Electronic Supplementary Information

On-line monitoring and active control of dye uptake in dye-sensitized solar cells

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Experimental

Experimental set-up for real-time monitoring of dye uptake

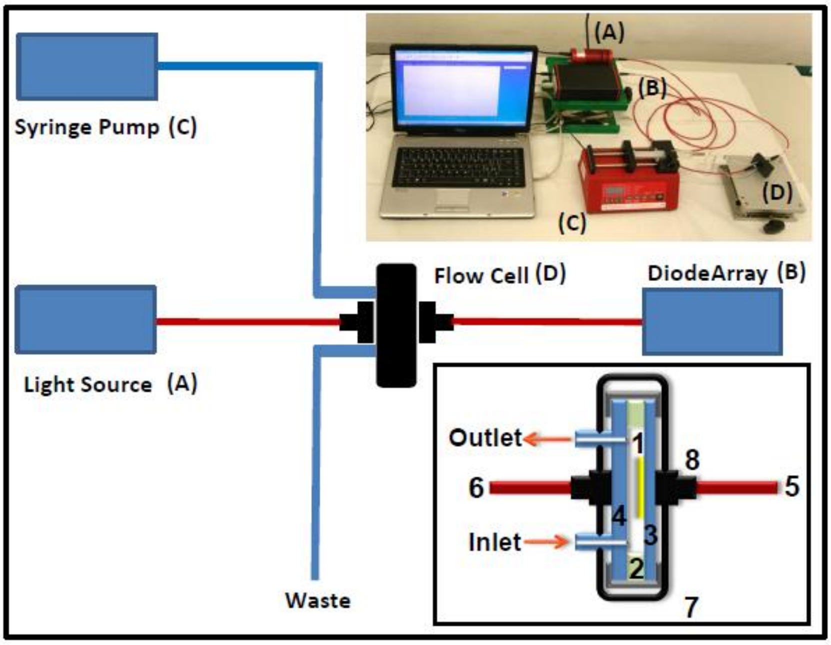

Figure S 1. Scheme of the flow-cell with an integrated UV-Vis monitoring system. In the inset a detail of the flow-cell components: 1) TiO_2 layer, 2) parafilm gasket, 3) FTO glass, 4) head of the microcell with tubings, 5) optical fiber to the spectrophotometer, 6) optical fiber to the light

source, 7) black box for shielding the flow-cell from ambient light, 8) optical lens for connection of the optical fiber to the flow-cell.

The fluidic part of the apparatus was made by using a previously reported fast prototyping procedure that exploits a commercially available photo-polymerizable, thiolene based, optical adhesive.[1][2] A “head” serving as an interface for the connection to the fluidic network is pressed against a FTO substrate carrying the TiO_2 layer by using a gasket cut in a parafilm sheet. A quick heating to ca. 60°C causes softening of parafilm that protects the flow-cell from leakages. The flow-cell is lined inside a black-plastic box carrying two built-in optical lenses that served as collimators for optical coupling the flow-cell with the light source (Avantes HL-2000-LL halogen lamp) and the UV-Vis spectrophotometer (AvaSpec-2048). A syringe pump (NE-300) is employed to flux the cell with ethanol (for conditioning the TiO_2 layer before the dyeing or removing excess dye after the sensitization) or with an ethanolic solution of the dye. The dyeing solution flows through the cell at a rate of 200 mL/min.

The real-time monitoring of dyeing process is achieved by the UV-Vis spectrometer connected to a personal computer. Data acquisition and elaboration is carried out with dedicated software (Avantes AvaSoft 7.5.3). In particular, absorption was monitored at three different wavelengths. It should be pointed that, although wavelengths corresponding to the absorption maxima of the dyes were monitored, the corresponding signals reach a saturation value (absorbance > 2.5 a.u.) well before the dyeing process is finished. Thus, absorbance was also monitored far from the absorption maxima. Since the dyeing solution is relatively diluted and the optical path of the flow cell is less than 100 mm, it is reasonable to assume that the recorded absorbance is proportional only to the dye uptake, without any need of considering the contribution of the dye in solution.

Device assembling and photovoltaic characterisation

Photoanodes were prepared by tape casting high transparent TiO_2 paste (T-nanoxide HT Solaronix, nominal particle diameter 9 nm) onto fluorine tin oxide coated glasses. Photoanodes were then fired at 450°C for 30 minutes.

Solar cells were prepared assembling the sensitised TiO_2 photoanodes with a Pt sputtered counteranodes and then sealed with 25μm thick plastic spacer. Voids inside the cells were filled by capillarity with the I^-/I_3^- redox couple electrolyte (Iodolyte AN-50 Solaronix).

Functional properties were investigated under simulated sun light irradiation using an ABET 2000 solar simulator at AM1.5G (100 mW·cm^{-2}).

