Carrier dynamics in photovoltaic nanostructures
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Chapter 7: Charge extraction in complete dye-sensitized solar cells

7.1 Motivation

In many fundamental studies on novel solar cell concepts, model systems are investigated that represent a specific sub-unit of the solar cell. For instance, to gain fundamental insight in Carrier Multiplication in QDs, ultrafast spectroscopic measurements are performed on suspensions of isolated QDs in a solvent (see chapter 4) instead of on QDs embedded in a real solar cell configuration. The reason is that in devices, many physical processes occur that can obscure the process of interest. In model systems, undesired physical processes can – in principle – be suppressed allowing one to focus on the physical process of interest. However, there is always the possibility that when the model system (e.g. the QD) is incorporated in an operating device, fundamental physical processes change as a result of interactions with the device environment.

In the final chapter of this thesis, the effect of the device environment on charge injection is investigated. As explained in Chapter 6, photo-generated carriers can be extracted from QDs by sensitizing mesoporous oxide films with QDs: in this approach, light is selectively absorbed by QDs and electrons are injected from the QDs into the oxide matrix, which serves as photoanode, and the remaining positively charged QDs are reduced by a suitable redox couple in the electrolyte. The oxidized redox species migrates towards the photocathode, where it is reduced by the electrons that re-enter the system via the external circuit. This configuration is analogous to the so-called Grätzel cell, the only difference being that the dye molecules are replaced by QDs. In chapter 6, we studied the dynamics of electron injection into a QD-sensitized oxide film that was embedded in an inert environment (N₂, toluene). In this chapter, we will investigate how the dynamics of charge extraction are altered when a dye-sensitized film is embedded in an electrolyte solution. The reason for sensitization with dyes instead of QDs is that dye-electrolyte combinations are known that are relatively stable against photo-oxidation: these combinations were optimized during years of research on dye-sensitized solar cells. In most Grätzel cells, ruthenium-based dyes are used in combination with an iodine/iodide redox couple (I₂/I⁻), but unfortunately, this redox couple causes severe photo-corrosion of QDs. In general, the photo-stability of QDs in the presence of an electrolyte redox couple is much less established, because the research on QD-sensitized solar cells started relatively recently and investigated QD-electrolyte combinations are still sub-optimal. In the search for non-corrosive electrolytes, several alternatives for the iodine/iodide couple are being.
explored including spiro-OMeTAD\(^3\), a sulfide/polysulfide couple (S\(_2-/S_n^{-}\))\(^{2,4,5}\), and a cobalt based complex\(^6\) ([Co(o-phen)]\(^{2+/3+}\)). Nonetheless, the effect of these various electrolytes on the QD stability is not yet well-established. Therefore, it is a logical choice to use dyes as light absorbers when studying the influence of the electrolyte on injection dynamics, since any perturbations of dynamical processes caused by photo-corrosion can be excluded. Here, we present a systematic study on the influence of the presence of an electrolyte on the dynamics of electron injection from two dye molecules, N3 and N719, into mesoporous oxide films.

### 7.2 Samples

Mesoporous TiO\(_2\) and SnO\(_2\) films were prepared by spreading out viscous dispersions of colloidal TiO\(_2\) and SnO\(_2\) particles on a microscope slide. For the TiO\(_2\) film, an ethanol based paste containing 15 nm TiO\(_2\) particles was purchased from Solaronix (T-LALT). A SnO\(_2\) paste was obtained by dispersing SnO\(_2\) powder (Aldrich, average particle size < 100 nm) in an ethanol solution containing NH\(_4\)OH (added to stabilize the colloidal suspension of SnO\(_2\) particles). After deposition of the paste, the films were dried at 115°C for 30 minutes and subsequently annealed in air at 450°C for 2 hours. Two commonly used ruthenium-based dye molecules were used to sensitize the oxide. The chemical formula of these dyes, usually denoted as N3 and N719, is given in Fig. 7.1. In both dye molecules, the central ruthenium atom is coordinated by two bipyridine and two thiocyanide ligands. The carboxylate groups result in strong binding of the dye molecules to the oxide surface. The difference between the dyes is that all four carboxylate groups in N3 are protonated, whereas two of the four carboxylate groups in N719 are deprotonated and stabilized with a tetrabutylammonium (TBA) group.

