

Charge Separation in Solid-State Dye-Sensitized Heterojunction Solar Cells

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Dye-sensitized nanocrystalline solar cells are presently under intensive investigation, as they offer an attractive alternative to conventional p–n junction devices.^{1,2} Solid-state versions have been described where the electrolyte present in the pores of the mesoporous oxide film is replaced by a large band gap p-type semiconductor.^{3–6} In this way, a solid-state heterojunction of very large contact area is formed. Light is absorbed by the dye that is located at the interface. Upon excitation, the dye injects electrons into the conduction band of the oxide and is regenerated by hole injection into the p-type conductor. High incident photon-to-electric current conversion efficiencies have been achieved recently with a cell consisting of a dye-derivatized mesoporous TiO₂ film contacted by a new organic hole conductor.^{7,8} The great advantage of such systems with regard to conventional p–n junctions is that only majority carriers are involved in the photoelectric conversion process. Moreover, these are generated by the dye precisely at the site of the junction where the electric field is maximal, enhancing charge separation. Photoelectric conversion by conventional solar cells involves minority carriers whose lifetime is restricted due to recombination. As they are generated throughout the semiconductor and away from the junction, expensive high-purity materials are required in order to maintain the minority carrier diffusion length at a level where current losses are avoided.

While the dynamics of photoinduced redox processes in photoelectrochemical systems have been studied in great detail, little is known about the electron-transfer dynamics in solid-state sensitized junctions. Here we report for the first time on the direct observation of photoinduced, interfacial charge separation across a dye-sensitized solid-state heterojunction by means of picosecond transient absorption laser spectroscopy.

The charge-transfer events taking place at the junction are depicted in Figure 1. Visible light is absorbed by the sensitizer, i.e., *cis*-RuL₂(SCN)₂ (where L is 4,4'-dicarboxy-2,2'-bipyridyl). Electron injection from the excited state of the dye into the conduction band of TiO₂ (eq 1) is followed by subsequent hole transfer from the photooxidized dye to the organic hole conductor, 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene or OMeTAD, regenerating the dye's original

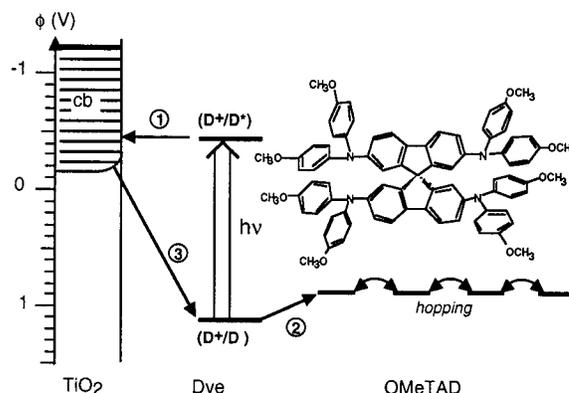


Figure 1. Scheme for the electron-transfer processes occurring in the dye-sensitized heterojunction together with the approximate redox potentials (vs NHE) and band energies of the different components.

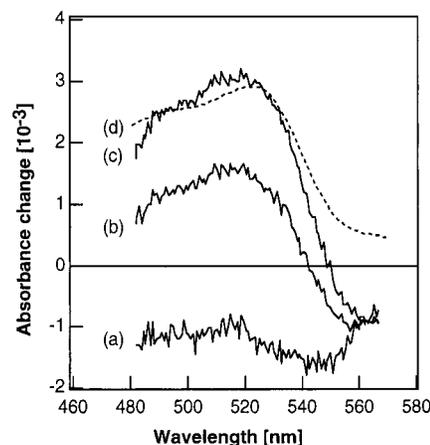
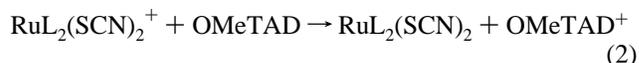


Figure 2. Transient absorption difference spectra obtained for solid TiO₂/OMeTAD heterojunctions, sensitized with RuL₂(SCN)₂, at different time delays to the exciting femtosecond pulse: (a) 3, (b) 300, and (c) 1000 ps. The excitation wavelength was 602 ± 7 nm, with pulse intensities of 600 ± 60 μJ/cm². For comparison, the absorption spectrum of chemically oxidized OMeTAD in chlorobenzene:acetonitrile = 90:10 (v/v) is also shown (d, arbitrary units).

ground state (eq 2).



The latter process competes with recapture of the injected electron by the oxidized dye:



The double-injection process described by eqs 1 and 2 generates mobile majority carriers in both the TiO₂ and the hole conductor phases, which are subsequently collected at the contact electrodes.

Figure 2 shows the time evolution of the transient absorption spectra observed with such a *cis*-RuL₂(SCN)₂-sensitized heterojunction. At a time delay of 3 ps after laser excitation, a broad negative feature is observed between 480 and 570 nm. This can be assigned to the bleaching of the RuL₂(NCS)₂ ground-state absorption due to excited-state formation and electron injection into the TiO₂.⁹ A positive feature with an absorption maximum at 520 nm grows in thereafter on the picosecond time scale. By

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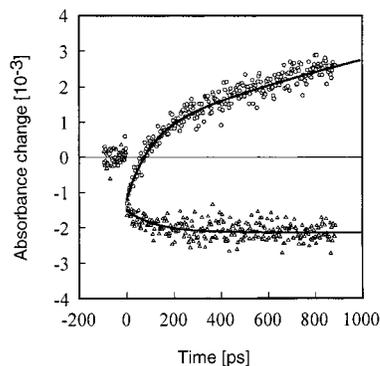


