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Ligand-Localized Electron Trapping at Sensitized Semiconductor Interfaces

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Charge-trapping processes are commonly invoked to rationalize the optical and electronic properties of semiconductor heterojunctions.[1−3] In most cases, however, the chemical nature of the "trap states" are poorly understood and are loosely described in terms of "surface states" or "impurity bands".[1−3] Herein we report compelling evidence that electrons injected into a semiconductor by molecular excited states can subsequently be trapped on ligands of the same compound. Trapping therefore yields products with well-defined molecular structure and redox properties. An additional advantage of the approach described herein is that trapping only occurs when electrons are injected into the semiconductor from upper vibrational excited states and thus serves as a direct probe of "hot electron" involvement in interfacial phenomena.[4−7] Furthermore, electron trapping yields charge-separated intermediates that can store ~2 eV of free energy for periods of minutes with potential applications in solar energy conversion,[8] photochromics,[9] and information storage.[10]

The molecular semiconductor interfaces of interest comprise nanocrystalline (anatase), mesoporous TiO_2 thin films[11] sensitized to visible light with $[Ru(bpy)_2(deebq)](PF_6)_2$ or $[Os(bpy)_2(deebq)](PF_6)_2$, where bpy is 2,2′-bipyridine and deebq is 4,4′-diethylester-2,2′-biquinoline. The coordination compounds have been characterized by ^1H NMR, M/S, and X-ray crystallography,[12] and the photophysical and electrochemical properties in acetonitrile are given in the Supporting Information. The absorption spectra shown in Figure 1 display two visible bands reasonably assigned to M → bpy (~440 nm) and M → deebq (~560 nm), and the Os compound shows an additional band in the near-IR region that has been assigned to a direct singlet-to-triplet transition (~860 nm).[13] Both compounds bind strongly to the nanocrystalline TiO_2 films, abbreviated Ru/TiO_2 and Os/TiO_2, with typical surface coverages of $7\ (\pm 2) \times 10^{-8}$ mol/cm^2.[14] The Ru compound is photoluminescent in fluid acetonitrile solution and on the nanocrystalline semiconductor surface.

Nanosecond transient absorption spectra measured after pulsed light excitation of M/TiO_2 are comprised of >80% metal-to-ligand charge-transfer (MLCT) excited states and a long-lived component that is discussed in the following paragraph. The MLCT excited-state assignment is confirmed by comparisons to the spectra observed in fluid solution and the coincidence of lifetimes measured by absorption and photoluminescence. The excited-state lifetime of Os^*/TiO_2 is unchanged within experimental error of that measured in fluid solution, $\tau = 10$ ns. For Ru/TiO_2, the long Ru* lifetime results in excited-state−excited-state interactions and nonexponential kinetics.[15] The electrochemical ($V_{appl} = -0.70$ V vs SCE) or photochemical ($\lambda_{exc} = 514.5$ nm, 0.5 M sacrificial donor triethylamine)[16] reduction of M/TiO_2 yields identical visible absorption spectra that are expected for the reduced form of the compounds, i.e., $[M^{II}(bpy)_2(deebq^{\bullet -})]^+$, with no spectroscopic evidence for the formation of $TiO_2(e^-)$, Figure 1.[17] This experimental data demonstrates that neither the emissive excited state or the reduced sensitizer efficiently injects electrons into TiO_2 because the conduction band edge position, E_{cb}, is energetically inaccessible, i.e., $E^0\ (M^{III/II*}) > E^0\ (M^{2+/+}) > E_{cb}$.[18]

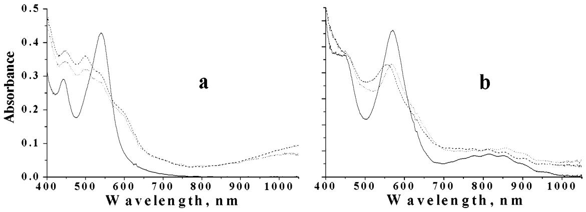

Figure 1. Absorption spectra for M/TiO_2 in argon-saturated CH_3CN shown as solid lines where (a) $M = [Ru(bpy)_2(deebq)^{2+}$ and (b) $M = [Os(bpy)_2(deebq)^{2+}$. Dashed lines were obtained after steady-state photolysis (514.5 nm) in 0.5 M triethylamine/CH_3CN. Dotted lines were measured after electrochemical reduction at −0.7 V vs SCE.

