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Spectral response mapping of co-sensitized dye-sensitized solar cells dyed processed using rapid adsorption/desorption



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ABSTRACT

Two-dimensional spectral response distribution maps in dye-sensitized solar cells (DSSC) are reported using 1×1 mm pixels for 0.5×2 cm DSSC devices by coupling external quantum efficiency (EQE) measurements with an X-Y scanning stage. The technique has been applied to singly dyed (D149 and N719) and co-sensitized (N719/SQ1 and D149/SQ1) devices. Dye desorption and re-dyeing processes have also been successfully mapped using this technique to help understand dye loading and dye location in multiply-sensitized cells.

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DSSC devices differ from Si and thin film photovoltaic devices because they separate light absorption from charge carrier transport by using dyes to harvest light and metal oxide particles to transport charge away from the dye [1]. The resulting photo-oxidized dyes are then reduced by a solid or liquid electrolyte. Controlling the dye-oxide interface is therefore key to improving DSSC efficiency [2] whilst ultra-fast dyeing is key to commercial scaling of DSSC technology to replace slow passive dyeing processes [3].

At the same time, whilst using multiple dyes to increase light harvesting generates higher open circuit voltage than panchromatic dyes [3–5], this complicates the dye-oxide interface because 2 or more dyes need to be positioned on the metal oxide surface especially in larger devices where variations in TiO₂ sintering and/or dye uptake are exacerbated.

Previous reports have shown that scanning microscopy techniques can be used to locally excite small (100 μm) areas of working DSSC devices using multiple lasers/wavelengths [6–8]. This measurement length is similar to the diffusion length in DSSC devices. Although information about pore filling cannot be obtained on the nano-scale using this method, larger scale inhomogeneities can be observed and correlated with photographic images of dyed films.

Here, we report studies of ultra-fast, co-sensitized 1 cm² (0.5×2 cm) DSSC devices using X-Y spectral response mapping

at two different wavelengths to study dye distribution across the TiO₂ meso-structure.

1. Experimental

Photo-electrodes were screen printed with TiO₂ paste (DSL-18-NRT, Dyesol) and sintered at 450 °C for 30 min. Counter electrodes were coated with Pt paste (PT1, Dyesol) and sintered at 400 °C for 30 min. The two electrodes (working area 0.5 cm × 2 cm) were sealed using a 30 μm Surlyn[®] gasket. Devices were dyed just before measuring using ultra-fast dyeing [3] before flushing with 99.99% ethanol to remove any un-adsorbed dye. The dyes used were the indoline dye – D149, the Ru (II) bipyridyl dye – N719 (both from Solaronix) and in-house synthesized squaraine – SQ1. Dyes were desorbed by tertiary-butyl ammonium hydroxide (tBu₄NOH) solution (1% by weight in 50:50 v/v ethanol-water) or ethanol, acetone or LiOH 0.1 M as described previously [2].

Spectral response measurements were conducted in plan-view with no light bias using a custom-built Bentham IPCE system in DC mode coupled with a motorised X-Y sample stage measuring every 1 mm over a 7 × 22 mm grid across each device (see ESI Figs. 2 and 3) using a spot size of 1.0 mm². EQE scans were recorded with 100 ms delay between wavelength switching (to allow for the photocurrent relaxation time) and with 1 mm step-size at a spectral resolution of 5 nm. To validate the EQE mapping data, data were measured for masked and unmasked N719 and co-sensitized N719/SQ1 devices (ESI Fig. 4) showing identical data within error (Table 1).

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Table 1
Dye-sensitized solar cell devices tested in this paper.

Device	Details
I	Device singly dyed with D149 Dye
II	Device dyed with N719 and then partially desorbed
III	Device II re-dyed with N719/SQ1, then N719 selectively desorbed before re-dyeing with SQ1
IV	Device co-sensitized with (1:1) SQ1/D149 dye solution before selective desorption of D149

2. Results and discussion

Mapped spectral response data for D149 dyed across the TiO₂ photo-electrode (Fig. 1a) show an even EQE response at 560 nm (0.20–0.25) across the whole device area apart from the device edges (EQE = 0.15) and the two fill holes at either end of the device (EQE = 0.10). This could reflect turbulent flow around the fill holes during dyeing which could reduce dye uptake but is more likely to be due to the absence of Pt-coated counter electrode above these regions which slows dye regeneration.

