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# 1 Finely tuning electrolytes and photoanodes in aqueous 2 solar cells by experimental design

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21  
22 **Abstract:** If opportunely developed and optimized, aqueous dye-sensitized solar cells  
23 can be considered a truly low impact photovoltaic device, with no toxic components.  
24 Here we report the use of design of experiments as a useful chemometric technique for  
25 the concurrent investigation of a series of experimental factors that directly influence  
26 the proper operation of these photoelectrochemical cells. Results obtained enlighten that  
27 a solid mathematical-statistical approach is fundamental to support the researchers and  
28 effectively drive the experiments towards the achievements of optimal operating  
29 conditions of any new energy device, thus bypassing the energy/time consuming of  
30 traditional monivariate one-factor-at-a-time method.

31  
32 **Keywords:** Dye-sensitized solar cell; Aqueous electrolyte; Sustainability; Design of  
33 experiments; Multivariate approach; Electrode/electrolyte interface.

## 34 35 36 1. Introduction

37 The introduction of aqueous electrolytes is contributing to the rebirth of dye-sensitized  
38 solar cells (DSSCs), the low-impact photoelectrochemical device for the conversion of  
39 solar energy into electricity (Bella et al., 2015). Aqueous DSSCs represent a truly  
40 sustainable and very limited environmental impact technology, which might  
41 successfully pinpoint the concept of artificial photosynthesis often been evoked within

42 the scientific community in the last two decades (Bella et al., 2017; Click et al., 2017;  
43 Imperiyka et al., 2014; McConnell et al., 2010; Yang et al., 2010).

44 Several research groups worldwide recently focused their efforts towards the  
45 investigation of a series of new factors, such as photoelectrode wetting (Dong et al.,  
46 2014; Galliano et al., 2017), novel sensitizers (Leandri et al., 2014; Li et al., 2017; Lin  
47 et al., 2015), the solubility and the diffusion behavior of various redox pairs in water  
48 (Daeneke et al., 2012; Xiang et al., 2013; Yang et al., 2015), the cathodic  
49 electrocatalytic reaction (Ellis et al., 2016). Clearly, in a new system (like the aqueous  
50 DSSC), the possibility to simultaneously study several of these experimental factors at  
51 the same time, bypassing the traditional one-factor-at-a-time (OFAT) process, would  
52 permit to effectively drive research towards well-defined paths supported by a solid  
53 mathematical/statistical justification. In this respect, despite being scarcely adopted by  
54 the energy-related research community (Gianotti et al., 2014; Miccoli et al., 2016),  
55 multivariate chemometrics, such as design of experiments (DoE) (Kennard et al., 1969),  
56 would represent a key-enabling method.

57 In this work, we propose a DoE for the simultaneous investigation of the  
58 characteristics of photoanode, electrolyte and photoanode/electrolyte interface of  
59 aqueous DSSCs. A simple experimental matrix based on 20 photoelectrochemical cells  
60 enables to comprehensively weight each of the experimental factors involved, and to  
61 easily identify the best conditions to maximize sunlight conversion efficiency. Amongst  
62 the powerful and intriguing aspects of the adopted approach, the ability to find two  
63 performance maximization strategies must be mentioned, which is the fundamental  
64 achievement of this work.

65

## 66        2. Experimental

67 Sodium iodide (NaI), iodine (I<sub>2</sub>), chenodeoxycholic acid (CDCA), ethanol, acetone,  
68 *tert*-butanol (*t*-BuOH) and acetonitrile (ACN) were purchased from Sigma-Aldrich.  
69 Deionized water (DI-H<sub>2</sub>O, 18 MΩ cm<sup>-1</sup> at 25 °C) was obtained by Direct-Q 3 UV Water  
70 Purification System (Millipore). Sensitizing dye 2-[[4-[4-(2,2-diphenylethenyl)phenyl]-  
71 1,2,3,3a,4,8b-hexahydrocyclopento[b]indole-7-yl}methylidene]-cyanoacetic acid  
72 (D131) was purchased from Inabata Europe S.A. FTO-glass plates (sheet resistance 7 Ω  
73 sq<sup>-1</sup>, purchased from Solaronix) were cut into 2 cm × 1.5 cm sheets and used as  
74 substrates for the fabrication of both photoanodes and counter electrodes.