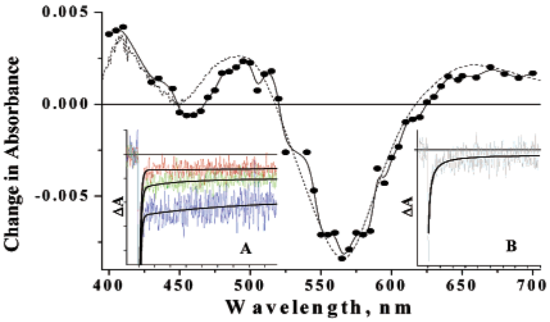

Figure 2. Time-resolved absorption difference spectrum recorded 2 μs after pulsed light excitation (417 nm, ~2.2 mJ/cm^2, 8 ns fwhm) of Os/TiO_2 in acetonitrile (solid line with circles). Dashed lines are calculated from the equation $\Delta A(\lambda) = A(Os^{III}/TiO_2) + A(Os^{+}/TiO_2) - 2A(Os^{II}/TiO_2)$. Inset A shows absorption decays on a 0.2 μs/division scale monitored at 570 nm following pulsed excitation at 417 nm (upper line), 532 nm (middle line), or 683 nm (lower line). To clearly show the wavelength dependence, the initial amplitudes shown are one-third their measured value. Inset B shows decay on a 2 ms/div time scale following 417 nm pulsed excitation with an overlaid second-order fit.

The absorption spectra of the long-lived component closely resemble the MLCT excited state, but no accompanying emission is observed, Figure 2. The intermediate is assigned to surfaces that contain an equal concentration of reduced and oxidized compounds, $M^{II}(deebq^-)(bpy)_2{}^+$ and $M^{III}(deebq)(bpy)_2{}^{3+}$. In situ spectroelectrochemical measurements allow us to directly measure the absorption spectra of both these compounds and simulate the transient data based upon the expected 1:1 stoichiometry. The simulations are in excellent agreement with the measured transient spectra as shown for Os/TiO_2. An estimate of the quantum yield for creating the charge-separated state (CSS) can be obtained from single

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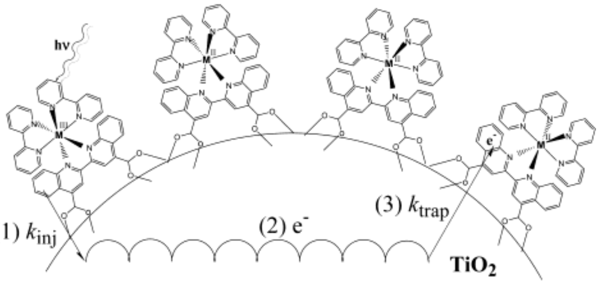
wavelength kinetics such as that shown in Figure 2, inset A.[5c] The quantum yield (ϕ_{CSS}) decreases with excitation wavelength: $\phi_{CSS}(417) = 0.14 \pm 0.03$, $\phi_{CSS}(532.5) = 0.08 + 0.03$, and, for Os/TiO$_2$, $\phi_{CSS}(683) = 0.05 \pm 0.01$. The ϕ_{CSS} values were independent of the excitation irradiance (from 1 to 20 mJ/pulse) and are zero in fluid solution, on insulating ZrO_2 films, or when the corresponding 4,4′-diethylester-bipyridine (deeb) compounds were used under otherwise identical conditions.

The proposed mechanism for formation of the charge-separated intermediates is shown schematically below and involves: (1) ultrafast interfacial electron injection from upper excited state(s) with a rate constant, k_{inj}, (2) transport of the injected electron, and (3) charge trapping (k_{trap}) on a ground-state compound. Other possible mechanisms, such as triple−triplet annhilation, are ruled out on the basis of the control experiments. The wavelength-dependent quantum yields are expected for injection from vibrationally hot excited states,[5] and their insensitivity to sensitizer (despite the fact that the Os Franck−Condon excited state is a stronger photoreductant by 400 meV) suggests a common injecting state. Electron trapping on a deebq ligand is expected to be thermodynamically downhill since these ligands are reduced before TiO_2. Trapping to regenerate the excited state is also energetically favored and could give rise to delayed emission.[6] We have observed no evidence for this, presumably because the injected electron is statistically more likely to reduce a ground-state compound then the oxidized compound it came from. This follows as there are ~1000 compounds anchored to each nanoparticle and pulsed laser excitation yields on average <1 injected electron per nanoparticle.



