

## Electronic Supplementary Information

Ultra-fast dye sensitisation of single or multiple dyes for Dye Sensitized Solar Cells

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This paper describes a method for ultra-fast dye sensitization of metal oxide photo-electrodes which can be achieved in under 5 minutes using small volumes of dye solution in a very controlled manner. This method has successfully been applied to dyeing with single dyes (e.g. N719 and SQ1). Importantly, this procedure has also been successfully applied to dyeing with more than one dye within a single photo-electrode in a simple and reproducible manner.

This ESI includes details of the methods used, details of the DSC devices prepared to illustrate the success of the method and also examples of the IV testing data for these DSC devices.

## Experimental

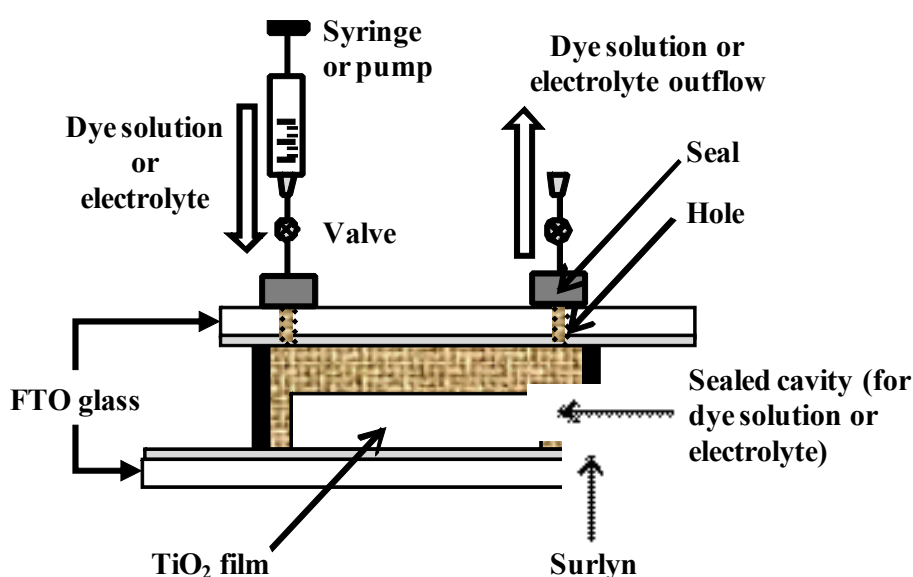
### Device manufacture

Photo-electrodes ( $0.5 \times 2 \text{ cm} = 1.0 \text{ cm}^2$ ) were prepared by doctor blading two layers of transparent titania colloid (DSL18NRT, Dyesol) followed by one layer of scattering titania colloid (WER4-O, Dyesol) onto fluorine tin oxide-coated glass (TEC15,  $15 \Omega \square^{-1}$ ). Each  $\text{TiO}_2$  layer was calcined at  $450^\circ\text{C}$  for 30 mins and also immersed in  $\text{TiCl}_4:\text{THF}_2$  in deionised water (50 mM) at  $70^\circ\text{C}$  for 30 mins, rinsed with de-ionised water, air-dried for 10min and re-sintered at  $450^\circ\text{C}$  for 30 mins.

Dyeing was carried out using one of two methods. For passive dyeing, after final sintering of the photo-electrode, this was allowed to cool to  $50\text{-}70^\circ\text{C}$  and then submersed in dye solution for 18 hours. Dye solutions containing N719, di-*tert* butyl pyridyl *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)dithiocyanato ruthenium(II), were prepared in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol (0.5 mM). Dye solutions containing SQ1 (5 mM) and

chenodeoxyxholic acid (5 mM, Aldrich) were prepared in ethanol. N719 dye was used as purchased from Dyesol. SQ1 was prepared as described in the literature (A. Burke, L. Schmidt-Mende, S. Ito and M. Grätzel, *Chem. Commun.*, 2007, 234). After dyeing, a Surlyn<sup>®</sup> (Du Pont) gasket was placed around the photo-electrode and a Pt-coated TEC 8 ( $8 \Omega \square^{-1}$ ) counter electrode which had been treated with Pt paste (PT1, Dyesol) and heated to 400 °C was placed on top and the two electrodes sealed together at 120 °C. For the passive dyed N719 device, electrolyte containing iodine/tri-iodide ( $I_2$  100 mM in distilled 3-methoxypropionitrile) was added through a hole in the counter electrode which was then sealed using Surlyn<sup>®</sup>. For the passive dyed SQ1 device, the electrolyte described by Grätzel *et al.* (A. Burke, L. Schmidt-Mende, S. Ito and M. Grätzel, *Chem. Commun.*, 2007, 234) was used.