![Figure 7.1 Molecular structures of the N3 and N719 dye.](image)
Sensitization was achieved by immersing the oxide films (stored at 90°C to remove the hydroxyl groups terminating the oxide surface) in a 0.1 mM dye solution in anhydrous methanol for several hours. The absorption spectra of TiO$_2$ films sensitized with N3 and N719 are given in Fig. 7.2(a) and (b), respectively. Clearly, the absorption spectrum of the dye-sensitized films (solid lines) is similar to that of a dye solution in methanol (dashed lines). The broad absorption band at ~ 535 nm originates from a metal-to-ligand charge-transfer (MLCT) transition from a ruthenium $d$-orbital to the $\pi^*$-orbital of the bipyridine ligands. Exciting the dye with visible photons in the 400-650 nm range brings the molecule in its singlet ($^1$MLCT) state, after which it will relax to the triplet ($^3$MLCT) state with a characteristic singlet-to-triplet intersystem crossing time of < 100 fs. This triplet state has been shown to be weakly luminescent with a ~nanosecond radiative lifetime. The tail in the absorption spectrum at longer wavelength has been attributed to direct excitation of this luminescent state.

![Absorption spectra for N3 and N719 dye](image)

**Figure 7.2** Absorption spectra for the N3 (a) and N719 (b) dye. The solid lines correspond to spectra for dye-sensitized TiO$_2$ films and the dashed lines are the spectra for the dyes dissolved in methanol. The inset in (b) shows that the absorption band at ~ 535 nm experiences a small blue-shift upon addition of electrolyte.
In this chapter, we use an I$_2$/I$^-$ redox couple dissolved in acetonitrile as electrolyte, which is commonly used in Grätzel solar cells. It has been reported that additives like lithium ions and 4-tert-butyl pyridine (TBP) lead to an enhancement of the solar cell performance$^{11,12}$. While the addition of lithium-salts leads to an increase of the short circuit current, the addition of TBP has been shown to result in larger open circuit voltages. To account for the effect of the various electrolyte components on injection dynamics, we investigated a number of electrolyte compositions, following Ref. 12:

- Electrolyte A: 0.6 M tetrabutylammonium iodide, 0.1 M lithium iodide, 0.5 M TBP, and 100 mM iodine dissolved in acetonitrile.
- Electrolyte B: similar as electrolyte A, but without the LiI.
- Electrolyte C: similar as electrolyte A, but without TBP

All chemicals were electrochemical or HPLC grade and were purchased from Fluka. To immerse the dye-sensitized film in the electrolyte, the microscope slide on which the oxide film was deposited was covered with a second microscope slide. Subsequently, the oxide matrix between the two microscope slides was interpenetrated with the electrolyte solution using capillary forces, resulting in a very thin electrolyte phase in the sample. This short path length was essential for the THz-TDS measurements, since THz light is strongly absorbed by polar solvents (like acetonitrile) that are commonly used for electrolyte solutions. We estimate that the thickness of the electrolyte phase amounted to ~10 $\mu$m, which was thin enough to have considerable transmission of THz light. After addition of electrolyte A, the absorption band of the dye sensitized film at 535 nm shifted slightly to shorter wavelengths, as can be seen in the inset of Fig. 7.2(b).

To demonstrate that dye-sensitized oxide films can be used to convert light into electrical current, we constructed a dye-sensitized solar cell with the same schematic layout as given in Fig. 6.1. Briefly, a TiO$_2$ film was deposited on conducting glass (indium-doped tin oxide, ITO) and sensitized with the N719 dye. The film was interpenetrated with electrolyte A and platinum was used as counter-electrode. Figure 7.3 shows the photocurrent action spectrum and the I-V characteristics for the fabricated dye-sensitized solar cell. Clearly, the spectral response from the photocurrent action spectrum closely matches the absorption spectrum in Fig. 7.2(b). The I-V characteristics of the solar cell are shown in Fig. 7.3(b) and indicate a short circuit current of 4.42 mA/cm$^2$, an open circuit voltage of 0.64 V, and a fill factor of 0.39.
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Figure 7.3 Photocurrent action spectrum (a) and I-V characteristics (b) of a N719-sensitized solar cell.

