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## 1 Nanocomposites of nickel oxide and zirconia for the preparation of photocathodes with 2 improved performance in *p*-type dye-sensitized solar cells

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#### 14 ABSTRACT

In p-type dye sensitized solar cells (p-DSCs) with nickel oxide (NiO) based photocathodes one of 15 16 the main causes of their relatively poor photoconversion performances is the fast recombination between the photoinjected holes in the valence band of the *p*-type semiconductor and the reduced 17 form of the redox shuttle (typically I). As a matter of fact, recombination phenomena at the 18 NiO/electrolyte interface heavily limit both photovoltage and photocurrent. Different approaches 19 have been adopted to minimize such an unwanted process: these range from the pretreatment of the 20 electrode surface with NaOH to the employment of passivating organic molecules (e.g. CDCA) in 21 the sensitizing solution and/or in the electrolyte solution. The present contribution describes the 22 23 implementation of the addition of zirconia (ZrO<sub>2</sub>) nanoparticles in nanostructured NiO films as antirecombination agent in p-DSCs due to the electro-inactivity of ZrO<sub>2</sub>. ZrO<sub>2</sub> nanoparticles with 24 diameter,  $\emptyset$ , of 20 nm, and NiO nanoparticles with  $\emptyset < 50$  nm were dispersed together in the paste 25 precursor for screen-printing. Different compositions of the mixture of NiO and ZrO<sub>2</sub> nanoparticles 26 were considered. From the combined analysis of the electrochemical and photoelectrochemical 27 properties of different nanocomposites it was concluded that the molar ratio ZrO<sub>2</sub>/NiO had the 28 optimal range of 2-5 % for realizing photocathodes more efficacious than sole nanostructured NiO. 29 Among the nanocomposite photoelectrodes the one obtained from the inclusion of 2% of ZrO<sub>2</sub> 30 nanoparticles produced the better photoelectrochemical performance being the short-circuit current 31 density  $J_{SC} = 2.037 \text{ mA/cm}^2$  and the overall efficiency  $\eta = 0.088\%$  when P1 is the sensitizer. These 32 results show an increase up to 40% compared to the un-modified NiO electrode. The unexpectedly 33 low efficiency of electrode with molar ratio of zirconia in nickel oxide of 5% was associated to an 34 insufficient dye-loading on NiO, in combination to the increase of the percentage of the 35 photoelectrochemically inert ZrO<sub>2</sub> additive. The electrochemical impedance spectroscopy (EIS) 36 data of the complete device under illumination confirmed that the improvement is mainly due to an 37 increase of the recombination resistance,  $R_{rec}$ , ongoing from sole nanostructured NiO ( $R_{rec} = 56.3 \Omega$ ) 38 to the electrode obtained from the nanocomposite with molar ratio  $ZrO_2/NiO = 0.02$  ( $R_{rec} = 70.3 \Omega$ ). 39

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#### 47 INTRODUCTION

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49 Among photovoltaic technologies the monocrystalline silicon-based devices and lead iodide based perovskite solar cells are capable to reach conversion efficiencies up to 20% under solar 50 irradiation<sup>1</sup>. When indoor illumination with diffuse features is considered as source of luminous 51 energy the dye-sensitized solar cell  $(DSC)^2$  appears as the most effective choice despite the fact 52 that the highest efficiency of a DSC is below 15%<sup>3</sup>. More recently, Gräetzel<sup>4</sup> and co-workers 53 reported overall efficiency up to 30% when the source intensity is as low as 100 lux. Conversions 54 up to 40% could be theoretically achieved by creating a p-n junction<sup>5</sup> (i.e. by coupling a photoanode 55 to a photocathode) when the solar radiation is considered as excitation source. Such a tandem 56 configuration would sensibly reduce also the costs of production of the corresponding device. The 57 theoretical limit of 40% is still far to be reached because of the generally poor performance of 58 59 photocathodes. To our knowledge, the best performance reported so far for a *p*-type DSC (*p*-DSC) is lower than 2% under 1 Sun of illumination<sup>6</sup>. One of the main causes of this is the fast 60 recombination reaction that occurs between the photoinjected holes in the valence band (VB) of the 61 photocathode (usually made of NiO)<sup>7-10</sup> and the reduced form of the redox shuttle (typically the 62 iodide anion)<sup>11–13</sup>. In fact, recombination phenomena at the NiO/electrolyte interface heavily limit 63 both photovoltage and photocurrent. The photoinjected holes are mainly localized onto NiO surface 64 in correspondence of the electron-deficient Ni<sup>3+</sup> sites. Different approaches have been adopted to 65 minimize such an unwanted reaction. The rational design of a sensitizer with bulky 66 substituents<sup>6,14,15</sup> could help to keep iodide distant from the holes localized on the electrode surface. 67 68 The implementation of a NiO compact layer has been proved to reduce recombination phenomena at the electrolyte/FTO interface<sup>16-18</sup>. Metal-doping or UV irradiation of NiO electrode are feasible 69 approaches to tune the opto-electronic properties of photocathode but are as not effective in 70 reducing the interfacial recombination<sup>19-21</sup>. An alternative route is the direct modification of the 71 photocathode. In a previous paper we showed that the treatment of NiO surface with soda has a 72 twofold effect: it reduces the surface concentration of superficial Ni<sup>3+</sup> sites and passivates the NiO 73 surface prior sensitization<sup>22</sup>. The success of this method has been confirmed by the achievement of 74 75 a less dark film. Unfortunately, the reduction of the number of Ni<sup>3+</sup> sites lowered also the amount of loaded sensitizer leading to a less performing device (lower photocurrent). We also tested CDCA 76 (chenodeoxycholic acid) in squaraines-based p-DSC<sup>23</sup>. In that work CDCA (acting as both 77 disaggregating and passivating agent) was added in the sensitizer solution with a concentration of 78 20 mmol. The overall efficiency was enhanced by 25% due to the depression of dye aggregation. 79 Nevertheless, the amount of chemisorbed dye was lowered because of the competition between 80 sensitizer and CDCA in binding Ni<sup>3+</sup> sites. To avoid the latter phenomena, Odobel et al.<sup>24</sup> dissolved 81 CDCA (50 mM) in the electrolyte. They reported an enhancement of the 20 % of the conversion 82 efficiency due mainly to a higher  $V_{OC}$  whereas the  $J_{SC}$  was substantially unchanged. The 83 employment of an insulating layer of Al<sub>2</sub>O<sub>3</sub> was proposed by Uehara and coworkers<sup>25</sup> but it 84 diminished the electron injection of surface chemisorbed sensitizer more than the desired 85 recombination phenomena Natu and co-authors reported the implementation of a more efficient 86 87  $Al_2O_3$  insulating layer directly deposited onto the NiO electrode by Atomic Layer Deposition<sup>26</sup>. Yet, the enhancement of photoelectrochemical properties is modest. As far as we are aware, no 88 research group previously attempted the nanometric approach in the framework of DSCs with the 89 90 preparation of the nanocomposites here reported. In particular, throughout this work we described, 91 for the first time, the employment of  $ZrO_2$  nanoparticles, NPs, with diameter  $\emptyset < 20$  nm) as not electroactive additive in NiO electrodes for p-DSC application. ZrO<sub>2</sub> is an insulating oxide with a 92 bandgap higher than 5 eV. We expect that the presence of zirconia nanoparticles, i.e. 93 a 94 nanostructured version of ZrO<sub>2</sub> with strong tendency of being finely dispersed on the electrode surface, diminishes the portion of NiO exposed to the electrolyte thus diminishing the probability 95 with which Ni<sup>3+</sup> sites on the surface recombine with the redox shuttle. The effect of NiO dilution 96 imparted by of zirconia nanoparticles on the electrode surface brings necessarily about the 97