75 FTO covered glasses were rinsed in mixed acetone/ethanol in an ultrasonic bath for  
76 10 min; solvent traces were removed by flash evaporation at 450 °C on a hotplate. Front  
77 electrodes were prepared by depositing a single layer of porous TiO<sub>2</sub> on top of the  
78 conductive substrate by means of a manual screen printer with a 43T mesh frame. After  
79 deposition of the paste (18NR-T, Dyesol) and 20 min rest to let it bed thoroughly, the  
80 TiO<sub>2</sub> layer was dried at 80 °C for 20 min; finally, it was sintered increasing the  
81 temperature up to 480 °C in 45 min. The fabricated photoanodes had a thickness of ≈6  
82 μm and active area of 0.25 cm<sup>2</sup>. They were finally reactivated by heating at 450 °C for  
83 20 min and, subsequently, soaked into a D131 dye solution (0.50 mM in *t*-BuOH:ACN  
84 1:1); CDCA was added to the dye solution as coadsorbent (its concentration represents  
85 one of the factors investigated in this work). Dipping in dye solutions was carried out at  
86 22 °C for 5 h under dark conditions and shaking in a Buchi Syncore platform equipped  
87 with a cooling plate. After dye loading, photoanodes were washed in acetone to remove  
88 residual dye not specifically adsorbed onto the TiO<sub>2</sub> layer.

89 As regards the preparation of counter electrodes, FTO conductive glasses were  
90 platinized by spreading a  $\text{H}_2\text{PtCl}_6$  5.0 mM solution on the plate surface and heating up  
91 to 400 °C.

92 Photoanodes were faced to the counter electrodes exploiting Surlyn<sup>®</sup> thermoplastic  
93 frames (internal area 0.6 cm × 0.6 cm) as spacers (60 μm thick), taking care of the  
94 overlapping of the active areas. All of these components were assembled by hot  
95 pressing (20 s) at 110 °C. The electrolyte solution (consisting of NaI and I<sub>2</sub> dissolved in  
96 water) was injected by vacuum backfilling process through a hole in the Surlyn<sup>®</sup> frame,  
97 which was then sealed by a commercial epoxy glue. The amounts of NaI and I<sub>2</sub>  
98 represent relevant factors in the aqueous DSSC field, thus they are investigated in this  
99 work.

100 Photovoltaic performances were evaluated recording three consecutive  $J-V$  curves  
101 on a Keithley 2420 Source Measure Unit. Cells were irradiated under simulated 1 sun  
102 light intensity (100 mW cm<sup>-2</sup>, AM 1.5G) after calibration by silicon diode, as it is  
103 typically done in the DSSC framework (Bella et al., 2017; Fan et al., 2017; Liu et al.,  
104 2017; Maçaira et al., 2017; Mengal et al., 2017). Electrochemical impedance  
105 spectroscopy (EIS) data were recorded using a potentiostat (CH Instruments Inc., Model  
106 680) in the frequency range between 10 kHz and 0.1 Hz. The amplitude of the AC  
107 signal was 10 mV. Spectra were recorded under dark conditions at applied DC  
108 potentials equal to the previously measured  $V_{oc}$  values under 1 sun (Buraidah et al.,  
109 2017; Mohan et al., 2017; Paušová et al., 2017; Subramanian et al., 2017; Vekariya et  
110 al., 2017).