7.3 Why THz-TDS measurements?

The dynamics of electron injection from ruthenium-based dyes into mesoporous oxide materials has been studied with a number of experimental techniques. In all experiments the absorbed dyes were excited with visible (femto-second) pump pulses with wavelengths ranging from 400 – 630 nm. In Refs. 10 and 13 the injection of electrons from excited dyes into oxides was monitored by probing the emergence of the spectral signature of the cationic dye (concurrently produced with injection) at near-infrared frequencies. Alternatively, mid-infrared frequencies (~ 5 μm wavelength) were used to probe the transient population of injected electrons in the oxide films directly⁸,¹⁴,¹⁵. In all these transient absorption studies, the dye-sensitized oxide films were measured in inert solvents without the electrolyte components being present. Recently, TA measurements (near-infrared probe) in combination with time-resolved single photon counting measurements were performed on complete dye-sensitized solar cells including the electrolyte¹²,¹⁶. These measurements indicated that the timescale of electron injection is retarded with a factor of 20 resulting from the influence of the electrolyte on conduction band energetics of the oxide. In this chapter, we employ THz-TDS to study the effect of the electrolyte on electron injection dynamics. THz-TDS measurements have been performed previously¹⁷-²⁰ on dye-sensitized TiO₂ films, indicating sub-picosecond injection dynamics in inert solvents. Analogous to TA measurements with a mid-infrared probe⁸,¹⁴,¹⁵, THz-TDS is a provides direct evidence of injected electrons, in contrast to TA measurements with a near-infrared probe or photon-counting experiments, in which injection timescales are inferred from transient signatures originating from the absorbed dye molecule¹⁰,¹²,¹³,¹⁶. The THz response to electrons in nanostructured oxide films has been discussed in section 2.4. In all THz measurements, we excited the sample with 590 nm light and recorded ΔEₜ₉ (corresponding to the real conductivity) as a function of pump-probe delay.
7.4 Charge injection in dye-sensitized TiO$_2$

Photo-physical processes in (absorbed) ruthenium-based dye molecules have previously been intensely investigated$^{9,21,22}$. An illustration of the different dynamic processes in a dye-sensitized oxide film after photo-excitation is given in Fig. 7.4. As a result of absorption of a visible photon by the dye, an electron is promoted from the ground state ($D$) to the singlet excited state ($^1$MLCT). The population of electrons in the $^1$MLCT state can decay via injection into TiO$_2$ (characterized by $\tau_1$). In parallel, the $^1$MLCT state can undergo intersystem crossing to the excited manifold of the triplet $^3$MLCT state, followed by intramolecular vibrational relaxation to the $^3$MLCT ground state. (characterized by $\tau_2$). Significant injection from the singlet state into TiO$_2$ will only occur when $\tau_1$ is small compared to $\tau_2$. In the situation where $\tau_1 > \tau_2$, the majority of the excited molecules in the $^1$MLCT state will decay to the $^3$MLCT state. From here, electrons can either be injected into TiO$_2$ or recombine to the ground state (characterized by $\tau_3$ and $\tau_4$, respectively). The injected electrons in TiO$_2$ will thermalize to the conduction band edge, from which they can recombine with the absorbed cationic dye molecule ($D^+$) or with the redox couple in the electrolyte (characterized by $\tau_5$ and $\tau_6$, respectively). The general theory to predict the rate of electron transfer between two chemical species was developed in the 1960’s by Marcus$^{23}$, amongst others. As discussed in Ref. 14, this theory can be adapted to describe electron transfer between dyes and bulk semiconducting oxides. Three parameters that in principle determine the rate of electron injection are given below$^{14}$:

1. electronic coupling between the electron-donating orbital of the absorbed dye and the electron-accepting orbitals of the semiconductor
2. the Density of States (DOS) in the conduction band of the electron-accepting semiconductor
3. the free energy gain for injection, i.e. the potential energy difference between the dye excited state and the conduction band edge of the oxide

Figure 7.4 Schematic diagram of the energy levels in a dye molecule with respect to the conduction band of the TiO$_2$ to which the dye is absorbed. All possible dynamic processes after photo-excitation of the dye are indicated by arrows (see explanation in text).
The dependence of the dye-semiconductor electron transfer rate on these parameters for the case of weak coupling (non-adiabatic limit) is given by the following expression:\(^8,^{14}\):

\[
K_{et} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} dE \rho(E) |H(E)|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp \left[ -\frac{\left( \lambda + \Delta G_0 - E \right)^2}{4\lambda k_B T} \right] 
\]

(7.1)

