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## Characterization of a Dye-Sensitised Titania Solar Cell Electrode

Tuquabo Tesfamichael<sup>a,\*</sup>, Geoffrey Will<sup>b</sup>, John Bell<sup>a</sup>, Kathryn Prince<sup>c</sup>, and Nick Dytlewski<sup>d</sup>

<sup>a</sup> Queensland University of Technology, Faculty of Built Environment and Engineering, School of Mechanical, Medical and Manufacturing, Box 2434, Brisbane Q-4001, Australia

<sup>b</sup> Queensland University of Technology, Faculty of Science, Centre for Instrumental and Developmental Chemistry, Box 2434, Brisbane Q-4001, Australia

<sup>c</sup> Environment Division, ANSTO, PMB 1 Menai, NSW 2234 Australia

<sup>d</sup> Physics Division, ANSTO, NSW 2234 Australia

e-mail:

[t.tesfamichael@qut.edu.au](mailto:t.tesfamichael@qut.edu.au); [g.will@qut.edu.au](mailto:g.will@qut.edu.au); [j.bell@qut.edu.au](mailto:j.bell@qut.edu.au);  
[kep@ansto.gov.au](mailto:kep@ansto.gov.au); [ndy@ansto.gov.au](mailto:ndy@ansto.gov.au)

### Abstract:

We have characterised a dye-sensitised nanoporous nanocrystalline titania film used in prototype photoelectrochemical solar cell production. From Transmission Electron Microscopy the particles were seen as mixtures of tetrahedral and rhombohedral geometries with size distribution in the range between 10 and 25 nm. These particles were identified by X-ray Diffraction as nano-crystals of anatase and brookite phases. The film was sensitised with a ruthenium (II) based chromophore for different times (between 0.5 and 24 hours) and the penetration and coverage of the dye was studied using Secondary Ion Mass Spectroscopy. The dye was found to percolate through the whole of the titania film and was distributed uniformly. Using Rutherford Back Scattering, the composition of the film was determined and found to be 1 wt% Ru on maximum sensitisation. The optical properties of the dye-sensitised films were also measured which resulted in an increase of absorbance and a decrease of transmittance for dyeing times up to 8 hours. Beyond this time the values remained unchanged and thus a semi-transparent film with luminous transmittance between 0.12 and 0.60 were obtained.

Key words: dye-sensitised titania, nanocrystalline, solar cell, optical properties.

### 1. Introduction

Recently, dye-sensitised photoelectrochemical solar cells have become an alternative photovoltaic technology which provides a technically and economically credible alternative to present day p-n junction photovoltaic devices. Due to the simple

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\* Corresponding author. e-mail: [t.tesfamichael@qut.edu.au](mailto:t.tesfamichael@qut.edu.au)

constructions of these solar cells, the production cost is expected to be lower than for conventional PV cells. Today the most extensively studied dye-sensitised solar cell is based on nano-structured titania semiconducting thin films [1, 2]. The films can be produced using techniques such as sol-gel, reactive DC magnetron sputtering, and chemical vapour deposition [2, 3, 4]. Titania is a cheap, non-toxic, hard, chemically stable material which only absorbs light in the UV region. Thus, by incorporating visible light photosensitising dye onto the surface of the titania thin films, the absorption can be extended into the visible region of the solar spectrum. The structure of the nanoporous nanocrystalline titania thin film yields a high surface area structure which can accommodate a large amount of sensitising dye. Depending on particle size and film thickness, an optimum effective internal surface area enlargement can be obtained [5]. Once the titania particles are sensitised with the dye, the chemical interaction between the dye and the surface results in an irreversible linkage to the film [6]. When light is incident, at a wavelength corresponding to the chemisorbed dye molecule, electrons are injected from the excited electronic state of the adsorbed dye molecules into the conduction band of the titania semiconductor. Positive charges are transferred from the dye to a redox mediator in the electrolyte solution with which the cell is filled 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.

