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## COMMUNICATION

## Supercritical carbon dioxide as a solvent for deposition of a tailored dye in dye sensitized solar cells<sup>†</sup>

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We report a new technique whereby dyes can be deposited onto metal oxide surfaces using supercritical carbon dioxide  $(scCO_2)$  for use in solar cell applications. This process eliminates the need for hazardous organic solvents and waste solvents generated during the dyeing process. The solubility of a perylene anhydride dye in  $scCO_2$  is enhanced by the incorporation of fluorinated alkyl subsituents and the use of masked carboxylic binding groups. This allows fast deposition of the dye onto the TiO<sub>2</sub> photoanode, resulting in efficient photovoltaic performance. The unreacted dye is then easily recovered in a solid form after the deposition process by venting the carbon dioxide.

Supercritical carbon dioxide (scCO<sub>2</sub>) is a non-toxic and nonflammable fluid that has received much attention as a green alternative to organic solvents.1-5 From an industrial perspective, scCO<sub>2</sub> is readily accessible at moderate pressures and temperatures (7.38 MPa and 31.1 °C). A major focus has been identifying systems that are readily amenable to scCO<sub>2</sub> conditions.<sup>5</sup> The current use of scCO<sub>2</sub> has been directed at small molecule synthesis,6,7 materials extraction (e.g. caffeine),8 materials loading,<sup>9,10</sup> catalysis,<sup>2</sup> and polymerization.<sup>11-13</sup> Recently there has been interest in the possible application of this medium to the field of organic electronics.<sup>14,15</sup> However, apart from deposition of fluoropolymers for photolithographic patterning<sup>16</sup> and surface treatment of dye-sensitized solar cell (DSSC) photoanodes<sup>17</sup> and quantum dots<sup>18</sup> with inorganic precursors, which have all shown encouraging results, this area remains under-explored with respect to the processing of small organic electronic materials.

Since their discovery by O'Regan and Grätzel,<sup>19</sup> DSSCs have become one of the most promising options as a cheap, nonsilicon-based device for harnessing solar energy. The system is based on the separation of a n-type material [*e.g.* mesoporous titanium dioxide (TiO<sub>2</sub>)], from a p-type system (*e.g.* consisting of the redox electrolyte or hole transport material) by a light harvesting dye that is self-assembled onto this metal oxide surface.<sup>20</sup>

Early dyes were based on ruthenium complexes, but recent research has focused on the development of new organometallic and organic dyes that exhibit superior spectroscopic and electronic properties.<sup>21,22</sup> Although many of the desirable electronic and structural features may be designed into the dye component, recent studies have shown the solvent<sup>23,24</sup> used to deposit the dye on the metal oxide surface can have a crucial impact on cell performance. For instance, Yang, Hagfeldt, Sun and coworkers23 have reported that the dye solvent influences the formation of dye aggregates in solution and on the metal oxide surface, the dye binding kinetics, variation in the functional group binding mode, overall dye loading and dye soaking times.<sup>23,25-28</sup> Although a range of solvents (e.g. EtOH, CH<sub>3</sub>CN, THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMF, DMSO and solvent combinations) can be evaluated in the laboratory, the approach is still very empirical and may not be ideal for industrial processes. Manufacturing parameters, such as cost, toxicity, flammability, scale, solubility, dye recovery and waste disposal need to be considered. In particular, there is a need to develop environmentally benign solvents that provide improved DSSC performance. We were attracted by the physical properties of  $scCO_2$ , such as high diffusion, low viscosity and low surface tension that make it an ideal solvent for the decoration of complex and intricate surfaces of materials.

Previously, Hayase and co-workers<sup>29</sup> investigated the deposition of ruthenium dyes from *t*-butanol/acetonitrile solutions with pressurized CO<sub>2</sub> for DSSC applications. Applying these conditions, N3 and N719 dyes were found to be extremely insoluble in both scCO<sub>2</sub> and scCO<sub>2</sub>-alcoholic mixtures. This limited solubility gave poor dye coated photoanodes that produced DSSC devices with much lower ECE compared with conventional solvent dye deposition. These observations were confirmed by CO<sub>2</sub> solubility measurements (both N3 and N719 showed no recordable solubility; by comparison the soluble reference compound *p*-tolylboronic acid exhibited a solubility of

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Synthetic procedures and characterization of **DOP** and **DOFP**, NMR spectra, CO<sub>2</sub> solubility studies data, UV-Visible spectroscopic data, CV data and DSSC performance data. See DOI: 10.1039/c1gc15864c

40.5 mg kg<sup>-1</sup> in CO<sub>2</sub> at 14 MPa and 50 °C). The poor solubility of N3 and N719 was attributed to the absence of sufficient CO<sub>2</sub> solubilizing groups and the presence of polar carboxylic acid binding groups.