In equation 7.1, \(\Delta G_0\) is the energy difference between the conduction band edge and the redox potential of the dye excited state, \(\rho(E)\) is the density of semiconductor states at energy \(E\) from the conduction band edge, \(H(E)\) is the average electronic coupling between excited dye state and the different states in the semiconductor at energy \(E\), and \(\lambda\) is the reorganization energy. Equation 7.1 clearly illustrates that the injection rate increases for higher density of acceptor states, stronger electronic coupling, and a larger free energy gain \(\Delta G_0\). Indeed, experimental reports show that injection from the dye singlet state into TiO\(_2\) is faster than injection from the dye triplet state\(^8,^{12-14}\); this observation has been be explained by the larger density of accepting states at the (higher) energy of the \(^1\)MLCT state\(^8\). The effect of electronic coupling has been investigated by introducing a varying number of CH\(_2\) units between the carboxylate linking group and the electron-donating bipyridine ligand. For increasing distance between the electron-donating ligand and the electron-accepting TiO\(_2\) (less electronic coupling), the rate of electron injection has been demonstrated to slow down considerably\(^14\). Finally, the expected influence of \(\Delta G_0\) on injection dynamics was confirmed by a systematic study of a series of dyes with different excited state potentials (but comparable electronic coupling properties)\(^14\).

It must be noted, however, that it is difficult to predict which of the three parameters in equation 7.1 is the rate-determining factor for electron injection from dyes into oxides. Recently, it has been argued that the DOS effect dominates over the effect of electronic coupling\(^15\). This was concluded by comparing the timescale of electron injection from Rhodamine with injection from the N3-dye. Despite large structural and electronic differences between Rhodamine and N3 (hence different electronic coupling), both dyes exhibited a similar semiconductor dependence, suggesting that DOS effects dominate\(^15\). As will be shown in section 7.5, a comparison between electron injection in N3-TiO\(_2\) and N3-SnO\(_2\) indicates that DOS arguments are also more important than the magnitude of \(\Delta G_0\).

Figure 7.5 shows the THz modulation for TiO\(_2\) films sensitized with N719- and N3-dye that were immersed in acetonitrile. The THz signal represents the population of injected electrons in TiO\(_2\). The data in Fig. 7.5 was obtained after exciting the films with 2 \(\mu\)J/mm\(^2\) 590 nm pulses. We verified that the shape of the THz signal remained the same for lower excitation fluences. Also, we checked that the high excitation fluence did not cause any photo-corrosion, by verifying that the amplitude and the shape of the THz signal remained the same during ~one hour of data acquisition. When the sensitized films were measured in
air, however, the amplitude of the THz signal strongly decreased as a function of data acquisition time. This observed photo-degradation has been explained previously by oxygen induced desulfurization of the thiocyanide (SCN) ligands\textsuperscript{10}.

Clearly, the data in Fig. 7.5 exhibits a fast rise of the THz signal, followed by an ingrowth of the signal at longer timescale. This ‘biphasic’ injection kinetics is typical for TiO\textsubscript{2} sensitized with ruthenium-based dyes\textsuperscript{8,10,12-14,20}. The fast component has been attributed to injection from the 1MLCT state (characterized by $\tau_1$ in Fig. 7.4), and the slower component was assigned to injection from the 3MLCT state (characterized by $\tau_3$)\textsuperscript{8}. Injection from the high-energy singlet state is only possible if it occurs on faster or equally fast timescales as intersystem crossing from the singlet to the triplet state (characterized by $\tau_2$ in Fig. 7.4). In literature, ultrafast injection from the singlet state in N3-TiO\textsubscript{2} was indeed reported with a time constant of $\sim 25 - 50$ fs\textsuperscript{24}, while intersystem crossing from the singlet to the triplet state was found to occur within 30 or 75 fs (for TiO\textsubscript{2}-N3 in air and ethanol, respectively)\textsuperscript{9}. The fast injection from the singlet state in Ru-TiO\textsubscript{2} systems can be explained by the very high electron effective mass in TiO\textsubscript{2} ($\sim 10 \cdot m_0$)\textsuperscript{25}, resulting in an extraordinary high DOS in the TiO\textsubscript{2} conduction band. Additionally, the conduction band of TiO\textsubscript{2} is formed from empty 3d orbitals of Ti\textsuperscript{3+} ions, having $\pi$ symmetry\textsuperscript{14}. Since the electron-donating orbital of the dye is the $\pi^*$ orbital of the bipyridine ligand, there is strong overlap between the donating and accepting orbitals, resulting in strong electronic coupling. The amplitude of the fast component in the biphasic injection is determined by the ratio of $\tau_1$ and $\tau_2$. The data in Fig. 7.5 is fit with the following equation:\textsuperscript{8}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.5.png}
\caption{THz modulation for nanostructured TiO\textsubscript{2} films sensitized with N719 and N3 (inset), following excitation with 590 nm pulses. The data can be described with biphasic injection kinetics (solid lines), as explained in the text.}
\end{figure}
\[ N_e = A(1 - \exp(-t/\tau_1)) + B(1 - \exp(-t/\tau_3)\alpha) \]  

