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Molecular Scale Characterisation of the Titania – Dye – Solvent Interface in Dye-Sensitized Solar Cells

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Abstract

Charge separation at the dye/titania interface in dye sensitised solar cells is strongly influenced by the thickness and homogeneity of the sensitizing dye layer, as this controls the potential drop across the interface, and the probability of an excited electron being transferred from the dye to the titania. In this study we use Atomic Force Microscopy (AFM) and the depth profiling method Neutral Impact Collision Ion Scattering Spectroscopy (NICISS) to investigate the thickness and homogeneity of N719 dye adsorbed to titania before and after rinsing with pure acetonitrile. Both experimental methods show that the dye layers are closed but inhomogeneous. Inhomogeneity is more pronounced for unrinsed samples.

Introduction

Energy supply has been identified as the most significant problem humanity will face in the next 50 years [1]. The depletion of fossil fuels, and the environmental and political issues associated with anthropogenic global warming, has led to increased demand for alternative energy sources. Solar energy is a clean, inexhaustible resource. The supply of solar energy to the earth is 3×10^{24} J per year, approximately 10,000 times greater than current global consumption, so covering just 0.1% of the Earth's surface with 10% efficient solar cells would produce enough energy to satisfy present global demand [2]. Conventional silicon-based solar cells have surpassed this efficiency standard, but are limited by their cost. The dye-sensitised solar cell (DSC) has recently attracted significant research attention. It is a relatively new and inexpensive device, and currently the only verified alternative to conventional solid-state photovoltaic devices [3].

The DSC employs a wide band gap semiconductor material, typically TiO_2 , in combination with a sensitizing molecular dye. In order to optimise light absorption TiO_2 nanoparticles are sintered to form a nanoporous matrix $\sim 10\mu\text{m}$ thick on which a layer of dye is adsorbed. Preferably, the dye layer should be a perfect monolayer with well anchored molecules in order to maximize the efficiency of injection

of photoelectrons into the semiconductor material. Photoexcitation of the dye leads to injection of electrons into the titania and leaves behind a hole in the dye. The dye is regenerated by electron donation from the electrolyte; typically an organic solvent containing a lithium salt and an iodide/triiodide redox couple. Dye regeneration prevents recapture of the conduction band electron by the oxidized sensitiser. The electron diffuses through the porous matrix to a transparent electrically conductive anode.

It is assumed that the thickness, composition and morphology of the dye layer at the dye/titania interface plays an important role in for the function of DSCs. The model for the titania/dye interface developed by Gregg et al. [4] assumes charge carriers are generated in a dye monolayer, inducing mobile electrolyte ions to rearrange – if possible - such that the charge carriers are screened. If electrolyte ions penetrate the dye layer they will screen the charges generated at the interface, and as a consequence restrict the potential drop between the electrolyte and the titania to just the region of the dye layer. If electrolyte ions do not penetrate into the dye layer, the potential drop will extend over a larger distance. In either case, the thickness of the titania layer will determine the gradient of the potential and thus the motion of the generated charge carriers. Thus, under this model, the operation and efficiency of the DSCs will be strongly influenced by the morphology of the dye layer. Further, if the dye layer is thicker than a monolayer, this will lead to photocurrent quenching [5]. As such the thickness and homogeneity of the dye layer adsorbed onto the titania will influence DSC efficiency. It is generally assumed that dye molecules form a monolayer on the titania matrix, [4, 6, 7, 8, 9] but there is little evidence for monolayer formation, and to our knowledge no evidence that the dye layer is homogeneous.

In the present study we investigate the lateral and normal structure of the N719 dye layer adsorbed on titania. Atomic Force Microscopy (AFM) imaging is used to follow the dye adsorption process *in situ*. Neutral Impact Collision Ion Scattering Spectroscopy (NICISS) is used to determine the elemental

concentration depth profile of the titania/dye interface. In combination these techniques allow conclusions to be drawn about the thickness and homogeneity of the adsorbed dye layer.

Materials and Methods

N719 dye ($[\text{RuL}_2(\text{NCS})_2]:2 \text{ TBA}$) with $\text{L} = 2,2'$ -bipyridil-4,4'-dicarboxylic acid and TBA = tetra-*n*-butylammonium) [10] was obtained from Dyesol (Queanbeyan, NSW, Australia) and used as received. When not in use all powdered dyes and dye solutions were stored in sample vials, sealed with Parafilm and wrapped in aluminium foil to minimize exposure to heat and light, which may decrease cell performance. [11, 12] 1-ethyl-3-methylimidazolium tetracyanoborate (EMIm-TCB, $\geq 98\%$, Merck, Germany), [13] acetonitrile (99.8%, Aldrich), 4-*tert*-butylpyridine (99%, Aldrich) and titanium dioxide nanoparticles (anatase, 98%, May & Baker) were used as received.