consequent minimization of recombination phenomena at the electrode/electrolyte interface as well 98 as flux of photoinjected charges in the photocathode. The purpose of this study is to evaluate to 99 which extent the presence of ZrO<sub>2</sub> NPs favors the suppression of recombination without being 100 excessively detrimental against dye-loading and photoinjection on the NiO portions of the 101 nanocomposite. ZrO<sub>2</sub> has been chosen because of its chemical inertness and long-term stability. The 102 formation of a mixed oxide of nickel and zirconium with a structure distinct from the ones of NiO 103 and  $ZrO_2$  has not been evidenced (vide infra)<sup>27</sup>. Therefore, the attainment of a solid solution from 104 the mixing and the sintering of NiO and ZrO<sub>2</sub> NPs is reasonably excluded. On these bases we 105 expect that the nanocomposites are actually constituted by two segregated oxides. 106

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# 108 EXPERIMENTAL PART

110 The chemicals ethylcellulose,  $\alpha$ -terpineol, NiO nanopowders, ethanol and acetonitrile (ACN) were 111 purchased from Fluka or Sigma-Aldrich whereas  $ZrO_2$  nanoparticles were purchased from US 112 Research Nanomaterials. All chemicals were used without any further treatment of purification.

The experimental procedure to produce NiO/ZrO<sub>2</sub> slurry consists on a modified version of the one 113 reported in our previous paper<sup>28,29</sup>: an ethanol solution of NiO nanopowders (6 g), ZrO<sub>2</sub> 114 nanospheres (variable amount),  $\alpha$ -terpineol as solvent (20 g) and ethylcellulose as crosslinker were 115 mixed together under continuous stirring. Then this solution was slowly heated at 50 °C to let 116 completely evaporate the solvent. The resulting slurries were screen-printed over 2.2 mm thick 117 FTO/glass substrates (TEC7 from NSG), which were previously cleaned in an ultrasonic bath with 118 acetone for 10 min and successively with isopropyl alcohol for 10 min. The electrodes with 119 geometrical area of 0.36 cm<sup>2</sup>, were annealed at 450 °C in oven for 30 minutes. The thickness of the 120 annealed samples ranged between 2 and 3 µm (evaluated with a Dektak 150® profilometer from 121 Veeco). The morphology has been investigated with a FESEM Auriga Zeiss Field Emission. EDX 122 (EDX Quantax Bruker, Resolution 123 eV (Mn  $K_{\alpha}$ ) was employed for the elemental analyses. The 123 amount of added ZrO<sub>2</sub> varied from 0 (pure NiO) to 856 mg (corresponding to the molar ratio 124  $ZrO_2/NiO = 0.11$ ). Six slurries have been prepared with different values of  $ZrO_2/NiO$  molar ratio: 125

- Pure NiO as reference
- $ZrO_2$ / NiO = 0.001, with 8 mg of  $ZrO_2$
- $ZrO_2/NiO = 0.010$ , with 85.6 mg of  $ZrO_2$
- $ZrO_2$ / NiO = 0.020, with 171.2 mg of  $ZrO_2$
- $ZrO_2/NiO = 0.053$ , with 428 mg of  $ZrO_2$
- $ZrO_2$ /NiO = 0.111, with 856 mg of  $ZrO_2$

The resulting slurries were chemically and physically stable for several months in ambient conditions. Throughout the paper, each electrode made starting from these slurries has been named as NiO\_ZrO<sub>2</sub>\_X where X represents the ZrO<sub>2</sub>/NiO molar ratio.

The electrochemical characterization of ZrO<sub>2</sub>/NiO samples consisted in the recording of cyclic 135 voltammetries (CVs), and electrochemical impedance spectra with Autolab potentiostat/galvanostat 136 Mod. PGSTAT12® from Metrohm. PGSTAT was remotely controlled from a computer by means 137 of the software Nova 1.9. The electrochemical cell had a three-electrode configuration with NiO 138 (either bare or ZrO<sub>2</sub>-modified as nanocomposite) as working electrode, a platinum wire as the 139 counter-electrode and Ag/AgCl electrode as the reference electrode. The supporting electrolyte was 140 0.1 M LiClO<sub>4</sub> in ACN. With regard to the CV measurements the applied potential has been varied 141 from -0.27 to 1.13 V with a variable scan rate (10, 20, 50, 100 or 200 mV\*s<sup>-1</sup>). Impedance spectra 142 were recorded in the same experimental set up by applying a frequency value ranging from 100 143 KHz to 0.1 Hz with a potential amplitude of stimulus of 20 mV. 144

WAXS experiments were carried out on a Bruker D8 Advance with DaVinci design diffractometer 145 (angle dispersive). The diffractometer is equipped with a Cu K $\alpha$  X-Ray tube ( $\lambda = 1.5406$  Å). The 146 instrument is fitted with focusing Göbel mirrors along the incident beam and Soller slits on both 147 incident and diffracted (radial) beams. Data were measured in step-scan mode in the 20-80° angular 148 range with a step of 0.02° within the Bragg-Brentano para-focusing geometry. Only the incident 149 beam slit was closed (0.2 mm width), while the diffracted beam slit was left open. The samples 150 were held on microscope slides within a humidity-controlled chamber purposely developed. The 151 scattered intensity was gathered with the Lynxeye XE Energy-Dispersive 1-D detector. 152

For the assembly of the DSC the different electrodes were sensitized by dipping them in a P1<sup>30</sup> solution (0.3 mM in ACN) for 16 hours. The electrodes were rinsed with ACN to remove the excess of not chemisorbed dye. Optical transmittance of sensitized photocathodes was measured with a double ray spectrometer [UV-2550 by Shimazdu, Kyoto (JP)].

