Supporting Information

Impact of Inkjet Printed ZnO Electron Transport Layer on the Characteristics of Polymer Solar Cells

José G. Sánchez[a], Víctor S. Balderrama[b], Salvador I. Garduño[c], Edith Osorio[d], Aurelien Viterisi[a], Magali Estrada[e], Josep Ferré-Borrull[a], Josep Pallarès[a] and Lluis F. Marsal[a]**

[a]Departament d'Enginyeria Electrònica Elèctrica i Automàtica, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain.

[b]Cátedra-CONACYT, Center for Engineering and Industrial Development (CIDESI), Micro-Electro-Mechanical Systems Department (MEMS), Av. Playa Pie de la Cuesta 702, Desarrollo San Pablo, 76125 Santiago de Querétaro, Querétaro, México.

[c]Cátedra-CONACYT, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional (CINVESTAV-I.P.N), Av. Instituto Politécnico Nacional 2508, 07360 Ciudad de México, México.

[d]Cátedra-CONACYT, Universidad de Quintana Roo, División de Ciencia e Ingeniería. Boulevard Bahía s/n esq. Ignacio Comonfort, C.P. 77019, Chetumal, Quintana Roo, México.

[e]Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional (CINVESTAV-I.P.N). Av. Instituto Politécnico Nacional 2508, 07360 Ciudad de México, México.

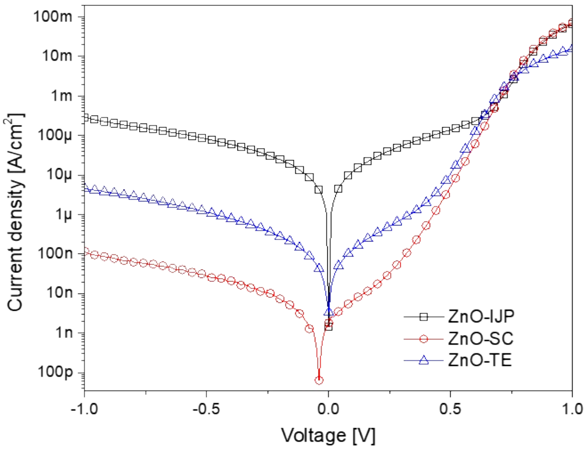

Fig. S1 Dark *J*–*V* characteristics for i-PSC with ZnO-IJP, ZnO-SC and ZnO-TE as ETL in a semi-log scale.

UV-Vis spectroscopy analysis

The reflection (%R) and transmittance (%T) spectra of ZnO-IJP, ZnO-SC and ZnO-TE layers were recorded on a Perkin Elmer UV-Visible-NIR Lambda 950 spectrophotometer using an integrator sphere. To complete the analysis we recorded the %R and %T spectra of ZnO-IJP/PTB7-Th:$PC_{70}BM$, ZnO-SC/PTB7-Th:$PC_{70}BM$ and ZnO-TE/PTB7-Th:$PC_{70}BM$. The absorbance of ZnO-IJP/PTB7-Th:$PC_{70}BM$, ZnO-SC/PTB7-Th:$PC_{70}BM$ and ZnO-TE/PTB7-Th:$PC_{70}BM$ layers were calculated by the equation:

$$1 = \rho + \tau + \alpha$$

by Kirchoff 's radiation law, where ρ is the reflectance, τ the transmittance and α the absorbance.

