

Interfacial electron transfer in dye sensitised nanocrystalline TiO₂ films

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Abstract. Sub-picosecond transient absorption study has been employed to study the electron transfer kinetics in the dye-sensitized TiO₂ films used in commercial photovoltaic devices. The electron injection in these dye sensitized films occurs on an ultrafast time scale with two components, 150 fs and 1.2 ps.

Keywords. Interfacial electron transfer; dye-sensitized films; sub-picosecond studies.

1. Introduction

The sensitisation of wide band gap semiconductors to visible irradiation by the adsorption of dyes to their surfaces is of widespread technological importance. Recently photoelectrochemical solar cells have been developed based upon dye sensitised nanocrystalline titanium dioxide (TiO₂) thin films. These devices have already achieved > 10% energy conversion efficiencies, and are now entering commercial production¹. High sensitisation efficiencies have, however, been achieved experimentally only for a very few dye/semiconductor systems and this is one of principal limitations of further technological development.

The sensitisation reaction involves an interfacial electron transfer from the optically excited dye molecule state to the conduction band of the semiconductor. The kinetics of this interfacial electron transfer are crucial to the efficiency of dye sensitisation, but have only attracted limited study to date. We present here a sub-picosecond transient absorption study of these interfacial electron transfer reactions. We employ this technique to study the electron transfer kinetics in the dye sensitised TiO₂ films employed in commercial photovoltaic devices.

Nanocrystalline TiO₂ films coated with the ruthenium (II) sensitizer dye Ru(2,2'-bipyridyl-4,4'-dicarboxylate)₂(NCS)₂ (1) were prepared as previously². ZrO₂ films coated with 1 were used as control samples. ZrO₂'s conduction band edge is ~ 1 V more negative than TiO₂, thus precluding electron injection from the excited dye. Transient absorption data were collected at room temperature using apparatus described previously³, with a 150 fs instrument response. An excitation wavelength of 605 nm was used.

Absorption difference spectra for the dye coated ZrO₂ and TiO₂ films at a time delay of 5 ps are shown in figure 1a. These spectra were taken using identical excitation

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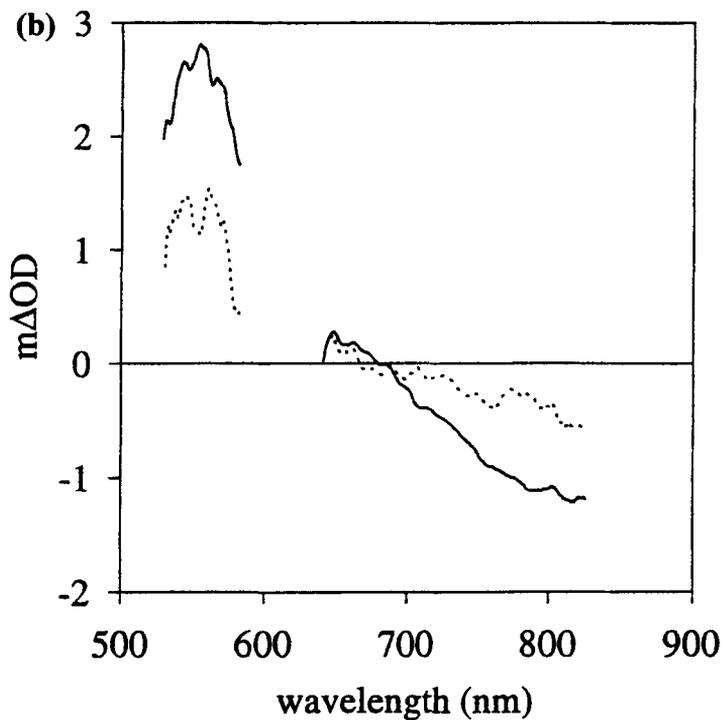
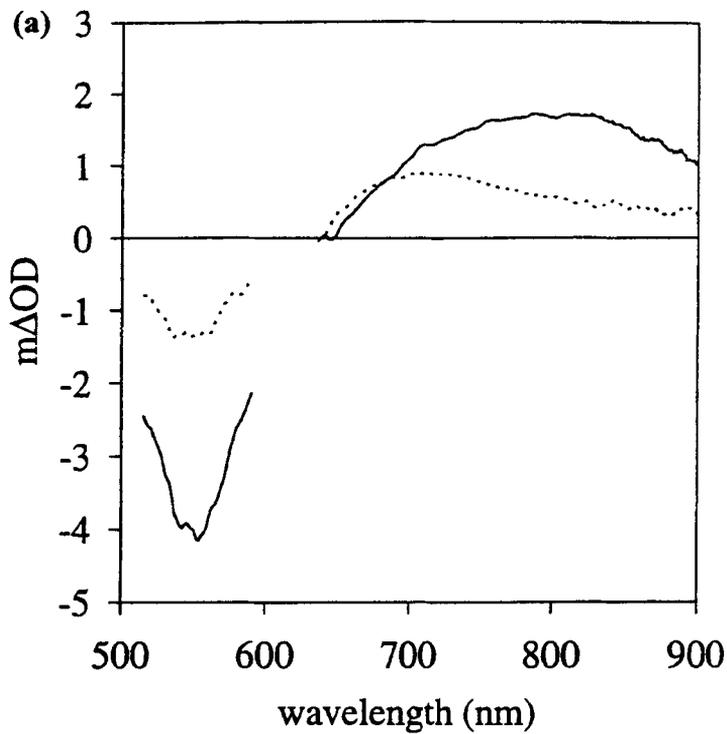


Figure 1. (a) Absorption difference spectra for dye coated TiO_2 (—) and ZrO_2 (·····) films at 5 ps time delay. (b) (—) difference between the two spectra shown in (a), and (·····) the spectrum of the amplitude of 1.2 ps component observed for the TiO_2 film.

