Photoanode and photocathode current matching toward tandem DSCs with higher photoconversion efficiency with respect to parent single-junction DSCs

Photoanode and photocathode current matching toward tandem DSCs with higher photoconversion efficiency with respect to parent single-junction DSCs

A.Y. Segura Zárate[a,b], M. Bonomo[a,c], E.J. Ekoi[d], A.G. Marrani[c], N. Barbero[a], D.P. Dowling[d], C. Barolo[a,e], D. Dini[c]

[a] *Department of Chemistry, NIS Interdepartmental and INSTM Reference Centre, Università degli Studi di Torino, Italy* , anayancy.segurazarate@unito.it

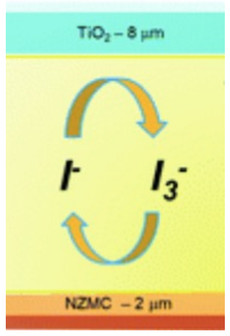
[b] *School of Physics, Technological Institute of Costa Rica, Costa Rica*

[c] *Department of Chemistry, University of Rome "La Sapienza", Italy*

[d] *School of Mechanical & Materials Engineering, University College Dublin, Ireland*

[e] *ICxT Interdepartmental Centre Università degli Studi di Torino, Italy*

INTRODUCTION

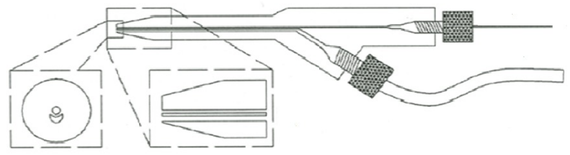


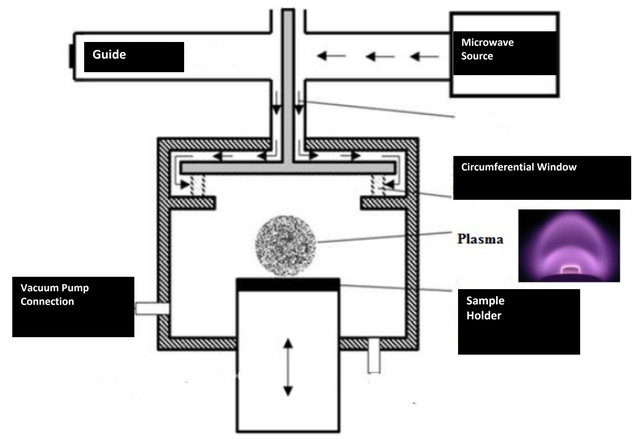
One of the reasons to research on dye-sensitized solar cells (DSCs) is to realize a photovoltaic device with (partial) optical transparency, attractive for the smart fenestration of buildings, as well as for the development of indoor light-activated powering devices that require low levels of luminous input. DSCs present three different configurations: n-type, p-type and tandem. In the first two types of solar cells are based on the nature of the semiconducting electrodes with nanostructured features; for a tandem configuration (t-DSCs) can be assembled by coupling a photoanode (sensitized TiO_2) with a photocathode (sensitized NiO), both photoelectrochemical active. Therefore, in t-DSCs both components of the redox couple are involved in the photoactivated processes of electron transfer in which the sensitizers act as mediators. Combining two sensitized photoelectrodes in the same cell represents a meaningful approach at the condition that the two sensitizers possess complementary absorption features and similar dynamics of excitation.

The NZNCs are actually solid solutions of NiO and ZrO_2 nanodomains, the use of spray-deposited nanostructured NiO/ZrO_2 composites as photocathodic material was extended also to t-DSCs when sensitized titania (TiO_2) was the photoanode. We report here the attainment of the maximum value for the overall efficiency of the t-DSC that employs VG10-C8 squaraine and P1 as anode and cathode sensitizers, respectively.

