

## Photoinduced charge transfer between Indoline D149 and porous ZnO detected in transient absorption

Egmont Rohwer<sup>1</sup>, Christian Litwinski<sup>2</sup>, Kerstin Strauch<sup>3</sup>, Nadine Heming<sup>1</sup>, Christoph Richter<sup>3</sup>, Tebello Nyokong<sup>2</sup>, Derck Schlettwein<sup>3</sup>, Heinrich Schwoerer<sup>1</sup>

<sup>1</sup>Laser Research Institute, Stellenbosch University, Stellenbosch, 7600, South Africa

<sup>2</sup>Department of Chemistry, Rhodes University, Grahamstown, South Africa

<sup>3</sup>Institute for Applied Physics, Justus-Liebig-Universität, Giessen, Germany

**Abstract.** The photophysics of charge transfer between the electron donating, surface adsorbed D149 dye and an electron accepting porous ZnO film was investigated by measuring excited state lifetimes using ultrafast transient absorption spectroscopy. We systematically varied the production scheme of the sample including the electrolyte.

### 1 Introduction

Modern dye sensitized solar cells (DSSCs) consist of a working electrode made of a semi-conducting material that can harvest and conduct electrons, with a dye bound to its surface that provides maximum sensitization to sunlight. The dye molecules absorb the sunlight and transfer the energy as electrons injected into the conduction band of the semiconductor electrode.

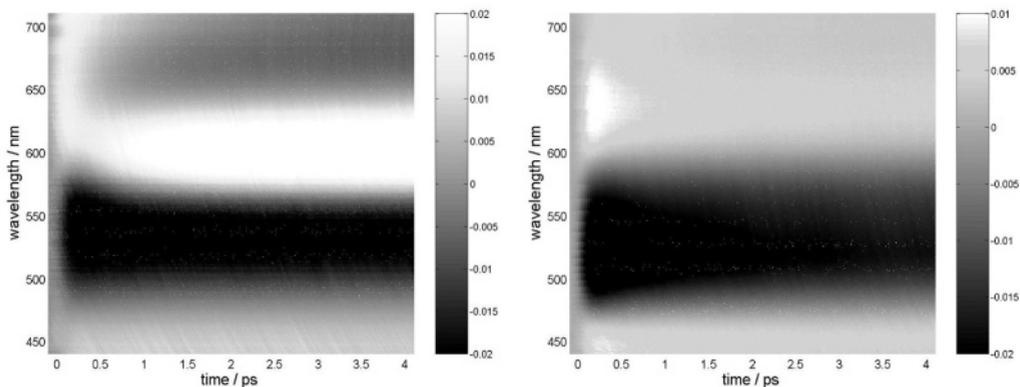
Indoline D149 Dye is to date the sensitizer molecule providing the highest solar energy conversion efficiencies when used in conjunction with ZnO as semi-conducting substrate [1]. ZnO does not require high temperature annealing in the production process, facilitating the use of plastic substrates, lower production costs and a large number of design options.

The working electrode consists of a conducting FTO layer on a glass plate that is first coated by electrochemical deposition with a crystalline ZnO layer that creates a buffer between the electrode and electrolyte without which the cell would short-circuit. Next a ZnO layer is electrochemically deposited with a structure directing agent (eosinY) that causes the ZnO layer to be highly porous. This creates a large surface area for dye sensitization. D149 is surface adsorbed to the porous ZnO layer and the dye loading can be maximized by adding a co-adsorbent, chenodeoxycholic acid [2,3]. This production scheme is slightly varied to produce 5 samples of different composition and in contact with either air or nitrogen.

Each sample is measured using pump-probe femtosecond transient absorption spectroscopy. D149 in solution is used as a reference. Samples are either excited with 530 nm or 388 nm laser pulses, corresponding to two electronic transitions of the D149 molecule namely the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  transition [4]. The probe pulse is a supercontinuum generated in  $\text{CaF}_2$  that allows us to monitor absorption changes in the spectral range of 330-720 nm with 120 fs temporal resolution.

This is an Open Access article distributed under the terms of the Creative Commons Attribution License 2.0, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

## 2 Results and Discussion



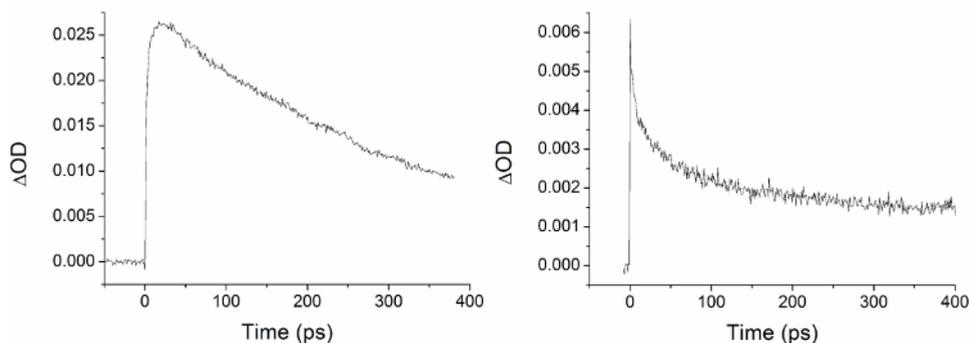
**Fig. 1.** Transient spectra of D149 (left) and sample 2 (right). Although the GSB, between 500 and 550 nm, of the D149 in solution and that of the D149 surface adsorbed to the ZnO layer is relatively long lived in both samples, the ESA around 600-650 nm is severely quenched when adsorbed to the ZnO layer due to electron transfer.

