

# Charge Dynamics following Dye Photoinjection into a TiO<sub>2</sub> Nanocrystalline Network

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Electrons can be injected into TiO<sub>2</sub> nanocrystals by a surface-adsorbed Ru-based dye in a well-known photosensitization process. Here we present time-resolved microwave conductivity measurements of the decay of electrons out of an electrically interconnected network of such TiO<sub>2</sub> nanocrystals, following charge injection, and in the presence of an electron donor to the dye cation that prevents direct recombination. The time scale for this decay process is hundreds of milliseconds to seconds and explains the high current collection efficiency in devices based on these materials, since the long time scale allows for slow charge transport through the network.

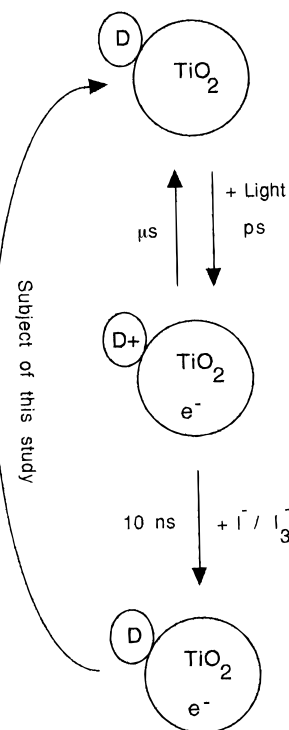
## Introduction

Semiconductor nanocrystals are crystals of semiconductor material that are on the order of tens of nanometers in dimension and have formed a fruitful field of study in recent years. Dye molecules adsorbed to the surface of titanium dioxide (TiO<sub>2</sub>) nanocrystals will inject electrons into the semiconductor conduction band from a photoexcited state of the dye.<sup>1</sup> Injecting charge into an electrically interconnected network of nanocrystals by dye sensitization and collection of the charge at an electrode contact forms the basis of the remarkable photoelectrochemical cell introduced by Grätzel and co-workers.<sup>1</sup> In the presence of an electron donor to the dye cation, injected charge is prevented from directly recombining with the cation and lives for some length of time on the nanocrystal; if this lifetime is long compared with the time for charge transport to a contact at one surface of the network, charge collection efficiency will be high, as it is for the Ru-based dye/TiO<sub>2</sub> cell.<sup>2</sup>

The underlying mechanisms of the cell are not well understood and have motivated a number of fundamental studies: The dye photoinjection process has been studied by Willig and co-workers and occurs on a time scale of a few picoseconds.<sup>3</sup> The back-reaction of the electron from the semiconductor to the dye cation occurs much more slowly, on a time scale of microseconds,<sup>2,8</sup> and allows the dye cation to be efficiently reduced by reaction with an electron donor such as I<sup>−</sup>, a reaction that occurs in tens of nanoseconds at molar concentrations of the ion.<sup>2</sup> These reactions and their time scales are summarized schematically in Figure 1. In this contribution, we focus on the electrons in the nanocrystals after the injection process, in the absence and presence of I<sup>−</sup>. We monitor the decay of charge in the semiconductor following the photoinjection process using a time-resolved microwave conductivity experiment. This technique has been described in detail elsewhere and is useful as a means of determining lifetimes of photogenerated charge carriers.<sup>4–7</sup> The photoconductivity is proportional to excess charge in the sample, and its decay in time mirrors the decay of the charge carriers

$$\Delta\sigma(t) = \Delta n(t)\mu_n \quad (1)$$

where  $\Delta\sigma(t)$  is the time-dependent change in microwave



**Figure 1.** Schematic diagram of the relevant reactions in the dye (D)–nanocrystal (TiO<sub>2</sub>) system with time scales indicated. The time scale for reduction of the dye cation by I<sup>−</sup> is given for a 0.5 M concentration of the ion.

conductivity,  $\Delta n(t)$  the excess photoinjected charge, and  $\mu_n$  the mobility of the injected charge at microwave frequencies.