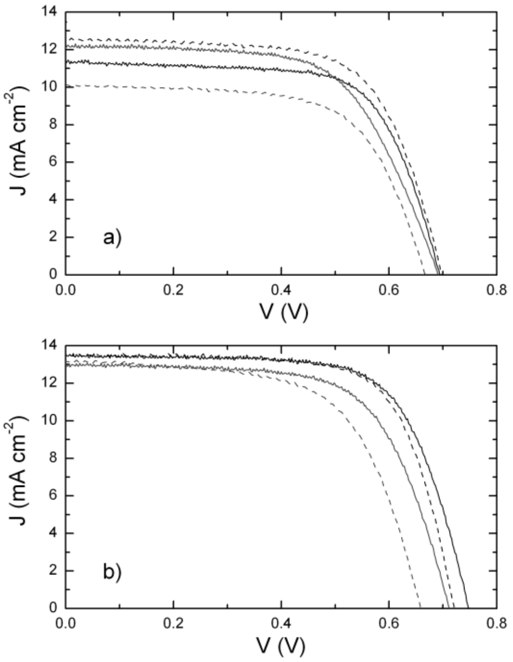

Figure S 2. Current-Voltage (*J-V*) curves. Comparison between the *J-V* curves of the cells reported in Table 1 in the text sensitized by different methods (static sensitization black lines, dynamic sensitization red lines) and different dye concentrations (5.0mM dye concentration solid lines, 0.5mM concentration dashed lines). (a) Characteristics of the cells sensitized with N3, (b) characteristics of the cells sensitized with N719.

Dye loading quantification

Absorption measurements were carried out in a T80 PG Instruments spectrophotometer using 1-cm quartz cells.

After the complete removal of adsorbed dye from oxide surface by washing with a 0.1 M NaOH aqueous solution, dye loading was determined by ultra-violet-visible (UV-Vis) spectrophotometry by comparison with calibrated solutions.

Infrared spectroscopy

Diffuse reflectance infrared Fourier transform spectra were collected on a Bruker VERTEX70v spectrometer (accumulating 32 scans at a resolution of 2 cm^{-1}) using a

MCT detector cooled with liquid nitrogen and displayed in the Kubelka-Munk unit.[3][4] Samples were analysed after removing the whole photoanode from the TCO-glass, mixed with KBr and loaded in the accessory for diffuse reflectance (Harrick Scientific); KBr was used as a background.

Dye coordination with titania surface has been evaluated by means of infrared spectroscopy.

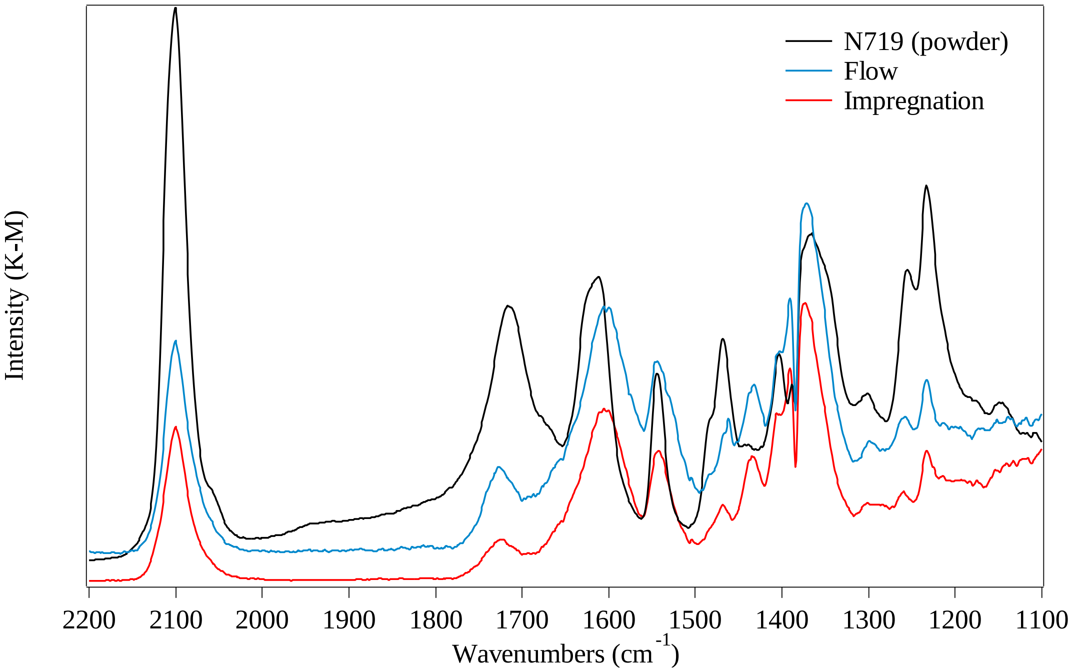

Figure S 3. DRIFT spectra of dye N719 (black line), dye sensitized photoanodes: dynamic (blue line) and static (red line).

