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Investigations of dye-sensitised titania solar cell electrode using confocal laser scanning microscopy

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We have characterised a dye-sensitised nanoporous nanocrystalline titania film used in prototype photoelectrochemical solar cell production. The film was sensitised with two types of ruthenium (II) based dyes for different times, between 0.5 and 24 hours. The penetration and coverage for each type of dye was studied using Confocal Laser Scanning Microscopy (CLSM). Varying laser powers were applied and fluorescence images from the film have been analysed. Both dyes were found to percolate through the whole of the nanoporous film irrespective of the dyeing time but the amount of dye increased with dyeing time. The CLSM is shown to be a valuable tool for the investigation of dye penetration and coverage in porous films.

1. Introduction

Conventional solar cells, such as single crystal silicon, perform absorption of light and separation of electric charges, simultaneously to convert light into electricity. To reduce recombination of charges the crystal should be highly pure and defect-free which requires expensive processes to manufacture the cell. Recently, dye-sensitised solar cells, based on nanoporous nanostructured films that work on a different principle have become an area of active research and development. The production cost of these types of cells is expected to be lower than for conventional PV cells. Today the most extensively studied dye-sensitised solar cell is based on a nanocrystalline titania film [1, 2]. The film can absorb a broad range of the visible spectrum, by incorporating a large amount of sensitising dye onto the large surface area of the nanoporous film. Photoexcitation of the dye molecules results in the injection of an electron into the conduction band of the titania semiconductor. Positive charge is transferred from the dye to a redox mediator in the electrolyte solution which fills the cell and the original state of the dye is subsequently restored by electron donation from the electrolyte. The injected electron percolates through the nano-structured electrode through the external circuit to the counter electrode where the redox couple is regenerated. In order to get maximum power output from the cell, among many factors, the coverage of the dye in the film is important. In addition, the optical absorption of the dye should coincide with the solar spectrum for optimum cell performance.

In this work, we have investigated the coverage of a dye in a dye-sensitised titania electrode using Confocal Laser Scanning Microscopy. These electrodes are representative of those used in prototype production of

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photoelectrochemical solar cells. The confocal laser microscope is capable of acquiring precise optical sections at far better lateral and axial resolution than a conventional light microscope. It can therefore provide vital structural information in the mesoscopic range of microstructures. The instrument has been used mainly for biological applications [3, 4] but is now also utilised widely in the area of materials science. It has been used as a tool for examining colloidal dispersions and crystals [5], mechanical properties of ceramics [6], surface and interface analysis of polymers, and measurements of micro-roughness and size of particles [7]. Confocal microscopy permits non-destructive imaging of translucent specimens or opaque surfaces [5, 7, 8]. Although a conventional spectrofluorometer is extremely flexible to study the fluorescence of dye solutions, information about the distribution and percolation of dye molecules in porous films cannot be obtained. In a confocal laser microscope, the dye can be excited by precise laser scans of the specimen and the dye localised by detecting the fluorescence from the dye. The aim of this experiment was to determine the distribution and penetration of the dye in the film using the above method and correlate the results with other well know techniques such as Secondary Ion Mass Spectroscopy (SIMS).

2. Experimental methods

2.1. Sample preparations

Samples of titania films with size 18 cm $\times$ 10 cm were obtained from Sustainable Technologies International Pty Ltd (STI). The samples were cut into 3 cm $\times$ 2 cm pieces and sensitised by soaking the films in a dye solution. Prior to the sensitisation process, the films were heated at a temperature of 130°C in air for 20 minutes. This can assist the absorption kinetics of the dye and also removes contaminants from the surface of the film. The samples were then immersed immediately (while still warm) into the dye for different periods of time ranging between 0.5 to 24 hours. After the dye treatment, the samples were rinsed with de-ionised water, blown with air to dry and were kept in a desiccators to protect from dust and moisture. Two types of dye with different absorption and/or emission characteristics have been used in this experiment. One of the dyes was $RuL_2(NCS)_2$ (L = 4,4′dicarboxy-2,2′-bipyridine) which is known as N3-dye and the second type of dye was RuL_3Cl_2. The N3-dye was prepared in ethanol at a concentration of 4.10×10^{-4} M whereas the RuL_3Cl_2 dye was prepared as an aqueous solution at a concentration of 3.27×10^{-3} M.

