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## COMMUNICATION

## *In situ* monitoring and optimization of room temperature ultra-fast sensitization for dye-sensitized solar cells

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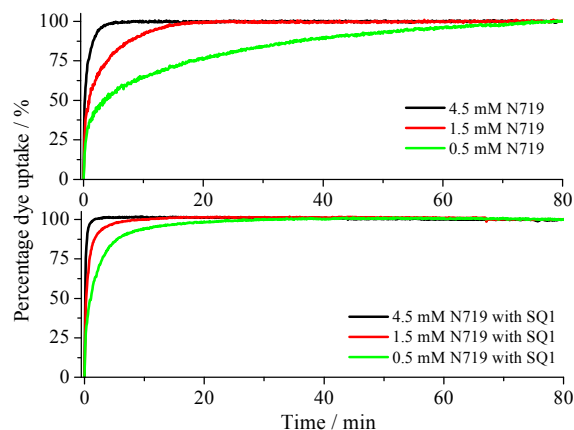
We describe the fastest dyeing of TiO<sub>2</sub> photo-electrodes for dye-sensitized solar cells reported to date (< 2 min) at room temperature giving  $\eta = 7.5\%$  for an N719/SQ1/CDCA mixture which is significantly higher than devices dyed for > 12 h using the same dye mixture ( $\eta = 5.5\%$ ). Time-lapse photography has been used to monitor the ultra-fast co-sensitization. The data show significantly different dye uptake between passive and pump dyeing reflecting competitive sorption between a Ru complex (N719) and an organic dye (SQ1).

The lower embodied energy and cheaper raw materials of dye sensitised solar cells (DSCs) makes them a potential competitor technology for Si photovoltaics but only if DSC device efficiency is improved and manufacturing processes are speeded up. In 1991, O'Regan and Grätzel made a key breakthrough in increasing DSC efficiencies by sensitizing nano-particulate TiO<sub>2</sub>, leading to higher surface area, dye loading and photocurrent<sup>1</sup>. Since then, research has focussed on increasing DSC device efficiency and stability to accelerate DSC commercialisation. This has, in part, focussed on improving the dye loading and light scattering of the TiO<sub>2</sub> layer<sup>2,3</sup> and the molecular engineering of new dyes, with the latter leading to a record efficiency for DSC ( $\eta = 13\%$ )<sup>4</sup>. A key challenge that remains for DSC is the development of rapid and scalable device processes that are compatible with continuous (roll-to-roll) processing<sup>5</sup>.

In this context, the dye sensitization of meso-porous TiO<sub>2</sub> photo-electrodes is the slowest process in DSC manufacture; typically taking 8-24 h by passive (immersion) dyeing<sup>3</sup>. Early methods to accelerate dyeing focussed on single dyes and included pumping N719 solution through DSC devices for 30-60 min under reflux<sup>6,7</sup> or rapid dipping of TiO<sub>2</sub> films in dye solution<sup>8</sup>. Co-sensitizing multiple dyes to improve device efficiencies has also been reported but using slow dyeing procedures<sup>9,10</sup>. We have combined these approaches and reported the first examples of ultra-fast co-sensitization (5 min) by pumping single or mixed dye solutions of either N719 and SQ1 with chenodeoxycholic acid - CDCA ( $\eta = 7.9\%$ )<sup>11</sup> or a triphenylamine

dye and N719 ( $\eta = 7.5\%$ )<sup>12</sup> or half-squaraine and squaraine dyes<sup>13</sup> through the device cavity at temperature. Recently we have also reported ultra-fast dyeing/desorption/re-dyeing procedures to control dye loading by selectively desorbing and replacing dyes<sup>14</sup>. Here we have focussed on room temperature (RT) dyeing, with dye uptake monitored via time-lapse photography, investigating the possibility of saturating a photo-electrode in a few minutes at RT.

Measuring dye loadings has typically been carried out by *ex situ* alkali desorption<sup>15</sup>. However, *in situ* measurements of dye loading are required to study dye uptake in real time. This has been achieved using either diffuse reflectance UV-visible spectroscopy or time-lapse digital photography and image analysis<sup>16</sup>. To date, this has been used to monitor passive N719 dye uptake over a period of hours by studying the underside of a TiO<sub>2</sub> electrode. In this paper, we report the first examples of *in situ* studies of ultra-fast co-sensitization of meso-porous TiO<sub>2</sub> photo-electrodes and the first insights into competitive dye sorption in the first minutes of dye uptake.