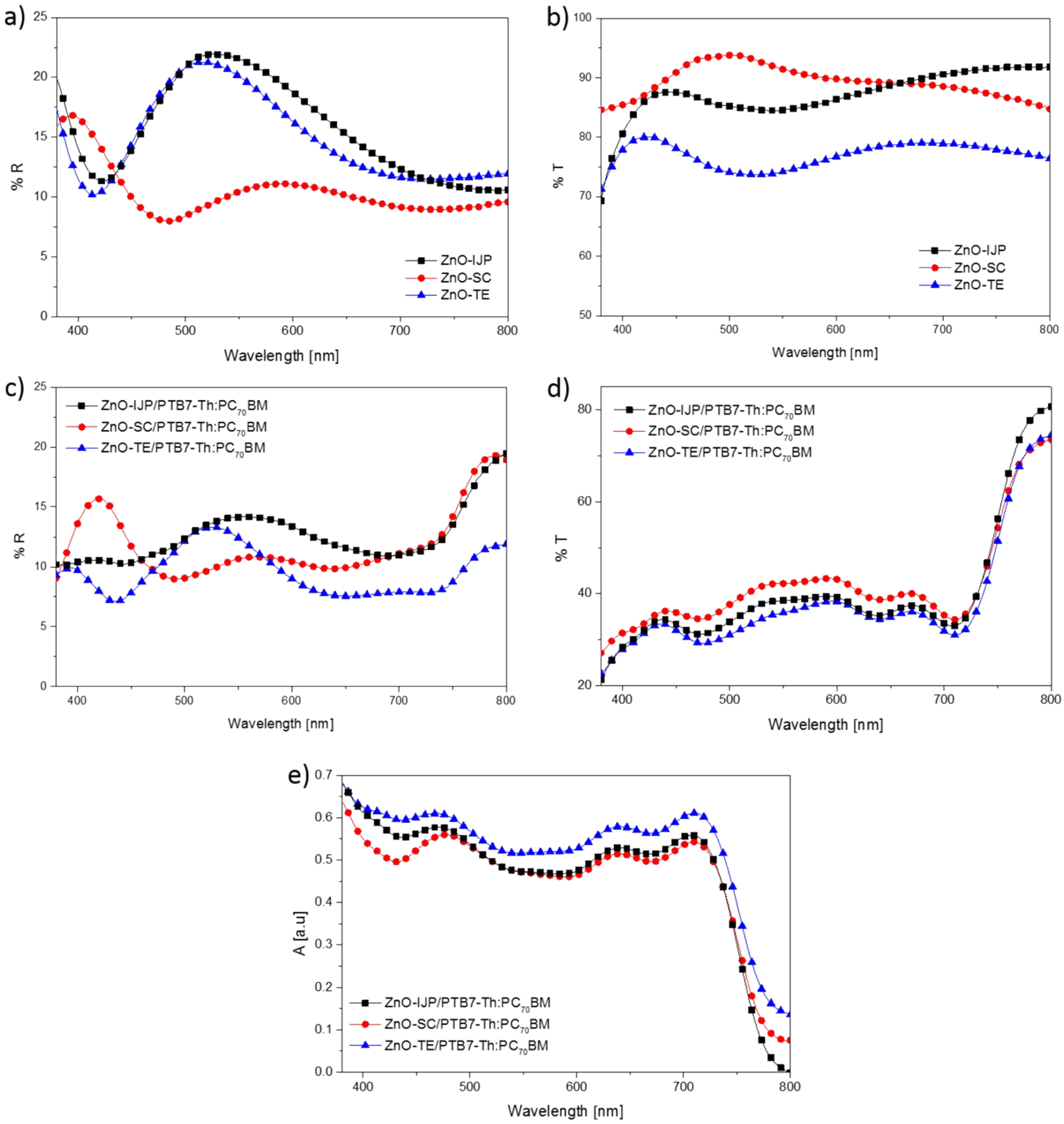

Fig. S2 Reflectance (a) and transmittance (b) spectra of ZnO-IJP, ZnO-SC and ZnO-TE layers. Reflectance (c) and transmittance (d) and absorbance (e) spectra of of ZnO-IJP/PTB7-Th:$PC_{70}BM$, ZnO-SC/PTB7-Th:$PC_{70}BM$ and ZnO-TE/PTB7-Th:$PC_{70}BM$.