2.2. Sample measurements

The absorbance of the dye-sensitised samples was measured using a Varian Cary 3 UV-Visible spectrophotometer in the wavelength range 300 to 900 nm at normal angle of incidence. A zero baseline reference was taken before any absorbance measurements were made. The absorbance measurements of the dye solutions were made in a standard optical cell (cuvette) with the zero baseline reference being taken when the cell was empty. Emission of the dyes in solution was also measured using Cary Eclipse Fluorescence Spectrophotometer in the wavelength range 400 to 900 nm. Different excitation wavelengths between 350 to 550 nm in steps of 5 nm were employed and the emission of the dye molecules recorded.

A Leica TCS 4D confocal laser scanning microscope (Leica Lasertechnik, Heidelberg, Germany) with a Leitz DM IRB light microscope was used for acquiring reflected and fluorescent light images from the thin film samples. The samples were illuminated with an Ar/Kr laser light source. Varying laser power settings (up to about 16 W) were employed in order to produce good image contrast in conjunction with an oil-immersion objective (63 $\times$ Plan Apo, 1.40 numerical aperture). The actual laser power incident on the sample is known to be very much lower than these settings due to dissipation through the optical path. Immersion oil with a refractive index of 1.518 was applied directly to the film surface. The instrument provides three laser excitation wavelengths but the shortest wavelength of 488 nm was used since it provided the best image contrast. Optical filters as well as detector voltages can be selected to vary the colour contrast of the fluorochrome in combination with fluorescent probe, objective lens or detector aperture [8]. In these experiments, appropriate optical filters and detector voltages were employed and a line scan was performed along the cross-section of the film. The emission filter used in these measurements was CY5 combined with a filter block mode of RSP510 which transmits above 510 nm but blocks below this wavelength. The emission maximum for this type of filter is 670 nm. Two methods of scanning the laser across the samples were used.

Method 1: by placing the surface of the film along x-y plane perpendicular to the incoming laser beam and scanned along the cross-section of the film in the x-z plane, and

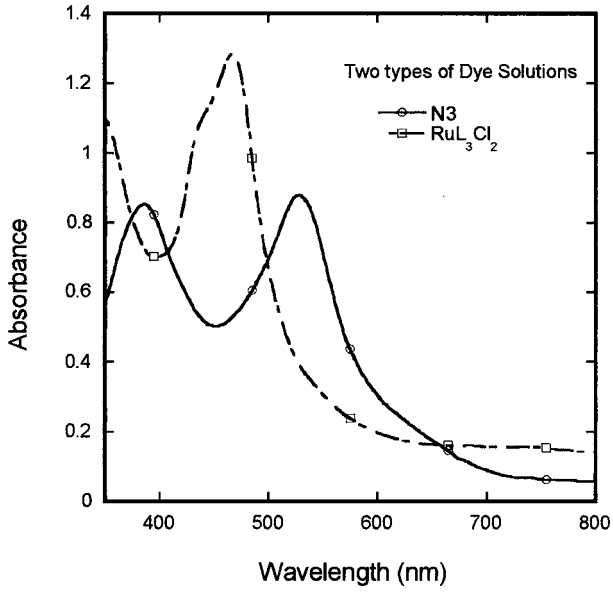
Method 2: by placing the cross-section of the film along the x-z plane parallel to the laser source and scanned along the cross-section of the film in the x-y plane.

Due to the simplicity of measurements, most of the results reported in this experiment were obtained using scan *Method 1* unless otherwise stated. The detector voltages and filter type used for analysing all the samples were set to be identical unless otherwise indicated. Two types of dye-sensitised titania films (one dyed with N3 and the second dyed with RuL_3Cl_2), as well as a titania film without any dye, were examined.

