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Direct Observation of Photodriven Intermolecular Hole Transfer across TiO_2 Nanocrystallites: Lateral Self-Exchange Reactions and Catalyst Oxidation

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Abstract: Photoselection of Ru(II)-polypyridyl sensitizers with polarized pulsed-light excitation, when anchored to TiO_2 nanocrystallites interconnected in a mesoporous thin film, results in an anisotropic distribution of excited sensitizers. Under conditions where excited-state sensitizers efficiently inject electrons into TiO_2, the resulting oxidized sensitizers exhibit an initial anisotropy in their absorption difference spectra. Over the course of the charge-separated lifetime for many sensitizers, the transient absorption anisotropy signal decays to nearly zero indicative of lateral self-exchange hole-transfer reactions at the interface. When a cobalt metalloporphyrin catalyst was coanchored to the sensitized nanocrystalline TiO_2 film, excited-state injection was followed by lateral hole transfer to oxidize the surface-bound catalyst.

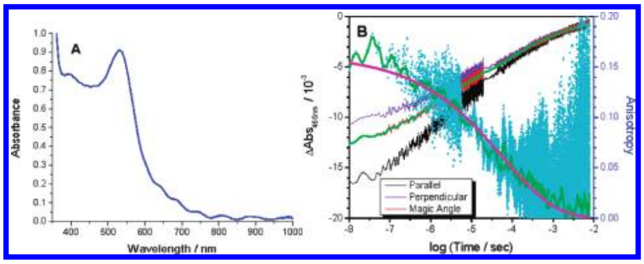

Figure 1. (A) Visible absorption spectrum of a Z907/TiO_2 thin film at 45° immersed in neat acetonitrile. (B) Transient absorption difference (left axis; black, purple, red) and anisotropy (right axis; light blue) changes monitored at 465 nm after 683 nm pulsed-laser excitation with absorbed fluence $\approx$ 700 $\mu J/cm^2$. Overlaid on the magic angle and anisotropy kinetics are adjacent-average smoothes (green) and a fit to a stretched exponential function (pink): $r = r_o \exp[-(kt)^{\beta}]$, where $k \approx 2 \times 10^4$ s^{-1} and $\beta \approx 0.34$.

Redox-active molecules anchored to TiO_2 nanocrystallites interconnected as the mesoporous thin films commonly used in dye-sensitized solar cells can be completely and reversibly oxidized with an appropriate bias provided that their surface coverage exceeds a percolation threshold.[1] Whether related lateral intermolecular sensitizer oxidation occurs after excited-state injection into TiO_2, or the extent to which such hole-transfer reactions might be exploited to accumulate redox equivalents for catalysis, remains unknown.[2] Self-exchange reactions are difficult to quantify at semiconductor interfaces due to the equivalence of reactants and products[3] and experimental challenges of conventional line-broadening measurements. Herein we report transient absorption anisotropy measurements,[4] a new spectroscopic tool for mechanistic characterization of photoinduced reactions at nanostructured semiconductor interfaces, that provide the first direct evidence for lateral self-exchange hole transfer across a semiconductor nanocrystallite after excited-state injection, behavior that was exploited to oxidize surface-anchored metalloporphyrin catalysts.

Figure 1a shows the absorption spectrum of *cis*-Ru(dnb)(dcb)$(NCS)_2$, where dnb is 4,4′-dinonyl-bpy and dcb is 4,4′-$(COOH)_2$-bpy (bpy is 2,2′-bipyridine), anchored at a saturation surface coverage of $\sim 5 \times 10^{-8}$ mol/cm^2 to a mesoporous, nanocrystalline (anatase) TiO_2 thin film, abbreviated Z907/TiO_2, immersed in neat acetonitrile. Nanosecond, polarized 683 nm light excitation of the sensitized thin film resulted in the prompt appearance of a transient absorption spectrum consistent with an interfacial charge-separated state, comprised of an injected electron in TiO_2 and an oxidized sensitizer, $k_{inj} > 10^8$ s^{-1}. Shown in Figure 1b are absorption transients monitored at 465 nm in a T format with a polarizer mounted either parallel or perpendicular to the vertical polarization of the laser excitation. The magic angle and anisotropy intensities shown were calculated in the usual manner; i.e. the magic angle is the average of the three orthogonal polarization axes while the anisotropy is the difference in the parallel and perpendicular signals divided by the total intensity.[4]

The wavelength-dependent amplitude of the anisotropy change was largest ($\sim$0.2) immediately after laser excitation and decayed slowly to near zero over time. Anisotropies less than the theoretical maximum of 0.4 are typical for Ru(II)-polypyridyl compounds where multiple and overlapping charge-transfer transitions are present.[5] Quantification of the anisotropy magnitude was only possible when the transient absorption difference signal was $> \sim 1 \times 10^{-3}$ due to noise. As the ruthenium coordination compounds are anchored to the TiO_2 nanocrystallites, thereby restricting molecular rotation, and a percolation threshold is known,[1,6] the transient anisotropy decay is reasonably attributed to lateral self-exchange hole transfer across the nanocrystalline TiO_2 surface.