Vibration Mode	**N719 (cm^{-1})**	**Photoanode (impregnation) (cm^{-1})**	**Photoanodes (flow) (cm^{-1})**
νSCN	2101	2100	2100
νC=O	1715 s	1725 m	1726 m
Bi-Py Ring stretching modes + ν_{asym} O-C-O	1624, 1613 (sh), 1545	1606, 1542, 1468	1606, 1544, 1484 (sh), 1466
δC-H(NBu_4^+)	1468	1468	1468
ν_{asym} O-C-O		1606	1606
TiO_2 vibration mode	----	1390	1390

ν_{sym} O-C-O	1367 (sh), 1358	1373	1372
ν C-O	1255, 1233 (doublet)	1260, 1233	1258, 1233

Table S 1. Infrared correlation table for N719 and related photoanodes. Abbreviations: ν (stretching); δ (bending); s (strong), m (medium), w (weak), sh (shoulder).

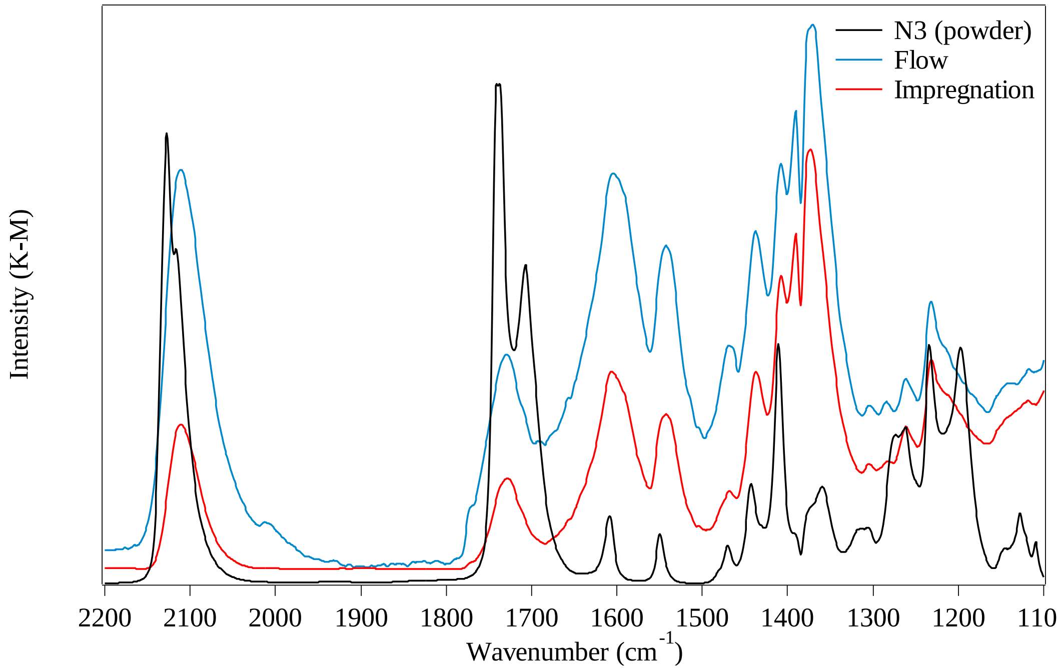

Figure 1. DRIFT spectra of dye N3 (black line), dye sensitized photoanodes: dynamic (blue line) and static (red line).

Vibration Mode	**N3 (cm^{-1})**	**Photoanode C (impregnation) (cm^{-1})**	**Photoanode A (flow) (cm^{-1})**
νSCN	2128, 2117 (doublet)	2112	2112
νC=O	1741, 1707 (doublet)	1727	1731
Bi-Py Ring stretching modes	1608, 1549, 1443	1605, 1543, 1438	1605, 1543, 1438
δC-H(NBu_4^+)	1470 (w)	1470 (w)	1470 (w)
TiO_2 vibration mode	----	1390	1390

ν_{asym} O-C-O	---	1605	1599
ν_{sym} O-C-O	1358 (w)	1367	1368
ν C-O	1276, 1261(sh), 1234	1261, 1232	1263, 1232

Table S 2. Infrared correlation table for N3 and related photoanodes. Abbreviation list: ν (stretching); δ (bending); s (strong), m (medium), w (weak), b (broad), sh (shoulder), v (very).

For both the dyes, ν_{asym} CO_2 and ν_{sym} CO_2 are shifted by coordination in opposite directions, being the first one gently pushed toward lower wavenumbers while the second one toward higher wavenumbers. This indicates that both dyes, irrespectively from the sensitisation technique, coordinate the TiO_2 surface in an asymmetric chelating or bridging configuration.

[1] T. Carofiglio, P. Donnola, M. Maggini, M. Rossetto and E. Rossi, Adv. Synth. Catal., 2008, 350, 2815.

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[4] G. Kortüm, Reflectance Spectroscopy, Springer, New York, 1969.