111

### 112 3. Results and Discussion

113 An experimental design was compiled to simultaneously investigate the effect of two  
 114 key parameters, such as the concentration of the redox mediator and the ratio between  
 115 the co-adsorbent CDCA and the dye-sensitizer in the photoanode dipping solution, of an  
 116 aqueous DSSC. As regards the electrolyte, two variables were identified: concentrations  
 117 of I<sub>2</sub> ( $x_2$ , from 10 to 30 mM) and NaI ( $x_3$ , from 1.0 to 5.0 M), respectively. The  
 118 CDCA/Dye molar ratio ( $x_1$ ) was the third variable, which ranged from 18 to 50. Such an  
 119 experimental domain was chosen accordingly to preliminary tests useful to identify the  
 120 most appropriate conditions to enable proper operation of lab-scale aqueous DSSCs  
 121 (Bella et al., 2016). In order to carry out a multivariate experimental design, the  
 122 software MODDE (version 11.0.2.2309, Umetrics) was chosen. A two-level full  
 123 factorial DoE was planned and the list of experiments is summarized in **Table 1**,  
 124 together with the measured responses of short-circuit current density ( $J_{sc}$ ), open-circuit  
 125 potential ( $V_{oc}$ ), fill factor (FF) and power conversion efficiency (PCE) (Abdul Rani et  
 126 al., 2014; Park et al., 2015). These experiments represent the most statistically  
 127 significant points of the investigated experimental domain as a whole, and design the  
 128 cubic geometry shown in **Fig. A.1 in Appendix A**.

129

130 **Table 1.** DoE model matrix consisting of 20 experiments, useful to investigate the three  
 131 selected experimental variables ( $x_1$ ,  $x_2$  and  $x_3$ ). The measured responses for  $J_{sc}$ ,  $V_{oc}$ , FF  
 132 and PCE are also shown.

| Exp.      | CDCA:Dye ratio [ $x_1$ ] | [Iodine] ( $x_2$ , mM) | [Iodide] ( $x_3$ , M) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (mV) | FF (%) | PCE (%) |
|-----------|--------------------------|------------------------|-----------------------|---------------------------------|---------------|--------|---------|
| <b>N1</b> | 18:1                     | 10                     | 1.0                   | 1.48                            | 564           | 54.7   | 0.46    |
| <b>N2</b> | 50:1                     | 10                     | 1.0                   | 2.21                            | 607           | 54.7   | 0.73    |
| <b>N3</b> | 18:1                     | 30                     | 1.0                   | 0.92                            | 476           | 54.9   | 0.24    |
| <b>N4</b> | 50:1                     | 30                     | 1.0                   | 1.71                            | 540           | 59.5   | 0.55    |
| <b>N5</b> | 18:1                     | 10                     | 5.0                   | 3.55                            | 528           | 56.0   | 1.05    |
| <b>N6</b> | 50:1                     | 10                     | 5.0                   | 1.73                            | 532           | 44.2   | 0.41    |
| <b>N7</b> | 18:1                     | 30                     | 5.0                   | 2.67                            | 450           | 58.3   | 0.70    |
| <b>N8</b> | 50:1                     | 30                     | 5.0                   | 2.27                            | 465           | 45.6   | 0.48    |