The cyclic nature of the photoelectrochemical reaction generates power through an external load without permanent chemical transformation [7]. To date laboratory devices have shown slightly above 10% overall solar to electric energy conversion efficiency [2]. The current measured efficiency for production is, however, limited to about 5%. In order to capture a significant market share, the conversion efficiency needs to be doubled, approximately equalling the efficiency of the laboratory prepared cells reported so far. Several factors determine the over all efficiency of the dye-sensitised solar cell. In optimising the performance of the cell, particle size [5, 8], shape, optical properties and porosity of the film [9] are key factors. Also important is the dye coverage, optical absorption of the dye [2], film thickness [10, 11], electrode material [12], distance between electrodes, and the electrolyte composition [13, 14, 15]. To fully understand and optimise the dye-sensitised solar cell, appropriate characterizations of every component in the cell and their effect when the cell is operating should be performed. To measure the effect of the components directly on the solar cell can be difficult. It can, however, be facilitated with the application of modelling provided each component is fully characterized [16, 17, 18, 19].

In this work we have characterized the dye-sensitised titania films used in prototype production of photoelectrochemical solar cells using a variety of techniques. The aim of these experiments was, to investigate the microstructure of the films; to determine the penetration and amount of the dye in the film; and to clearly understand the properties of each element in the film. This will provide a fundamental strategy for further improvements in the efficiency of the cell. Transmission Electron Microscopy (TEM) was used to investigate the microstructure of the films, including particle size, shape, and crystalline properties. The average crystallite size and phases of the films were studied using X-ray Diffraction (XRD) and the thickness of the films were

measured using a profilometer. The penetration and coverage of the dye in the films were analysed by Secondary Ion Mass Spectroscopy (SIMS). The amount of the dye in the film has been quantified by Rutherford Back Scattering (RBS). Conventional Spectrophotometers were used to measure the optical properties (absorption and transmittance) of the dye-sensitised titania films.

## 2. Experimental Methods

### 2.1. Sample Preparation:

Samples of titania films were obtained from Sustainable Technologies International Pty Ltd (STI) which has been extensively researching and commercialising the dye-sensitised titania solar cell. The titania electrode is produced by screen-printing a colloidal titania paste onto a sheet of conducting (SnO<sub>2</sub>:F coating) glass substrate. A subsequent heat treatment of the paste yields a mechanically -robust, high surface area, mesoporous titania layer. The nanometer-sized particles have been sintered together at 550 °C for 30 minutes forming a sponge-like porous structure. The porosity and transparency of the films can vary with sintering temperatures [11]. In this experiment transparent films with some small degree of light scattering were used. Scattering can increase the path-length of light in the film and enhance the optical absorption. A detailed experimental procedure for production of titania electrodes have been described elsewhere [1].

Samples of the titania film were sensitised by soaking the film 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. Then the samples were immersed immediately (while still warm) into the dye for different period 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. The dye used was Ru(II)L<sub>2</sub>(NCS)<sub>2</sub>Cl<sub>2</sub> (L=2,2'-bipyridine-4,4'-dicarboxylic acid) commercially known as Solaronix-dye. The dye solution was prepared in ethanol at a concentration of 4.1X10<sup>-4</sup> M.

### 2.2. Sample Characterization:

The microstructures of two titania films (a bare titania and titania with dye) were analysed using Philip CM 200 Transmission Electron Microscopy (200 keV) with an EDX system. From this investigation, the particle size, shape and distribution have been obtained. Philips X'Pert Multi-Purpose X-ray Diffractometer (MPD) with special accessories for thin film analysis was used to determine the crystalline phase and average particle size of the film. In this investigation, the samples were scanned with respect to the Bragg angle, 2θ using X-ray beam at a grazing incidence of Ω=1 degree.

Using Cameca ims5f SIMS, the depth profiling and distribution of dye from the surface of the film to the film-substrate interface were studied. The instrument was

equipped with duoplasmatron and caesium sources. Dye-sensitised titania samples were bombarded with  $O_2^+$  ion beam which knocks out (sputtering) secondary ions from the sample surface and mass analysed. Oxygen ion-beam etching was carried out at a primary ion beam voltage of 15 keV and a beam current of about 500 nA. The ion beam raster over an area of about 150x150 microns and secondary ions were detected over an area of 30 microns. Sputtering was stopped when the crater reached the conducting substrate. The thickness (crater) of the film was measured using Alpha step 200 mechanical stylus profilometer. The composition of the dye-sensitised films were determined by RBS using  $^4He^+$  ion beam at normal angle of incidence. The accelerator was set up to deliver an ion energy of 2 MeV, with the backscattered ions being detected at an angle of 169 degrees. The backscattered ions were collected by a silicon surface-barrier charged particle detector and energy analysed using a multi-channel analyser.