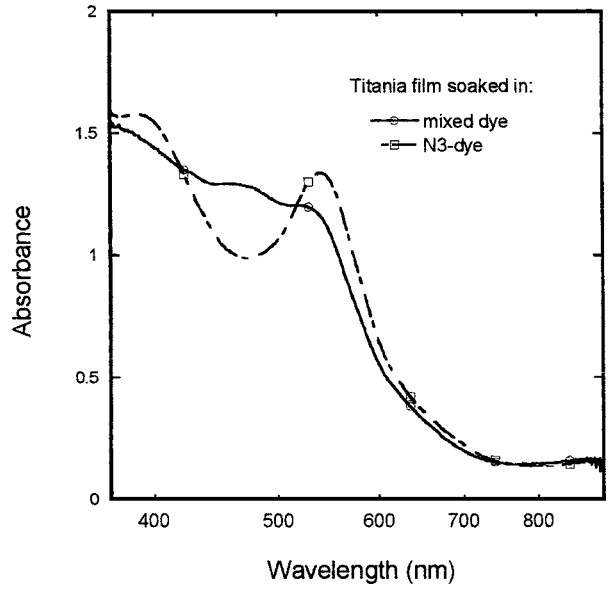
3. Results and discussion

3.1. Optical absorption and emission

Fig. 1a shows absorption spectra of N3-dye in solution measured in the wavelength range 350 to 800 nm. A standard glass optical cell (cuvette) was used for the measurement of the dye solution. Absorption maxima at two wavelengths, 385 and 525 nm, were measured. These are two optical transitions in the visible region which are attributed to a metal to ligand charge transfer



(a)



(b)

Figure 1 (a) Absorbance of two types of dye solutions (N3-dye and RuL_3Cl_2-dye solutions). (b) Absorbance of titania film immersed in 50% mixture of these two dyes compared to spectra of a film soaked in N3-dye only.

(MLCT) [2] i.e., from the highest occupied molecular orbital (π orbital) of Ru (II) to the lowest unoccupied molecular orbital (π^* orbital) of the bipyridyl groups. A similar measurement was done on the RuL_3Cl_2 which showed an absorption maximum at 465 nm. The minimum absorbance value of the N3-dye almost lies at the maximum value of the RuL_3Cl_2. By mixing these two dyes the absorbance minimum of the N3-dye in Fig. 1a was occupied by the MLCT band of the RuL_3Cl_2 and consequently the entire visible spectrum can be absorbed. This is shown in Fig. 1b for titania film immersed in 50% mixture of each of these dyes and the result is compared with absorbance of titania film soaked in the N3-dye only. As shown in the figure the absorbance minimum of the film dyed in the N3-dye disappears when mixed with RuL_3Cl_2 and thereby improved the absorbance of the film.