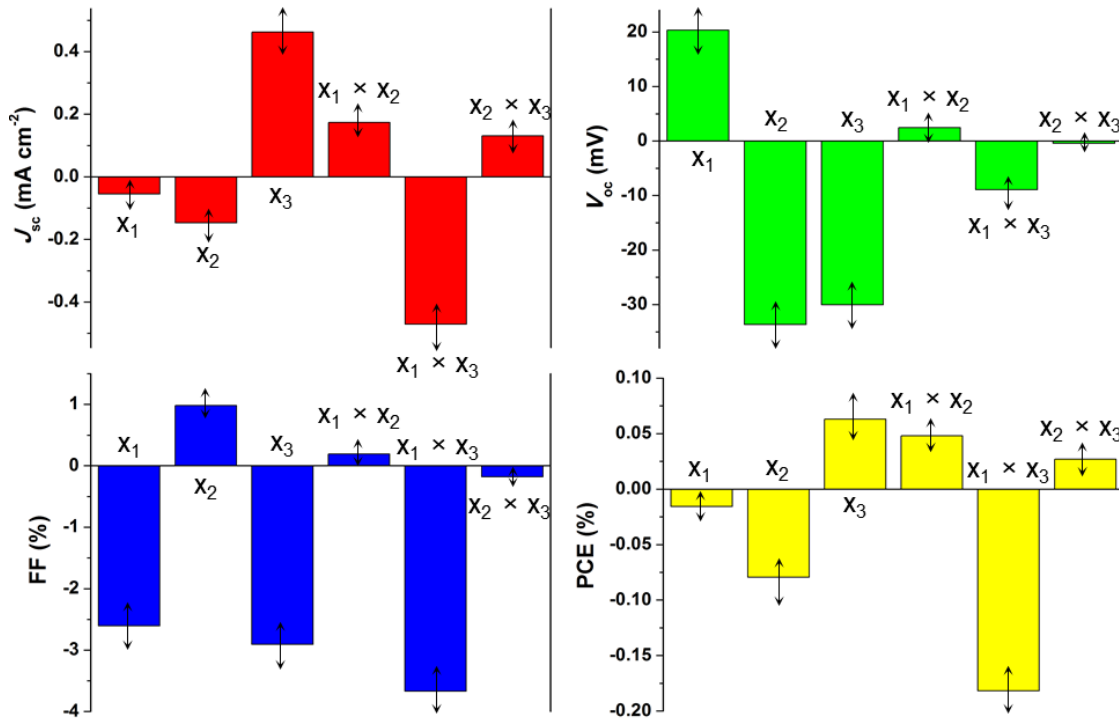
|            |      |    |     |      |     |      |      |
|------------|------|----|-----|------|-----|------|------|
| <b>N9</b>  | 34:1 | 20 | 3.0 | 0.70 | 425 | 53.4 | 0.17 |
| <b>N10</b> | 34:1 | 20 | 3.0 | 1.35 | 453 | 56.9 | 0.35 |
| <b>N11</b> | 18:1 | 10 | 1.0 | 1.56 | 549 | 55.6 | 0.48 |
| <b>N12</b> | 50:1 | 10 | 1.0 | 2.57 | 613 | 57.1 | 0.90 |
| <b>N13</b> | 18:1 | 30 | 1.0 | 1.08 | 494 | 57.3 | 0.30 |
| <b>N14</b> | 50:1 | 30 | 1.0 | 1.88 | 557 | 59.7 | 0.63 |
| <b>N15</b> | 18:1 | 10 | 5.0 | 3.47 | 502 | 56.1 | 0.98 |
| <b>N16</b> | 50:1 | 10 | 5.0 | 1.72 | 534 | 44.0 | 0.42 |
| <b>N17</b> | 18:1 | 30 | 5.0 | 2.82 | 434 | 58.2 | 0.71 |
| <b>N18</b> | 50:1 | 30 | 5.0 | 2.58 | 474 | 44.6 | 0.55 |
| <b>N19</b> | 34:1 | 20 | 3.0 | 1.12 | 463 | 56.2 | 0.29 |
| <b>N20</b> | 34:1 | 20 | 3.0 | 1.44 | 468 | 57.8 | 0.39 |

133

134 The model was fitted with the obtained experimental responses listed in **Table 1** and  
135 the *summary of fit* plot, i.e. a bar graph showing the values of the  $R^2$ ,  $Q^2$  and  
136 reproducibility parameters, is shown in **Fig. A.2 in Appendix A**. By the analysis of the  
137 data, it is evidenced that the resulting regression model provides a significant  
138 description of the relationship between the independent variables and the responses,  
139 which means an optimal analysis of the investigated photoelectrochemical system, as  
140 also shown in **Fig. A.3 in Appendix A**.