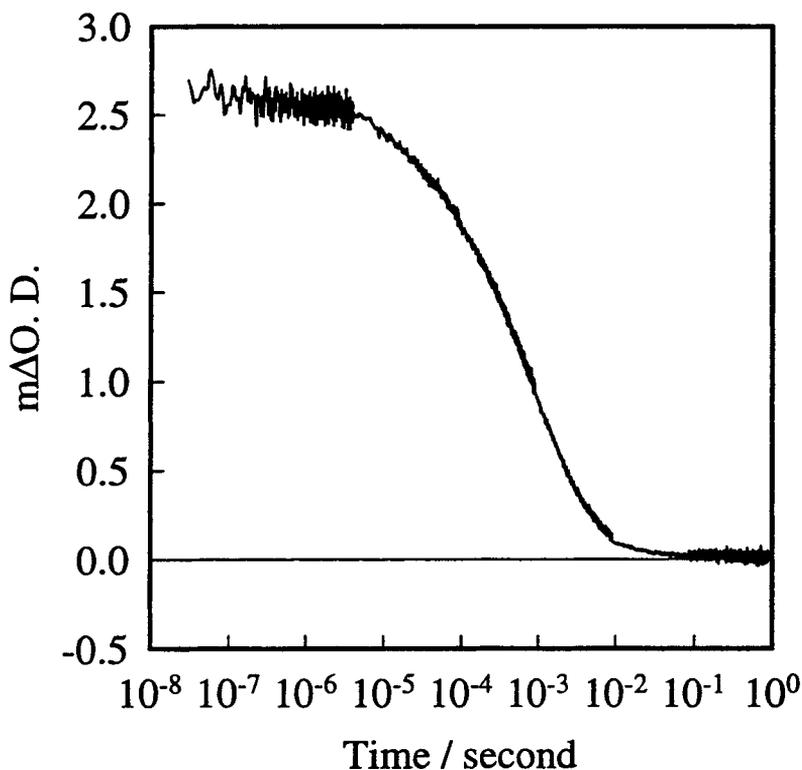


Figure 2. The kinetics of charge recombination the dye coated TiO₂ film, monitored decay of the cation absorption band at 820 nm. The data are shown on a lin/log plot and exhibit multiphasic kinetics on the micro-millisecond timescales.

conditions, and have been normalised to take account of small differences in the absorption of the excitation pulses between the two films. Comparison with the spectroscopy of 1 in solution allows assignment of these spectra⁴. The spectrum obtained for the ZrO₂ film exhibits a positive maximum at ~ 700 nm, characteristic of the excited state of this dye. For the TiO₂ film, the positive maximum appears at ~ 800 nm, indicating that this spectrum results from formation of the dye cation, and the concomitant injection of an electron into the TiO₂ conduction band.

Transient spectra were collected on 0–3 and 0–12 ps timescales. Spectra obtained with the ZrO₂ films were found to be independent of time delay on these timescales. In contrast, data collected with the TiO₂ film indicated the presence of an exponential component with a 1.2 ± 0.2 ps lifetime. The spectrum of the amplitude of this component is shown in figure 1b (dotted line).

The two difference spectra shown in figure 1a are assigned to the states before and after electron injection. Therefore, kinetics associated with electron injection should exhibit an amplitude proportional to the difference between these two spectra. This comparison is made in figure 1b. It is apparent that the spectrum of the 1.2 ps component has the expected shape for electron injection, but only $\sim 50\%$ of the predicted amplitude. We thus conclude that this component is due to electron injection into the TiO₂, but accounts for only 50% of the total charge separation. As electron injection is complete after this component, we conclude that the remaining 50% of

electron injection occurs prior to the 1.2 ps component, and within our instrument response (150 fs). We thus conclude that electron injection in these dye sensitised films occurs on an ultrafast timescale (50% in < 150 fs and 50% with a time constant of 1.2 ± 0.2 ps).

In the absence of a redox couple to re-reduce the oxidised dye (such as the I^-/I_3^- couple employed in functioning photovoltaic devices), charge recombination occurs on the microsecond-millisecond time scale. These recombination kinetics are illustrated in figure 2, exhibiting multiphasic kinetics on timescales up to 10^{-3} s. Thus this two component system exhibits charge separation and recombination rates differing by up to 10^{10} .

Implications of these observations for the mechanism of sensitisation and the function of photoelectrochemical solar cells are discussed in detail elsewhere⁴.

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