The adsorption isotherm was prepared by the solution depletion method.[14, 15]. Samples containing 5 mL of N719 solution and a defined amount of particulate titania (anatase) were stirred end-over-end for 24 hours, then centrifuged at 30 rpm for 15 minutes. The concentration after adsorption is determined spectrophotometrically and the surface excess is determined by the change in solution concentration.

The titania surfaces for AFM and NCISS investigations were prepared by Luke Parkinson at the Ian Wark Research Institute, South Australia. The substrates were ITO-coated glass slides containing an insulating layer of mica. The titania surface was then deposited onto the substrate by sputtering with DC magnetron at 470 V and 1.7 A for 10 minutes in 30 sccm argon and 10 sccm O_2 at 1.2×10^{-3} mbar.

Dye adsorption to surfaces used for NCISS was carried out on the clean titania surfaces. A 0.5 mM solution of N719 dye in acetonitrile was prepared and placed in a clean sample vial. [16] The surface was placed in the solution immediately after UV irradiation to prevent exposure to air and other contaminants. The vial was sealed with Parafilm and wrapped in aluminium foil to prevent light

exposure; the typical dye adsorption time was 24 hours. After the required time had elapsed, the surface was removed from the dye solution and rinsed with copious acetonitrile immediately prior to analysis.

AFM images and force curves were measured using a Digital Instruments Nanoscope III Multimode AFM in soft contact mode [17]. Dye adsorption was carried out *in-situ*. Scan rates between 0.1 and 1 Hz were used. Si₃N₄ standard cantilevers with sharpened tips were irradiated with ultraviolet light for 20 minutes before use. All cantilevers used were from the same batch and had an average spring constant of 0.32 ± 0.005 N/m. A fluid cell with a silicone O-ring was used to house the solvent. These were cleaned by ultrasonication for 20 minutes, rinsed with ethanol and Milli-Q water, and then dried with nitrogen before use. All data was collected at 21°C. Temperature was maintained using an incubator. All experiments were repeated at least three times.

In a NCISS experiment the target is bombarded with a pulsed beam of inert gas ions - mostly helium ions - with a kinetic energy of several keV [18]. The energy of the projectiles backscattered from the atoms in the target is determined by their time of flight from the target to the detector. The projectiles lose energy during the backscattering process, and the energy transfer depends on the mass of the target atom. This first type of energy loss is used to identify the element from which a projectile is backscattered. The projectiles also lose energy on their trajectory through the bulk due to small angle scattering and electronic excitations of the molecules constituting the target (stopping power). This energy loss is used to determine the depth of the atom from which a projectile is backscattered. In combination, these two types of energy losses are used to determine the concentration depth profiles of the elements.

A typical NCISS spectrum consists - apart from the broad background of sputtered hydrogen - of energy loss spectra for each element constituting the sample. The shape of the spectrum measured of a single element is determined by its concentration depth profiles in the sample. The spectra are also influenced by the distribution of inelastic energy losses during the back scattering process [19] and the

straggling of the energy loss due to the stopping power [20]. The data evaluation is described in references 18 and 19.

The measurements were averaged over a sample size of about a few square millimetres to keep the damage due to the impact of the ions low. The helium ion dose was kept below $5 \cdot 10^{13}$ ions/cm².

Results and Discussion

A single step adsorption isotherm for N719 dissolved in acetonitrile on anatase titania is presented in Figure 1. The surface excess is below detection limits for concentrations less than 0.3 mM. A gradual increase in adsorption is noted between 0.3 mM and 0.45 mM, but the surface excess increases very rapidly between 0.45mM and 5 mM, indicative of cooperative adsorption, [21] perhaps due to attractive van der Waals interactions between adsorbed dye molecules. The surface excess appears to slowly increase between 0.5 mM to saturation levels at 0.7 mM as the remaining adsorption sites on the substrate are filled. The surface excess increases more slowly with concentration in this region on account of steric interactions between dye molecules. The AFM and NICISS experiments detailed below use a dye concentration of 0.5 mM as this is the concentration generally used to prepare devices, [22] and the ~ 10% increase in surface excess that occurs above this concentration may be within experimental error.