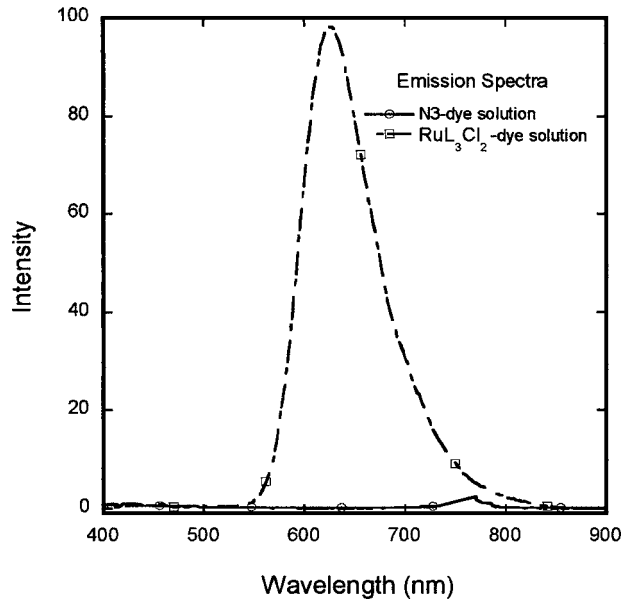


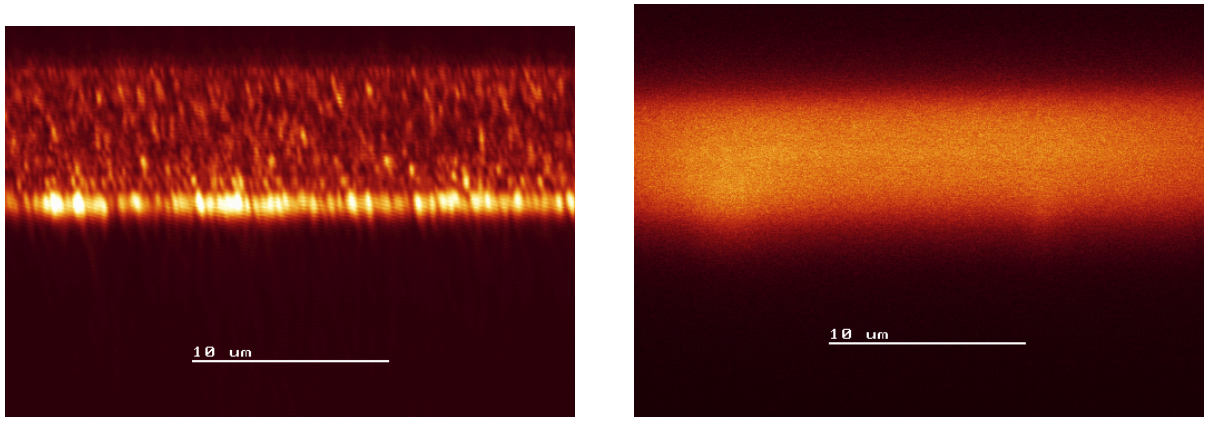
Figure 2 Emission spectra of N3-dye and RuL_3Cl_2-dye solutions measured using Fluorescence Spectrophotometer in the wavelengths range 400 to 900 nm at excitation wavelength of 440 nm (RuL_3Cl_2 dye) and 540 nm (N3-dye).

Emission of the two dye solutions was carried out by scanning the excitation wavelengths between 350 to 550 nm in steps of 5 nm. From these scan ranges, the results with maximum emission have been selected. Fig. 2 shows emission spectra for the RuL_3Cl_2 and N3-dye at excitation wavelengths of 440 nm and 540 nm, respectively. These excitation wavelengths are near their absorption maximum at 465 nm (RuL_3Cl_2) and 525 nm (N3-dye). From Fig. 2, it can be observed that the RuL_3Cl_2 emits strongly at 625 nm. A weak emission spectrum at around 753 nm was detected for the N3-dye, consistent with similar dyes reported to fluoresce at 750 nm [2]. These two types of dye were used to study the penetration and distribution of dye molecules in titania films using Confocal Microscopy as discussed below.

3.2. Fluorescence

Fig. 3a shows a cross-sectional image of a bare (undyed) titania film obtained using Confocal Laser Scanning Microscopy in reflection mode. Since titania has a high refractive index, the backscattering of the layer is high which provides sufficient contrast. A fractal surface with a compact microstructure can be seen from Fig. 3a. From the reflection mode measurement, thickness of the titania films was easily determined. The samples analysed in this experiment had film thicknesses of about 8 μm. This is in good agreement with the results obtained using a profilometer. In comparison to the strongly scattered signal obtained from the bare titania layer (Fig. 3a), the titania film with a dye appeared to show a weaker reflected image probably due to the re-absorption of the reflected light by the adsorbed dye molecules. With increasing dyeing time, the absorption in the film increases and hence the reflected image contrast reduces.