The absorbance and transmittance of the dye-sensitised samples were measured using Varian Cary 3 UV-Visible spectrophotometer in the wavelength range 300 to 900 nm at normal angle of incidence. As a reference, zero and 100% baseline signals were displayed before placing the samples for measurement of absorbance and transmittance, respectively.

### 3. Results and Discussions

#### 3.1 Film Microstructure

Figure 1 shows TEM cross-sectional image of a bare titania film. The particles were seen to form a porous-structure with adjacent nanocrystallites having made contact between each other through small necks. The contact between individual particles and between particles and the conducting substrate is necessary to allow efficient electronic conduction. The nano-crystallites making up the film have a particle size distribution in the range of 10 to 25 nm comprised mainly of tetrahedral shape crystals with some small rhombohedrals present. The predominant structure of anatase nanoparticles are described as square-bipyramidal and pseudocubic [2]. Tetrahedral bipyramids and truncated tetragonal geometries have also been reported for this type of phase therefore indicating a predominantly anatase phase present [20]. From Electron Diffraction analysis, circular rings of electron diffraction patterns have been obtained as shown in Fig. 1b. The average intensity of the diffraction patterns over each circular region has been extracted and plotted as a function of the radius of the rings (see Fig. 1c). The intensity peaks obtained from the diffraction rings after the background subtraction, were compared to standard data for polycrystalline diffraction patterns [21] and found best fit to those for anatase and brookite phases. The two phases appear to be randomly distributed over the entire film forming a compact porous microstructure when observed from both the cross-sectional and top views of the film. A similar microstructure as in Fig. 1 was observed for titania films which had been dyed with a Ru(II) sensitizer indicating no changes in morphology of the film on derivatisation.

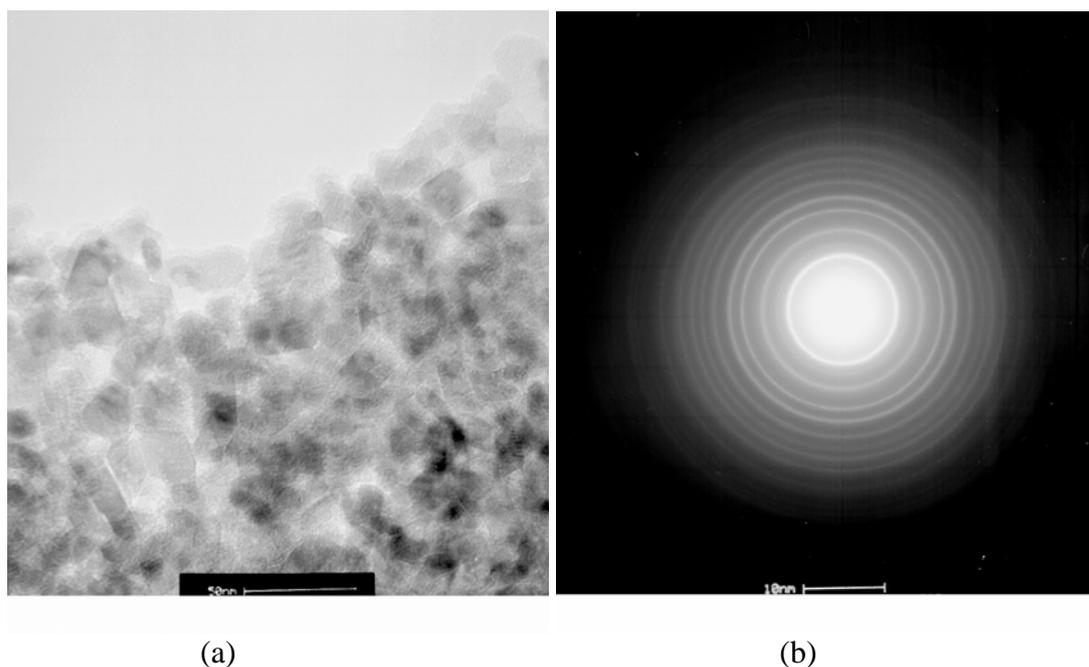


Fig. 1 (a) Cross-sectional TEM image of nanocrystallite titania film and (b) Electron Diffraction of the nanocrystallite film.