## Experimental Section

Titanium oxide nanocrystals were purchased from Degussa AG, Germany and have been previously characterized as a mixture of 80% anatase and 20% rutile phase with an average particle diameter of about 20 nm<sup>2</sup>. *cis*-Di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) dye was purchased from Solaronix Co. (Switzerland). A colloid of the nanocrystals was prepared, spread on a glass slide, and sintered at 450 °C

according to a published procedure.<sup>8</sup> The dye adsorption was performed by soaking the sintered electrode overnight in a 0.5 mM solution of dye in ethanol. Excess dye was rinsed off the electrode with ethanol, and the electrode was allowed to dry under nitrogen. The electrode of nanocrystals with adsorbed dye was then scraped off the glass slide with a razor blade to give macroscopic pieces of material; these were then placed in a glass capillary ( $\sim 1$  mm i.d.) in electrolyte (a 1:1 weight mixture of ethylene carbonate/propylene carbonate with 0.5 M KI and 0.05 M  $I_2$ , referred to as the electrolyte or ECPC) or in ethylene carbonate or acetonitrile (Aldrich) as a solvent without an electron donor into the microwave cavity at a position of maximum electric field strength.

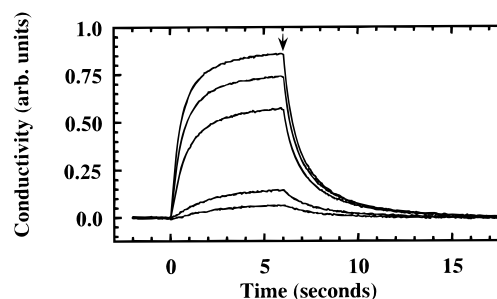
The microwave cavity consisted of a ca. 15 cm section of rectangular waveguide between an adjustable tuning pin and a shorted end consisting of a metal grid. Optical access was through the metal grid, and the sample was inserted in a thin slot in the wide section of the cavity. The tuning pin was adjusted to achieve critical coupling between the loaded cavity and the external microwave circuitry; in this way, the reflection of microwave power from the cavity is zero in the absence of light. Excess photogenerated charge in the sample leads to an increase in microwave absorbance and a small microwave reflection from the cavity. The reflected signal was detected via direct downconversion in a phase-sensitive double-balanced mixer (Miteq M0614F) followed by a home-built high-gain amplifier and a Lecroy 9450 digitizing oscilloscope (350 MHz bandwidth). The microwaves were generated by a Gigatronics synthesizer (Model 610) operating at 9.5 GHz and amplified to 10 mW before being directed to the cavity. The quality factor,  $Q$ , of the loaded cavity was about 200, giving a cavity time response  $\tau = 3$  ns (using  $\tau = Q/2\pi f$ , with  $f = 9.5$  GHz) and an electric field strength on the order of  $10^4$  V/cm at the sample.

For continuous illumination we used a Bosch 50 W halogen lamp fitted in a Zeiss housing equipped with optical lenses to provide a parallel beam. The light was passed through a KG3-2 IR filter (700 nm cutoff, Schott, Germany) and a UV filter (395 nm cutoff, Schott, Germany) to produce white light with an intensity of 100 mW/cm<sup>2</sup>, as measured with a Scientech AC5001 power meter. The light intensity could be varied with neutral density filters (Melles Griot). For pulsed illumination the light source was a Quanta Ray Nd:YAG laser, operating at 50 Hz. The frequency-tripled (355 nm) output pumped an optical parametrical oscillator (OPO, Spectra Physics), generating 530 nm pulses of about 10 ns duration with an energy of about 2 mJ/pulse over an area of 2 cm<sup>2</sup>. The repetition rate of the pulsed system could be varied using a synchronized shutter system that was triggered via an adjustable frequency divider; the same system was used to shutter the light in the continuous illumination experiment.

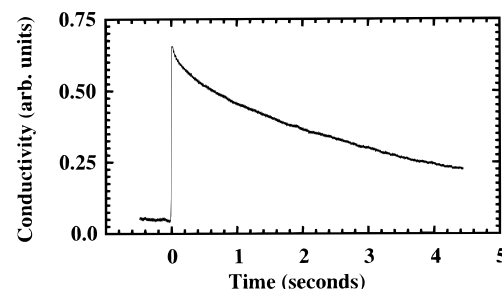
All experiments were performed at room temperature.