**Fig.1** Percentage dye uptake for 0.5-4.5 mM N719 (top graph) and N719/SQ1/CDCA (bottom graph) over 80 min. For the N719/SQ1/CDCA mixes the concentrations of the dyes are 0.5 mM N719/1.3  $\mu$ M SQ1, 1.5 mM/3.8  $\mu$ M SQ1 and 4.5 mM/11.3  $\mu$ M SQ1 with a CDCA concentration of 1.67 mM in all cases. Data extracted from images taken every 5 s.

**Table 1.** Saturation times for 17  $\mu\text{m}$   $\text{TiO}_2$  electrodes with selected dyes at room temperature using passive or fast dyeing. The CDCA concentration is 1.67 mM.

Dye(s)	Dye conc.		Saturation time/min	
	N719/ mM	SQ1/ $\mu\text{M}$	Fast dyeing	Passive dyeing
N719	0.5	-	77.3	504
	1.5	-	27.0	
	4.5	-	8.3	
N719/SQ1/CDCA	0.5	1.3	38.0	132
	1.5	3.8	9.8	
	4.5	11.3	1.8	
SQ1/CDCA	-	50.0	5.4	162

Our approach has been to analyse the RGB values of digital images with time and to present these data as % dye loading *versus* dye saturation. Fig. 1 shows sorption data for pump dyed N719 solutions showing dye saturation taking place between *ca.* 5 and 80 min. Extracting dye saturation data (Table 1) shows that pump dyeing N719 gives rise to significantly faster dye saturation compared to passive dyeing; e.g. at 0.5 mM N719 fast dyeing takes 77.3 min compared to 504 min by passive dyeing. Table 1 also shows that increasing the N719 concentration by nine times (0.5 to 4.5 mM) also accelerates dye saturation by *ca.* nine times (77.3 to 8.3 min). Increasing N719 concentration by three times (0.5 mM to 1.5 mM) accelerates dye saturation by *ca.* three times (77.3 to 27.0 min). These data suggest a linear relationship between dye concentration and saturation time which, in turn, suggests that the rate of ultra-fast pump dyeing of N719 as a single dye is only limited by dye concentration. An even greater acceleration in dyeing time is observed for 50  $\mu\text{M}$  SQ1 with 1.67 mM CDCA from passive to fast dyed (162 to 5.4 min). Table 1 also shows much faster dyeing (either by passive or pump dyeing) for SQ1 than N719.

Interestingly, Table 1 shows that passive and fast dye saturation times are significantly accelerated even further when SQ1 and CDCA are added to the N719 solution. For example, for 0.5 mM N719, adding 1.3  $\mu\text{M}$  of SQ1 and 1.67 mM CDCA reduces passive dyeing time by almost four times (504 to 132 min) and halves the fast dyeing time (77.3 to 38.0 min). Increasing the dye concentrations to 4.5 mM N719 and 11.3  $\mu\text{M}$  SQ1 reduces the dye saturation time to 1.8 min which brings dye sensitization within the realms of scaleable roll-to-roll processing.

Table 2 shows I-V testing data for passive and fast dyed DSC devices and shows lower  $\eta$  for passive dyed devices using either N719 or N719/SQ1/CDCA when compared to the pump dyed system. The latter shows slightly higher  $J_{\text{sc}}$  attributed to improved light harvesting efficiency due to dye loading but lower  $V_{\text{oc}}$  presumably due to increased recombination due to non-optimised dye loading. By comparison, fast dyeing N719/SQ1/CDCA in *ca.* 2 min shows the highest efficiency ( $\eta = 7.5\%$ ) in line with the highest  $J_{\text{sc}}$  and comparable  $V_{\text{oc}}$  to the passive dyed N719 device (ESI Fig.3). The high  $J_{\text{sc}}$  is attributed to the presence of CDCA, which reduces dye aggregation<sup>17</sup>. It is clear that *via* the fast-dyeing pump method there is an optimised loading of N719/SQ1/CDCA that is difficult to achieve *via* passive dyeing consistent with previous reports.<sup>11</sup> EQE data for the N719/SQ1/CDCA fast dyed device and the N719 passively dyed device are given in ESI Fig.4. These data highlight the enhanced spectral response from the co-sensitized device.