Fig. 1b shows an image and the spectral response map of Device II which was first dyed with N719 before dye was desorbed from

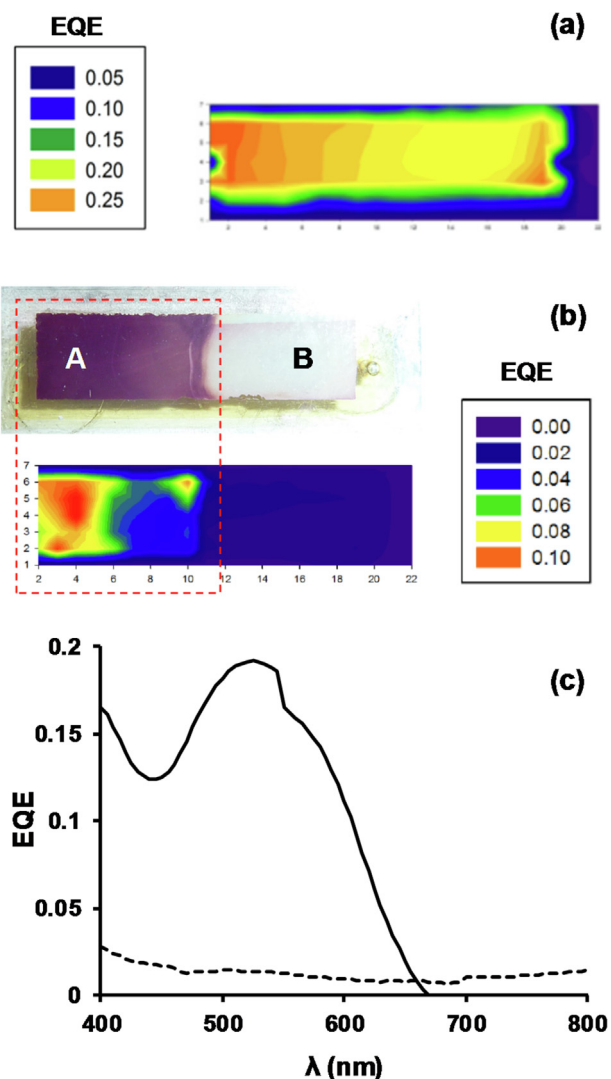


Fig. 1. (a) current map of Device I at $\lambda = 560$ nm showing light harvesting response of D149, and data for Device II showing (b) image and EQE map at $\lambda = 580$ nm of device showing N719 dyed and desorbed areas and (c) EQE point scans from A (solid line = N719 dyed TiO₂) and from B (dashed line = undyed TiO₂).

half of the photoelectrode using 0.1 M LiOH_(aq). The colour image clearly shows the red-brown, N719-dyed area (labelled A on Fig. 1b) and the desorbed white area (labelled B on Fig. 1b). The corresponding spectral response map shows the highest EQE (0.10) on the far left-hand-side of the device (i.e. furthest from the desorbed area) which drops to EQE = 0.04–0.06 closer to the centre of the photoelectrode. This is believed to correlate with partial N719 desorption which arises from capillary action of LiOH_(aq) being drawn into the mesoporous TiO₂ film beyond the midpoint of the photoelectrode. Then, on the right-hand-side (labelled B), the EQE is zero in line with complete dye desorption. Point scan EQE