As stated previously, these sensitized thin films can be fully oxidized electrochemically.[1,6] Potential-step experiments have allowed an effective diffusion constant for self-exchange hole transfer to be quantified on a minutes time scale. Since the entire mesoporous film was oxidized, the data were expected to be influenced by interparticle hole transfer across necking regions between anatase nanocrystallites. Since hole-transfer reactions between sensitizers on different TiO_2 nanocrystallites seem less likely on the time scale probed herein, these combined techniques represent a powerful approach for the characterization of lateral charge transfer on semiconductor materials. It was of specific interest to see whether the available electrochemical data were correlated in any way to those from these anisotropy measurements.

The Z907/TiO_2 sensitized material was selected as it has one of the highest effective $Ru^{III/II}$ diffusion constants ever measured, $(4-7) \times 10^{-9}$ cm^2/s, behavior attributed to the orientation of the Ru-NCS

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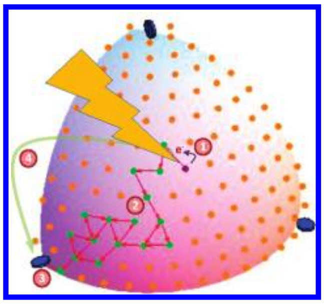
groups.[6b] Strikingly, the corresponding diffusion constant for the well-known N3 sensitizer, *cis*-Ru(dcb)$_2$(NCS)$_2$, is at least an order of magnitude smaller, behavior attributed to the sensitizer−surface orientation wherein two carboxylic acid groups on opposite dcb ligands, *trans* to the isothiocyanato ligands, bind to the surface.[6b] Polarized light excitation of N3/TiO$_2$ immersed in 100 mM LiClO$_4$/CH$_3$CN resulted in an anisotropy signal that remained nearly constant throughout the charge-recombination process. Therefore, consistent with previous potential-step measurements made on much longer time scales,[6b] significant anisotropy kinetics indicative of lateral self-exchange hole transfer were observed for Z907$^+$/TiO$_2$ but not N3$^+$/TiO$_2$.

Time-resolved anisotropy changes were also quantified for Ru(dcb)(dtb)$_2$/TiO$_2$, where dtb is 4,4′-di-*tert*-butyl-bpy. Heteroleptic ruthenium compounds of this type are known to have effective Ru$^{III/II}$ diffusion constants of $\sim 3 \times 10^{-10}$ cm^2/s,[6b] roughly an order of magnitude smaller than that of Z907/TiO$_2$, presumably due to electron tunneling through the bipyridine ligands.[3] Interestingly, the anisotropy measured after polarized light excitation of Ru(dcb)(dtb)$_2$/TiO$_2$ at 465 nm was essentially time independent when neat acetonitrile was used as the external solvent bath, but a surface-coverage-dependent rate of decay was observed when 100 mM LiClO$_4$ was introduced. In contrast, time-resolved anisotropies measured for Z907/TiO$_2$ were within experimental error the same in the presence and absence of 100 mM LiClO$_4$. This presumably occurs because ions are required to decrease the work terms associated with self-exchange hole transfer[3] in the more highly charged tris-diimine compound.

Lateral hole-transfer reactions after excited-state injection can potentially be exploited in redox catalysis for the generation of solar fuels.[2] In a small step toward this goal, and to test whether lateral hole transfer to a catalyst would occur prior to charge recombination, Co^{III}TCPP$^+$ was coanchored to a Z907/TiO$_2$ thin film and electrochemically reduced to its Co^{II} state (TCPP is tetracarboxyphenyl porphyrin). The strategy was that, after excited-state injection into TiO$_2$, the Z907$^+$ formed would oxidize the cobalt porphyrin from the formal oxidation state of (II) to (III) by lateral hole transfer. While the reaction is thermodynamically favored, $\Delta G° = -1.1$ eV, it must compete kinetically with TiO$_2$(e$^-$) + Z907$^+$ charge recombination. For an isotropic distribution of molecules at maximum packing and the ∼100:1 molar ratio of Z907 to Co^{II}TCPP employed, as determined by the Beer−Lambert Law, Z907$^+$ would be separated from the nearest porphyrin by an average of four Z907 sensitizers. (In other words, approximately six porphyrins would be bound to each nanocrystallite with one at either end of each orthogonal pole.) The true number of hops is likely much larger than four due to the random-walk nature of the self-exchange process, Scheme 1, and was found to be ∼60 based on 10^5 Monte Carlo iterations with symmetry boundary conditions.