Figure 1

The titania substrates for AFM and NICISS experiments were prepared by sputter coating 200 nm TiO₂ particles onto ITO coated glass. There are two key reasons for using these substrates and not a sintered titania matrix. Firstly, the porosity of the working electrode complicates AFM and NICISS data interpretation. Secondly, the sputter coated layer will have fewer impurities than the sintered substrate, as a sintered titania layer is fabricated from a paste of a solvent/titania nano-particle mixture, and residues of the solvent could remain. 200 nm particles were used to prepare the sputtered surface.

These particles are about ten times larger than those used to fabricate the sintered substrate, but both electron microscopy and atomic force microscopy images of the titania matrix reveal features with dimensions around 200 nm [23]; particles may coalesce and grow during sintering. Our model sputtered surfaces therefore have roughness and topography similar to the working electrode, but are non-porous and are also more easily cleaned prior to experiment.

Contact mode images of the titania substrate before dye adsorption, during the dye adsorption process and following rinsing with pure acetonitrile are presented in Figure 2. Figure 2a shows the bare titania surface (before dye adsorption) in the presence of acetonitrile, revealing a characteristic pattern consistent with titania particles approximately 200nm in diameter. These particles appear relatively homogeneous in size and shape, resulting in surface corrugations approximately 20 nm in height.

Figure 2

Figure 2b shows the surface three hours after a 0.5 mM dye in acetonitrile solution was passed into the AFM cell. For time periods less than three hours the surface had the same appearance as the pure acetonitrile result (Figure 2a); adsorption will certainly begin before three hours, but cannot be detected using AFM. Given that the calculated diameter of the N719 molecule is only 1.5 nm, and that surface corrugations are ~ 20 nm high, if the dye adsorbed in a true monolayer the appearance of the surface should be quite similar to that shown in Figure 2a. However, in Figure 2b parts of the surface appear much smoother such that individual titania particles can no longer be resolved. This indicates gross accumulation of dye between titania particles. Dye adsorption continues with time, and after 24 hours (Figure 2c) the “smoothing-off” effect dominates most of the surface, such that the characteristic pattern of titania particles is no longer visible. The conclusion from these images is that much of the surface is indeed coated with dye, but that the thickness is far greater than an ideal monolayer. AFM force curves (not shown) were obtained in the areas where the particulate nature of the surface was clear and for smoothed regions. Both force curves were dominated by a short range van der Waals

attraction, but there was evidence of compressibility in the compliance region of force curves obtained in the smooth over region, consistent with gross dye adsorption.

It is common to rinse the dye-coated surfaces with ethanol [2,24] or acetonitrile [25] to remove aggregated dye prior to device assembly. This step has also been completed in the AFM cell, and an image obtained after rinsing with copious quantities of acetonitrile is shown in Figure 2d. Clearly rinsing has removed a significant amount of the adsorbed dye, revealing the particulate titania surface in some places, but in other areas a thick dye coating remains.

NICISS measurements have been performed on sputtered titania surfaces after immersion in 0.5 mM N719 dye in acetonitrile solutions for 24 hours. In Figure 3 concentration depth profiles for carbon (a), ruthenium (b) and titanium (c) are shown for samples before and after rinsing with pure acetonitrile. The roughness of the sputtered titania substrate complicates interpretation of NICISS data, as the measurement averages over the entire sampled surface (the sampled area is $\sim 0.5 \text{ cm}^2$). This complicates conclusions regarding homogeneity. However, comparison of rinsed and non-rinsed samples allows inferences regarding the surface composition to be made.

The titanium depth profiles for the rinsed and non-rinsed samples are presented in Figure 3a. It is clear that rinsing markedly affects the data. The depth at which the titanium concentration begins to rise is shifted by about $15 \text{ \AA}$ for the non rinsed sample relative to the rinsed sample, and the rate at which the titanium concentration increases with depth (the slope of the concentration depth profile) is also reduced; the mid-point of the non-rinsed sample is at $45 \pm 10 \text{ \AA}$ compared to $25 \pm 5 \text{ \AA}$ for the rinsed sample. The reduced depth at which the titania concentration begins to increase for the non-rinsed sample is consistent with a thicker dye layer, while the reduced slope of the increasing region shows the dye layer is less homogeneous.

The concentration depth profiles of carbon (Figure 3 b) and ruthenium (Figure 3 c) both increase sharply at the surface plane and reach a maximum within a few nanometers. As expected, the

concentration of ruthenium is two orders of magnitudes less than that of carbon reflecting the relative composition of the dye. The maximum concentration of both carbon and ruthenium are higher in the non-rinsed sample, once again consistent with greater dye adsorption. For both elements, the FWHM of the non-rinsed sample ($25 \pm 5 \text{ \AA}$) is greater than that of the rinsed sample ($15 \pm 5 \text{ \AA}$), and the rate at which the concentration decreases with depth is lower for the non-rinsed samples. Both results are consistent with the dye layer being thicker and less homogeneous in the non-rinsed sample.