141 To figure out the most significant within all of the variables under study, a  
142 *coefficients plot* for the selected response was elaborated as shown in **Fig. 1**. We noticed  
143 that the increase in the concentration of  $I_2$  and NaI negatively affected the  $V_{oc}$ , while the  
144 opposite effect was obtained by raising CDCA concentration. On the contrary,  $J_{sc}$   
145 values increased upon NaI addition, unless when also CDCA was added in high  
146 amounts. Overall, the PCE substantially increased at increasing amounts of NaI, while  
147 decreased upon increasing the concentration of  $I_2$ . The worst situation is highlighted by  
148 the interaction coefficient  $x_1 \times x_3$ , i.e. when concentration levels of CDCA and NaI are  
149 kept both at the highest level. **Fig. 1** truly helps in identify the most relevant

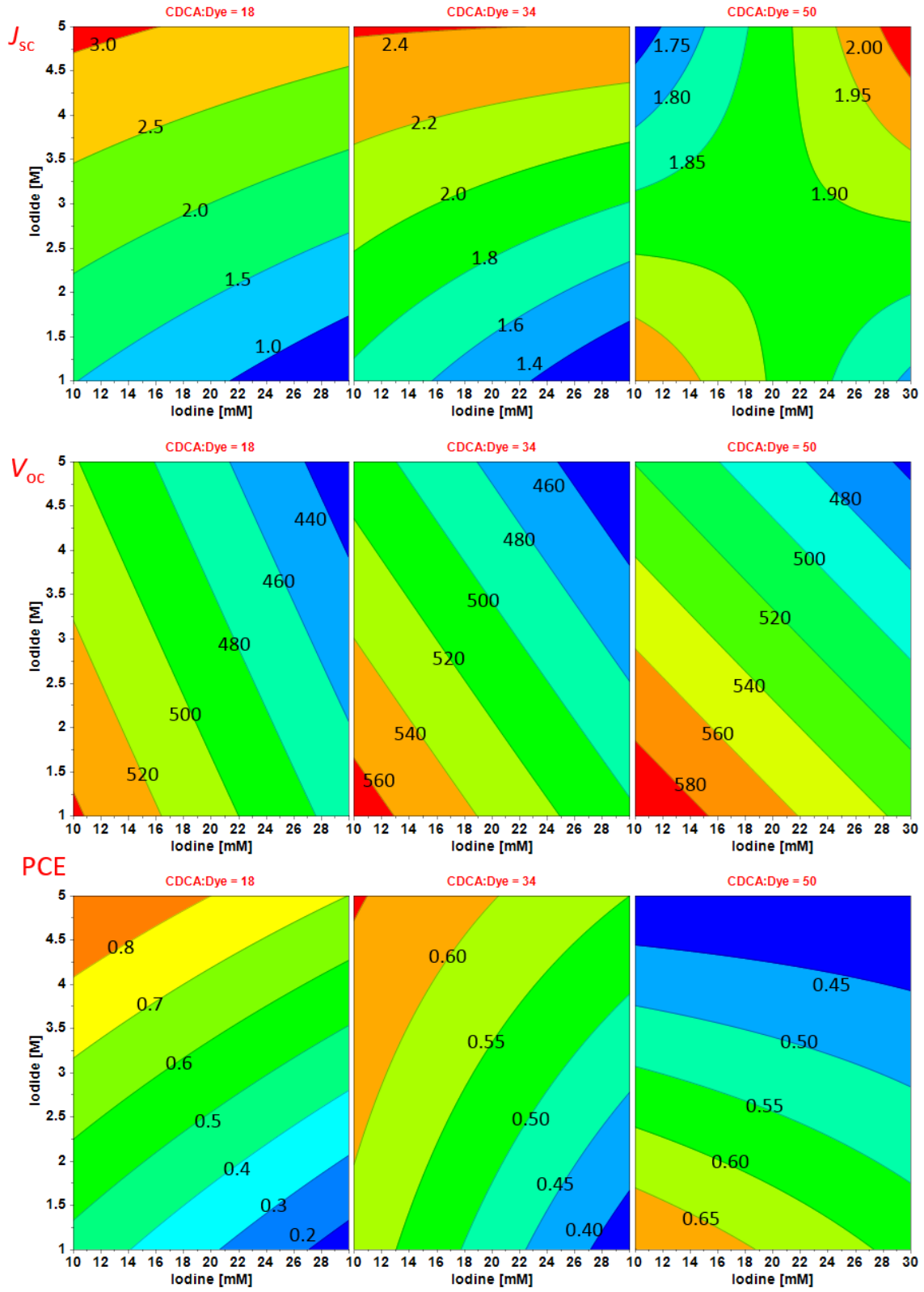
150 experimental factors affecting each of the photovoltaic parameters measured by  $J-V$   
 151 analysis.  
 152