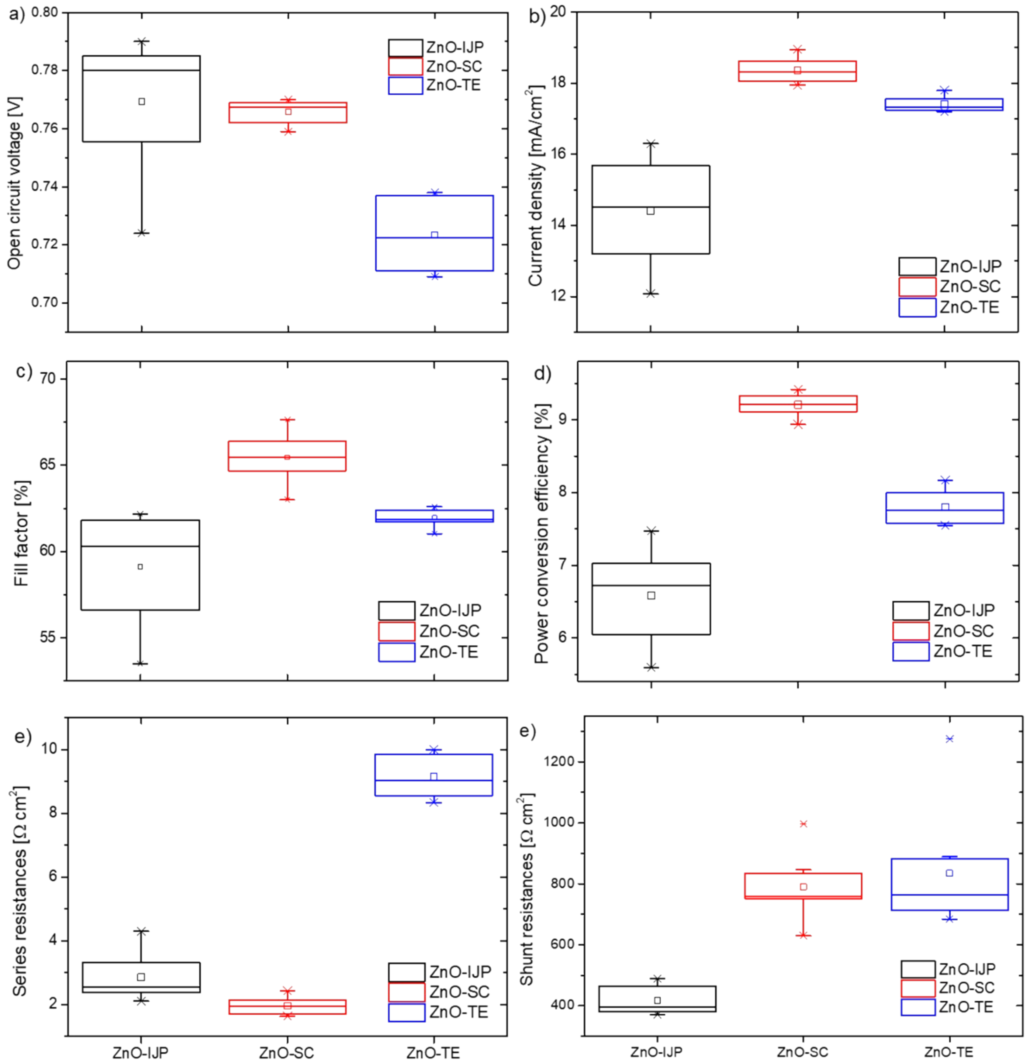

Fig. S3 Statistics of the a) V_{OC}, b) J_{SC}, c) FF, d) PCE, e) R_S f) R_{Sh} of i-PSCs with ZnO deposited via IJP (black box), Spin coating (red box) and thermal evaporation (blue box).

Table 1 RMS and peak to peak roughness of i-PSCs with ZnO-IJP, ZnO-SC and ZnO-TE calculated from AFM topography (5x5 µm and 1x1 µm) measurements.

AFM tapping	ZnO film	Annealing temperature [°C]	Roughness	
			RMS [nm]	peak to peak nm]
5x5 µm	ZnO-IJP	115	16.82	134.77
	ZnO-SC	110	16.19	116.61
	ZnO-TE	110	5.08	100.95
1x1 µm	ZnO-IJP	115	7.18	60.88
	ZnO-SC	110	8.62	58.74
	ZnO-TE	110	4.26	31.81

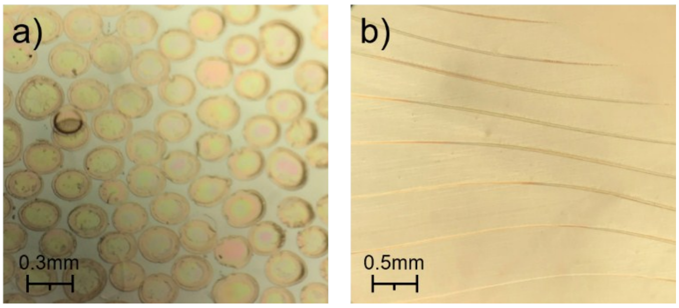

Fig. S4 Micrography of ZnO-IJP layer (a) on ITO and (b) on glass.