## Results

The decay of the excess charge was followed after injection into the semiconductor by the light-absorbing dye. Four experiments were performed. First, the sintered dye-nanocrystals were immersed in the electrolyte with the electron donor  $I^-$  and illuminated with a CW source that could be switched on or off within about 1 ms. The constant illumination allowed the semiconductor nanocrystals to be charged to steady-state, with the dye cation reduced after each injected charge from the pool of electron donors in solution. The changes in sample photoconductivity (reflected microwave power) as a function of incident light intensity are plotted in Figure 2. Light turned



**Figure 2.** Transient microwave photoconductivity of the dye-nanocrystal system in electrolyte (a 1:1 mixture of ethylene carbonate/propylene carbonate by weight with 0.5 M KI and 0.05 M  $I_2$ ) under continuous white light illumination. The light is turned on at  $t = 0$  and turned off at  $t = 6$  s, indicated by the arrow. The topmost trace was measured with 100 mW/cm<sup>2</sup> illumination intensity; the ones below it were obtained by placing neutral density filters of OD 0.1, 0.3, 1.0, and 1.3 in the beam.



**Figure 3.** Transient microwave photoconductivity of the dye-nanocrystal system in electrolyte (a 1:1 mixture of ethylene carbonate/propylene carbonate by weight with 0.5 M KI and 0.05 M  $I_2$ ) exposed to a flash of 530 nm light from a YAG laser. The laser light intensity was  $\sim 2$  mJ/pulse, and data was collected as single shots with a 1 min waiting period between shots.

on leads to an increase in sample conductivity (microwave power reflection increase) with time, rising to a steady-state level; light turned off leads to a decay of the signal on a time scale of seconds. The decays can be fitted well by a sum of two exponentials for each different light intensity, with time constants in the range of 500 ms to 3.7 s. In the case with the lowest light intensity, the decay is nearly monoexponential with a time constant of 1.6 s. No change in microwave conductivity was detectable with nanocrystals without adsorbed dye in electrolyte, indicating that the observed signal is due to the photoinjected charge by the dye. Furthermore, no change in microwave power was detectable from the nanocrystals with adsorbed dye in solvent (acetonitrile or ethylene carbonate) without an electron donor ( $I^-$ ), due to insufficient charging of the semiconductor particles to be detectable at these light intensities.

The second experiment involved exposing the network of dye-nanocrystals immersed in electrolyte to a flash of light from a YAG laser. This experiment prepares a charge-separated state with sufficient numbers of electrons in the particles to produce a detectable signal in a single flash as shown in Figure 3. Subsequent reduction of the dye cation due to the presence of the electron donor traps the injected electron in the nanocrystal for a period of hundreds of milliseconds to seconds, consistent with the results of the first experiment. The decay can be fitted to a sum of two exponentials with time constants of 270 ms and 4 s and relative amplitudes of 0.15 and 0.85, respectively. The signal rise is instantaneous on a 100 ns time scale, and further resolution is limited by the time resolution of the experimental apparatus (about 50 ns, limited by the detection electronics). The signal magnitude is roughly linear with the

laser power intensity in the region we are working in ( $\sim 2$  mJ/pulse), which was verified by varying the light intensity. Again, no change in microwave power was detectable with nanocrystals without dye in the electrolyte, indicating that the observed changes are due to charge injected into the semiconductor by the dye. A signal was also detectable with dye–nanocrystals in solvent (acetonitrile or ethylene carbonate) without a redox couple, indicating that in this case a single flash produced a detectable amount of excess charge in the semiconductor. The decay of this signal represents recombination between the injected charge and the dye cation and occurs on a microsecond time scale.