It was not possible to get an image from the bare titania film in fluorescence mode, and thus no



(a) (b)

Figure 3 Images obtained using confocal laser scanning microscopy at a laser power setting of 3 W. (a) Reflected light of bare (undyed) titania film measured using reflectance mode and (b) fluorescence of titania film dyed in RuL_3Cl_2-dye for 5 minutes obtained using fluorescence mode.

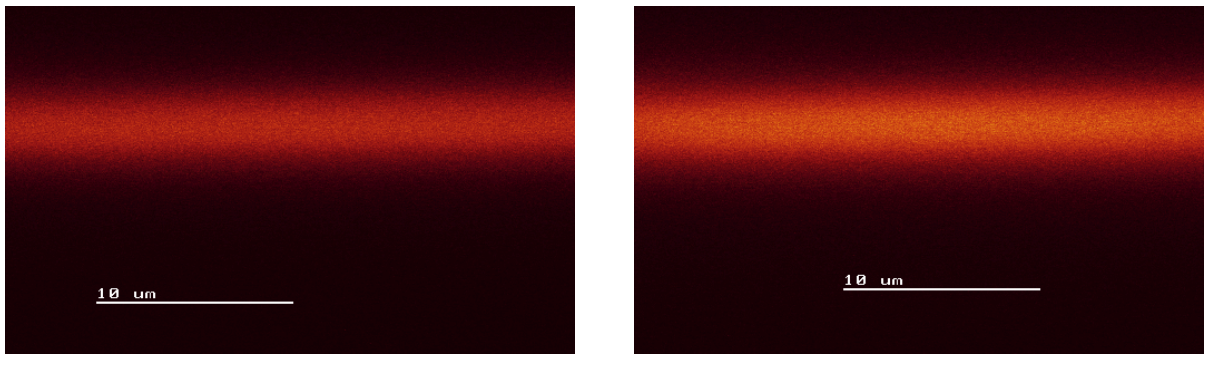
auto-fluorescence was observed. But when the film was dyed a fluorescence image was observed. With a very small amount of dye the fluorescence was homogenously distributed throughout the film, but the intensity from the film was low as indicated in the pseudo-thermal scale used for the images. Increasing the amount of dye gave an increase in the fluorescence intensity, indicated on the thermal scale. Fig. 3b shows a cross-sectional image in fluorescence mode of titania film soaked in the RuL_3Cl_2 for about 5 minutes analysed at a laser power setting of 3 W. From the figure, the dye appeared to percolate through the whole of the nano-structured titania film.

Very weak fluorescence were observed when the 3 W laser power was applied on titania films dyed with N3-dye and consequently poor images were found. However, at higher laser power the intensity and contrast of the fluorescence image have been improved dramatically. Fig. 4a–b, shows fluorescence images of a titania film dyed with N3-dye for 0.5 hour at laser power setting of 9 W and 16 W, respectively. As shown in the figure the contrast of the fluorescence image improved with increasing the laser power setting from 9 W to 16 W. Due to the small amount of dye in the film (dyed for only 0.5 hour) the images appeared to be thinner than the actual thickness of the film. With increasing the dyeing time the fluorescence from the whole film can be observed.

Fig. 5a–b, shows fluorescence images of two samples soaked in N3-dye for 1 and 8 hours, respectively, at a laser setting power of 9 W. These two films were found to have similar fluorescence images and the intensity difference between these films is small irrespective of their dyeing time. The fluorescence intensity can be saturated for the given laser power which can show similar results. From the overall investigations, both types of dye (RuL_3Cl_2-dye and N3-dye) have been shown to percolate through the whole of the nano-structured film. This observation correlates well with results found by SIMS analysis [9].