Figure 3. Transient absorption kinetics obtained for dye-sensitized TiO₂ films covered with OMeTAD (○) and with PC/EC (△) at a probe wavelength of 520 nm after excitation at 602 nm with pulse intensities of $600 \pm 60 \mu\text{J}/\text{cm}^2$. The solid lines show results of exponential fitting to the data. For the sensitized TiO₂/OMeTAD heterojunction, a double-exponential fit yielded component lifetimes of 100 and 2300 ps.

comparison with the absorption spectrum of chemically oxidized OMeTAD (Figure 2, trace d), we can assign this transient to the formation of the OMeTAD⁺ radical cation.⁷ The spectral changes in Figure 2 are, therefore, due to electron injection from excited *cis*-RuL₂(SCN)₂ into TiO₂ (eq 1), followed by dye regeneration via hole transfer to OMeTAD (eq 2). The first process is known to occur very rapidly, with most of the reaction being completed within 1 ps.^{9–11} Hence, it is not resolved on the time scale employed in Figure 2.

In view of the finding that the rate of photoinduced electron injection from *cis*-RuL₂(SCN)₂ into TiO₂ was similar in a vacuum and in propylenecarbonate,¹² it seems to be insensitive to the nature of the contact medium. Hence, the injection in the presence of OMeTAD is expected to occur also on a femtosecond time scale.

Figure 3 compares the transient absorption kinetics of the 520-nm absorption for the *cis*-RuL₂(SCN)₂-sensitized mesoporous TiO₂ films in the presence and absence of the OMeTAD hole conductor. In the absence of OMeTAD, only the expected bleaching of the *cis*-RuL₂(SCN)₂ ground-state absorption is observed due to electron injection into the TiO₂ conduction band. The small increase in this signal at early times is attributed to residual slow (10–100 ps) phases of the electron injection process into the TiO₂. In the presence of OMeTAD, the initially negative bleaching signal is replaced at later times by the positive OMeTAD⁺ cation radical absorption due to hole injection from the oxidized sensitizer into the hole conductor. The hole injection kinetics observed in the presence of OMeTAD could be fitted by a biexponential time law with component lifetimes of 100 and 2300 ps. We further note that the spectrum observed at 3 ps in Figure 2 suggests the formation of some (5–10%) OMeTAD⁺ cations, even at this early time. We thus conclude that the hole injection from the RuL₂(SCN)₂⁺ cation to the OMeTAD proceeds over a broad time range from <3 ps to >1 ns.

The fact that the hole transfer kinetics do not follow a single-exponential time law is attributed to a statistical distribution of the dye/hole conductor distances, as well as a variation in the total number of OMeTAD molecules contacting each dye molecule. The wide time range over which the hole injection proceeds suggests that the dye is not perfectly contacted by the hole conductor. In particular, this may arise from incomplete filling of the mesoporous TiO₂ structure with the organic

semiconductor. In support of this possibility, we note that SEM studies on cross sections recently revealed that pore-filling is, indeed, incomplete when OMeTAD is applied via the spin-coating technique (data not shown). We further note that, for dye molecules not in contact with the OMeTAD, regeneration of the dye ground state may proceed via lateral hole migration between neighboring dye molecules until a dye molecule in close contact with the OMeTAD is reached. Such lateral charge transport has recently been observed in monolayers of surface-adsorbed molecules on nanoporous TiO₂, such as aromatic amines¹³ and ruthenium polypyridyl complexes.¹⁴ Lateral hole hopping prior to dye regeneration by the hole conductor might, therefore, contribute to the dye regeneration kinetics and could be the underlying mechanism for its slower components.

From consideration of the relative amplitudes of the traces shown in Figure 3, we can estimate the quantum yield of hole injection into OMeTAD. Based on a difference in molar extinction coefficients of $5800 \text{ L mol}^{-1} \text{ cm}^{-1}$ for $[\epsilon_{520}(\text{dye}^+) - \epsilon_{520}(\text{dye}^0)]$ ¹⁵ and an extinction coefficient of $18\,700 \text{ L mol}^{-1} \text{ cm}^{-1}$ for $\epsilon_{520}(\text{OMeTAD}^+)$,¹⁶ we conclude that, 900 ps after laser excitation, the hole injection yield is about 50%. The presence of some residual dye cation states at this time is further supported by the small, 560-nm negative feature observed in Figure 2, attributed to a residual bleaching signal of the RuL₂(SCN)₂ dye cation. Extrapolation of the fit to the kinetics shown in Figure 3 suggests that, at long times (~10 ns), the efficiency of hole transfer approaches unity. Such a high yield of charge separation is consistent with the rapid rate of hole transfer from the RuL₂(SCN)₂⁺ to the OMeTAD reported here. The competing recombination reaction (eq 3) typically proceeds on the micro- to millisecond time scale^{17–19} and is, therefore, likely to be much slower than the hole injection reaction (eq 2) studied here.

In conclusion, it was possible to directly observe hole transfer from a photooxidized dye to a solid organic charge transport material, resulting in regeneration of the dye ground state. The dye regeneration could be time-resolved and shown to proceed primarily on the picosecond time scale with multiphasic kinetics. It is, therefore, at least 1 order of magnitude faster than the dye regeneration process involving iodine/iodide electrolytes.^{2,19} The high rate of the hole injection reaction into the OMeTAD ensures that the quantum efficiency for the overall charge separation process across the junction is close to unity. This may be a key factor behind the high external quantum efficiencies for charge carrier collection obtained with OMeTAD compared to other solid-state hole conducting materials studied to date.⁷

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Supporting Information Available: Device preparation and femtosecond transient absorption spectroscopy setup (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org> JA9915403

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