As proof-of-concept, we investigated whether scCO<sub>2</sub> soluble dyes could be made to adsorb onto the titania surface in the presence of scCO<sub>2</sub> to produce efficient DSSCs. To address the solubility issues associated with polar functional groups, "masked" carboxylic binding groups, such as the anhydride in the perylene dye **DOP** (8) (developed by Ferrere and  $\text{Gregg})^{26}$ and DOFP (9), incoporating fluoroalkyl chains, were studied. To the best of our knowledge, there has only been one report of a perfluoroalkyl dye that has been tested in a liquid DSSC, but unfortunately, this ruthenium dye performed poorly when compared to an alkylated ruthenium analogue.<sup>30</sup> However, in organic electronics, such as bulk heterojunction OPVs,<sup>31</sup> OLEDs<sup>32</sup> and OFETs,<sup>33,34</sup> fluorinated substituents have been incorporated to tune the electronic properties and provide device stability. Nevertheless, the syntheses of compounds DOP (8) and DOFP (9) were completed and are shown in Scheme 1. The perylene bromide (1) was prepared following the method of Langhals and co-workers.35 Hartwig-Buchwald amination of bromide (1) with dioctylamine (2) gave the perylene (4), and subsequent imide hydrolysis to the carboxylic acid (6) followed by anhydride formation provided **DOP** (8). To further enhance the solubility of the dye in scCO<sub>2</sub>, the dioctyl groups were replaced with partially fluorinated octyl-groups following the same synthetic strategy outlined in Scheme 1. Thus, the partially fluorinated amine precursor (5) was synthesized by coupling the perfluoroalkyl-amine (3) with the bromide (1), and the imide was similarly converted *via* the carboxylic acid (7) into the fluorinated anhydride DOFP (9) in moderate yields (see Supporting Information for full synthetic details<sup>†</sup>).



Scheme 1 The synthesis of **DOP** (8) and **DOFP** (9) perylene dyes. Reagents and conditions: (i)  $Pd_2(dba)_3$ ,  $P('Bu)_3$  HBF<sub>4</sub>, Na'OBu, anhydrous toluene, 90 °C, overnight; (ii) KOH, 'BuOH, reflux, overnight, followed by (iii) AcOH, 40 °C, 4 h.

The physical and spectroscopic properties of **DOP** (8) and **DOFP** (9) were compared. Both **DOP** (8) and **DOFP** (9) are more soluble in scCO<sub>2</sub> than the ruthenium dyes, as determined by solubility measurements; 0.1 and 3.3 mg kg<sup>-1</sup>, respectively at 14 MPa and 50 °C (Supporting Information†). Analysis of the UV-Visible spectra of both **DOP** (8) and **DOFP** (9) showed significant solvatochromism (Supporting Information†).<sup>26</sup> To gain further understanding of the electronic characteristics of these dyes, cyclic voltammograms (CV) were recorded in CH<sub>2</sub>Cl<sub>2</sub> (Supporting Information<sup>†</sup>) following methods used for other perylene anhydride dyes.<sup>36</sup> **DOP** (8) has one reversible oxidation wave near  $E_{1/2}$  0.37 V, and **DOFP** (9) has a quasi-reversible oxidation at  $E_{1/2}$  0.31 V and one reversible oxidation wave near  $E_{1/2}$  0.63 V vs. Fc/Fc<sup>+</sup> (ferrocene/ferrocenium). The  $E_{1/2}$  of the first oxidation peaks were used to calculate the HOMO energy levels, which appear very similar in both dyes. **DOP** (8) and **DOFP** (9) also show two similar reduction waves near  $E_{1/2}$  –1.32 V and  $E_{1/2}$  –1.93 V, and  $E_{1/2}$  –1.39 V and  $E_{1/2}$  –1.86 V vs. Fc/Fc<sup>+</sup> respectively. This implies that the presence of the two methylene carbon spacers in the fluoroalkyl chain of **DOFP** (9) reduces the strong electron withdrawing nature of the fluorine atoms.<sup>37</sup>