The transient absorption spectrum of D149 in a 1:1 solution of acetonitrile and tert-butyl alcohol are shown in Figure 1. The D149 solution shows a decrease in optical density due to the photo-initiated ground state bleaching (GSB) in a band centred around 530 nm. An increase in optical density can be observed over the entire probe spectrum red-shifted of the GSB signature for 500 fs after excitation due to excited state absorption (ESA). After this initial broadband absorption a strong ESA band centred at 600 nm emerges along with a fluorescence signal of decreased optical density on the longer wavelength side of the ESA band. Analysis of the GSB, Fluorescence and ESA decay traces of pure D149 in solution show equal decay times of  $300 \pm 50$  ps (extracted from longer scans than presented here), suggesting that electrons from the observed excited state decay directly into the ground state.

Another significant feature of the observed photodynamics of the dye in solution is the red shift of the fluorescence signal within 1 ps from 640 nm to 660 nm with a concomitant blue shift of the ESA maximum from 620 to 600 nm. This is attributed to the solvation dynamics of the solvent molecules that respond to the dipole of the excited dye molecule. The fluorescence signal and ESA signal reach a maximum after 18 ps due, in part, to their spectral separation and the continued red shift of the fluorescence signal after 1 ps. This shift continues to shift reaching 700 nm after 100 ps and may be due to collisional cooling or the decay of vibrationally hot states.

On the right panel of Figure 1, the transient spectrum of a D149-adsorbed ZnO electrode in contact with air is plotted. It has ESA and GSB signatures in similar wavelength regions to those observed for dissolved D149, but the decay times are no longer equal. The Fluorescence signal is also completely absent. Adsorbed D149 clearly shows severe shortening of the ESA lifetime due to the presence of a competing decay mechanism, the desired electron injection into the ZnO layer.

The fastest and most significant component of the ESA decay trace is measured to be 150 fs, close to the temporal resolution of our setup, and is attributed to the electron injection. Slower components ( $170 \pm 20$  ps) of the decay trace are due to the relaxation of dye molecules that do not undergo charge transfer, typically by radiationless mechanisms like phonon coupling. The slowest component of the decay trace, which is in the ns regime, is attributed to the absorption of the oxidised dye. To illustrate this a comparison of the ESA maxima for samples in solution and samples adsorbed to ZnO is shown in figure 2.



**Fig. 2.** The decay trace of the ESA maximum at 600 nm of samples in solution is plotted on the left panel, a maximum is reached after 18 ps due to overlapping with the fluorescence band and the decay is fitted with a  $306 \pm 16$  ps time constant. The decay trace of the ESA maximum at 650 nm is plotted on the right; the fastest decay component is due to electron injection whilst the long-lived component is due to the absorption of the oxidised molecule.

Further evidence for electron transfer can be seen in the spectral signatures assigned to the one electron oxidised D149 molecule. The absorption peaks of the oxidised molecule are reported to occur at 445 nm and 651 nm [5]. At both 445 nm and 651 nm the dye in solution exhibits ESA (decay constant  $\sim 300$  ps), although significantly weaker at 445 nm.

In the DSSC samples, a long lived component ( $\sim$  ns) is observed at both wavelengths that is not present in the dissolved dye molecules, which is attributed to the absorption of the one-electron oxidised dye molecule. This is indicative of a long lived charge separated state in samples adsorbed to ZnO, consistent with the proposed charge transfer mechanism.

ZnO surface adsorbed D149 were also placed in cells where the dye molecules are exposed to a redox mediator. The mediator, an iodine solution, is added to complete the solar cell circuit. The iodine solution reduces the oxidised dye molecules after charge transfer and is itself reduced at the counter electrode. The effect of the redox mediator was observed by monitoring the lifetime of the absorption band of the oxidised molecule which shortened from ns to few hundred ps.

### 3 Conclusions

In conclusion, we have observed an ultrafast, light induced charge transfer from Indoline D149 to a porous ZnO electrodes using transient absorption spectroscopy. The lifetimes of the excited and intermediate states were determined for systematically varied sample properties, and support the conclusion, that D149 on ZnO is a promising candidate for a dye sensitized solar cell.

### References

1. T. Dentani, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, H. Minoura, H. Miura, M. Matsui, *New J. Chem.* **33**, 93-101 (2009)
2. E. Michaelis, K. Nonomura, D. Schlettwein, T. Yoshida, H. Minoura, D. Wöhrle, J. Porphyrins Phthalocyanines. **8**, 1366-1375 (2004)
3. T. Yoshida, M. Iwaya, H. Ando, T. Oekermann, K. Nonomura, D. Schlettwein, D. Wöhrle, H. Minoura, *Chem. Commun.* 400-401 (2004)
4. T. Le Bahers, T. Pauporte, G. Scalmani, C. Adamo, I. Ciofini, *Phys. Chem. Chem. Phys.* **11**, 11276-11284 (2009)
5. A. Fattori, "*Electrochemical and Spectroelectrochemical Studies of Dyes used in Dye-sensitized Solar Cells*," PhD Dissertation, University of Bath (2010)