Figure 2b shows X-ray diffraction peaks of titania film as a function of  $2\theta$  between 20 and 60 degrees. The peaks have been identified from standard diffraction data [21] and they were predominately of anatase (A) phase with A(101) the most exposed orientation. The least square fit of the XRD data also shows a small diffraction peak, B(121), at  $30.8^\circ 2\theta$  that is characteristic of brookite (B) phase. The phases were also identified by Electron Diffraction analysis as discussed previously (Fig.1c). By modelling the diffraction patterns, the composition of each phase was calculated. From the calculation a significant amount of brookite (about 24%) was present. The average crystal size of the titania particles can be determined using Scherrer's equation [22] from the broadening of the diffraction lines measured at half its maximum intensity. The average particle size was found to be about 12 nm for the anatase phase and 16 nm for the brookite. These values are within the size distribution range obtained from TEM and relate to the typical particle sizes used in solar cell applications, 5 to 30 nm [23, 24].

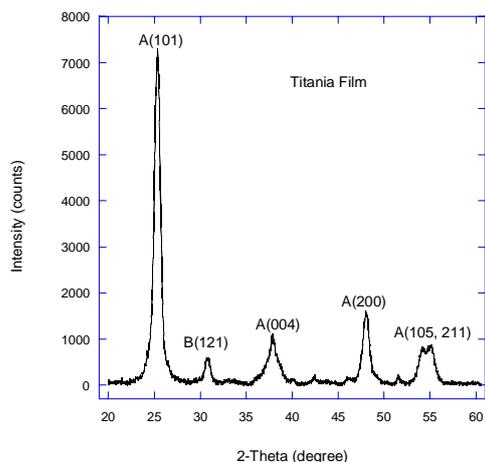


Fig. 2. X-ray diffraction of titania film deposited on conducting (SnO<sub>2</sub>:F) glass substrate as a function of Bragg angle, 2θ, between 20 and 60 degrees. Diffraction peaks for anatase (A) and brookite (B) phases are shown.

### 3.2 Dye Sensitisation

The concentration and distribution of the Solaronix-dye within the sensitised film was studied using Secondary Ion Mass Spectroscopy. By comparing the intensity of <sup>102</sup>Ru to that of <sup>48</sup>Ti an indication of the relative concentration of both can be determined. Figure 3 shows the <sup>102</sup>Ru:<sup>48</sup>Ti intensity ratio plotted as a function of depth from the film surface for different dye impregnation times. As shown in the figure the dye penetrates in the porous film right up to the film-substrate interface and is uniformly distributed. For samples dyed for longer times, a slightly lower quantity of dye at the front of the film than in the rest of the film can be observed. This could be due to the fluctuation of the instrument in the beginning of the sputtering process. By taking the values of the <sup>102</sup>Ru:<sup>48</sup>Ti intensity ratio averaged over the whole distribution profile, the overall Ru:Ti ratio has been determined and is shown in Fig. 4. The ratio increases with increasing dyeing time and about 0.2 % of relative concentration was obtained for films dyed for 24 hours.

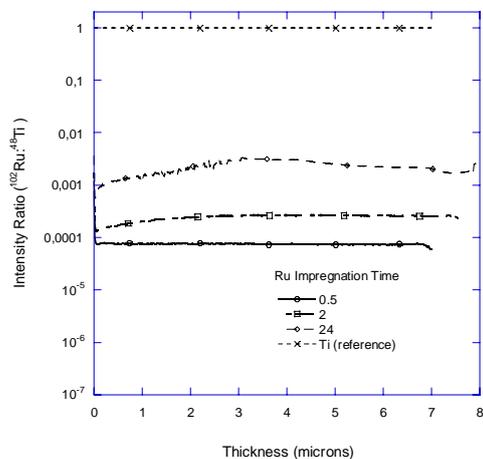


Fig. 3 Depth profile of dye-sensitised titania film analysed using SIMS as a function of thickness of the film for varying dyeing time.