In the third experiment, we repeated the first two experiments with a nonsintered  $\text{TiO}_2$  (not electrically interconnected) nanocrystal sample with adsorbed dye. The measured decay rates were compared with those of the sintered sample and found to be the same. A fourth experiment measured the recombination rate of injected electrons with the dye cation in ethanolic solution without a redox couple (occurs on a  $10\ \mu\text{s}$  time scale), and this is in qualitative agreement with that obtained by transient absorption measurements ( $10^{-7}$ – $10^{-5}$  s).<sup>2,8</sup>

## Discussion

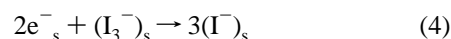
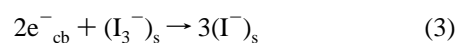
In this study we have monitored the decay of the electrons out of the nanocrystals, following dye photoinjection and in the presence of the  $\text{I}^-/\text{I}_3^-$  redox couple. There are two means of estimating the absolute amount of excess charge injected into the nanocrystals. One means depends on making a calibration of excess charge with the conductivity signal and requires knowledge of the local electric field strength in the sample, the  $Q$ -factor of the cavity, and the mobility of the injected charge in the nanocrystals. Since neither the local electric field strength nor the mobility of the injected charge is known, we estimate an upper limit for excess amount of charge generated in our first (CW illumination) experiment via a second means using the average photon flux on the sample (about  $10^{18}$  photons/s). The charge generation rate in the sample ( $G$ ) at full light intensity is at maximum on the order of  $10^{18}$  electrons/s; with the measured recombination rate constant of  $k \approx 1\ \text{s}^{-1}$ , a recombination rate of  $R = -kn_{\text{ss}}$  with  $n_{\text{ss}}$  the steady-state charge density, and the condition that at steady-state,  $G = R$ , the upper limit of steady-state excess charge density (per sample volume) at full light intensity is on the order of  $10^{21}$  electrons/ $\text{cm}^3$ . The excess charge density in our experiments is substantially lower than this taking into account that not all photons are absorbed. The light intensity in this experiment was varied by a factor of 20 from highest to lowest illumination. In this range, the steady-state microwave conductivity (and therefore the excess steady-state charge density) varied over a factor of 13 but the half-time for charge decay from the semiconductor nanocrystals is nearly constant, about 1 s. Since the process we are monitoring represents a drain of charge from the nanocrystalline network, the charge collection efficiency from such a network will depend on the balance between the rate of this process and the rate of charge transport through the network to an electrode contact; the half-time for charge decay thus provides an estimate for the upper limit of the transport time, 1 s, for charge collected through a  $10\ \mu\text{m}$  thick nanocrystalline layer given the known current collection efficiency in such cells ( $\sim 0.6$ ) and similar conditions of electrolyte and illumination levels.<sup>10</sup>

In the second experiment with the laser flash, the signal is linear in the region of light intensity in which we work. An upper limit for the number of injected charges per laser flash can be estimated at 100 charges per particle if all adsorbed dye

molecules donate one electron to the particle, considering that this is approximately the average number of dye molecules per particle,<sup>9</sup> and this corresponds to an upper limit of  $10^{18}$  electrons/ $\text{cm}^3$  for the excess charge density given the average size of a particle (20 nm diameter). Alternatively, the total number of photons per laser flash is  $5 \times 10^{15}$  (2 mJ/pulse), and given the sample volume (on the order of  $10^{-3}\ \text{cm}^3$ ) one also obtains an upper limit of  $10^{18}$  electrons/ $\text{cm}^3$  for the excess charge generated. Since we are not working under saturating conditions with respect to the laser intensity, the charge density corresponding to our observed signal is below this. We emphasize that the excess charge density in both the CW and laser flash experiments may be comparable in magnitude since in the CW case the nanocrystals are being charged to steady-state over a period of seconds (see Figure 2). There is no significant decay of the reflectivity signal on time scales faster than hundreds of milliseconds.