Pulsed-light excitation of Z907 resulted in subnanosecond excited-state injection to yield Z907$^+$/TiO$_2$(e$^-$) and a small fraction of Co^{III}TCPP$^+$, Figure 2. Over hundreds of microseconds, a sharp absorption growth at ∼440 nm and bleach at ∼420 nm expected for oxidation of Co^{II} to Co^{III} appeared. Spectral modeling indicated that, by 85 μs, ∼10% of the porphyrins were oxidized with a hole-transfer quantum yield of ∼3% based on the number of Z907$^+$ initially created. The slow time scale and low metalloporphyrin surface coverage support the hypothesis that Co^{II}TCPP/TiO$_2$ oxidation was preceded by lateral Ru$^{III/II}$ self-exchange hole transfer. The low Co^{II} oxidation yield was rationalized by the large number of hops, kinetic competition with charge recombination, and possible nonuniform loading of CoTCPP. By 1 s, the TiO$_2$(e$^-$) had recombined with Co^{III}TCPP$^+$ to restore the initial state, Figure 2b. To the best of our knowledge this is the first observation of lateral hole transfer across a semiconductor surface to oxidize a molecular catalyst.[7]

Scheme 1. Hole-Transfer Simulation at Maximum Packing[a]



[a] (1) Excited-state electron injection from Z907* (purple) into TiO$_2$, (2) Monte Carlo simulated lateral self-exchange hole-transfer reactions between Ru^{III} and Ru^{II} (orange/green), (3) nearest-neighbor oxidation of Co^{II}TCPP (blue), and (4) ultimate recombination of TiO$_2$(e$^-$) + Co^{III}TCPP$^+$ to yield the initial state, Ru^{II}/TiO$_2$/Co^{II}.

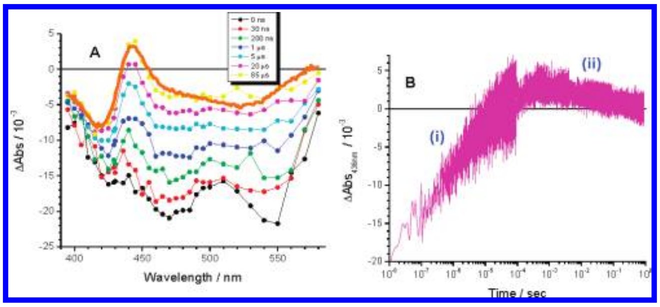


Figure 2. Transient absorption difference signals after 683 nm pulsed-laser excitation of a TiO$_2$ thin film electrode cofunctionalized with Z907 and CoTCPP in an ∼100:1 molar ratio and immersed in 100 mM TBAClO$_4$/CH$_3$CN (absorbed fluence ≈ 2.65 mJ/cm^2). (A) Spectra at the indicated delay times; the 85 μs data are modeled by spectral addition of Co^{II}, Co^{III}, TiO$_2$(e$^-$), and Ru^{III} in a −1:1:9:8 molar ratio (orange). (B) Kinetics monitored at 436 nm that correspond to (i) Z907$^+$ + Co^{II} followed by (ii) Co^{III} + TiO$_2$(e$^-$) to yield the initial state, Ru^{II}/TiO$_2$/Co^{II}.

In conclusion, pulsed-light excitation of Ru(II)-sensitized TiO$_2$ thin films with polarized light resulted in rapid excited-state electron injection into TiO$_2$ ($k_{inj} > 10^8$ s^{-1}) to yield a Ru^{III}/TiO$_2$(e$^-$) charge-separated state that displayed significant absorption anisotropy. Under most experimental conditions, the anisotropy decayed on a micro- to millisecond time scale. Given the known percolation threshold,[1,6] previously reported potential-step results,[6b] and the carboxylate-type linkage between the Ru compounds and TiO$_2$,[8] the anisotropy decay was assigned to a lateral Ru$^{III/II}$ self-exchange "hole-hopping" process across the anatase surface. The observation of lateral hole transfer has clear implications for fundamental studies of sensitized thin films for applications in solar energy conversion. First, mechanistic models of interfacial charge recombination between TiO$_2$(e$^-$)s and oxidized sensitizers must take into account diffusion of the injected electron[9] *and* the oxidized sensitizer,[6b] not simply the injected electron.[10] Second, lateral hole transfer can be utilized to translate holes present as oxidized sensitizers[11] to catalysts such as the cobalt porphyrins reported here. Such hole transfer is not necessary for iodide oxidation in dye-sensitized solar cells.[12] However, for water oxidation four holes must be accumulated on a single catalytic site[2] and lateral hole hopping after excited-state injection represents a viable approach. Finally, we anticipate that transient absorption anisotropy will be a useful tool for the study of a wide variety of lateral self-exchange reactions across nanocrystalline materials.

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