Commercially available pre-sintered TiO<sub>2</sub> photoanodes were used for dve deposition in conventional solvents and scCO<sub>2</sub>. The photoanode was made from a blended 20 and 400 nm titania particle paste, with an average thickness of 13 µm and active area of 0.88 cm<sup>2</sup>. The photoanodes were not pre-treated with TiCl<sub>4</sub><sup>26</sup> nor was any attempt made to optimize device performance through use of additives. For the conventional solvent deposition experiment the photoanodes were reactivated by heating to 450 °C, cooled and immersed in the dye solution overnight.<sup>23,25-28</sup> Ethanol was an unsuitable solvent for deposition of both DOP (8) and DOFP (9), and the resulting solar cells exhibited low performance. CH<sub>2</sub>Cl<sub>2</sub> was a better solvent for deposition of DOP (8) and DOFP (9), and the resulting photoanodes produced solar cells with energy conversion efficiency (ECE) of  $1.24 \pm$ 0.04% (for **DOP** (8) which is comparable with the literature)<sup>26</sup> and  $1.41 \pm 0.007\%$ , respectively. The latter result was attributed to an increase in the open-circuit voltage  $(V_{\rm oc})$  and fill factor (FF), when compared with DOP (8) (Fig. 1). The improved efficiency is also attributed to dark current-voltage for DOFP (9) having a higher onset than **DOP** (8) indicating a lower charge recombination rate.



Fig. 1 Current–voltage curves measured in the dark and under simulated AM 1.5 sunlight at 100 mW cm<sup>-2</sup> for **DOP** (8) and **DOFP** (9) deposited onto TiO<sub>2</sub> using conventional dye soaking with  $CH_2Cl_2$  (0.5 mM, 15 h).

The absorption maxima of the dyes **DOP** (8) and **DOFP** (9) in  $CH_2Cl_2$  occur at 570 nm and 521 nm, respectively (Supporting Information<sup>†</sup>), but these differences are not apparent in the incident photon-to-current conversion efficiency (IPCE) curves (Fig. 2). The behavior of the adsorbed dyes on titania are



Fig. 2 IPCE curves of DOP (8) and DOFP (9) deposited onto  $TiO_2$  using conventional dye soaking with  $CH_2Cl_2$  (0.5 mM, 15 h).

relatively similar, both showing effective energy conversion over the wavelength range 400–580 nm. This implies that the electronic properties of both dyes are largely unchanged when bound onto  $TiO_2$ .

The deposition of **DOP** (8) and **DOFP** (9) perylene dyes in  $scCO_2$  batch mode was evaluated at a pressure and temperature of 14 MPa and 50 °C and showed promising results. Dye deposition could be achieved in  $scCO_2$  with short contact times of only a few hours. Both dyes produced a photovoltaic response in a DSSC, (Fig. 3) and **DOFP** (9) outperformed **DOP** (8). **DOFP** (9) was more effectively adsorbed on titania than **DOP** 



Fig. 3 Example of current–voltage curves of DSSCs fabricated using titania photoanodes prepared by deposition of **DOP** (8) and **DOFP** (9) using  $scCO_2$  (14 MPa, 50 °C) with 1 h dye deposition time.

(8) in scCO<sub>2</sub> solution as judged by qualitative observation of the intensity of the coloration of the titania as viewed through the sapphire window of the scCO<sub>2</sub> reaction chamber. The coloration of the dyes in scCO<sub>2</sub> is also consistent with solubility data measurements at 14 MPa and 50 °C (**DOP** (8) = 0.1 mg kg<sup>-1</sup> and **DOFP** (9) = 3.3 mg kg<sup>-1</sup>).

To probe the scCO<sub>2</sub> dye deposition process, the influence on DSSC performance was studied as a function of dyeing time and dye loading. Table 1 illustrates DSSC device performance for photoanodes coated with a more CO<sub>2</sub>-soluble dye **DOFP** (9) (5 and 20 mg) for periods of 1–3 h in scCO<sub>2</sub> solution. Increased deposition time produces increased energy efficiencies as a result of the enhanced short-circuit current ( $J_{sc}$ ). Similarly, higher quantities of dye result in higher loading for a given exposure time. The improvement in the dye loading is evident in the qualitative observation of intense coloration of the photoanode after the dye deposition process.