Bare and P1-sensitized photocathodes were assembled in a sandwich configuration with platinised-157 158 FTO as counter-electrode. A double layer of Platinum (3D-nano) was screen-printed onto the counter-electrodes. The first layer was dried at 120 °C for 10 min before printing the second one. 159 As the first, the second layer was dried at 120°C in order to burn the solvents. Successively the 160 counter-electrodes were fired at 480 °C in oven for 30 min for the thermal reduction of the Pt 161 precursor<sup>31</sup>. A thermoplastic resin (Surlyn<sup>®</sup>, from Dupont), was used as spacer and sealant. The 162 electrolyte (Iodolyte-H from Solaronix) was injected inside the two sandwiched electrodes by 163 vacuum backfilling technique through a drilled hole -one for each cell- in the Surlyn® mask. These 164 holes were sealed with a specific UV-curable resin (TB3035B from ThreeBond®). 165

Photoelectrochemical characterization of the *p*-DSCs consisted in the recording of the JV characteristic curves, incident photon-to-current conversion efficiency (IPCE) spectra and in-light EIS data. All the measurements were recorded with a Sun Simulator AM 1.5G at 1 SUN (Incident Power = 1000 W m<sup>-2</sup>) using a Keithley 2420 as a source-meter in ambient conditions. The light source was calibrated with s SKS1110 sensor (Skye Instruments Ltd).

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# 172 **RESULTS AND DISCUSSION**

Figure 1 shows the voltammograms of bare NiO and NiO ZrO<sub>2</sub> 2%, which were recorded within 173 the potential range -0.5 - 1 V vs Ag/AgCl at different scan rates (range:10-200 mV s<sup>-1</sup>). In both 174 series of CVs two main peaks are observed: the peak at lower potential corresponds to the reversible 175 solid state oxidation of NiO with occurrence of Ni<sup>2+</sup> $\rightarrow$  Ni<sup>3+</sup> + 1  $e^-$  (named O1); the peak at higher 176 potential is assigned to the formal oxidation of preexisting  $Ni^{3+}$  sites into  $Ni^{4+}$  (named O2)<sup>32</sup>. The 177 current peak of O1 was more than doubled in going from bare NiO to the sample NiO ZrO<sub>2</sub> 2%. 178 Moreover, a sensible variation of the O2/O1 ratio is observed in the compared analysis of NiO and 179 NiO ZrO<sub>2</sub> 2% electrodes being the O2 peak less pronounced when the electrode is 180 doped/combined with ZrO<sub>2</sub>. This combination of findings leads us to suppose that the presence of 181 zirconia as a fine dispersion diminishes the surface concentration of Ni(III) in the as deposited 182 sample. Beside the diminution of the portion of defective NiO, i.e. the portion containing Ni(III) 183 sites, the presence of zirconia would favor the relative increase of the surface concentration of 184 Ni(II) sites with respect to bare NiO. The latter statements are going to be verified in a successive 185 186 study through the adoption of the XPS technique for the speciation of these NiO/ZrO<sub>2</sub> nanocomposites. In Table 1, the charge density exchanged during the occurrence of O1 and O2 as 187 well as their relative ratio are reported. The O2/O1 ratio decreases regularly upon increase of ZrO2 188 content up to the composition NiO\_ZrO<sub>2</sub>\_2%. When the ZrO<sub>2</sub>/NiO ratio becomes higher (samples 189 NiO  $ZrO_2$  5% and NiO  $ZrO_2$  10%), the ratio O2/O1 increases again. This is a consequence of the 190 fact that zirconia should form aggregates at relatively high concentrations thus becoming a 191

segregated phase, i.e.  $ZrO_2$  is not longer homogeneously dispersed in the form of nanoparticles within the NiO nanostructure. In the aggregated state zirconia, i.e. the component representing the passivating and non-electroactive agent of the composite, becomes less efficient in blocking the Ni<sup>3+</sup> sites. Simultaneously, the presence of  $ZrO_2$ -based macrostructure on the NiO surface decreases the active surface area of the electrode. In this context the presence of  $ZrO_2$ -based macrostructure on NiO surface can explain both the detrimental effect on NiO electrochemical activity of the electrode as well as the increase in O2/O1 ratio.



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Figure 1. CVs of (right) NiO bare and (left) NiO\_ZrO<sub>2</sub>\_2% at different scan rates [10 mV/s (light blue), 20 mV/s (red), 50 mV/s (green), 100 mV/s (light red) and 200 mV/s (dark blue)]. The supporting electrolyte was 0.1 M LiClO<sub>4</sub> in ACN. CE was a platinum rod and RE is SSE (+0.220 mV vs NHE).

Electrode	O1 peak (mC cm <sup>-2</sup> )	O2 peak (mC cm <sup>-2</sup> )	02/01 (%)
NiO	0.195	0.207	106.2
NiO_ZrO <sub>2</sub> _0.1%	0.206	0.178	86.4
NiO_ZrO <sub>2</sub> _1%	0.461	0.144	31.2
NiO_ZrO <sub>2</sub> _2%	0.990	0.200	20.2
NiO_ZrO <sub>2</sub> _5%	0.686	0.162	23.3
NiO_ZrO <sub>2</sub> _10%	0.096	0.033	34.3

**Table 1.** Charge density exchanged during the processes identified as O1 and O2 and relative ratio.

From Table 1, it could be evidenced that NiO\_ZrO<sub>2</sub>\_2% showed both the better electrochemical activity, i.e. the higher value of exchanged charge, and the relatively lower extent of Ni<sup>3+</sup> in the sample being this characteristic associated with the lower O2/O1 ratio. Because of that, sample NiO\_ZrO<sub>2</sub>\_2% appeared as the most suitable electrode to be employed as photocathode in a *p*-DSC<sup>33</sup>.

For the detection of the eventual presence of these ZrO<sub>2</sub>-based macrostructures we performed combined SEM-EDX measurements. SEM (Figure 2) evidenced all samples possessed a quite open morphology with a lot of nanometer size voids: such a morphological feature is essential to assure a sufficiently high dye-loading for DSC purposes. The presence of ZrO<sub>2</sub> macrostructures was detected in all samples. For the determination of the actual chemical nature of the macrostructures we analyzed the elemental distribution on the electrode surface with Energy Dispersive X-ray (EDX, figure 3) spectroscopy. The analysis concerned the search of the elements Ni, O and Zr. The

- eventual presence of Sn from FTO substrate was also checked to evaluate the porosity of the screen-
- 217 printed electrodes. Are here shown the SEM and EDX images of NiO, NiO\_ZrO<sub>2</sub>\_2% and
- 218 NiO\_ZrO<sub>2</sub>\_5%. Additional images have been collected in the supporting information (Figures
- 219 ESI1-ESI4).