In the fast dyeing method, the titania photo-electrode was prepared in the same manner. However, before dyeing, a Surlyn<sup>®</sup> (Du Pont) gasket was placed around the photoelectrode and a Pt-coated counter electrode, prepared as before, was placed on top and the electrodes were sealed together at 120 °C. Dye solutions were then pumped through the device cavity either individually, sequentially or as a dye solution mixture through a hole in the counter electrode for between 5 and 10 minutes at 50 °C. After cooling to room temperature, iodine/tri-iodide electrolyte ( $I_2$  100 mM in distilled 3-methoxypropionitrile) was then pumped into the cell cavity within 5 mins of the dye(s) and the holes sealed using Surlyn<sup>®</sup> (Du Pont).



**Figure 1** Schematic of the design of the dye-sensitised solar cell used in these studies from side view showing pumping procedure

## Device Examples

### Device A

A titania photo-electrode was submerged in a acetonitrile:tertiary butanol (1:1 v/v) solution containing N719 ( $5 \times 10^{-4}$  M) for a period of 18 hours. The electrode was then removed from the dye solution and the cell was constructed as described for passive dyeing.

### Device B

A titania photo-electrode was submerged in an ethanol solution containing SQ1 ( $1.075 \times 10^{-4}$  M) and CDCA (5 mM) for a period of 18 hours. The electrode was then removed from the dye solution and the cell was constructed as described for passive dyeing.

### Device C

1 ml of N719 dye in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol (8.6 mM) was pumped through the DSC cell over a period of 5 minutes at a temperature of 50 °C followed by electrolyte at ambient temperature.

### Device D

1 ml of a mixture of SQ1 (5 mM) and CDCA (5 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by electrolyte at ambient temperature.

### Device E

A titania photo-electrode was submerged in a solution comprised of both N719 and SQ1-CDCA (1:1 v/v) and dyed for a period of 18 hours. For N719, this dye was dissolved in acetonitrile:tertiary butanol (1:1 v/v) to give a concentration of  $5 \times 10^{-4}$  M. For SQ1-CDCA, the dye and so-sorbent were dissolved in ethanol to give a solution containing SQ1 ( $1.075 \times 10^{-4}$  M) and CDCA (5 mM) solutions. After dyeing, the electrode was removed from the dye solution and the cell was constructed as described above for passive dyeing.

### Device F

1 ml of N719 dye in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol (8.6 mM) was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by the addition of 1 ml of a mixture of SQ1 (5 mM) and CDCA (5 mM) in ethanol, also pumped

for 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

#### Device G

1 ml of a mixture of SQ1 (5 mM) and CDCA (5 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 mins at a temperature of 50 °C followed by the addition of 1 ml of N719 dye in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol (8.6 mM), also pumped for 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

#### Device H

1 ml of 5 mM SQ1 dye (without CDCA) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C followed by the addition of 1 ml of N719 dye in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol (8.6 mM), also pumped for 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

#### Device I

2 ml of a 1:1 v/v mixture of N719 (8.6 mM) in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol) and SQ1 (5 mM) and CDCA (5 mM) in ethanol was pumped through the DSC cell cavity over a period of 10 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

#### Device J

2 ml of a 1:1 v/v mixture of N719 (8.6 mM) in a 1:1 mixture of acetonitrile/*tert*-butyl alcohol) and SQ1 (5 mM) and CDCA (5 mM) in ethanol was pumped through the DSC cell cavity over a period of 5 minutes at a temperature of 50 °C. The electrolyte was added straight after the dye solutions at ambient temperature.