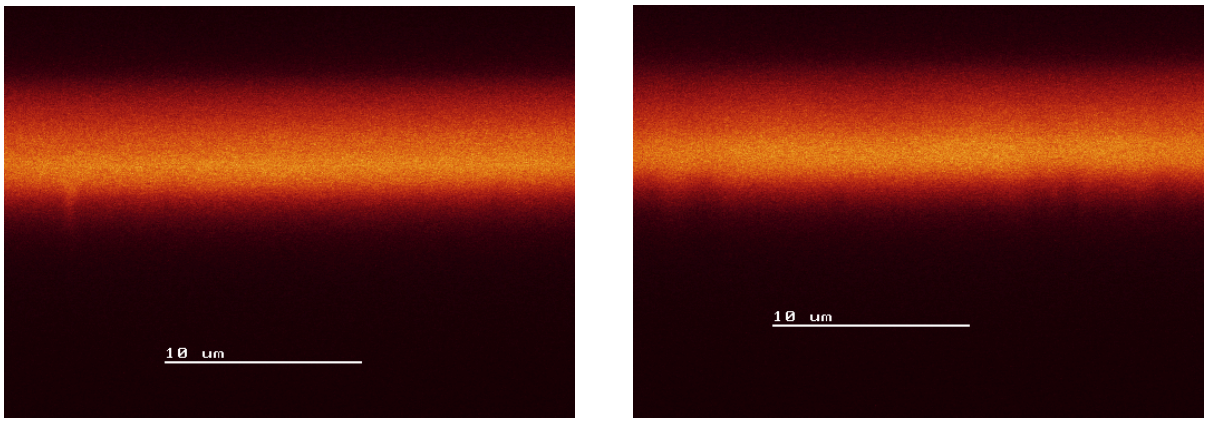
In Fig. 6a the distribution of Ru-based dye determined using by SIMS as a function of thickness for all the films was found to be uniform. A small increased value in the middle of the film (Fig. 6a) can be seen for the thicker film and this could be attributed to the nature and geometry of the sample. Unlike the SIMS results, the distribution of the fluorescing dye along the film cross-section as measured by CLSM varies considerably. Fig. 6b shows the intensity profile for the dye-sensitised sample extracted from the fluorescence images (grey scale) of the confocal laser microscope. As shown in the figure (Fig. 6b), the intensity is higher in the middle of the film for both types of dye and drops towards the surface as well as the film-substrate interface.

The point-spread function, the light distribution within the sample, is elongated in the axial direction,



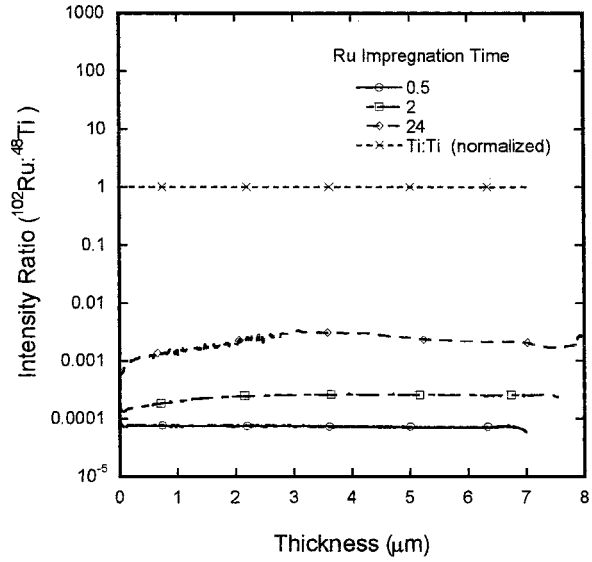
(a) (b)

Figure 4 Fluorescence images of titania film soaked for 0.5 hour in N3-dye obtained using confocal microscopy at laser power setting of (a) 9 W and (b) 16 W.

