Photoinduced Absorption Spectroscopy of Dye-Sensitized Solar Cells

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The precise working mechanism of dye-sensitized solar cells (DSCs) based on nanostructured TiO_2 is still not well understood, despite many investigations in the past 15 years. Some of the remaining questions are the nature of the electrons in the nanostructured film (trapped / free in the conduction band) and the recombination mechanisms. A better understanding will be necessary in order to break the current 10% efficiency limit. One of the techniques that is frequently used to study the recombination kinetics in DSCs is pulsed laser spectroscopy. The kinetics in the DSC are very complex and strongly dependent on light intensity. It is difficult to translate the recombination kinetics found in the laser experiments to the actual solar cell. We therefore developed photoinduced absorption (PIA) spectroscopy in order to obtain spectroscopic and kinetic information of the DSC under realistic solar cell conditions.

In the PIA setup the DSC is excited with a modulated diode laser (λ= 635 nm, 10 mW cm^{-2}). The resulting changes in absorption are monitored using white light from a halogen lamp, a monochromator with appropriate detectors, and a lock-in amplifier. Figure 1 shows the PIA spectrum of a *cis*-Ru(dcbpy)$_2$(NCS)$_2$–sensitized TiO_2 film on glass, in contact with redox electrolyte consisting of 0.5 M NaI, 0.05 M I_2 in propylene carbonate. This system is analogous to a DSC in open circuit. The PIA spectrum is a difference spectrum of the system with laser on and laser off. Upon laser excitation, dye molecules are excited, leading to injected electrons in the TiO_2 and oxidized dye molecules. No features of the oxidized dye are visible in Fig. 1, as the reduction of the oxidized dye by iodide is very rapid. Instead the products of this reduction step are visible:

$D^+ + 2\,I^- \rightarrow I_2^-$ (eq. 1)
$2I_2^- \rightarrow I_3^- + I^-$ (eq. 2)

The sharp peak at 410 nm and a broad peak around 800 nm can be attributed to the I_2^- intermediate. The shoulder at 520 nm is attributed to I_3^- (or I_2). The spectrum of the electrons in TiO_2 is relatively featureless and is nearly flat in the near-infrared. The lifetime of the electrons, 0.15 s, can be calculated from the frequency response of the PIA signal.

PIA spectroscopy is one of the techniques in our 'toolbox' of non-destructive techniques for the study of DSCs. By combining the toolbox-techniques we hope to get a complete picture of the solar cell.

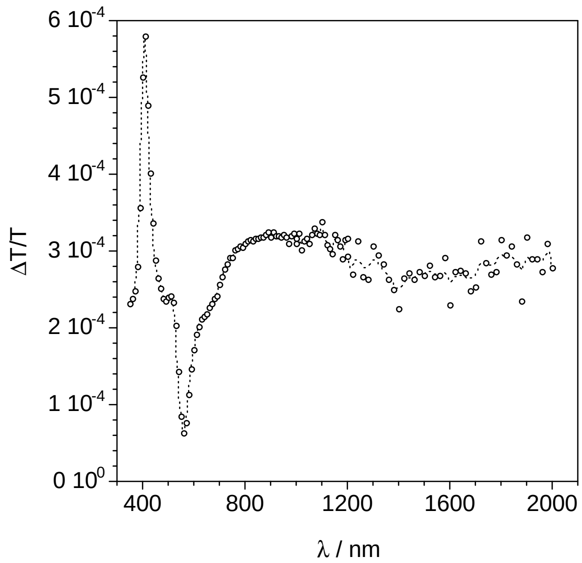

Figure 1. Photo-induced absorption spectrum of a *cis*-Ru(dcbpy)$_2$(NCS)$_2$–sensitized TiO_2 film on glass, in contact with redox electrolyte consisting of 0.5 M NaI, 0.05 M I_2 in propylene carbonate. Modulation frequency is 7 Hz.