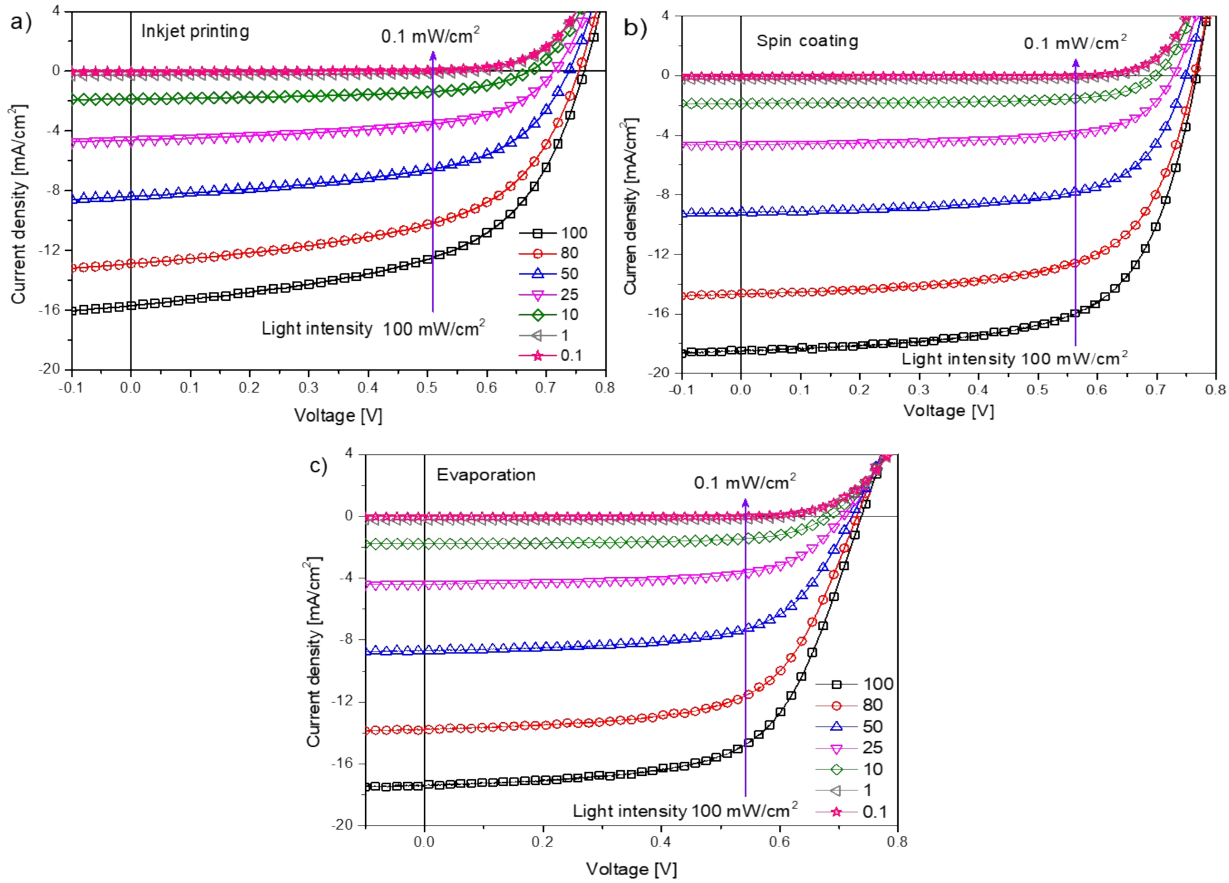

Fig. S5 Current density versus voltage characteristics of i-PSCs with a) ZnO-IJP, b) ZnO-SC and c) ZnO-TE under simulated AM 1.5G illumination (100 mW/cm^2) measured at several light intensities. The light intensity was varied using neutral density filters.

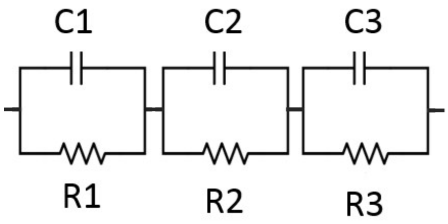

Fig. S6 Schematic RC circuit model used for IS fitting procedure.

Table S2 Dielectric constants, thickness and calculated capacitance for bulk, ZnO and V_2O_5 layers.

Layer	ε_{layer}	d_{layer} [nm]	Capacitance [nF]
ZnO	4[1]	40	8
V_2O_5	5[2]	5	78
Bulk	3.9[3]	100	2.5

CE/TPV analysis

Charge extraction (CE) was employed to probe the charge density within the active layer of the device under working conditions using a homebuilt system. Devices were held at open circuit by applying bias from a focused array of LEDs. Once the device reached steady state it was then short-circuited with the LEDs switched off simultaneously (switch-off time / relay = 300 ns), leaving the charge stored in the active layer to decay through a small 50 Ω resistor. A Yokogawa 2052 digital oscilloscope was used to record the voltage decay across the resistor. Using Ohm's law the voltage transient could be turned into a current transient, which was subsequently integrated to calculate the total charge in the active layer at each light applied bias. In general the device is measured from open circuit voltage values corresponding to >1 Sun conditions to dark condition (0 V). The charge carrier density was corrected for the charge stored at the electrodes. To do so the capacitance of the devices was calculated according to $Q_{electrodes} = C\,\Delta V$, and the charge density present in the photo-active layer of the device is given by: $n_{active} = n_{measured} - Q_{electrodes}/e\,A\,d$; where $C = \varepsilon\,A/d$ where ε is the dielectric constant (fixed to 3), A is the area and d is the thickness of the device. [4]