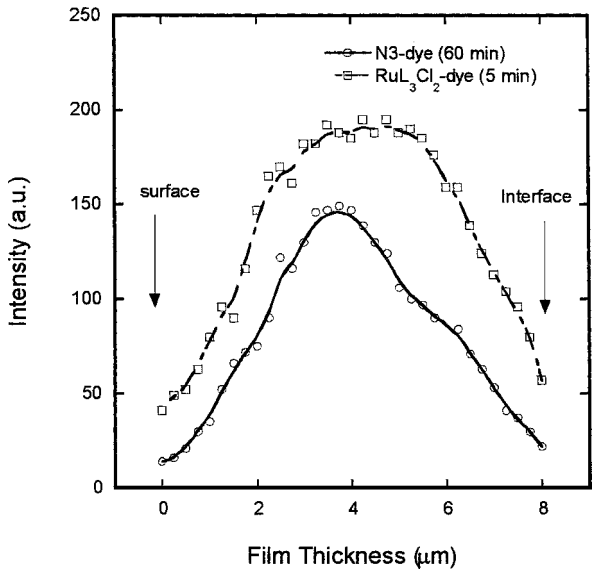


(a) (b)

Figure 5 Fluorescence images of N3-dyed titania films obtained using confocal microscopy at laser power setting of 9 W. The films were dyed for (a) 1 hour and (b) 8 hours.



(a)

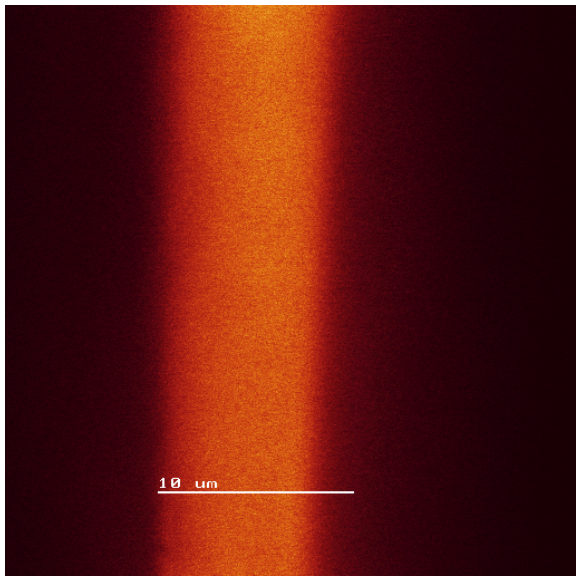


(b)

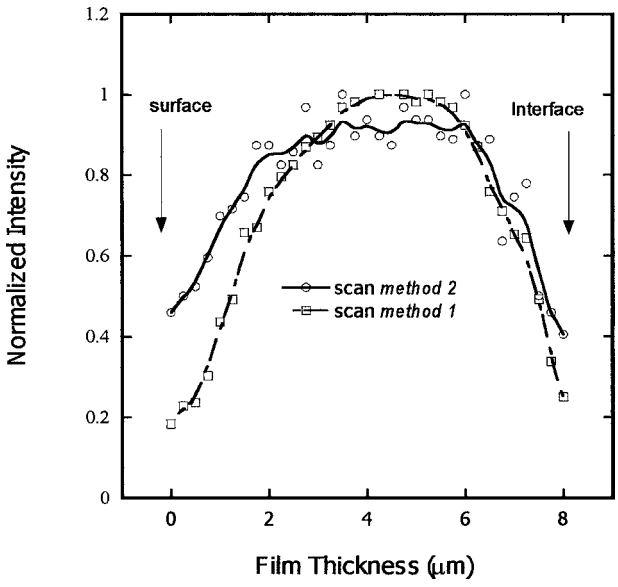
Figure 6 (a) Depth profile of Ru:Ti intensity ratio in dye-sensitised titania film analysed using SIMS. The Ru was introduced by immersing bare titania samples in N3-dye for different times as shown in the legend. (b) Intensity profile extracted from the confocal fluorescence images (grey scale) as a function of depth into of the films for N3 and RuL_3Cl_2 dyed films.