153  
 154 **Fig. 1.** Coefficient plot for the DoE. Each plot displays the coefficients, when changing  
 155 from level 0 to a higher level, for the selected response (i.e., the photovoltaic  
 156 parameters).  
 157

158 *Contour plots* (isoresponse graphs) are shown in **Fig. 2** (for  $J_{sc}$ ,  $V_{oc}$  and PCE) and in  
 159 **Fig. A.4 in Appendix A** (for FF). They graphically show the relevance of each factor in  
 160 influencing the measured response. In particular, highest values of  $V_{oc}$  were obtained at  
 161 low concentrations of NaI and  $I_2$  ad high amount of CDCA. This was due to the  
 162 inhibition of electron- $I_2$  and electron- $I_3^-$  recombination processes usually observed in  
 163  $I_2$ -rich electrolytes (Mathew et al., 2013); moreover, it is known from Nernst equation  
 164 that an increase in NaI concentration reduces the working potential value (Fabregat-  
 165 Santiago et al., 2005).





168 **Fig. 2.** *Contour plots* of the fitted DoE considering  $J_{sc}$ ,  $V_{oc}$  and PCE as response; their  
169 values are written onto the contour lines. Values range from low (blue) to high (red)  
170 values.  
171

172

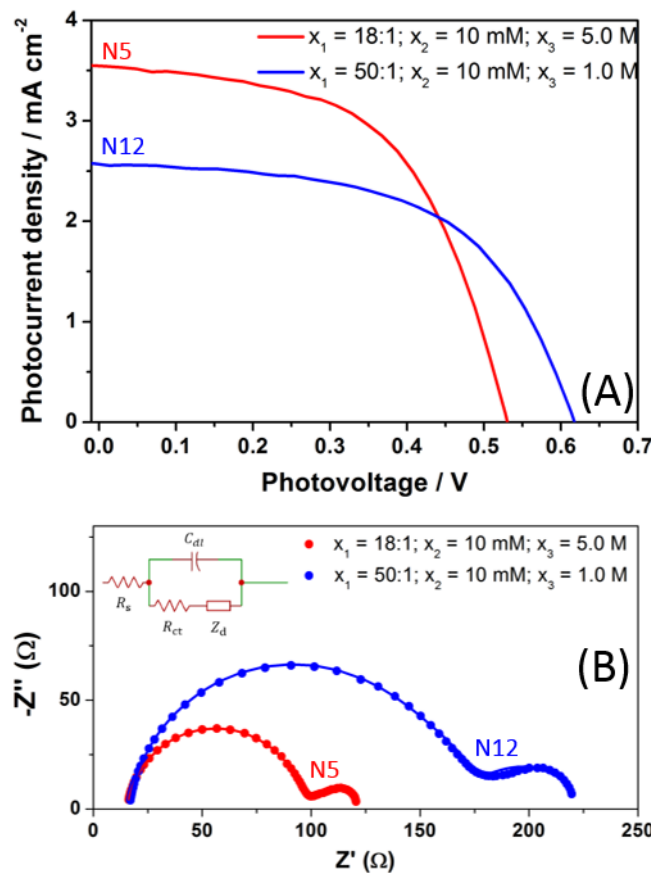
173 As regards  $J_{sc}$ , in the presence of medium-low CDCA:Dye ratios the maximum  
174 current density values were achieved at high NaI content, with a rather little effect given  
175 by the selected concentration of  $I_2$ . Conversely, at high CDCA:Dye ratios,  $J_{sc}$  trend  
176 showed two maxima: i) at low [NaI] and [ $I_2$ ], and ii) at high [NaI] and [ $I_2$ ] values,  
177 respectively. Also PCE values showed a peculiar trend, with high values obtained in the  
178 presence of low  $I_2$  and high NaI contents at medium-low CDCA:Dye ratios, while the  
179 best PCE values resulted at high CDCA levels in the presence of low concentrations of  
180 iodine species. This performance trend is basically related to the amount of dye  
181 molecules anchored at the surface of the  $TiO_2$  electrode. Actually, at low dye loading  
182 (high ratio CDCA:Dye), little amounts of iodide ions are sufficient for the regeneration  
183 of the oxidized sensitizer molecules; conversely, at low CDCA:Dye ratios, increased  
184 iodide concentration is required to enable the efficient reduction of  $Dye^+$  species.