To begin to understand the reasons behind the increase in the rate of dyeing in the presence of SQ1, it is useful to remember that pure SQ1 exhibits faster dye uptake than pure N719 (Table 1). For the N719/SQ1 combination, it might be expected that both dyes chemisorbing in a competitive environment might either exhibit a combined saturation time between that of pure N719 and SQ1 or that competitive sorption might slow the overall process. Alternatively, the two dyes might sorb independently. What is surprising is that the combination of N719 and SQ1 results in more rapid dye uptake. This suggests that there is a beneficial interaction by having the two dyes simultaneously in contact with the  $\text{TiO}_2$ . This phenomenon occurs in the N719/SQ1/CDCA system during both passive and pump dyeing suggesting that the beneficial interaction is independent of “through-film” diffusion and instead is more closely related with the dyes at the  $\text{TiO}_2$  surface.

**Table 2.** Photovoltaic performance of DSC devices dyed using either passive or rapid dyeing. The concentrations of the dye solutions are 4.5 mM N719 and 4.5 mM N719 with 11.3  $\mu\text{M}$  SQ1 and 1.67 mM CDCA. The data is an average from at least 5 devices; the statistical spread of the data is given in ESI Fig.5.

Device	Dye time	$\eta/\%$	FF	$J_{\text{sc}}/\text{mA cm}^{-2}$	$V_{\text{oc}}/\text{V}$
Passive dyed					
N719	18 h	6.1	0.66	12.08	0.77
N719/SQ1/CDCA	18 h	5.5	0.61	12.72	0.70
Pump dyed					
N719/SQ1/CDCA	2 min	7.5	0.59	16.63	0.77

To study the roles of the individual components on the rate of dyeing, dye saturation times have been recorded for various mixtures of N719, SQ1 and CDCA which have been sequentially pump dyed through a DSC device cavity in different orders (Table 3). The data show similar saturation times (*ca.* 41  $\pm$  3 min) for N719 either in a mixed solution with SQ1 or CDCA or with a pre-wash of either SQ1 or CDCA. However, pre-washing the  $\text{TiO}_2$  surface with SQ1 and CDCA in combination halves the dyeing time to 19 min.

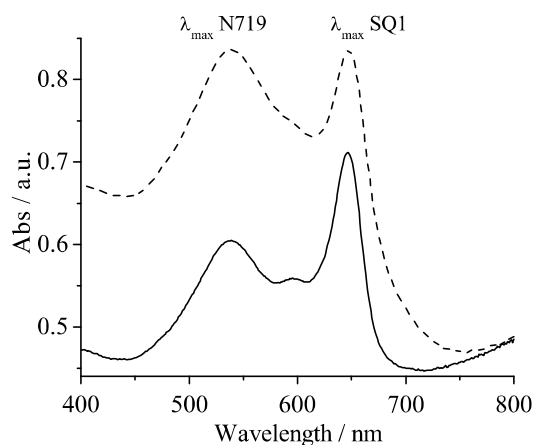
**Table 3.** Saturation point times for 1 mM N719 with 2.5  $\mu\text{M}$  SQ1 or 1.67 mM CDCA as additives or with selected surface pre-treatments of the  $\text{TiO}_2$ .