with a full-width half maximum (FWHM) which is roughly 3 times that of the lateral FWHM. With the 63 × objective, the axial FWHM may be about 0.5–0.6 μm. The axial (z) resolution is thus worse than the lateral resolution in x-z scans (*Method 1*). Therefore scan *Method 2* (described in section 2.2) was used to ascertain whether the apparent fluorescence distribution was mainly a consequence of the poorer axial resolution. Fig. 7a shows a fluorescence image for a RuL_3Cl_2 dyed titania film obtained using scanning *Method 2*. The film was held in the vertical direction but the fluorescence image from the x-y scan was qualitatively similar to that from scan *Method 1*. Fig. 7b shows the normalized intensity profile for Fig. 7a as compared to the normalized intensity distribution shown in Fig. 6b for the RuL_3Cl_2 dyed film. The intensity profiles using the two scan methods were similar, but the drop-off at the boundaries of the film was less pronounced with *Method 2*, demonstrating that the poorer z-resolution in x-z scans did have some effect on the observed intensity profile. However the observed fluorescence distribution was more peaked than that measured for the Ru/Ti ratio by SIMS (Fig. 6a). The emission wavelengths of the N3-dye and RuL3Cl2-dye as measured using the fluorescence spectrophotometer are 753 nm and 625 nm, respectively. At these wavelengths the absorbance of the two dyes is small (Fig. 1a) and thus optical attenuation in the intensity profile (Fig. 7b) can be very small.

Hell and Stelzer [10] have investigated intensity profiles obtained from homogeneous layers of fluorophore using x-z scans. However their test layers were considerably thicker (40–80 μm) than the titania films used here. Their edge-response curves indicated a drop-off over about 1–2 μm. There was also a decline in fluorescence intensity as the focal plane was shifted deeper into the film which was dependent on the refractive index of the film. Thus the observed decline in intensity towards the film-glass interface in Fig. 7b may be at least partially due to a difference in refractive index between the titania and the immersion oil. Spherical aberration may also have an effect on the shape of the intensity profile. Finally there remains the slight possibility that some dye may dissolve into the immersion oil at the external surface of the film. Thus the physical



(a)



(b)

Figure 7 (a) Fluorescence images of RuL_3Cl_2 dyed film obtained using scan *Method 2*, and (b) normalized intensity depth profile of RuL_3Cl_2 dyed films extracted form the fluorescence images (grey scale) of Figs 6a and 7a obtained using scans *Method 1* and *method 2*, respectively.

effects that define the observed fluorescence intensity profile in confocal microscopy are quite different from those pertaining to the SIMS measurements. However the results from the confocal microscopy clearly show that the dyes had penetrated throughout the film thickness. In summary, confocal microscopy requires little sample preparation, and provides rapid information on the film thickness and dye distributions. It has therefore proved a useful technique to study the mesoscopic structure of porous films doped with fluorescing dyes.

4. Conclusions

We have investigated the penetration and coverage of dye in a dye-sensitised nanostructured titania films. The films were dyed for different times (between 0.5 and 24 hours) and fluorescence images were acquired using Confocal Laser Scanning Microscopy (CLSM). At lower laser power setting (3 W), a bright fluorescence images were obtained from the RuL_3Cl_2 dyed film but very weak images when the N3-dyed films were analysed. The contrast of the N3-dyed films was increased by increasing the laser power setting to 9 W and this indicated that the N3-dye was weakly fluorescing. Using fluorescence spectrophotometer, the RuL_3Cl_2 dye solution was found to emit strongly at 625 nm while a weak emission at around 753 nm was detected from the N3-dye-solution. From fluorescence intensity profiles of the dye-sensitised titania films, a relatively lower intensity was observed at the surface and at the film-substrate interface in comparison to the interior part of the films. The observed profile may be a consequence of the more limited axial resolution in x-z scans, differences in refractive index between the titania film and the immersion oil, and effects of spherical aberration. The spatial resolution for detection was improved when x-y scans were used (*Method 2*). From the overall measurements, the two types of the dye molecules were found to percolate quickly up to the film-substrate interface irrespective of the dyeing time. The finding by confocal microscopy that the dye molecules penetrated up to the glass-film interface was consistent with previous results obtained by SIMS [9].

Acknowledgments

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