From Rutherford Back Scattering analysis the composition of the dye-sensitised film was obtained by considering the film matrix as  $\text{TiO}_2\text{Ru}_x$ , where  $x$  is a variable parameter to be determined. Using RBS simulation package RUMP and applying an automatic iterative procedure the concentration of Ru in weight percent (wt%) for films dyed for different times was determined by varying the stoichiometry,  $x$ . The Ru uptake is faster in the early stages of the dyeing process and appears to saturate rapidly for dyeing times longer than about 8 hours as shown in Fig. 4. For the longest dye impregnation time (24 hours), the concentration of the dye was found to be 1 wt% of Ru. Particle Induced X-Ray Emission (PIXE) run with He ion beam was also performed on the above samples and the results were found in reasonable agreement with those obtained from RBS. In Fig. 4, the Ru concentration determined by RBS and Ru:Ti intensity ratio obtained from SIMS show similar trends.

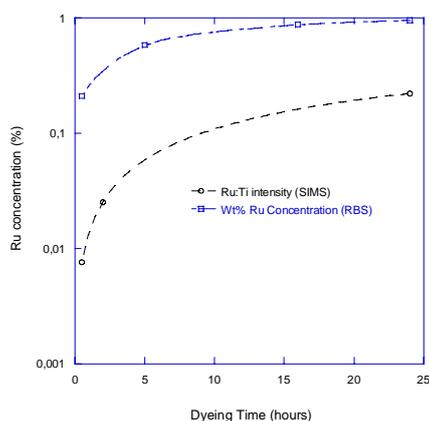


Fig. 4 Concentration of Ru as a function of dyeing time analysed by RBS and Ru:Ti overall intensity ratio obtained from SIMS.

Spectrophotometers are routinely used instruments for the investigation of the optical properties of solar cells. Figure 5a shows absorbance of titania films soaked in a Solaronix-dye for the indicated time intervals between 0.5 to 24 hours. The titania film absorbs only in the UV wavelength spectrum whereas the absorption can be seen to extend to longer wavelengths when the film is derivatised with the dye molecule. The absorbance of the film increases with increasing dyeing time and after 8 hours the absorbance of the film remained unaltered. The absorbance peak of the ruthenium dye is red-shifted (from 480 to 550 nm) when the dyeing time is increased. The flattened shoulder curve observed for the shorter dyeing time became a sharp distinct peak when the dyeing time increased. In order to give an optimum solar absorption the absorbance peak of the dye-sensitised films should coincide with the maximum intensity of the solar spectrum. In this respect the absorbance maximum (540 nm) of the Ru(II) dye is very close to the maximum intensity of the solar spectrum (550 nm). However, a significant absorption from the solar spectrum is lost from the absorbance minimum occurring at 475 nm.

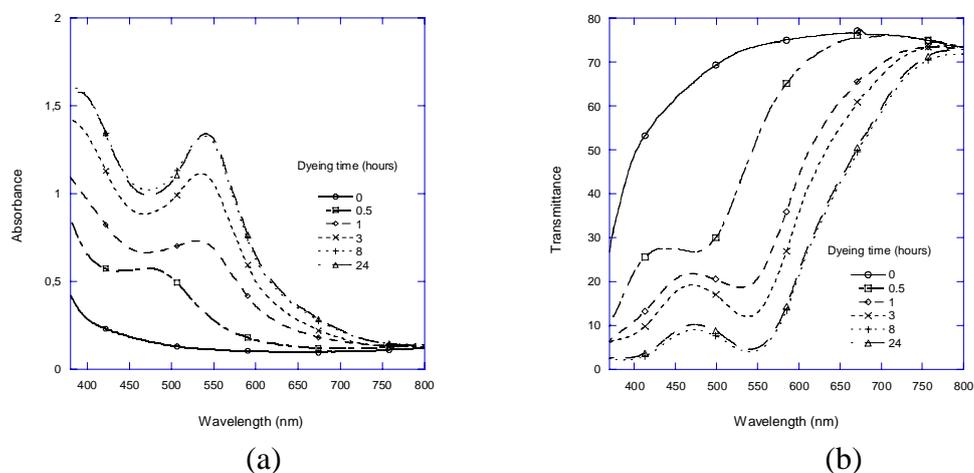


Fig. 5 (a) Absorbance and (b) transmittance of a dye-sensitised titania film as a function of wavelength. Various films were soaked in the dye for different times as shown in the legend.

