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Molecular control of recombination dynamics in dye sensitised nanocrystalline TiO_2 films†

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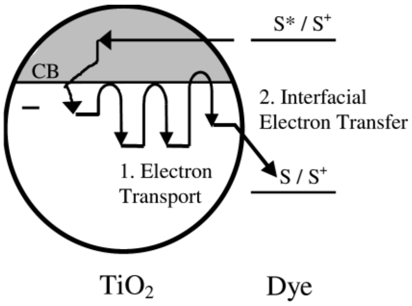
Received (in Cambridge, UK) 25th February 2002, Accepted 17th April 2002
First published as an Advance Article on the web 9th May 2002

Modification of the structure of a porphyrin dye shows a significant change in the rate of charge recombination between injected electrons in the TiO_2 and the oxidised dye anchored to it following optical excitation, offering an insight into fundamental understanding of processes occuring at the dye/semiconductor interface.

A key challenge in the development of molecular electronics is the electrical interfacing of molecular redox species with inorganic metal or semiconductor surfaces. An area attracting particular interest at present is the functionalisation of nanocrystalline metal oxide films by the adsorption of molecular redox dyes. This interest derives both from the suitability of such films for fundamental spectroscopic studies of interfacial electron transfer processes,[1] and also from their importance in technological applications ranging from electrochromic windows to photoelectrochemical solar cells.[2]

In this paper we are concerned with the charge recombination dynamics observed in dye sensitised nanocrystalline TiO_2 films. This recombination is observed following the photoinduced electron injection from adsorbed dye molecule into the conduction band of film, as illustrated in Scheme 1. Such recombination dynamics are of particular importance in the development of dye sensitised photoelectrochemical solar cells, where interfacial recombination reactions are the principle loss mechanism limiting device function.[1] Several groups have focussed upon the importance of the interfacial electron transfer step in controlling the dynamics of this recombination reaction (step 2 in Fig. 1),[3] and have modelled such dynamics in terms of non-adiabatic electron transfer theory as developed by Marcus, Gerischer and co-workers. In contrast, our own studies, employing similar dye/semiconductor materials, have emphasised the importance of electron transport with the semiconductor nanoparticles (step 1 in Fig. 1) in controlling the recombination dynamics.[4] Our observed recombination dynamics have been successfully modelled in terms of a random walk of electrons within the metal oxide film between an energetic distribution of trap states,[5] and found to be consistent with independent experimental observations of the occupancy of these trap states as a function of applied bias.[4]



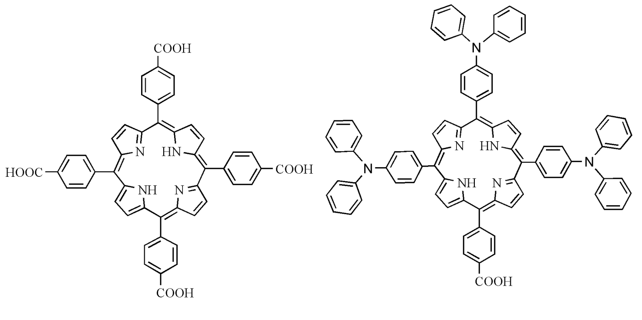
Scheme 1

In this paper we provide data which suggest that by appropriate design of the sensitiser dye, it is possible to move between transport limited (step 1) and interfacial electron transfer limited (step 2) recombination dynamics under the same spectroscopic conditions by appropriate design of the molecular sensitiser dye.

Our studies employed two different sensitiser dyes as illustrated in Scheme 1. Dye **1**, *meso*-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (Scheme 2) was bought from Porphyrin Products Inc. Dye **2,** *meso*-5-(4-carboxyphenyl)-10,15,20-tris(4-diphenylaminophenyl)porphyrin, differs from the dye **1** by the substitution of three carboxyphenyl peripheral groups with triphenyl amine (TPA) electron donor groups. Synthesis[6] and characterisation of dye **2** is detailed in the supporting information. Dye sensitised nanocrystalline TiO_2 films were prepared as described previously.[7] Absorption spectra of the dye sensitised TiO_2 films were indistinguishable from solution spectra (after subtraction of background absorption/scatter from the TiO_2 alone), indicating negligible dye aggregation.

Transient absorption spectroscopy was used to monitor the charge recombination dynamics following π–π^* photoexcitation of the dyes. Details of the apparatus employed have been given previously.[4] The films were incorporated as the working electrode of a three electrode photoelectrochemical cell, employing anhydrous, degassed 0.1 M $LiClO_4$ in propylene carbonate, and held at 0 V *vs.* the Ag/AgCl reference electrode. All experiments were conducted at room temperature. Experiments employed low intensity (20 μJ cm^{-2}) 600 nm excitation pulses. At this excitation wavelength the optical density of all films employed was ~ 0.1, resulting in equal excitation densities for both sensitiser dyes (<0.1 excited dyes/nanoparticle). For both sensitiser dyes, electron injection was observed with a high yield on a timescale faster than the apparatus time resolution, consistent with our previous studies.[8]

Recombination dynamics were monitored by observation of the decay of the photoinduced absorption in the near-IR attributed to dye cation absorption and induced absorption of injected electrons. Typical data for the two sensitiser dyes are shown in Fig. 1, employing probe wavelengths of 800 and 900 nm for films sensitised by dyes **1** and **2**, respectively. It is