185 *Contour plots* clearly show the advantages of the DoE approach in the rapid and  
186 effective characterisation of an electrochemical power source, highlighting that device  
187 performance can be maximized by different combinations of the same experimental  
188 parameters. **Fig. 3** shows the  $J-V$  and Nyquist plots of N5 and N12, which are the two  
189 best cells of the experimental matrix detailed in **Table 1**. Clearly, even if the two cells  
190 provided similar PCE values (1.05% and 0.90%, respectively), their figure of merits are  
191 rather different. Indeed, cell N5 shows high  $J_{sc}$ , low  $V_{oc}$ , recombination resistance ( $R_{ct} =$   
192  $82.5 \Omega$ ) and redox couple diffusion resistance ( $R_d = 23.3 \Omega$ ) as expected for DSSCs  
193 based on liquid electrolytes containing high amount of iodine species; conversely, the

194 lower redox mediator content in cell N12 leads to lower  $J_{sc}$ , higher  $V_{oc}$ ,  $R_{ct}$  (154  $\Omega$ ) and  
195  $R_d$  (44.4  $\Omega$ ).

196 In our opinion, the experimental conditions adopted for cell N12 are preferable than  
197 those of cell N5, since the use of lower amounts of dye and redox mediator would lower  
198 the final cost of the solar cell, without affecting the overall sunlight conversion  
199 efficiency.

200



201

202 **Fig. 3.** (A)  $J$ - $V$  curves and (B) corresponding Nyquist plots of aqueous DSSCs (N5 and  
203 N12 of **Table 1**) measured under 1 sun irradiation (AM 1.5G). Inset of B) represents the  
204 equivalent circuit used to fit experimental data.

205

#### 206 4. Conclusions

207 A multivariate study of photoelectrode sensitization, electrolyte formulation and  
208 interface phenomena in aqueous DSSCs has been proposed in this work. The proposed

209 approach enlightened that the concurrent evaluation of several experimental factors  
210 affecting the overall performance is fundamental to support the researchers in finding  
211 the optimal operating conditions of any new energy device with solid mathematical and  
212 statistical bases (Ccorahua et al., 2017; D'Angelo et al., 2017; Feng et al., 2017; Miao et  
213 al., 2017; Zhu et al., 2017). The lab-scale aqueous DSSCs, that were assembled based  
214 on the optimised parameters resulting for chemometrics, provided a reproducible  $\approx 1\%$   
215 sunlight conversion efficiency without the addition of additives, and can therefore be  
216 used as a solid benchmark for future studies aimed at boosting its performance.

217

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221

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