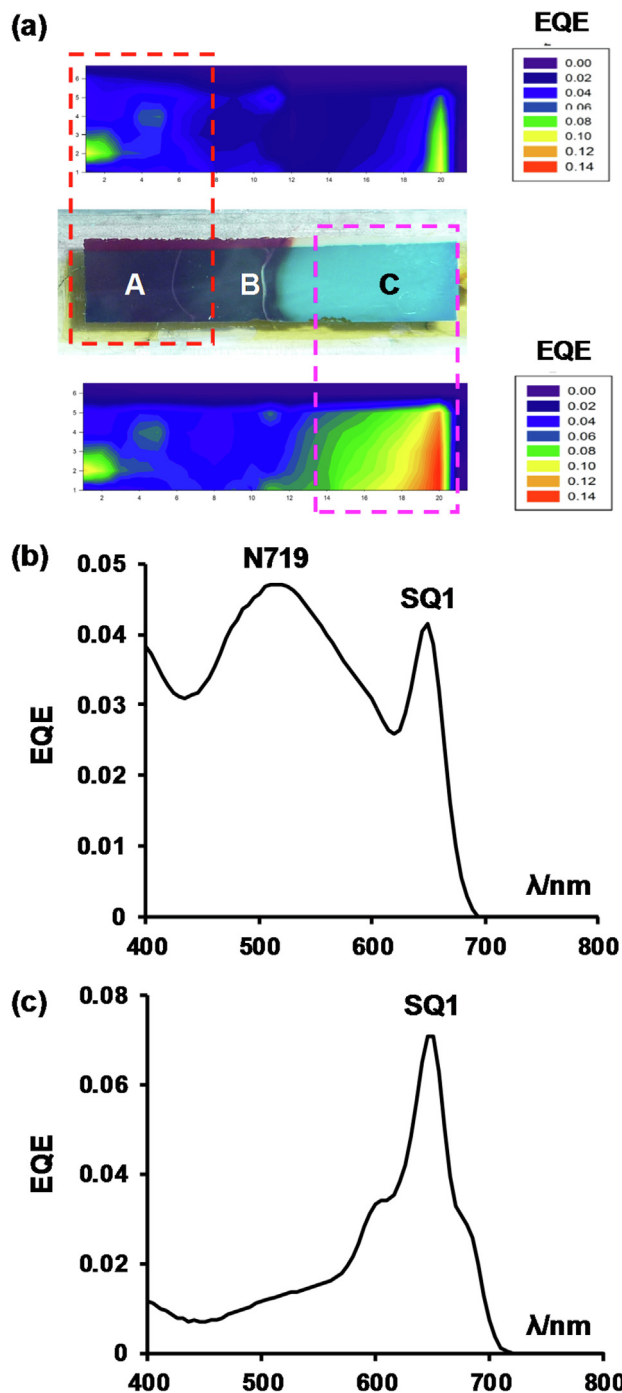


Fig. 2. Device III showing (a) top - EQE map of at $\lambda = 580$ nm showing response of N719, middle - image of device, bottom - EQE map at $\lambda = 650$ nm showing response of SQ1, (b) EQE point scan at A and (c) EQE point scan at C.

data are also in line with these assertions (Fig. 1c) showing a typical N719 spectral response for point A and no spectral response for point B.

Device II was then co-sensitized with N719/SQ1 to produce Device III before N719 was selectively desorbed [2] from the right-hand-side of the photoelectrode by holding the device at ca. 45° and adding $t\text{Bu}_4\text{NOH}$ drop-wise onto the photoelectrode surface. After rinsing, squaraine dye (SQ1) was pumped through the cavity (5 min, 200 $\mu\text{L}/\text{min}$) and the device was mapped at two wavelengths; 580 nm and 650 nm (Fig. 2a). The left-hand-side of the device remains red-brown in colour (labelled A) and shows EQE = 0.04–0.10 at 580 nm in line with N719 colour and light harvesting. The EQE data (Fig. 2b) agrees with this showing spectral response for N719 as well as a signal for SQ1 at 650 nm. The right-hand-side of the device (labelled C) only has SQ1 because N719 has been selectively desorbed. The blue colour and EQE = 0.08–0.14 at 650 nm are in line with SQ1 colour and light harvesting. Interestingly, the colour of the middle of the device (labelled B) is a mixture of red-brown and blue suggesting partial N719 desorption has occurred here presumably due to $t\text{Bu}_4\text{NOH}$ spreading within the mesoporous TiO_2 film as seen for $\text{LiOH}_{(\text{aq})}$.