Figure 2. SEM image of the NiO electrodes differing for the amount of ZrO<sub>2</sub>: (top left) NiO; (top right) NiO\_ZrO<sub>2</sub>\_2% and (bottom left) NiO\_ZrO<sub>2</sub>\_10%. A magnification of NiO\_ZrO<sub>2</sub>\_2% has been shown (bottom right) to evidence the dispersion of ZrO<sub>2</sub> NPs onto the NiO surface.

225 By the comparison of images in Figure 2 and ESIX, one can see that a ZrO<sub>2</sub>/NiO molar ratio higher than 2% leads to the growth of some macrostructures. The latter feature became more evident in 226 227 NiO  $ZrO_2$  10%. Interestingly, the presence of nanoparticles randomly dispersed onto the electrode surface was evidenced too with EDX spectroscopy. EDX confirmed also that the ZrO<sub>2</sub> 228 229 macrostructures were formed by the aggregation of ZrO<sub>2</sub> NPs in the samples with the largest concentration of zirconia. As shown in figure ESIX, a concentration of Zr and a lower amount of 230 Ni was revealed in the analyzed area. Moreover, this structure is not porous since the signal of Sn 231 could not be detected. The presence of superficial Zr could not be found in NiO\_ZrO<sub>2</sub>\_0.1% (Figure 232 233 ESI1) because of the too high dispersion of ZrO<sub>2</sub> NPs, which is below the sensitivity of the EDX instrument (0.065 mmol per unit area). The signal of Sn was detected for all nanocomposites with 234 235 molar content of Zr smaller than 10% (See ESI5).

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Figure 3. EDX images of (left column) NiO\_ZrO<sub>2</sub>\_1%, (middle column) NiO\_ZrO<sub>2</sub>\_2% and (right column) NiO\_ZrO<sub>2</sub>\_5%. The surface distribution of different elements has been marked with different colors: violet-blue = O (first row of images); green = Ni (second row of images); pink = Zr (third row of images); red = Sn (fourth row of images). The bottom row represents the morphology of the three different samples of nanocomposites here considered.

The *Tauc's plot* was employed to determine the optical band gap of not sensitized electrodes upon variation of zirconia content (Figure 4).



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Figure 4. Tauc's plot for the extrapolation of the optical bandgap in the different nanocomposites of NiO and ZrO<sub>2</sub>. Black circles:
NiO; light blue squares: NiO\_ZrO<sub>2</sub>\_0.1%; dark blue diamonds: NiO\_ZrO<sub>2</sub>\_1%; orange triangles: NiO\_ZrO<sub>2</sub>\_2%; red triangles:
NiO\_ZrO<sub>2</sub>\_5%; green triangles: NiO\_ZrO<sub>2</sub>\_10%.

In the present case, the bandgap  $E_g$  for this series of nanocomposites tends to increase monotonically on going from NiO to NiO\_ZrO<sub>2</sub>\_5% whereas the bandgap of NiO\_ZrO<sub>2</sub>\_10% is very similar to the one of NiO. More precisely, the calculated bandgap is 3.62, 3.61, 3.68, 3.71, 3.75 and 3.63 for NiO, NiO\_ZrO<sub>2</sub>\_0.1%, NiO\_ZrO<sub>2</sub>\_1%, NiO\_ZrO<sub>2</sub>\_2%, NiO\_ZrO<sub>2</sub>\_5% and NiO\_ZrO<sub>2</sub>\_10%, respectively. The blue-shifted  $E_g$  of the ZrO<sub>2</sub> /NiO electrode with respect to NiO leads to more transparent films of the nanocomposites with respect to NiO in the visible range. A larger number of defects in the lattice corresponds to a system with a tighter the optical band gap.

257 Electrochemical impedance spectra were recorded in a three-electrode cell configuration in dark condition in order to avoid any modification induced by the eventual photoactivity of NiO working 258 electrode. The applied potential ranged in the interval -0.2 - 1.1 V (vs Ag/AgCl) (Figure 5). 259 Experimental data have been fitted with the equivalent circuit depicted in Figure ESI5: the first 260 element simulates charge-transfer phenomena occurring at the electrode/electrolyte interface whilst 261 the second accounts for the charge transport through the electrode with its characteristic charge 262 transport resistance and capacitance. In the present context, we focus our attention and discuss 263 mainly the former type of phenomenon, i.e. interfacial charge transfer since this represents the 264 process at the basis of recombination in the actual *p*-DSC device and constitutes the problem which 265 266 is here tackled through the introduction of nanocomposites of electroactive NiO and electrochemically inert ZrO<sub>2</sub>. The electrolyte composition in the experiments of electrochemical 267 impedance is the same as the one employed in the experiments of cyclic voltammetry. 268

In Table 2  $R_{CT}$  represents the charge transfer (CT) resistance at the electrolyte/electrode interface, C<sub>INTER</sub> is the double layer capacitance whereas C<sub>electrode</sub> is the capacitance of the electrode layer. EIS data evidenced that  $R_{CT}$  diminishes with the applied potential irrespective of the amount of zirconia in the electrode. This is expected since the increase of the applied potential is accompanied by the concomitant increase of the number of holes, i.e. the mobile charged species that are injected

electrochemically in the film of NiO during its oxidation. Beside the improvement of the charge 274 transfer properties these holes contribute to the double layer capacitance CINTER at 275 electrode/electrolyte interface and to the capacitance Celectrode of the electrode bulk. When CT is 276 relatively fast it promotes the formation of a diffuse double layer instead of a compact one. The R<sub>CT</sub> 277 values decrease sharply when the applied potential approaches the values of NiO redox processes, 278 i.e. between 0 and 0.25 V and between 0.5 and 0.7 V for  $Ni^{2+} \rightarrow Ni^{3+}$  and  $Ni^{3+} \rightarrow Ni^{4+}$  reactions, 279 respectively. A similar behaviour has been already reported for NiO when is polarized in aqueous 280 electrolytes<sup>34</sup>. Among the various formulations of the nanocomposites in the pristine state, the 281 system NiO\_ZrO<sub>2</sub>\_2% showed the lowest  $R_{CT}$  (2218  $\Omega$ ), and the largest values of the capacitive 282 terms Celectrode and CINTER. These findings denote the existence of a quite defective material with a 283 relatively high number of native charges in starting NiO\_ZrO<sub>2</sub>\_2%. Upon completion of the 284 oxidation processes ( $E_{appl} = 1.10$  V vs Ag/AgCl) NiO\_ZrO<sub>2</sub>\_2% presented also the largest value of 285 R<sub>CT</sub> (twice the value of bare NiO one): this is an indication of the stronger tendency of this 286 particularly formulation of nanocomposite to suppress efficaciously recombination at the 287 electrode/electrolyte interface with respect to the other combinations. 288





Figure 5. EIS data of (top left) NiO bare, (top right) NiO\_ZrO<sub>2</sub>\_1%, (bottom left) NiO\_ZrO<sub>2</sub>\_2% and (bottom right) NiO\_ZrO<sub>2</sub>\_10% at different applied potential: -0.20 (dark red circles), 0.00 (dark green squares), 0.25 (dark blue diamonds), 0.50 (red triangles), 0.70 (purple triangles), 0.90 (orange triangles) and 1.10 V vs Ag/AgCl (light blue triangles). The fittings have been reported as full lines.