METHODOLOGY

Spray deposition method / Sintering process



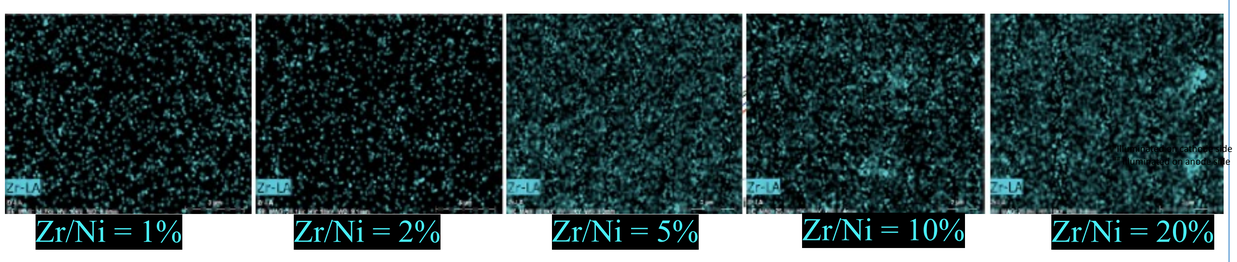


- **Heat generation from inside**
- **High homogeneity (no DT)**
- **Lower Sintering Time**

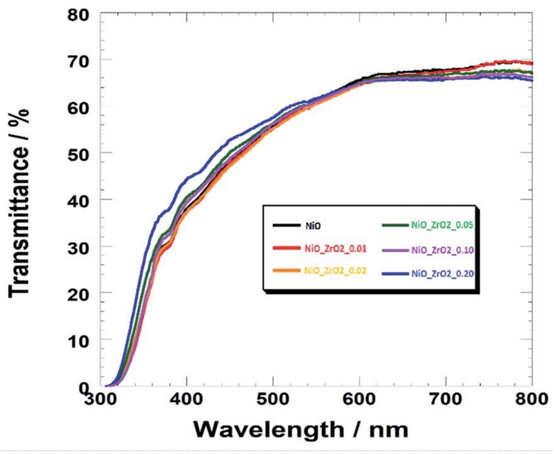
The dispersion to be sprayed had the mass concentration of 10 mg of NiO NPs precursor per mL of solvent. Dispersion was sprayed with a constant flow rate of 30 µL/min at 0.55 mPa of operating pressure with nitrogen gas as atomizer. The scan rate of the nozzle was set at 10 mm/s while the distance between the nozzle and the substrate was 15 mm. During deposition, the substrate was heated up and its temperature was maintained at 70 °C.

RESULTS AND DISCUSSION

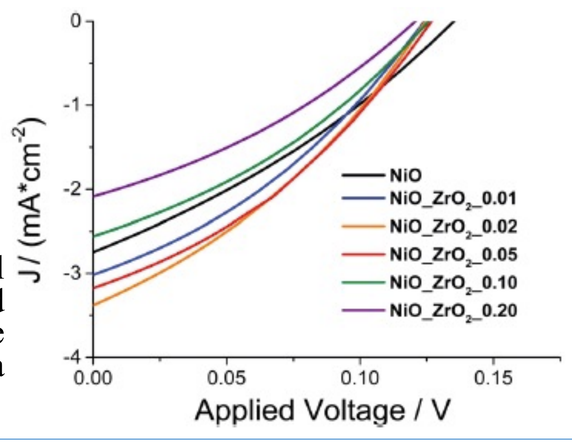
Physical properties of NZNCs



The EDX images show the localized presence of Zr through the cyano colored areas and Zr atoms increases in passing from lower to higher Zr/Ni ratio. The dispersion of ZrO_2 NPs results uniform on nanocomposite surface when Zr/Ni < 10%. Only at larger concentrations of ZrO_2 (Zr/Ni ≥ 10%) there is the verification of ZrO_2 macrostructures formation. The SD samples do not show the signal of Sn (from underlying FTO) in the EDX images. This implies that the coverage of the transparent conductive substrate through the SD procedure is much more uniform than in case of the coatings obtained via screen-printed NZNCs.

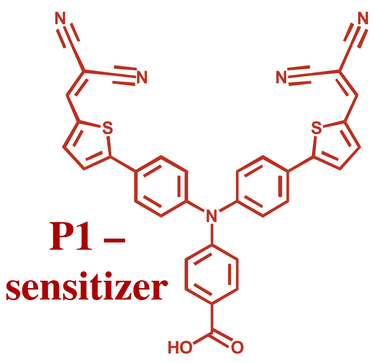


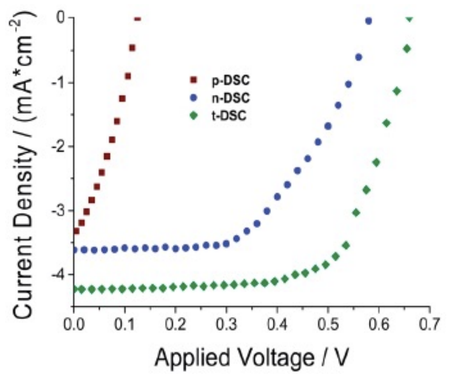
Inclusion of ZrO_2 in the NiO matrix does not affect the optical properties of the resulting SD nanocomposite thin films as verified by the comparison of the transmittance spectra for the various NZNCs.