The coverage of the titania surface with dye molecules can be determined quantitatively by integrating the ruthenium concentration depth profiles. The integration yields in the case of the rinsed sample a surface coverage of $(2.6 \pm 1) \cdot 10^{13} \text{ molecules/cm}^2$ (1 molecule per 3.8 nm^2) and in the case of the non rinsed sample $(4.2 \pm 1.5) \cdot 10^{13} \text{ molecules/cm}^2$ (1 molecule per 2.4 nm^2). These numbers are similar in their order of magnitude to those determined by using models to fit the quantum yield of photoelectrical experiments [26, 27].

Taking the difference between the concentration depth profiles can be used to cross check whether the results are consistent. The difference shows in case of the titanium how the layer thickness of the layer adsorbed on titania reduces when rinsing the sample. A similar result should be obtained for ruthenium and carbon. The difference between the concentration depth profiles peak in the case of ruthenium and titanium indeed at the same depth of about 50 Angstrom. However, the total count rate of the ruthenium signal in the measurements shown here is too low to allow a rigorous comparison.

The filling of the troughs seen in the AFM images in figure 2 and the estimation of the dye layer thickness in a trough region might seem to be a bit larger than the range of the layer thickness found in the concentration depth profiles in figure 3. There might be various reasons for this observation though a conclusion could be drawn only by performing a rigorous analysis. Firstly, we did not investigate the same samples with AFM and NCISS but compare samples prepared under the same conditions. Variations between samples prepared under same conditions are possible. Secondly, the depth scale in

a NICISS experiment has an uncertainty in the scaling of the depth scale of about 20% and needs to be taken into account when comparing AFM images and NICISS experiments. However, it must be emphasised that the uncertainty in the scaling of the depth scale does not influence results like the total amount of the dye adsorbed on the surface as such values are calibrated within a single NICIS spectrum. Thirdly, for a rigorous analysis of layer thickness variations we would need to obtain statistics for layer thicknesses estimated from the AFM images and compare the distribution of layer thicknesses – the areas of filled troughs and areas with very thin layers – with the concentration depth profiles obtained with NICISS. Thus the current analysis is qualitative rather than quantitative.

Surface roughness impacts the concentration depth profiles of carbon, ruthenium and titanium. A rough substrate means that NICISS averages over all slopes of the titania substrate, and even a homogeneous dye layer would yield a concentration depth profiles consistent with inhomogeneous dye layers. However, in this work the interpretation is based on comparison of slopes before and after rinsing. Moreover, as the corrugation of the substrate is much smaller than the lateral structure (20 nm versus 200 nm), the corrugation of the substrate has only a minor influence on the concentration depth profiles measured with NICISS. Thus we can conclude that even the profiles of the rinsed sample show evidence for a non-homogeneous dye layer thickness.

The data presented here may suggest that 0.5 mM is not the optimal concentration for preparing devices. This issue will be elucidated by planned NICISS and optical reflectometry experiments, which will determine the adsorption kinetics, the surface excess per unit area at equilibrium, the mass of material removed from the surface during rinsing, and the desorption kinetics.

Conclusions

The adsorption isotherm of the dye N719 on titania was determined. A dye concentration of 0.5 mM was chosen for further study as this is the concentration where the adsorption isotherm plateaus. The thickness and homogeneity of the dye layer was studied with AFM and the depth profiling method

NICISS. Samples were studied after dye adsorption on the titania, both before and after. Both samples reveal closed but inhomogeneous dye layers, but the rinsed sample is more homogeneous than the non-rinsed sample. Critically, this study shows that the pores between particles on the titania substrate are filled during dye adsorption. It may be anticipated that that devices with this dye layer structure have less than optimum function.

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Figure 1: Adsorption Isotherm for N719 dye on titania nanoparticles (anatase).

Figure 2. 10 μm x 10 μm AFM topography images showing the progress of dye adsorption on sputtered TiO₂ surfaces over 24 hours, showing key surface changes: (a) t=0 hrs, (b) t=3 hrs, (c) t=24 hrs, (d) after rinsing with pure acetonitrile.

Figure 3. Concentration depth profiles of titanium (A), carbon (B) and ruthenium (C) measured with NISS. Surfaces were examined before and after rinsing with acetonitrile.

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