(7.2)

In this equation, \( N_e \) corresponds to the population of injected electrons, \( A \) and \( B \) are the amplitudes of injection from the singlet and triplet state, respectively, and \( \alpha \) is the so-called stretch parameter. The use of the latter parameter is required since injection from the triplet state is not mono-exponential because of local inhomogeneities in the sensitized film (leading to local shifts of the conduction band edge, electronic coupling, etc.). The multi-exponential nature of the slow injection component is usually described by a stretched exponential, characterized by the stretch parameter \( \alpha \). For \( \alpha = 1 \), the stretched exponential is equal to a mono-exponential ingrowth. Fitting the data in Fig. 7.5 with equation 7.2 yields values for \( \tau_3 \) of 11.2 \( \pm \) 1.5 ps for TiO\(_2\)-N3 and 9.4 \( \pm \) 1.5 ps for TiO\(_2\)-N719. For both samples, the value of \( \alpha \) was fixed to 0.7: this value resulted in much better fits than for using \( \alpha = 1 \). An upper limit for the time constant \( \tau_1 \) of 150 fs was obtained for both samples, which was determined by the instrument response function of the THz-TDS setup. Next we measured the transient THz modulation for dye-sensitized TiO\(_2\) films immersed in electrolyte solution with three different compositions (specified in section 7.2). For both N3- and N719 sensitized films, the observed trends are similar, as can be seen in Fig. 7.6.

![Figure 7.6](image)

**Figure 7.6** Transient THz modulation for TiO\(_2\)-N3 (a + b) and TiO\(_2\)-N719 (c + d) in different electrolytes. The composition of electrolytes A, B, and C is given in section 7.2.
When the films were immersed in electrolyte A (both Li\(^+\) ions and TBP added) or in electrolyte B (only TBP added), the fast component of the biphasic kinetics in Fig. 7.5 is reduced markedly. However, when immersing the samples in electrolyte C (only Li\(^+\) ions added), the injection dynamics were comparable to the dynamics observed for films immersed in (inert) acetonitrile. In the presence of electrolyte A, the value of \(\tau_3\) (obtained from fitting the data in Fig. 7.6) was found to be 50 ± 10 ps for TiO\(_2\)-N3 and 60 ± 10 ps for TiO\(_2\)-N719 for \(\alpha = 0.7\). Since the injection was not completed at \(\tau = 300\) ps, the error in the extracted time constants was larger than in Fig 7.5, but the data in Fig. 7.6 suggest clearly that the injection dynamics are strongly retarded in the presence of electrolyte A and B, compared to immersion in acetonitrile or electrolyte C where the majority of electrons is injected within ~ tens of picoseconds. The results in Fig. 7.6 are consistent with previous reports on the effect of electrolyte composition on injection dynamics\(^{12,16}\). In these reports, exactly the same electrolyte compositions were used, but electron dynamics were monitored by time-resolved single photon counting. In this technique, the emission from excited dye molecules absorbed to TiO\(_2\) (injection possible) or ZrO\(_2\) (control sample, injection energetically not allowed) is monitored for different electrolyte compositions. Since emission from the dyes is quenched when electron injection occurs, the amplitude and the dynamics of the emission from the TiO\(_2\)-dye sample (relative to the control sample) give information about the efficiency of electron injection and the corresponding dynamics. The trends observed in the time-resolved single photon counting experiments\(^{12,16}\) are fully consistent with the THz-TDS measurements presented in Fig. 7.6. The authors in Refs. 12 and 16 have argued that the slower injection dynamics can be explained by the influence of the electrolyte additives (i.e. TBP and Li\(^+\) ions) on the energetics of the TiO\(_2\) conduction band. Briefly, spectro-electrochemical studies have indicated that the presence of TBP in the electrolyte leads to shifts of the TiO\(_2\) conduction band to higher energies\(^{11}\). Similar studies have revealed that addition of Li\(^+\) ions has the opposite effect: for increasing Li\(^+\) concentration, the conduction band of TiO\(_2\) shifts to lower energies. These shifts in the position of the conduction band cause variations in the density of TiO\(_2\) acceptor states relative to the singlet and triplet dye excited state, as is visualized in Fig. 7.7. For the Li\(^+\) and TBP concentrations used in this study, the induced shift of the conduction band can be as high as 300 meV\(^{11,12}\), resulting in a 20-fold decrease or increase of the number of accepting TiO\(_2\) states\(^{12}\). Hence, the addition of Li\(^+\) (electrolyte C) facilitates fast electron injection, which is also corroborated by the presence of a fast injection component in Fig. 7.6(b) and (d). The fact that there is still a dispersive slow injection component in the presence of electrolyte C can be attributed to local variations of the Li\(^+\) concentration in the homogeneous film\(^{12,16}\). Addition of TBP to the electrolyte strongly retards the injection dynamics, even in the case where Li\(^+\) ions are present (electrolyte B). This observation can be explained by the higher concentration of TBP (0.5 M) than that of Li\(^+\) (0.1 M).
In Fig 7.6(a) and 7.6(c), it can be seen that the fast injection component decreases in the presence of electrolyte A and B. This observation can also be explained by the reduction of the density of accepting states at the position of the 1MLCT level, slowing down ultrafast injection from dye molecules in the 1MLCT state. Hence, intersystem-crossing from the 1MLCT to the 3MLCT state (characterized by $\tau_2$ in Fig. 7.4) is likely to become the dominating decay pathway for excited dye molecules in the singlet state, as was also argued in Ref. 16. Future studies should reveal that the fast injection component completely disappears upon increasing the TBP concentration.