The decays are nearly monoexponential for the experiments with CW light at lowest illumination intensity (about 10 mW/ $\text{cm}^2$ ) and the YAG laser ( $\sim 2$  mJ/pulse) and biexponential for the other cases, suggesting that at higher light intensity electrons in two types of states (possibly due to heterogeneity in particle size and therefore state energies) are reducing the electron acceptor in the electrolyte ( $\text{I}_3^-$ ). Since there is not a hole generated in the semiconductor by the dye sensitization process, we are only monitoring the decay of the electrons. In these experiments with the  $\text{I}^-/\text{I}_3^-$  redox couple, there is no observable difference between the decay rates measured for both sintered and nonsintered samples, suggesting that grain boundaries do not play a significant role in the lifetime of excess charge in the nanocrystals.

A detailed understanding of the mechanism underlying the decay time scale will depend on further studies, particularly on the role of semiconductor surface states and how the redox couple influences the process, but an outline of the process can be drawn. Assuming the electron acceptor species is  $\text{I}_3^-$ , the relevant reactions for the decay process are as follows



where  $\text{e}^-_{\text{cb}}$  and  $\text{e}^-_{\text{s}}$  are electrons in the conduction band and surface states and subscripts s and bulk denote species in the bulk of the electrolyte and at the semiconductor surface within distance for an electron transfer to occur. Reaction 1 in the above scheme is the equilibrium between conduction band and surface-state electrons, reaction 2 is the electron-transfer process from a conduction band electron to the electron acceptor in the electrolyte, reaction 3 is the same process as in reaction 2 for electrons in semiconductor surface states, and reaction 4 is the equilibrium between the bulk and surface-localized electron acceptor species. There is experimental evidence for  $\text{Ti}^{3+}$  surface states at an energetic depth of  $\sim 70$  meV below the semiconductor conduction band.<sup>11</sup> At room temperature, this energy difference is small enough to allow for fast equilibration compared with a time scale of seconds, so reaction 1 involving these states is not likely to be the rate-limiting step. Surface adsorbates are also known to be important in modulating the rate of electron transfer from the semiconductor nanocrystals

to acceptors in solution, so the presence of the dye itself may play an important role in determining the rate.<sup>2,12</sup>

A phenomenological equation for the measured decay of photoinjected charge from the nanocrystals is  $D(t) = -kn(t) - [I_3^-]_s$  where  $D(t)$  is the time-dependent rate,  $n(t)$  represents the time-dependent surface-state or conduction band electron density,  $k$  is the rate constant for electron transfer to occur, and  $[I_3^-]_s$  is the concentration of the species at the semiconductor surface. Assuming that reaction 2 is not rate-limiting, the product of  $k$  and  $[I_3^-]_s$  determines the time scale of the decay process and is on the order of hundreds of milliseconds to seconds. Whether the rate for charge decay is limited by  $[I_3^-]_s$  or by  $k$  may be best answered by further experiments; calculations of  $k$  must take into account that the system is in a photoexcited state, not in equilibrium, and therefore predictions of the rate constant based on fluctuations to positions near equilibrium are probably not valid.

### Conclusions

Transient microwave reflectivity measurements were performed on a dye-TiO<sub>2</sub> nanocrystal system to monitor the dynamics of photoinjected charge in the semiconductor. This system has been intensively studied by others, and rate constants for charge injection, recombination with the dye cation in the absence of electron donors, and reduction of the dye cation by an electron donor have been measured. This study presents measurements on the time scale for electron decay from the nanocrystals, following photoinjection by a dye and reduction of the dye cation by an electron donor. In an I<sup>-</sup>/I<sub>3</sub><sup>-</sup> ethylene carbonate:propylene carbonate electrolyte like that used in dye-TiO<sub>2</sub> photoelectrochemical cells, this decay rate occurs on a time scale of hundreds of milliseconds to seconds. This remarkably long lifetime for injected charge explains the high quantum yield of current collection in such devices, since the

decay process represents a "short-circuit" pathway in the cell. A detailed elucidation of the physical-chemical mechanism underlying the decay will depend on further experiments, particularly how the rate constant of the process depends on the amount of excess charge in the semiconductor, the role of semiconductor surface states, or the liquid (solvent or electrolyte) used to create the interface.

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### References and Notes

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