To further analyse dye placement, Device IV was co-sensitized with D149/SQ1 and measured bifacially; i.e. either through the Pt electrode or through the TiO_2 photo-electrode. The EQE data are dominated by D149 when the device is illuminated through the Pt electrode (Fig. 3a) suggesting that D149 adsorbs preferentially at the top of the mesoporous film. This is backed up by the EQE map at 580 nm which shows EQE = 0.20–0.25 across the device (ESI Fig. 5a). By comparison, approximately equal spectral response for D149 and SQ1 are observed when the device is illuminated through the TiO_2 side (Fig. 3b). If it is assumed that D149 adsorbs faster than SQ1, then these data suggest that the percolation of SQ1

through the mesoporous TiO_2 film is faster than D149 so that both dyes adsorb at a more even rate at the bottom of the TiO_2 film. The photocurrent generated at the bottom of the TiO_2 film (Fig. 3b) is also smaller than at the top (Fig. 3a) because dye molecules at the top of the film are closer to the electrolyte and so are regenerated faster. After partial desorption of D149 from Device IV using $t\text{Bu}_4\text{NOH}$ and acetone, the EQE map at 580 nm (ESI Fig. 5b) and EQE data (ESI Fig. 5d) from the Pt electrode again shows a reduced spectral response compared to the fully dyed device electrode and only for D149. Interestingly, the EQE map at 650 nm (ESI Fig. 5c) and spectral response data (ESI Fig. 5e) for the desorbed device illuminated from the TiO_2 electrode again shows a much smaller response but only for SQ1 showing that all the D149 and some SQ1 dye has been desorbed.

3. Conclusions

The data show that combining a motorized XY sample stage with EQE is a useful technique to map the spectral response of singly and co-sensitized DSSC devices to produce 2D current maps at 1 mm spatial resolution of 0.5x2cm devices. Using this technique, spectral response data are produced for each 1x1mm pixel and these data can be used to generate wavelength-specific EQE maps which can be used to study dye location across devices in plan view. Combining this approach with bifacial EQE measurements from either the Pt electrode or TiO_2 photoelectrode side of the device also enables vertical dye location across the mesoporous TiO_2 film to be studied. These approaches have been used to study both co-sensitization and selective desorption techniques in DSSC devices which has important implications for the further development of co-sensitization techniques to extend spectral response and increase device efficiency.

Declaration of Competing Interest

There are no conflicts of interest related to this paper for the authors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mblux.2019.100015>.

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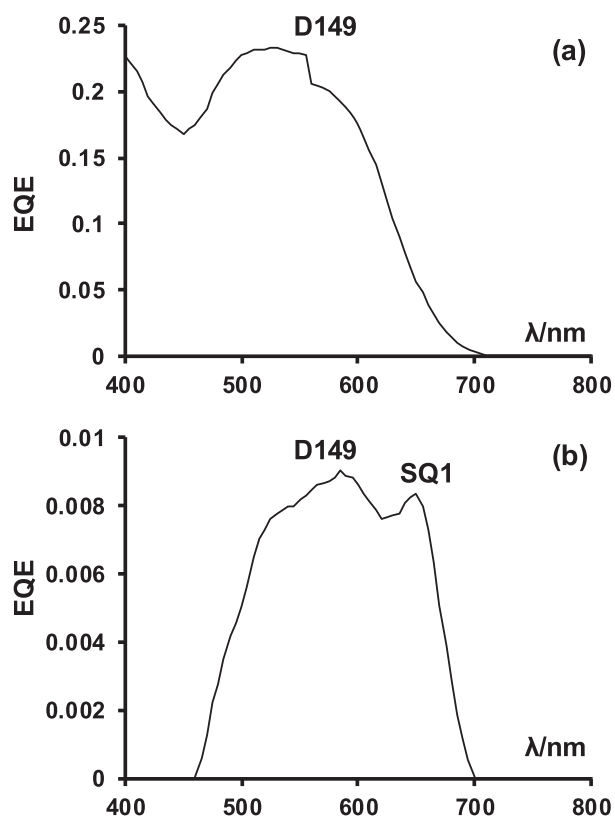


Fig. 3. Device IV co-sensitized with D149 and SQ1 showing EQE data for illumination through (a) Pt counter electrode and (b) through TiO_2 photo-electrode.

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