At first sight, one might be tempted to conclude that the device performance of a dye-sensitized solar cell is sub-optimal in case of slower electron injection. The argumentation in this reasoning is that charge separation should occur as fast as possible to reduce any losses from recombination of excited dyes to the ground state (characterized by $\tau_4$ in Fig. 7.4). However, it is known that the addition of TBP to the electrolyte solution significantly benefits the solar cell operation by increasing the $V_{oc}$, in spite of slower injection dynamics reported here and in Refs 12 and 16. This contradiction can be explained by the concept of ‘kinetic redundancy’. When the TiO$_2$ conduction band edge is shifted downwards, electron injection will occur on ultrafast (< 100 fs) time scale. However, for efficient charge separation, electron injection on a sub-picosecond time scale is not required, since the lifetime of excited dye is on the order of ~ 50 ns, indicating that the system is ‘kinetically redundant’. The disadvantage of positioning the TiO$_2$ conduction band edge at lower energy

*Figure 7.7* Schematic representation of shifts of the TiO$_2$ conduction band edge induced by addition of Li$^+$ ions or TBP. Clearly, these shifts lead to variation in the DOS of the TiO$_2$ at the position of the dye excited states (1MLCT and 3MLCT), hereby influencing injection dynamics.
values is that the conduction band edge moves towards the Fermi level, as a result of which the occupancy of trapped states and conduction states increases\textsuperscript{11}. This is important since recombination of electrons in TiO\textsubscript{2} with the cationic dye or the redox couple (characterized by $\tau_5$ and $\tau_6$ in Fig. 7.4, respectively) has been shown to depend strongly on the occupancy of trap and conduction states\textsuperscript{11}. Hence ultrafast ($< 100$ fs) electron injection from dyes into TiO\textsubscript{2} is accompanied by increased recombination and does not automatically lead to higher solar cell efficiency. Addition of TBP, on the other hand, increases the time scale of electron injection from $< 100$ fs to $\sim 100$ ps, but this is still fast enough to extract the majority of the electrons from the excited dyes. Since the conduction band has shifted to higher energies ($\sim$ hundreds of meV, depending on the TBP concentration), hence moving away from the Fermi level, the time scale of recombination of electrons in the TiO\textsubscript{2} is reduced by orders of magnitude\textsuperscript{11}. The above discussion illustrates that ultrafast electron injection is not a prerequisite for optimal solar cell efficiency, but that an optimal efficiency is obtained by achieving a balance between efficient charge separation and suppression of recombination of injected electrons: for optimal solar cell efficiency, ‘kinetic redundancy’ needs to be avoided.