Figure 5b shows transmittance of the dye-sensitised titania film as a function of wavelength for varying dyeing time. The transmittance in the shorter wavelength range decreases sharply with increasing dyeing time and after 8 hours no change in transmittance value was recorded. The films dyed for longer time possess a maximum and a minimum absorbance at 480 and 550 nm, respectively. For the longest dyed films, the on-set of transmittance is 600 nm at which point the absorption of the dye is weaker. Luminous transmittance of the dye-sensitised titania films were determined by weighting the transmittance of the films (Fig. 5b) in the wavelength range 380 to 760 nm to the intensity of the corresponding visible spectrum for air mass 1.5. Figure 6 shows luminous transmittance,  $T_{lum}$  of titania films immersed in a dye between 0.5 to 24 hours. The titania layer without dye is fairly transparent in the measured wavelength range and has a luminous transmittance of about 0.77 which is less than the value of the conducting glass substrate (0.86). On the other hand the dye sensitised titania films became semi-transparent and depending on the dyeing time their luminous transmittance varied between 0.12 and 0.60. As shown in Fig. 6, the luminous transmittance,  $T_{lum}$  decreases sharply for the shorter dyeing time and remained almost constant (0.12) above 8 hours of dyeing time. In the figure the value of  $1-T_{lum}$  as a function of the dyeing time is also plotted and can be observed with sharp increase for the shorter dyeing time but remained almost constant when the dyeing time becomes longer. The trend of the  $1-T_{lum}$ , in Fig. 6 is directly proportional to the optical absorption and is found to be similar to the dye uptake as a function of time determined by RBS and SIMS analyses (Fig. 4).

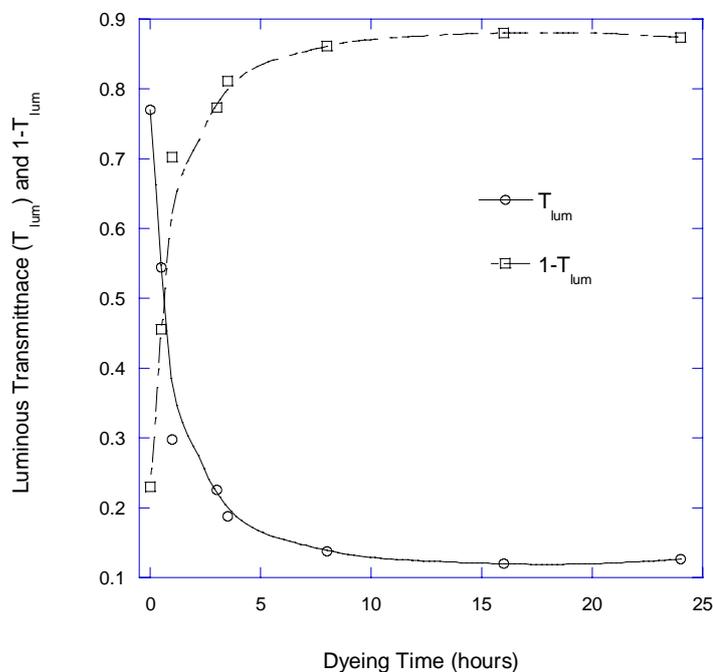


Fig. 6 Luminous transmittance,  $T_{lum}$  as a function of dyeing time obtained by weighting the transmittance of the dye-sensitised titania films in the wavelength range 380 to 760 nm to the intensity of the visible spectrum. In addition the value of  $1-T_{lum}$  is also shown.

#### 4. Conclusions

We have investigated the microstructure, optical properties and dye coverage of a nano-crystalline dye-sensitised titania film. The titania film has particle size between 10 to 25 nm with a tetrahedral and a rhombohedral shaped particles. The film is primarily of anatase phase with substantial amount (24%) of brookite phase. Titania films when immersed in ruthenium based dye solution for different time intervals resulted in an increase in absorbance and decrease in transmittance up to 8 hours of immersion time. Beyond this time the optical properties did not changed significantly. The Ru uptake, as analysed by RBS and SIMS, is faster in the beginning of the dyeing process and remains almost constant when the samples kept in the dye for longer times. This trend is found to be similar to the results obtained from optical measurements. About 1 wt% of Ru was determined by RBS investigations from a film dyed for 24 hours. The dye molecules percolate quickly up to the film-substrate interface and are found uniformly distributed in the porous titania film. The penetration of the dye molecules up to the interface is important for the flow of the injected electrons to the conducting substrate with minimum losses. Despite the quick penetration of the dye in the film, we observed that an optimum time is needed to allow the maximum amount of dye coverage.

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