In general, DSSC device performance is improved by thermal reactivation of the photoanode immediately before dye deposition. To determine whether the photoanode "heat-reactivation" step was also required in the scCO<sub>2</sub> process, comparison studies were undertaken. With the conventional dye soaking method, there is significant improvement in ECE using a pre-heated  $TiO_2$  photoanode (1.22 ± 0.01%) rather than a non preheated one  $(0.84 \pm 0.16\%)$ . This improved efficiency is largely influenced by an increase in  $J_{sc}$  and FF (Fig. 4a). In contrast, repeating this experiment using scCO<sub>2</sub> batch conditions resulted in essentially no benefit when pre-heating the photoanodes prior to dye deposition. Both the non pre-heated and the pre-heated photoanodes gave ECE of  $1.24 \pm 0.03\%$  and  $1.26 \pm 0.04\%$ , respectively (Fig. 4b). The current results suggest that CO<sub>2</sub> acts to activate the surface of the TiO<sub>2</sub>, presumably by deabsorbing soluble contaminants and water.38 This "active" surface is then ready for the adsorption of dye. Further work is necessary to gain a better understanding of this process, and this could be addressed through batch and continuous flow studies.



Fig. 4 Current–voltage curves of DOFP (9) on pre-heated and non pre-heated titania using (a) conventional ( $CH_2Cl_2$ , 0.5 mM, 15 h) and (b) scCO<sub>2</sub> (14 MPa, 50 °C, 20 mg dye, 2 h) methods.

Table 1 DSSC performance parameters of DOFP (9) recorded for cells at various dye deposition time and dye quantity using  $scCO_2$  deposition method in a 25 mL reaction chamber at 14 MPa and 50 °C

	Dye quantity (mg, µmol)	Dye time (h)	$J_{\rm sc}~({ m mA~cm^{-2}})$	$V_{\rm oc}~({ m mV})$	FF	ECE (%)
1	5. 4.86	1	2.08	568	0.62	$0.72 \pm 0.01$
2	5, 4.86	3	3.64	548	0.63	$1.24 \pm 0.03$
3	20, 19,43	1	2.86	548	0.60	$0.97 \pm 0.11$
4	20, 19,43	2	3.70	575	0.58	$1.25 \pm 0.03$
5	20, 19.43	3	2.66	538	0.58	$0.83 \pm 0.14$

scCO<sub>2</sub> soluble dyes can be accessed by using masked binding groups, such as anhydrides, for use in DSSC applications. The solubility of the dye in  $scCO_2$  can be further enhanced by the incorporation of fluoroalkyl substituents, which replace the analogous alkyl substituents. DOP (8) and DOFP (9) dyes were studied in liquid DSSC devices, where dyes were deposited by conventional and under scCO<sub>2</sub> conditions in batch mode. In conventional solvents, DOFP (9) showed slightly better performance than the alkyl analogues with an overall improvement of 14% in ECE, which is an advantageous discovery for application to other dyes in DSSCs. When the dyes were deposited using scCO<sub>2</sub>, both dyes produced photovoltaic responses as a result of the masked anhydride group. Although the solubility of **DOP** (8) in  $scCO_2$  is improved in the presence of this masked binding group, it is still low and thus hinders satisfactory dye adsorption. In contrast, the modified perylene dye DOFP (9) has greater solubility in scCO<sub>2</sub>, attributed to the presence of both the masked binding group and the fluorinated substituent, resulting in better dye deposition. With the scCO<sub>2</sub> deposition method, **DOFP** (9) (ECE = 1.25%) showed similar cell performance to the alkyl analogue **DOP** (8) (ECE = 1.24%). This performance is comparable when DOFP (9) is deposited using conventional solvent (ECE = 1.41%).

In conclusion, the replacement of organic solvents with scCO<sub>2</sub> for depositing dyes onto photoanodes provides several fabrication benefits. By employing the  $scCO_2$  process we have dramatically reduced dye deposition times from 15 h for conventional organic solvents to only 2 h. No additional photoanode rinsing step is required, as conducted in the conventional deposition step.<sup>39</sup> The energy intensive heat reactivation step (450 °C) required with conventional solvents has been eliminated by use of the  $scCO_2$  process. The valuable dye material can be easily recovered in a solid form after the scCO<sub>2</sub> process simply by venting of the CO<sub>2</sub> gas, which can also be recycled. This is in stark contrast to the costly and laborious processes with the conventional solvent method, which generates large quantities of unreacted dye and solvent and requires separation and disposal of waste solvent. We have demonstrated an effective dye deposition method for DSSCs using  $scCO_2$  with a comparable photovoltaic response to that of conventional deposition methods. Current work is directed at applying these concepts to other dyes and investigating alternative non-fluorinated CO<sub>2</sub>-solublizing groups.<sup>40</sup>

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