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	E / V vs Ag/AgCl	-0.20	0.00	0.25	0.50	0.70	0.90	1.10
NiO	<b>R</b> <sub>CT</sub> / <b>Ω</b>	3715	1942	284	131	88	71	62
	CINTER / µF	33.2	28.6	24.4	16.2	11.9	10.2	9.2
	Celectrode / µF	53.8	178.2	198.5	212.1	225.2	236.7	239.8
NiO_ZrO2_0.1%	$R_{CT} / \Omega$	3134	707	312	198	131	99	84
	CINTER / µF	37.3	31.7	22.3	20.7	14.1	13.5	12.4
	Celectrode / µF	55.3	184.4	218.8	232.2	242.6	252.9	254.6
NiO_ZrO <sub>2</sub> _1%	$R_{CT} / \Omega$	2540	635	328	237	151	126	102
	CINTER / µF	<b>43.8</b>	35.9	26.1	21.3	17.9	15.3	13.6
	C <sub>electrode</sub> / µF	65.1	223.2	293.2	301.2	332.9	336.5	362.8
NiO_ZrO <sub>2</sub> _2%	$R_{CT} / \Omega$	2218	<b>593</b>	248	179	148	130	119
	CINTER / µF	<b>49.7</b>	33.7	26.5	20.4	17.6	15.6	14.8
	C <sub>electrode</sub> / µF	170.1	332.2	383.3	393.8	436.4	446.0	470.7
NiO_ZrO <sub>2</sub> _5%	$R_{CT} / \Omega$	2649	741	346	264	164	133	112
	CINTER / µF	<b>47.9</b>	36.0	26.5	<b>19.7</b>	17.3	15.1	13.8
	Celectrode / µF	132.0	248.9	340.8	342.8	367.9	384.6	402.3
NiO_ZrO <sub>2</sub> _10%	$R_{CT} / \Omega$	4135	1002	422	280	136	117	108
	CINTER / µF	46.6	31.7	23.7	17.2	14.4	12.6	11.7
	Celectrode / µF	72.2	191.8	198.6	204.6	228.9	230.9	236.9

Table 2. Electric parameters derived from the fit of experimental impedance spectra. The errors on the fitting parameters are less than 3%.

In order to check the crystallographic structure of our modified samples and the eventual arising of 299 some NiO/ZrO2 mixed phase, we performed X-Ray Diffraction measurements. The results have 300 been reported in figure 6: as one can see, the XRD spectrum of bare NiO (JCPDS card No. #47-301 1049) shows one main peak corresponding to the 111 plane (at 37.2°) and a smaller peak at 75.1° 302 corresponding to the 311 plane. All the peak indexed with \* arising from the FTO employed as 303 substrate<sup>35</sup>. The addition of ZrO<sub>2</sub> NPs leads to a slight modification of the XRD pattern: two small 304 peaks could be evidenced at 42.8° and 62.5° ascribable to the 200 and 220 plane of cubic NiO 305 (JCPDS card No. #47-1049), respectively. Furthermore, there is not any evidence of peak due to 306 ZrO<sub>2</sub> or NiO/ZrO<sub>2</sub> mixed phases. The XRD pattern of monoclinic ZrO<sub>2</sub> usually presents two main 307 peaks at 28.1° (110) and 31.4° (111), JCPDS card No. #78-1807, whereas the spectrum of 308 tetragonal zirconia is composed by three main peaks centred at  $30.2^{\circ}$  (101),  $50.2^{\circ}$  (112) and  $60.2^{\circ}$ 309 (211), JCPDS card No. #79-1769. The absence of any crystallographic peak of ZrO<sub>2</sub> is ascribable to 310 the homogenous dispersion of the nanoparticles (figure 3) that not allow the occurrence of large 311 ZrO2 crystallographic domains. Therefore, the effect of the addition of ZrO2 results in the growth of 312 the NiO matrix in additional crystalline planes. More interestingly, the rise of NiO/ZrO<sub>2</sub> mixed 313 phase could be completely ruled out. 314



#### 316

**Figure 6.** XRD spectra of bare NiO (black line), NiO\_ZrO2\_2% (orange line) and NiO\_ZrO2\_5% (red line) films. The peak due to the presence of crystalline NiO are indexed by the name of the corresponding plane. \*-indexed peak refers to FTO substrate.

319 The JV curves of the p-DSCs with the six formulations here considered have been recorded for both pristine and P1-sensitized electrodes to stress eventual changes in the operating features of the NiO-320 321 based electrode after sensitization. When dye is not loaded onto the NiO surface, the only accessible pathway to produce photocurrent is the excitation of an electron from the VB of NiO to its CB at 322 323 the approximate wavelength of excitation  $\lambda_{exc} \approx 320$  nm. To reduce the current losses due to recombination phenomena, Ni<sup>3+</sup> sites should be inaccessible to the reducing species that are present 324 in solution: the implementation of ZrO<sub>2</sub> NPs avoids that the surface of nickel oxide with its 325 recombination defects is fully exposed to the electrolyte. The practical effect of the introduction of 326 ZrO<sub>2</sub> NPs is the increase in the powered photocurrent: +123% on going from pristine NiO to 327 NiO\_ZrO<sub>2</sub>\_2% (Figure 7 and Table 3) accounting for a huge decrease in recombination phenomena. 328 NiO and NiO ZrO<sub>2</sub> 2% produced a photocurrent of 0.448 mA\*cm<sup>-2</sup> and 0.994 mA cm<sup>-2</sup>, 329 respectively. The trend of photocurrent is not monotonic: it reached its maximum when ZrO<sub>2</sub> to 330 NiO have a molar ratio of 2% and it decreased for NiO\_ZrO<sub>2</sub>\_5% and NiO\_ZrO<sub>2</sub>\_10% ( $J_{SC} = 0.747$ 331 and 0.414 mA cm<sup>-2</sup>, respectively). This trend is in accordance with the CV and EIS data (vide 332 supra). Such a combination of findings shows how revealing is the analysis of the electrochemical 333 properties in case of nanostructured NiO electrodes for the successive evaluation of their 334 photoelectrochemical performance. When compared to sole NiO, the sample of NiO ZrO<sub>2</sub> 0.1% 335 does not show any significant difference in terms of electrochemical and photoelectrochemical 336 behavior due to the fact that zirconia NPs are too dispersed to effectively influence the 337 (photo)electrochemical properties of the corresponding nanocomposite electrode. NiO\_ZrO<sub>2</sub>\_1%, 338 NiO\_ZrO<sub>2</sub>\_2% and NiO\_ZrO<sub>2</sub>\_5% manifested similar electrochemical behavior and displayed 339 similar morphologies. In case of NiO\_ZrO<sub>2</sub>\_1% such a concentration of ZrO<sub>2</sub> does not allow a good 340 dispersion of the nanoparticles throughout the NiO film whereas molar percentage values higher 341 than 2% causes the formation of pure ZrO<sub>2</sub> macrostructure that can prevent the exposure of the Ni<sup>3+</sup> 342 343 sites. Among the doped electrode NiO ZrO2 10% showed the worst performance: the electrode mainly suffered for an extremely low Fill Factor (FF  $\approx 25\%$ ). Such a result could be ascribed to the 344 presence of large aggregates of zirconia that produce as main effect the inhibition of the process of 345