Dye system	Pre-wash	Saturation time/min
N719/SQ1	None	39
N719/CDCA	None	42
N719	SQ1	39
N719	CDCA	44
N719	SQ1/CDCA	19

In considering why the combination of SQ1 and CDCA causes an increase in dye loading, it is first necessary to consider whether it is possible to decipher individual colour components from the multiply-dyed  $\text{TiO}_2$  surfaces. In this case, N719 and SQ1 have overlapping dye bands between *ca.* 580-650 nm making it difficult to separate out signals for the individual dyes. However, it is known that squaraine molecules have a very strong tendency to aggregate and that CDCA can be used to reduce SQ1 aggregation on  $\text{TiO}_2$  surfaces<sup>17</sup>. In ESI Fig.6 the diffuse reflectance UV of  $\text{TiO}_2$  films saturated with SQ1 and SQ1/CDCA are shown. The data show the clear difference in the presence of CDCA with a higher and narrower

absorption band with CDCA due to less aggregated SQ1 molecules. Thus, there will be significant differences between the surfaces pre-washed with solely SQ1 or CDCA on their own and an SQ1/CDCA mixture. The surfaces are likely to be dominated with aggregated SQ1 molecules or not sorbed SQ1 molecules when CDCA is not used. Reducing SQ1 aggregation produces a more optimal spatial arrangement for N719 sorption and only the SQ1/CDCA surface will exhibit segregated SQ1 molecules. This has a number of effects that may increase the probability of N719 adsorption; (i) the surface charge will be reduced because the SQ1 and CDCA molecules will have chemisorbed to some surface hydroxyls on the TiO<sub>2</sub>, (ii) evenly segregated, pre-sorbed molecules reduce the TiO<sub>2</sub> surface tension, which helps bring the N719 solution into more consistent contact with the surface. Contact angle measurements show that there is a lower surface tension when the surface is pre-sorbed with SQ1/CDCA (ESI Fig.7). There is significantly improved wetting of N719 on SQ1/CDCA/TiO<sub>2</sub> when compared to bare TiO<sub>2</sub>.

Having shown that SQ1 saturates TiO<sub>2</sub> more rapidly than N719 and that an SQ1/CDCA pre-wash accelerates N719 sorption, colour image analysis of a mixed N719/SQ1/CDCA solution (1.5 mM/3.8  $\mu$ m/1.67 mM, respectively) shows that the initially white TiO<sub>2</sub> becomes blue after 20 s of dyeing indicating much faster SQ1 uptake compared to N719 (ESI Fig. 8). However, after 1 h, the purple colour indicates significant N719 sorption as well. This is confirmed by DRUV of a passive dyed N719/SQ1/CDCA system (Fig. 3) which shows that initially ( $t \leq 5$ min) the absorbance ratio N719:SQ1 is *ca.* 1:2, whilst at saturation of the TiO<sub>2</sub> electrode ( $t > 10$  h) this absorbance ratio is 1:1. This suggests that the mechanism of dye sorption from the mixed N719/SQ1/CDCA solution may be similar to the step-wise SQ1/CDCA followed by N719 process with initial SQ1/CDCA sorption giving rise to secondary N719 sorption (but which is more rapid than for N719 solution alone).



**Fig. 3** Diffuse reflectance UV of N719/SQ1/CDCA (at concentrations of 1.5 mM/ 3.8  $\mu$ m/ 1.67 mM respectively) dye sorption to a TiO<sub>2</sub> electrode with time. The spectrum at  $t \leq 5$ min (solid line) exhibits a higher SQ1:N719 absorbance ratio than the saturated electrode at  $t > 10$  hours (dashed line).

In summary, we have shown that it is possible to saturate a photo-electrode in less than 2min with a combination of N719/SQ1/CDCA producing high efficiency devices. Time-lapse photography and image analysis can be used to study ultra-fast dye sensitization onto meso-porous TiO<sub>2</sub> photo-electrodes in real time for single dye

dyeing, sequential dyeing and mixed dye co-sensitization. These data have been used to understand the mechanism of dye uptake in a multiple component system. The time-lapse method can also measure dye uptake with almost any chosen time resolution from seconds to hours and on a range of length scales making it suitable for in-line measurements for quality control of DSC by roll-to-roll manufacturing. The time-lapse method is cost effective relative to other methods to measure dyeing kinetics such as nanoplasmonic sensing<sup>18,19</sup> or quartz crystal micro-balance with dissipation (QCM-D)<sup>20</sup>.

## Notes and references

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† Electronic Supplementary Information (ESI) available: Device manufacture details, time-lapse and DRUV methods for measuring dye uptake, device characterisation details, I-V and EQE data and digital images of dyed TiO<sub>2</sub> electrodes at different stages of the dyeing process. See DOI: 10.1039/b000000x.

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