovskite layer).



Figure S5: Measured  $V_{OC}$  as function of light-intensity of reference and nanoarchitectured CPSCs, showing a slight difference in ideality factor *n* 



Figure S6: JV-curves of champion reference and nanoarchitectured perovskite solar cells with JV-parameters shown in the table (on the right).



Figure S7: Tauc plot of the reference and nanoarchitectured cells based on the external quantum efficiency (EQE) data in Fig. S2, showing the energy bandgap ( $E_G$ ) of 1.59 eV corresponding to a wavelength of ~778 nm.

## References

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