photoinjection rather than preventing recombination. Moreover, the electrode formulation NiO\_ZrO<sub>2</sub>\_5% showed a relatively low FF ( $\approx 28\%$ ) too. Open circuit potential ( $V_{OC}$ ) values ranged from 78 to 85 mV without showing any clear trend with the amount of dispersed zirconia.



Figure 7. (Left) JV curves and (right) IPCE spectra of the p-DSCs employing bare electrodes with different doping degree: 0%
 (black), 0.1% (light blue), 1% (dark blue), 2% (orange), 5% (red) and 10% (green).

By definition the IPCE (Incident Photo-to-current Conversion Efficiency) is the ratio of the number 352 of collected carriers to the number of all the incident photons on the device active area at a given 353 wavelength. The differences in the spectra reported in figure 7 evidence that the probability with 354 which the photoinjected holes reach the current collector  $(\eta_{tr})$  varies with the content of zirconia 355 and follows the trend of the photocurrent, i.e. the higher the photocurrent powered by the device, 356 the higher the maximum of the IPCE spectra. Some little shifts of the wavelength corresponding to 357 IPCE maximum are expected for the different electrodes due to the blue-shift of the optical bandgap 358 introduced by the presence of zirconia, as previously outlined. 359

P1 was the sensitizer of our p-DSCs<sup>36</sup> (sensitization conditions: 16 hours in a 0.3 mM solution of 360 the dye in ACN). NiO\_ZrO<sub>2</sub>\_10% has been excluded from the analyses because of its poor 361 electrochemical and photoelectrochemical performance. Upon sensitization the enhancement of the 362 photocurrent is clear in going from NiO to NiO\_ZrO<sub>2</sub>\_2%. Yet the magnitude of such an increase is 363 lower compared to the corresponding increase when un-sensitized electrodes are employed (+ 46% 364 vs +123%, respectively). This difference was mainly due to the presence of the sensitizer: the dye 365 partially acts as a passivating agent by reducing the free Ni<sup>3+</sup> sites that represent the actual sites of 366 anchoring. Some of the Ni<sup>3+</sup> sites are actively involved in binding P1 onto the NiO surface, whereas 367 other are simply covered as a consequence of the steric hindrance of the organic molecule.  $J_{SC}$ 368 values varied from 1.447 mA cm<sup>-2</sup> to 2.037 mA cm<sup>-2</sup> in passing from bare NiO to NiO\_ 369 ZrO<sub>2</sub>\_0.020. To our knowledge the efficiency value of 0.088% here obtained with P1-sensitized 370 371 NiO\_ZrO<sub>2</sub>\_0.020. is the highest reported for a P1-sensitized screen-printed NiO electrode without the integration of a NiO compact layer<sup>37,38</sup>. NiO\_ZrO<sub>2</sub>\_0.1% and NiO\_ZrO<sub>2</sub>\_1% have shown quite 372 similar performances (1.611 and 1.690 mA cm<sup>-2</sup> of short circuit current density, respectively) but 373 far from the record value. 374

375

	Dye	J <sub>SC</sub> / mA*cm <sup>-2</sup>	V <sub>OC</sub> / mV	FF / %	η / %	Dye Loading / 10 <sup>8</sup> *mmol*cm <sup>-2</sup>
NiO	-	$0.448 \pm 0.012$	83 ± 2	$33.8\pm0.9$	0.012	-
NiO_ZrO <sub>2</sub> _0.001	-	$0.480 \pm 0.020$	83 ± 2	$34.1 \pm 0.7$	0.014	-
NiO_ZrO <sub>2</sub> _0.010	-	$0.618 \pm 0.023$	78 ± 1	$33.2 \pm 0.7$	0.016	-
NiO_ZrO <sub>2</sub> _0.020	-	$0.994 \pm 0.033$	78 ± 2	$33.7 \pm 0.6$	0.026	-
NiO_ZrO <sub>2</sub> _0.053	-	$0.747 \pm 0.028$	$75 \pm 3$	$27.9 \pm 0.9$	0.017	-
NiO_ZrO2_0.111	-	$0.414 \pm 0.056$	84 ± 3	$25.3\pm0.8$	0.009	-
NiO	<b>P1</b>	$1.447 \pm 0.120$	$129 \pm 2$	$32.5 \pm 0.6$	0.060	$3.19 \pm 0.62$
NiO_ZrO2_0.001	<b>P1</b>	$1.611 \pm 0.089$	$130 \pm 2$	$32.4 \pm 0.5$	0.068	$3.16 \pm 0.52$
NiO_ZrO <sub>2</sub> _0.010	<b>P1</b>	$1.690 \pm 0.103$	$130 \pm 3$	$34.4 \pm 0.5$	0.075	$3.27 \pm 0.39$
NiO_ZrO <sub>2</sub> _0.020	<b>P1</b>	$2.037 \pm 0.095$	$129 \pm 2$	$33.6 \pm 0.6$	0.088	$3.22 \pm 0.41$
NiO_ZrO <sub>2</sub> _0.053	<b>P1</b>	$1.313 \pm 0.063$	$126 \pm 1$	$30.5\pm0.3$	0.050	$2.65 \pm 0.53$
NiO ZrO <sub>2</sub> 0.111	<b>P1</b>	-	-	-	-	-

376 Table 3. Photoelectrochemical parameters of the *p*-DSCs with the differently doped ZrO<sub>2</sub>-NiO nanocomposite photoelectrodes. The

377 reported values are obtained from averaging the performances of five devices. The errors on the efficiency values are lower than

378 0.001 and have not been reported.

379



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Figure 8. JV curves of the complete devices built up with P1-sensitized electrodes with different doping degree: 0% (black), 0.1% 381 382 (light blue), 1% (dark blue), 2% (orange) and 5% (red).