### 7.5 Charge injection in dye-sensitized SnO\textsubscript{2}

To further investigate the effect of the parameters determining electron transfer rates (density of accepting states in the oxide, electronic coupling, and the magnitude of $\Delta G_0$), we studied electron injection dynamics in N3-sensitized SnO\textsubscript{2} films. Fig. 7.8 shows a comparison of the THz modulation for N3-sensitized SnO\textsubscript{2} and TiO\textsubscript{2} films. Although the energy of the SnO\textsubscript{2} conducting band edge is roughly 0.5 eV lower than the TiO\textsubscript{2} conduction band edge\textsuperscript{26}, electron injection into SnO\textsubscript{2} is slower compared to injection into TiO\textsubscript{2}. This observation can be explained by the considerably lower electron effective mass in SnO\textsubscript{2} ($\sim 0.28 m_e$)$\textsuperscript{27}$, leading to a much lower DOS in the SnO\textsubscript{2} conduction band\textsuperscript{8,14,15}. Furthermore, the conduction band of SnO\textsubscript{2} is formed by empty 5s orbitals of the Sn\textsuperscript{4+} ions. As a result, the overlap between the electron-donating $\pi^*$ orbitals of the bipyridine ligands and the electron-accepting orbitals in the SnO\textsubscript{2} conduction band is not optimal and electronic coupling is relatively weak\textsuperscript{14}. Apparently, DOS and electronic coupling arguments have a more pronounced influence on injection kinetics than the potential difference between the excited state dye and the conduction band edge.
Figure 7.8 THz modulation for N3-sensitized SnO$_2$ (grey dots) and TiO$_2$ (black lines) following excitation with 590 nm pulses. In contrast with injection into TiO$_2$, electron injection into SnO$_2$ is not bi-phasic and can be fit with a stretched exponential ingrowth. The dynamics of the THz data are attributed to injection from the $^3$MLCT state, as explained in the text. The inset shows a comparison of injection dynamics into SnO$_2$ in acetonitrile and electrolyte A.

The data in Fig. 7.8 can be fit with a single stretched exponential ingrowth ($N_e = B(1 - \exp(-t/\tau_e))^{\alpha}$), fits represented by dashed black line in Fig. 7.8). This indicates that the kinetics of electron injection into SnO$_2$ is not bi-phasic, in contrast to injection in the Ru-TiO$_2$ system. The fit yields a time constant associated with electron injection of $\sim 16 \pm 1$ ps for $\alpha = 0.7$. We attribute this kinetics to injection from the $^3$MLCT state, since the time constant is in good agreement with injection from the triplet state in the Ru-TiO$_2$ system. The absence of biphasic injection kinetics in the Ru-SnO$_2$ system indicates that injection from the $^1$MLCT state is no longer fast enough to compete with relaxation to the $^3$MLCT state ($\tau_1 \gg \tau_2$).

The inset of Fig. 7.8 shows a comparison of injection dynamics of the N3-sensitized SnO$_2$ immersed in acetonitrile (black solid line) and electrolyte A (grey dots). Clearly, electron injection in the presence of electrolyte A is slowed down significantly. Analogous to the Ru-TiO$_2$ system immersed in electrolyte A, this retardation of electron injection is likely caused by a positive shift of the SnO$_2$ conduction band edge, leading to reduced DOS of electron-accepting energy levels in SnO$_2$. The data in the inset of Fig. 7.8 is fit with the stretched exponential function yielding a time constant of electron injection of $\sim 160 \pm 20$ ps. The data in Fig. 7.8 indicates that the presence of electrolyte A reduces the rate of electron injection with at least one order of magnitude, which is in agreement with Ref. 12.
The similar trend for Ru-TiO$_2$ and Ru-SnO$_2$ when immersing the films in electrolyte indicates that the main effect of the electrolyte (shifting of the oxide conduction band edge, leading to changes of the DOS in the oxide at the position of the 1MLCT and 3MLCT states) can likely be generalized to other dye-oxide systems.

