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Electronic Supporting Information

Title: NiO/ZrO₂ nanocomposites as photocathodes of tandem DSCs with higher photoconversion efficiency with respect to parent single-photoelectrode p-DSCs

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Figure S1. Top-down SEM images of NZNC electrodes with different ZrO₂/NiO ratio: 0% (top left), 1% (top right), 2% (middle left), 5% (middle right), 10% (bottom left) and 20% (bottom right). Scale 200 nm.



Figure S2. Zr 3d photoionisation region of two relevant samples: NiO_ZrO₂_0.02 (red), and NiO_ZrO₂_0.05 (blue).



Figure S3. Chemical structure of (left) P1 and (right) VG10-C8. P1 and VG10-C8 represent the dyesensitizers of the cathode and anode, respectively, for the various types of DSCs here assembled and characterized.



Figure S4. Absorption spectra of (top) P1 in ACN and (bottom) VG10-C8 in ethanol.



Figure S5. IPCE profiles t-DSC when the NZNC cathode with X = 0.2 is sensitized with P1 and the TiO2 anode is sensitized with VG10-C8. Dotted lines in the right frame refer to the Jsc integrated curve recorded during the collection of the IPCE spectra. The t-DSC was illuminated from the side of the photoanode.



Figure S6. Electrochemical Impedance Spectra of single junction and tandem DSSCs devices as both Nyquist's (top frames) and Bode's plot (bottom frame): single junction n-type (blue), single junction p-type (wine), tandem device illuminated from photocathode (green) or from photoanode (purple).

ZrO ₂ (%)	0	2	0	2
Deposition method	Screen-printing		Spray-Deposition	
$R_{CE}(\Omega)$	13.0 ± 0.1	13.0 ± 0.1	4.1 ± 0.2	4.1 ± 0.3
C_{CE} (µF)	12.7 ± 0.3	12.4 ± 0.2	10.9 ± 0.4	10.2 ± 0.5
$R_t(\Omega)$	27.3 ± 0.5	20.8 ± 0.2	42.9 ± 0.5	31.0 ± 0.5
$R_{rec}(\Omega)$	56.3 ± 0.5	70.3 ± 0.7	76.7 ± 1.1	102 ± 0.8
$C_{\mu}(\mu F)$	89 ± 3	115 ± 4	164 ± 4	198 ± 3
$\tau_{\rm h}~({\rm ms})$	2.4 ± 0.1	2.3 ± 0.1	7.0 ± 0.3	6.1 ± 0.4
$\tau_{\rm rec}(\rm ms)$	5.0 ± 0.1	8.1 ± 0.1	12.6 ± 0.6	20.2 ± 0.9
$L_h(\mu m)$	2.9 ± 0.3	3.7 ± 0.2	2.7 ± 0.4	3.6 ± 0.2
$D_{\rm h}$ (cm ² /s) *10 ⁻⁵	3.4 ± 0.1	5.7 ± 0.2	1.0 ± 0.1	2.2 ± 0.1

Table S1. Microscopic parameters with the relative errors as determined by the interpolation of EIS spectra of NZNC electrodes with different ZrO2 content (i.e. 0 or 2%) and deposited by two different approaches (i.e. screen-printing, SP, and spray-deposition, SD). The reported values are averaged considering the measurements conducted on three different cells with the photoelectrodes from the same batch.