Transient Photoconductivity of Dye-Sensitized TiO$_2$ Nanocrystalline Films Probed by Optical Pump-THz Probe Spectroscopy

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Dye sensitized solar cells (DSCs) offer a promising alternative to traditional silicon-based solar cells, in particular due to their low cost and low energy consumption during manufacturing process [1]. DSCs consist of a porous network of titanium dioxide nanoparticles sensitized by a molecular dye and an electrolyte or hole transporter material (HTM) filling the pores.

The electron diffusion and transport within the TiO$_2$ network affect directly the device performance and, therefore, these phenomena have been studied over the past decades using different techniques and different charge transport models, such as Drude's, and modified Drude's models or effective medium theory. Here we employed optical pump THz probe spectroscopy (OPTP) to monitor the temporal evolution of the photoconductivity of a mesoporous anatase nanocrystalline film. Ru^{II}(dcbpy)$_2$(SCN)$_2$ complex dye (N3) was used as a redox photosensitizer.

OPTP spectroscopy offers the advantage of being an all optical, contact-free method. It allows for probing the photoconductivity without the necessity to attach contacts to the sample or fill the pores with an electrolyte to complete the electrical circuit. Furthermore, the technique affords a rather high temporal resolution, in the ps time range. Photoconductivity transients and spectra were recorded with a setup described in ref. 2.

Electron injection and trapping dynamics in a dye-sensitized pure anatase film have been more particularly scrutinized. Figure 1 shows the change in transmission of the THz probe pulse observed following pump excitation at $\lambda = 600$ nm.

The change in the THz transmitted signal amplitude can be related to the photoconductivity using the following equation [3]:

$$\Delta\sigma(t) = -\frac{(n_a + n_b)c\varepsilon_0}{L}\frac{\Delta T(t)}{T(t)}$$

where n_a and n_b are the refractive indexes of the materials on the front- and back-side of the photoexcited material (in our case air and quartz), c the speed of

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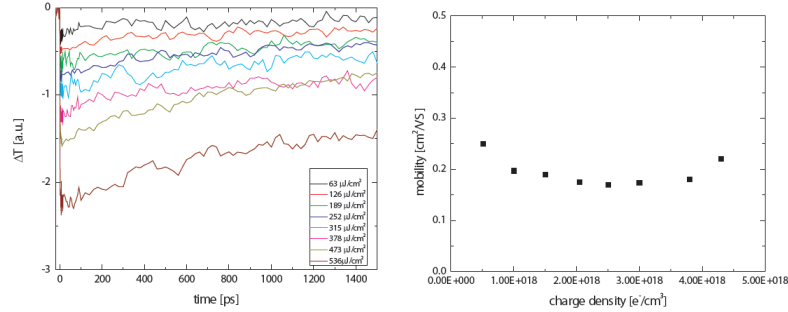
Figure 1. *Transient photoinduced changes in THz transmission of N3 dye-sensitized mesoporous TiO$_2$ films excited with various energy fluences at a central pump wavelength of 600 nm (left). Electron mobilities were extracted from the values at the peak of the transient signal (right).*

light, ε_0 the free space permittivity and L the thickness of the photoexcited material. Charge mobilities were extracted from the values measured at the maximum of the photoconductivity transients using the relation :

$$\mu = \frac{\Delta\sigma}{eFN}$$

where e is the elementary charge, F the fraction of absorbed photons, and N the incident photon density. We made here the assumption that the electron injection efficiency is unity.

The carrier mobility extracted from these measurements is ~ 0.2 cm^2/(V · s). This value is comparable to that found by Tiwana et al [4]. Other groups, however, reported values of 0.01 cm^2/(V · s) [5] and 15 cm^2/(V · s) [6]. Recently, Němec et al found a mobility of ~ 8 cm^2/(V · s) at 1.4 THz [7]. The large discrepancy between these values is probably due to different experimental conditions. In our case, the extracted carrier mobility appears to be constant over the investigated range of excitation energy densities. This is interpreted as being due to the fact that the mobility is extracted at a time delay before carrier trapping has occurred and that data were measured within a sufficiently low energy fluence range to avoid charge-charge interaction.

Recombination between electrons injected into the conduction band of TiO2 and oxidized dye species adsorbed on the surface typically takes place at the ms-ms time scale. The decay of the THz absorbance is therefore attributed to carrier trapping. Fitting the decay by a single exponential decrease leads to time constants of the order 3 ns, independent of the excitation wavelength. Similar kinetics were observed by Tiwana et al [4]. Here, the time constant was observed to increase slightly from 2.5 ns to 3.5 ps with increasing the visible light excitation energy fluence. This effect might be rationalized by trap filling at higher carrier densities.
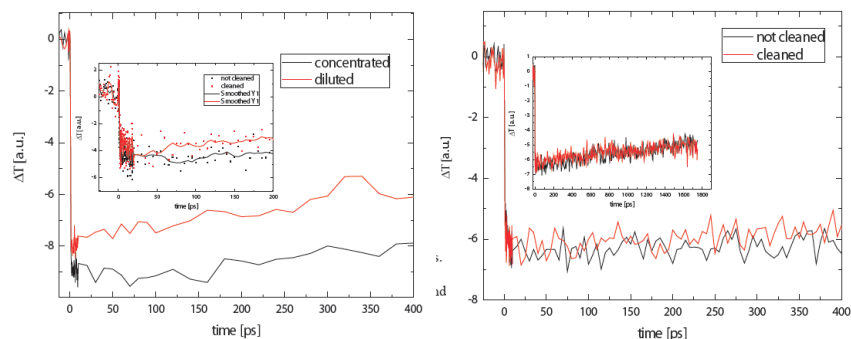
Figure 2. *a) Transient change in THz transmission for samples prepared from concentrated and diluted N3 solutions. Inset: Effect of rinsing a sample for 2 days in pure ethanol. b) Transient THz transmission of samples containing N719 as sensitizer. Inset: same measurements displayed on a longer time scale.*

To investigate the relationship between charge injection dynamics and dye aggregation on the surface, we prepared samples by soaking TiO_2 films in sensitizer solutions of various concentrations. Transients observed with samples prepared from concentrated dye displayed a fast decrease of the THz transmittance, followed by a slow component of the injection dynamics extending over ~150 ps. This second component disappears when samples are stored for two days in pure ethanol and is absent for films soaked in diluted dye solutions. Similar experiments were conducted using the doubly deprotonated analog of N3 dye, N719, as a sensitizer. Lacking the ability to form hydrogen bonds, this dye is less prone to aggregate. In the case of N719, no difference was observed between samples measured directly after preparation and after storing them for two days in ethanol. These observations are congruous with results of optical pump - optical probe measurements [8] and support the conclusion that a slower injection rate arises from dye sensitizer molecules weakly coupled to the surface. Kinetic heterogeneity could result from increased electron transfer distances, intermolecular charge transfer and/or exciton migration within aggregated dye molecules. As slow quenching of singlet dye excited states must compete with intersystem crossing, electron injection from aggregated dye molecules is likely to arise from triplet states. Our observation are thus compatible with the previously proposed two-states injection mechanism [9].

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