7.6 Discussion

In the previous sections, some essential parameters in charge transfer processes at the dye-semiconductor interface were discussed including electronic coupling between donating and accepting orbitals, density of accepting states, and the gain in free energy. These parameters are strongly influenced by several material characteristics such as the effective mass of the electron-accepting oxide (defining the density of states), the energies of the oxide conduction band edge and the excited states of the dye, and the dielectric constant of the solvent, amongst others. In many studies on dye-sensitized oxides, it has been suggested that density of states characteristics are dominating the rate of electron transfer, and electronic coupling to a lesser extent$^{12,14-16}$. It is conceivable that similar arguments are important in charge transfer processes at QD-oxide interfaces. Presumably, electronic coupling at the QD-oxide interface is weaker than the coupling at the dye-oxide interface: in the excited dye, the electron is localized on the bipyridine ligand which is in intimate contact with the oxide via a carboxylate group, whereas the molecules used to link QDs to oxides typically span longer distances. The effect of the density of accepting states on injection dynamics from QDs has not been systematically addressed in literature. In one study, the injection dynamics were monitored for different QD sizes and faster injection was observed for smaller QDs$^{28}$. This observation was explained by the larger value of $\Delta G_0$ for smaller QDs (higher energy of 1S$_e$ level compared to the conduction band edge), but it is conceivable that higher density of accepting states at the energy of the 1S$_e$ level in small QDs also plays a role. This latter explanation is consistent with Fig. 7.8, where faster injection was observed in the TiO$_2$-N3 system than in SnO$_2$-N3, in spite of the higher value of $\Delta G_0$ for SnO$_2$-N3, but in agreement with the higher density of states in TiO$_2$.

The observed changes of injection dynamics in dye-sensitized films in the presence of an electrolyte are also to be expected in a QD-sensitized system. There is no reason why additives like TBP or Li$^+$ would not lead to shift of the conduction band edge of QD-sensitized oxides. Of course, an optimal electrolyte composition has to be determined for QD-sensitized solar cells, hence it is currently not clear what the effect of the optimized electrolyte on injection dynamics from QDs will be. A possible retardation of injection dynamics in a QD-sensitized cell is not always detrimental for the overall cell efficiency. Slow injection dynamics will only reduce light-to-current conversion efficiencies if the
timescale of injection approaches the radiative lifetime of excitons in QDs. In future research, a systematic investigation of the parameters affecting electron injection in QD-sensitized oxides should be performed, as well as a correlation between injection dynamics, electrolyte composition, and device performance.

7.7 Conclusions

We have studied the dynamics of electron injection from ruthenium-based dyes into mesoporous oxide films. In an inert environment (air or acetonitrile), electron injection in dye-TiO$_2$ was found to occur with ‘biphasic kinetics’, in which the fast injection component (< 150 fs) corresponds to injection from the excited dye singlet state and the slow injection component (~ 10 ps) corresponds to injection from the excited triplet state of the dye. Electron injection into SnO$_2$ films is likely occurring from the triplet state only: although the energy difference between the dye excited state and the SnO$_2$ conduction band edge is larger than for dye-TiO$_2$, the density of accepting states is much lower in SnO$_2$, as a result of which injection from the singlet state is no longer fast enough to compete with intersystem crossing from the singlet to the triplet state.

For both the dye-TiO$_2$ and the dye-SnO$_2$ system, electron injection was significantly retarded when adding electrolyte solutions with compositions that have been reported to optimize solar cell efficiency$^{12}$. By varying the electrolyte composition, we found that especially the addition of TBP (4-tert-butyl pyridine) causes slower injection. The explanation for this observation is that the addition of TBP shifts the oxide conduction band to higher energies, as a result of which the density of states at the energy position of the excited dye states decreases, leading to slower injection dynamics. Slower electron injection is not automatically detrimental for solar cell efficiency, since injection on ultrafast (< 100 fs) is ‘kinetically redundant’$^{12}$ and is inherently associated with larger recombination of electrons in TiO$_2$ with the cationic dye or the redox couple. Positioning the conduction band at higher energies leads to slower electron injection (but still fast enough to extract the majority of photo-generated carriers), but significantly reduces recombination of electrons in TiO$_2$. It is conceivable that parameters like the density of states in the conduction band of the electron-accepting oxide and the composition of the electrolyte are also crucial in the design of efficient QD-sensitized solar cells.
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References

(22) Yeh, A. T.; Shank, C. V.; McCusker, J. K. Science 2000, 289, 935-938.