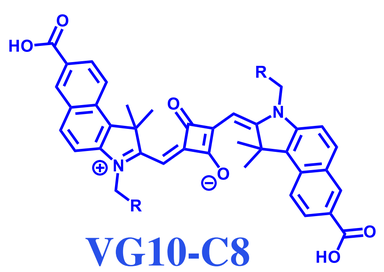


The best performing photoelectrochemical cell was the p-DSC with P1-sensitized NiO_ZrO2_0.02 photocathode with the higher photocurrent and efficiency, ed in a tandem device.

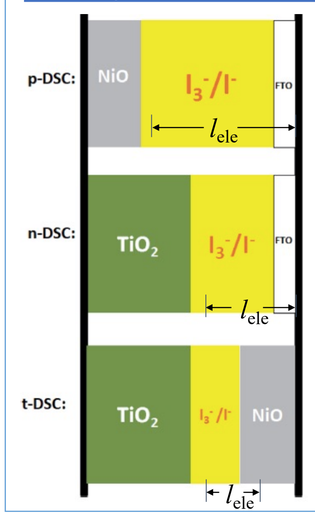
Characterization of DSC







Device (photocathode material)	V_{oc} / mV	J_{sc} / mA cm^{-2}	FF / %	η / %
p-DSC (NiO)	128	2.738	0.33	0.12
p-DSC (NZNC)	124	3.523	0.34	0.15
n-DSC	580	3.621	0.68	1.43
t-DSC (NZNC) # spacer thickness: 15 mm	678	4.198	0.66	1.88
t-DSC (NZNC) ## spacer thickness: 15 mm	682	2.800	0.66	1.26
t-DSC (NZNC) # spacer thickness: 25 mm	684	3.012	0.63	1.30
t-DSC (NZNC) ## spacer thickness: 25 mm	688	2.352	0.59	0.95



The photoconversion efficiencies are 1.43% and 0.15% for the n-DSC and p-DSC, respectively. The t-DSC displayed better photoconversion properties in comparison to the parent n- and p-DSCs, for the open circuit voltage. The V_{OC} value is the result of the difference between the upper edge of the valence band of the p-type semiconductor (ZrO2/NiO nanocomposite) and the lower edge of the conduction band of the n-type semiconductor (TiO2). Current density is explained in terms of inter-electrodes thickness in the device with the different configurations considered (n-, p- and t-) DSC. In the experimental conditions, the spacer interposed between the DSC electrodes as a frame has a fixed value of thickness. The t-DSC has the larger sum of electrodes thickness, and this implies the thinnest electrolytic layer (l_{ele}) with respect to the others [l_{ele} (t-DSC) < l_{ele} (n-DSC) < l_{ele} (p-DSC)], given a higher current density.

CONCLUSION

The combined analysis of XRD patterns and SEM pictures demonstrated that spray-deposited NiO/ZrO_2 nanocomposites are solid solutions of ZrO_2 nanodomains embedded into a matrix of nanostructured NiO. Such an optimal composition of the nanocomposite cathode was employed also for the production of photocathodes in t-DSCs with squaraine-sensitized TiO_2 as photoanodes. The resulting tandem device had a maximum conversion efficiency of 1.88% and 4.2 mA cm^{-2} as photocurrent density, these values are among the largest reported insofar for a t-DSC based on NiO and TiO_2 photoelectrodes.

REFERENCES

Mozaffari, S et al. Solar Cells. *Renew. Sustain. Energy Rev.* **2017**, 71, 675–686;

Liu, J. et al. *Science China Materials*, **2019**, 62(2), 173-180.

Bonomo M. et al. *J. Electrochem. Soc.* **2019**, 166 (8), D290–D300.

Bonomo, M. et al. *Sustainable Energy and Fuels*, **2021**, DOI: 10.1039/D1SE00566A

Mariotti, N. et al. *GreenChemistry*, **2020**, 22, 7168-7218