NiO\_ZrO<sub>2</sub>\_5% displayed the worst performance in terms of current density and open circuit 383 voltage. The lower values of  $J_{SC}$ ,  $V_{oc}$  and FF are mainly due to an insufficient dye-loading (see 384 Table 3): zirconia macrostructures, even if they are not as extended as in case of NiO\_ZrO<sub>2</sub>\_10% 385 (see SEM pictures in Figure 2), seem to prevent the full penetration of the sensitizer throughout the 386 porous structure of the electrode with consequent insufficient dye-loading. Similar to not sensitized 387 devices, no substantial variations of  $V_{OC}$  could be observed. The highest values of fill factor (34.4%) 388 and 33.6%), have been reported when the fraction of ZrO<sub>2</sub> are 1% and 2%. This evidence confirms 389 390 the optimal dispersion of zirconia NPs in the fraction range of 1-2 % as already outlined by the 391 electrochemical measurements. IPCE spectra of the P1-sensitized devices (Figure 9), confirmed the trend shown by JV curves. 392



#### 393

Figure 9. IPCE spectra of the complete devices built up with P1-sensitized electrodes with different doping degree: 0% (black), 0.1%
 (light blue), 1% (dark blue), 2% (orange) and 5% (red).

The different performances of the *p*-DSCs differing for the composition of the nanocomposite 396 electrodes could be ascribed to a minimization of the recombination reactions involving the reduced 397 species in the electrolyte, i.e. I, and the surface localized holes in the NiO electrode. The similar 398 399 values of dye loading and bandgap for the series of electrodes here considered indicate that the kinetics of charge injection is not sensibly altered by the fraction of zirconium oxide. The 400 electrochemical impedance spectra of the different photelectrochemical cells are presented in Figure 401 9. For sake of simplicity the impedance spectrum of the DSC with NiO\_ZrO<sub>2</sub>\_0.1% photocathode is 402 not shown due to the similarity with the spectrum of the cell having sole NiO photocathode. 403

The electric parameters reported in Table 4 could be extracted from experimental data when the 404 equivalent circuit<sup>28</sup> of the inset of Figure 10 is adopted as model. In this model  $R_s$  is the resistance 405 of all the external elements. It should be constant within the experimental error. R<sub>CE</sub> is the resistance 406 407 of charge transfer through the electrolyte/counter electrode interface and corresponds to the process of oxidation of the reduced species of the redox shuttle (i.e.  $\Gamma$ ) at Pt electrode. C<sub>CE</sub> is the capacitance 408 at the electrolyte/counter electrode interface. The following circuital elements have been defined in 409 410 the transmission line element adapted by Bisquert to analyze the impedance response of *n*-type DSCs <sup>39</sup> and successfully employed for the analysis of the impedance spectra of p-type DSCs<sup>28</sup>: 411

- Rt is the (transport) resistance of the electronic charge carriers, i.e the holes, to traverse the
   NiO electrode and reach the FTO back contact (charge collector).
- R<sub>rec</sub> is the resistance of recombination the charge carriers experience after photogeneration.
   Patterns of recombination can be due either to the recombination of the excited/oxidized dye
   with the hole or to the recombination of the photogenerated hole with a reducing species in
   the electrolyte, namely I<sup>-</sup>.
- 418  $C_{\mu}$  is the (chemical) capacitance of the NiO-based photocathode and is related to the content 419 of charge that is present inside the illuminated photocathode.

The employment of the transmission line element is consistent with the mesoporous nature of the photocathodes. The pure capacitive elements are here replaced with the CPE (constant phase 422 element) that allows an easier fit of the experimental data without influencing the reliability of the 423 obtained parameters. The actual capacitance ( $C_{real}$ ) could be calculated applying the following 424 equation:

425 
$$C_{real} = \frac{(C_{CPE} * R)^{\left(\frac{1}{n}\right)}}{R}$$

in which  $C_{CPE}$  and *n* are the two parameters describing the capacitive properties of the CPE element whilst R is the value of the resistance associated to CPE. If *n* is equal to 1, the CPE acts a pure capacitance.



429

Figure 10. EIS spectra of the complete devices built up with P1-sensitized electrodes differing for the fraction of zirconia dopant: 0%
(black dots), 1% (dark blue diamonds), 2% (orange triangles) and 5% (red triangles). In the inset, the equivalent circuit employed for the experimental data interpolation is reported.

The determination of these electrical parameters allows the direct calculation of the followingmicroscopic parameters:

- $\tau_h (= R_t * C_\mu)$ , i.e. the time the photoinjected holes take to reach the FTO charge collector;
- 436  $\tau_{rec} (= R_{rec} * C_{\mu})$ , i.e. the holes lifetime that corresponds to the time the photoinjected holes 437 spend before undergoing any type of recombination process;
- 438  $L_h = l (R_t/R_{rec})^{1/2}$ , where *l* is the nominal film thickness] is the mean free path of the 439 photoinjected holes before being involved in recombination reactions;
- $D_h (=L_h^2 / \tau_h)$  is the average diffusion coefficient of the photoinjected holes through the photocathode.
- 442 The values of both R<sub>CE</sub> and C<sub>CE</sub> did not vary considerably with the concentration of ZrO<sub>2</sub> NPs in the
- 443 nanocomposite electrode. The modification in electronic and photoelectronic properties of the
- 444 working photoelectrode do not influence the kinetics of charge transfer processes at the counter-
- electrode.
- 446 In the *p*-DSCs the value of  $R_t$  decreased with the increase of  $ZrO_2$  molar content in the 447 photocathode in agreement with the ameliorated electronic transport properties of the NiO electrode