Dye 1 **Dye 2**

Scheme 2

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† Electronic supplementary information (ESI) available: synthesis and characterisation data for dye **2**. See http://www.rsc.org/suppdata/cc/b2/b201855a/

DOI: 10.1039/b201855a

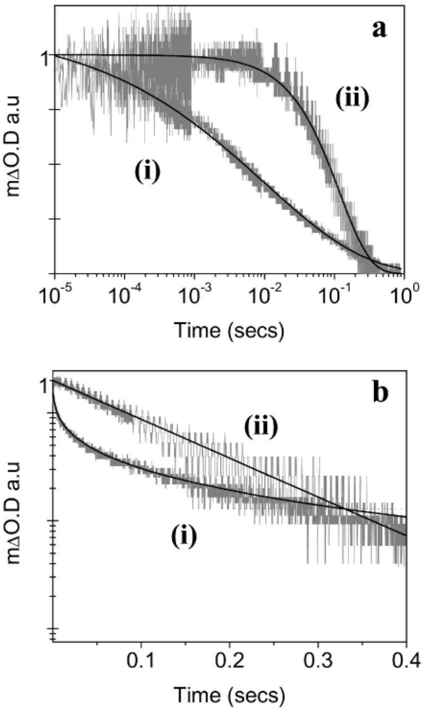

Fig. 1 (a) and (b): Transient absorption data monitoring charge recombination dynamics for TiO_2 films sensitised with dye **1** (i) and dye **2** (ii). Both figures are the same data with (a) being a lin/log plot and (b) being a log/lin plot. The black lines are the fits to the decay kinetics corresponding to (i) a stretched exponential ($\Delta OD \propto \exp(-(t/\tau)^{\alpha})$, $\alpha = 0.31$) and (ii) a monoexponential decay. The signals have been normalised for comparison purposes.

apparent that the recombination dynamics observed employing dye **2** are significantly slower than those observed for dye **1**, exhibiting recombination half times $t_{50\%}$ of 80 and 4 ms, respectively. It is further apparent that the temporal shape of the recombination dynamics differ significantly between these two dyes. For dye **1** a decay kinetics fit well to a stretched exponential ($\Delta OD \propto \exp(-(t/\tau)^{\alpha})$, with $\alpha = 0.31$. Such stretched exponential recombination dynamics are typical of those we have observed previously for a range of different dyes under similar experimental conditions.[8] In contrast, for dye **2** the recombination dynamics show an excellent fit to a monoexponential decay ($\Delta OD \propto \exp(-t/\tau)$, $\alpha = 1$) as illustrated by the log/linear plot shown in Fig. 1b.

We have previously demonstrated that stretched exponential recombination dynamics, as observed here for nanocrystalline TiO_2 films sensitised by dye **1** are consistent with the charge recombination dynamics being rate limited by electron transport within the metal oxide film, step 1 in Scheme 1. The stretched exponential nature of these kinetics have been attributed to an inhomogeneous distribution of trap depths in the film, resulting in a broad distribution of detrapping (and therefore recombination) times. Our observation that sensitiser **2** exhibits recombination dynamics an order of magnitude slower than sensitiser **1** in itself suggests that for this sensitiser interfacial electron transfer, step 2 in Scheme 1, is critical to determining the overall recombination dynamics. Strong support for this conclusion comes from our observation of monoexponential recombination kinetics with this dye. In the limit of slow interfacial electron transfer, the injected electrons are expected to have sufficient time to equilibrate thermally between all available trap sites prior to recombination, resulting in the inhomogeneous distribution of recombination times collapsing to the observed homogeneous monoexponential decay.

The slower recombination dynamics observed for the dye **2** sensitised TiO_2 films most probably derives from a larger physical separation of the dye cation state from the film surface rather than differences in dye redox potential. Cyclic voltammetry studies dyes **1** and **2** in solution indicate that the oxidation potential of dye **2** was less positive than dye **1**, consistent with the expected electron donating function of the TPA moieties of this dye. Comparison with theory (the recombination reaction is thought to lie in the Marcus inverted region) and with previous experiments[9] suggests that this shift in redox potential should result in faster recombination dynamics, in contrast to the observed retardation of the dynamics for this dye. In contrast the large size of the TPA groups, the reduction in the number of carboxylate binding groups and the potential supersensitising function of the TPA moieties can all be expected to contribute to increasing the physical separation of the cation species of dye **2** from the film surface. The strong distance dependence of interfacial electron transfer dynamics as been well documented previously, although it has not previously been employed to move between transport and interface limited recombination as reported here.

We conclude that by suitable design of the molecular sensitiser dye we appear to be able to move between regimes in which the recombination dynamics of dye sensitised, nanocrystalline TiO_2 films are controlled either by electron transport dynamics within the metal oxide film or by the rate of the electron transfer across the dye/semiconductor interface. This control has been achieved by sufficiently retarding the rate of the interfacial electron transfer step such that it becomes the rate determining step in the overall recombination process.

We thank Richard Willis and Thierry Lutz for fabrication of the TiO_2 films, Colin J. Campbell for help in electrochemistry, Jenny Nelson and Saif Haque for may helpful discussions and Richard Monkhouse for assistance with the transient absorption spectrometer. Funding from the EPSRC is gratefully acknowledged.

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