### Device Testing

Current-voltage characteristics were measured using a Universal Photovoltaic Testing System (UPTS, Dyesol) at 100 mW cm<sup>-2</sup> or 1 Sun between 0 and 1 V (see Table 1 and Figure 2). For comparison, selected devices were also measured using an Oriel Sol3A (94023A) utilising a Xenon arc lamp (150 W), an AM1.5 filter and a Keithley 2400 source meter (Table 2)

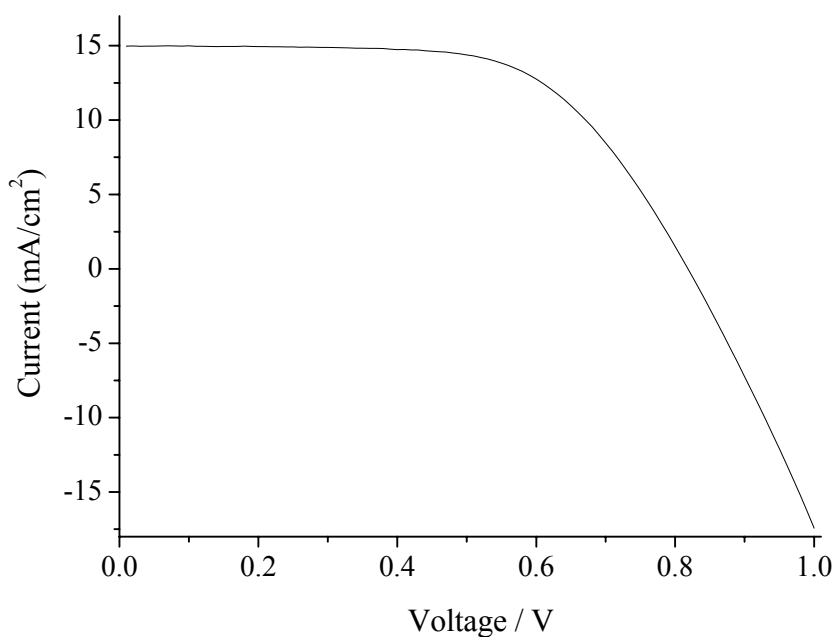
showing slightly different efficiencies but similar trends in the data. A certified (Oriel 91150V) monocrystalline silicon reference cell traceable to the National Renewable Energy Laboratory (NREL) was used to adjust the solar simulator to one sun ( $100 \text{ mW cm}^{-2}$ )

**Table 1** IV testing data measure at 1 Sun ( $100 \text{ mW cm}^{-2}$ ) on Dyesol UPTS testing system at Bangor University

Device	$\eta$ / %	Fill factor	$J_{sc} / \text{mA cm}^{-2}$	$V_{oc} / \text{V}$
A	6.4	0.62	14.2	0.73
B	2.9	0.57	9.0	0.56
C	6.0	0.69	11.1	0.79
D	3.7	0.67	8.1	0.68
E	5.2	0.59	12.1	0.69
F	5.3	0.51	14.6	0.71
G	7.5	0.60	16.1	0.78
H	4.9	0.55	12.4	0.71
I	7.0	0.58	15.7	0.77
J	7.9	0.63	15.0	0.82

**Table 2** IV testing data for selected devices measure at 1 Sun ( $100 \text{ mW cm}^{-2}$ ) on Oriel Sol3A testing system at Swansea University

Device	$\eta$ / %	Fill factor	$J_{sc} / \text{mA cm}^{-2}$	$V_{oc} / \text{V}$
A	5.7	0.65	11.4	0.78
B				
C	6.0	0.64	12.1	0.78
D	2.1	0.66	4.6	0.69
E	5.2	0.70	10.5	0.70
F				
G	6.3	0.66	12.5	0.76
H				
I	6.0	0.64	12.2	0.77
J	6.5	0.64	12.9	0.8



**Figure 2** I-V curve data for Device J dyed by pumping a 1:1 (v/v) solution of SQ1-CDCA and N719 for 5 min (device measured at 1 Sun, 100 mW cm<sup>-2</sup> on Dyesol UPTS testing system at Bangor University)

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