Transient photovoltage (TPV) measurements were carried out on working devices through applying a light bias (the same ring of LEDs used in CE) and holding the device at steady state in open circuit conditions. Once the device reached steady state conditions, a low-intensity laser pulse (PTI GL-3300 Nitrogen Laser) irradiated the sample to allow a small excess number of charge carriers to be generated. As the device is being held at open-circuit, the excess charge generated has no choice but to recombine. The transient decay of the charge carriers is recorded using a Yokogawa 2052 digital oscilloscope. Sweeping from high-applied bias (high illumination) to low-applied bias (low illumination) allows a correlation between charge carrier lifetime and voltage to be made. The irradiation wavelength was chosen to be close to but not at the maximum of the donor absorption spectrum (650 nm). A graded neutral density filter was used to adjust the intensity of the small perturbation, keeping the value as low a possibly measurable with high accuracy under 1 Sun illumination (typically 5 mV).

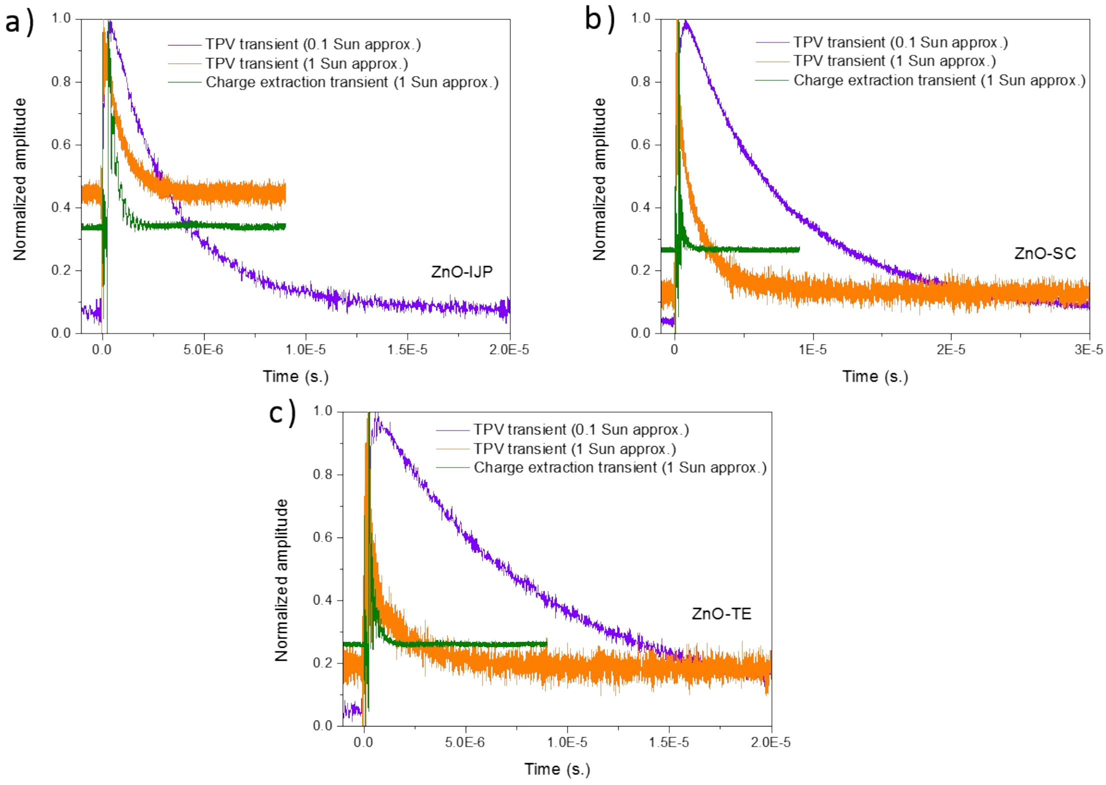

Fig. S7. Comparison of Charge extraction transients (at 1 Sun approx..), and TPV transients (at 0.1 and 1 Sun approx.) for each type of device studied in this article.

References

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