due to the controlled doping with zirconia when the three-electrode cell was analyzed. The presence 448 of zirconia NPs onto the NiO surface reduces the number of free trap sites (i.e. Ni<sup>3+</sup> surface located 449 sites) which contribute to the chemical capacitance of the electrode. This is proved by the higher 450 value of C<sub>µ</sub> reported for NiO\_ZrO<sub>2</sub>\_1% and NiO\_ZrO<sub>2</sub>\_2% (101 µF and 115 µF, respectively) 451 compared to the un-doped NiO electrode (89 µF). The relatively low value of chemical capacitance 452 (i.e. 97  $\mu$ F) recorded for NiO ZrO<sub>2</sub> 5% is probably due to the insufficient dve loading that prevents 453 the photoinjection of a high number of carriers. The low value of R<sub>rec</sub> for the NiO\_ZrO<sub>2</sub>\_5% 454 electrode is associated with a relatively low amount of dye. Both un-doped NiO and NiO\_ ZrO<sub>2</sub>\_5% 455 electrode showed the lowest  $R_{rec}$  values (56.3  $\Omega$  and 57.3  $\Omega$ , respectively) while NiO\_ZrO<sub>2</sub>\_1% 456 with 63.8  $\Omega$  and NiO ZrO<sub>2</sub> 2% with 70.3  $\Omega$  gave the best performing cells in combination with 457 the higher resistance of recombination (see JV curves in Figure 7). The analysis of the data showed 458 a linear correlation between  $R_{\rm rec}$  and  $J_{\rm SC}$ : the higher the former the higher the latter. Such a linear 459 correlation does not hold when  $\eta$  is correlated to  $R_{\rm rec}$  (and  $J_{\rm SC}$ ). The values of  $\tau_{\rm rec}$  followed the same 460 trend of  $R_{\rm rec}$ . A remarkably long time of recombination of 8.1 ms for the charge carriers diffusing 461 through NiO\_ZrO<sub>2</sub>\_2% has been found in combination with long diffusion length (3.7 µm) and high 462 diffusion coefficient (5.7  $*10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>). This is a consequence of the fact that the photoinjected 463 holes have a longer mean free path and a higher rate of diffusion throughout the NiO film in 464 presence of zirconia nanoparticles with respect to undoped NiO. The Ni<sup>3+</sup> trap states are expected to 465 be masked and eventually annihilated upon addition of zirconia nanoparticles. For the confirmation 466 of the latter statement the analysis of the surface with XPS will be necessary and is planned in a 467 successive study. The photoelectrode formulation NiO\_  $ZrO_2_5\%$  presented a low value of  $\tau_{rec}$ , as 468 well as the lowest value of  $\tau_h$  within the series of the electrodes. It is expected that such a content of 469 zirconia prevents the homogeneous sensitization of the anchoring sites of NiO, which also behave 470 471 as trapping species. Such sites in the not sensitized state contribute to lower the hole diffusion time with the consequent attainment of high values of  $D_h$  (Table 4). 472

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<b>ZrO</b> <sub>2</sub> (%)	0	1	2	5
$\mathbf{R}_{\mathrm{CE}}\left(\mathbf{\Omega} ight)$	$13.0 \pm 0.1$	$13.3 \pm 0.2$	$13.0 \pm 0.1$	$12.8 \pm 0.1$
Cce (µF)	$12.7 \pm 0.3$	$13.1 \pm 0.2$	$12.4 \pm 0.2$	$12.3 \pm 0.1$
$\mathbf{R}_{t}(\mathbf{\Omega})$	$27.3 \pm 0.5$	$23.0 \pm 0.4$	$20.8\pm0.2$	$18.6\pm0.5$
$\mathbf{R}_{\mathrm{rec}}(\mathbf{\Omega})$	$56.3 \pm 0.5$	$63.8 \pm 0.8$	$70.3 \pm 0.7$	$57.3 \pm 0.8$
$C_{\mu}(\mu F)$	89 ± 3	$101 \pm 3$	$115 \pm 4$	97 ± 3
$\tau_{h}$ (ms)	$2.4 \pm 0.1$	$2.3 \pm 0.1$	$2.3 \pm 0.1$	$1.8 \pm 0.1$
$\tau_{rec}$ (ms)	$5.0 \pm 0.1$	$6.4 \pm 0.2$	8.1 ± 0.1	5.6 ± 0.1
$L_{h}(\mu m)$	$2.9\pm0.3$	$3.3 \pm 0.2$	$3.7 \pm 0.2$	$3.5 \pm 0.2$
$D_h (cm^2/s) * 10^{-5}$	$3.4 \pm 0.1$	$4.8 \pm 0.2$	$5.7 \pm 0.2$	$6.9 \pm 0.3$

474 Table 4. Microscopic parameters with the relative errors as determined by the interpolation of EIS spectra of Figure 9. The
475 reported values are averaged considering the measurements conducted on five different cells with the photoelectrodes from the same
476 batch.

Treatments like the deposition of a blocking layer between the FTO and the photocathode or the post-sintering surface modification of NiO based electrodes are expected to further enhance the performance of *p*-DSCs. For this reason, further experiments in the direction of the modification of the photocathode with inclusion of a blocking compact layer and consideration of post deposition treatments will be planned. The main motivation of the conduction of this type of studies is the implementation of the best performing photocathodes in tandem DSCs when comparable current densities and efficiencies are achieved at the corresponding photoelectrodes of p- and n-type devices.

485

#### 486 CONCLUSIONS

The nanocomposites obtained from the sintering of nanoparticles (NPs) of nickel oxide (NiO) and 487 zirconia (ZrO<sub>2</sub>) have been employed as photocathodes of p-type dye-sensitized solar cells (p-488 DSCs), P1 being the sensitizer. NiO represented the component in large excess whereas ZrO<sub>2</sub> 489 constituted the doping species of the nanocomposite with a percentage of less than 10%. Nano-490 dispersed ZrO<sub>2</sub> minimized recombination phenomena at the electrode/electrolyte interface of the p-491 DSC when the redox shuttle was the couple  $I^{-}/I_{3}^{-}$ . The best performance of the photoelectrochemical 492 cell was obtained with the electrode having the 2% of ZrO<sub>2</sub> in the NiO matrix. This enhancement 493 (due to the addition a controlled amount of ZrO2 NPs) was firstly ascribed to a minimization of the 494 recombination phenomena occurring at the electrode/dye/electrolyte interface. Electrochemical 495 impedance measurements were employed to prove this hypothesis: recombination resistance was 496 improved by 25% (from 56.3 to 70.3  $\Omega$ ); additionally, hole transport resistance was reduced to 20.8 497  $\Omega$  (from 27.3  $\Omega$  of bare NiO). These evidences lead to slower recombination time, faster hole 498 transport, longer hole diffusion length and higher diffusion coefficient. The efficiencies of the p-499 DSCs with NiO/ ZrO<sub>2</sub> nanocomposites were 123% and 48% higher than un-doped NiO for the bare 500 and sensitized electrode, respectively. SEM-EDX experiments have been performed to visualize the 501 pattern of dispersion of ZrO<sub>2</sub> NPs in the NiO matrix. The values of 0.1 and 1% of zirconia do not 502 503 assure a uniform dispersion. When the concentration of zirconia was higher than 5%, the NPs merged to form macrostructures. This phenomenon of ZrO<sub>2</sub> NPs aggregation on the electrode 504 surface prevented surface passivation and efficient dye-loading. The enhancement here reported 505 506 consists in a considerable breakthrough as far as the lowering of charge recombination phenomena p-DSCs is concerned. On the other hand, the optimization of the other cell elements, e.g. dye, 507 electrolyte etc., will be mandatory to further improve the conversion performance of this type of 508 devices in perspective of assembling tandem devices with nanocomposite photocathodes. 509

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