Rate-limiting intermolecular charge-transfer "hopping" across the nanocrystalline semiconductor surface eventually leads to encounters between the charge-separated pairs and to the highly energetically favored recombination to yield ground-state products, i.e., $M^{II}(deebq^-)(bpy)_2{}^+/TiO_2 + M^{III}(deebq)(bpy)_2{}^{3+}/TiO_2 \rightarrow 2\ M/TiO_2$. Transient absorption experiments performed on the millisecond time-scale were adequately fit to a second-order kinetic model plus a nonzero baseline from which $k_{obs} = 1.3 \times 10^6\ s^{-1}$ for both Ru/TiO$_2$ and Os/TiO$_2$, Figure 2B. Here k_{obs} is related to the true second-order rate constant by the extinction coefficient and path length, $k = k_{obs}/\epsilon l$. $Ru^{III/II}$ hopping has previously been observed under potentiostatic conditions in related sensitized materials[11b,19] and is sufficiently slow that the concentration of the charge-separated intermediates can be increased by continued pulsed excitation at 10 Hz.[20] Under these conditions the sample can be removed from the laser beam, and the charge-separated intermediate appears as a green color, easily observed by the human eye for a few hundred seconds before regeneration of the initial color. Transient images of different shapes and sizes were created by masking the excitation light.

The ability to observe the trapped products on a seconds time scale allows one to explore their response to chemical stimuli. For example, the addition of 0.1 M $LiClO_4$ results in rapid electron transfer to yield ground-state products (<10 s). Li^+ is a known "potential-determining ion" that shifts E_{cb} to promote electron injection and, in this case, rapid recombination.[19,20] In fact, 0.1 M Li^+ quenches the Ru/TiO$_2$ photoluminescence intensity by ~30% and trapping is absent, indicating that E_{cb} is energetically proximate to $E^0(M^{III/II*})$ under these conditions.[14,15,17]

An important feature of ligand-localized trapping is that it yields reducing and oxidizing equivalents in known concentrations with well-defined molecular structures and reduction potentials on the semiconductor surface. The Ru/TiO$_2$ CSS stores ~2.1 eV of potential energy for periods of minutes and Os/TiO$_2$ stores ~1.6 eV. In three previous literature reports, researchers have identified conditions where thermally equilibrated excited states are energetically proximate to E_{cb}, thereby giving rise to wavelength-dependent electron injection yields.[5] A key to the observations reported here is that the first reduction potential lies below E_{cb}. To our knowledge this has not been previously accomplished, and this finding opens the door toward fundamental studies of charge trapping at semiconductor interfaces. It is likely that other examples will emerge as solar energy researchers utilize ligands with low-lying π^* orbitals and tune E_{cb} to optimize the spectral sensitivity and power conversion efficiencies of dye-sensitized solar cells.[22]

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Supporting Information Available: A table of the photophysical and electrochemical data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Shockley, W.; Read, W. T. *Phys. Rev.* **1952**, *87*, 835.
(2) (a) Sze, S. M. *Physics of Semiconductor Devices*; Wiley: New York, 1969. (b) Kittel, C. *Introduction to Solid State Physics*, 7th ed; Wiley: New York, 1996.
(3) Pankove, J. I. *Optical Processes in Semiconductors*; Dover: New York, 1971.
(4) Nozik, A. J. *Annu. Rev. Phys. Chem.* **2001**, *52*, 193.
(5) (a) Ferrere, S.; Gregg, B. A. *J. Am. Chem. Soc.* **1998**, *120*, 843. (b) Islam, A.; Hara, K.; Singh, L. P.; Katoh, R.; Yanagida, M.; Murata, S.; Takahashi, Y.; Sugihara, H.; Arakawa, H. *Chem. Lett.* **2000**, 490. (c) Moser, J. E.; Grätzel, M. *Chimia* **1998**, *52*, 160.
(6) Huber, R.; Sporlein, S.; Moser, J. E.; Grätzel, M.; Wachtveitl, J. *J. Phys. Chem. B* **2000**, *104*, 8995.
(7) Benko, G.; Kallioinen, J. E.; Korppi-Tommola, J. E. I.; Yartsev, A. P.; Sundstrom, V. *J. Am. Chem. Soc.* **2002**, *124*, 489 and references therein.
(8) (a) Slama-Schwok, A.; Ottolenghi, M.; Avnir, D. *Nature* **1992**, *355*, 240. (b) Hoyle, R.; Sotomayor, J.; Will, G.; Fitzmaurice, D. *J. Phys. Chem. B* **1997**, *101*, 10791.
(9) Bonhote, P.; Moser, J.-E.; Humphry-Baker, R.; Vlachopoulos, N.; Zakeeruddin, S. M.; Walder, L.; Grätzel, M. *J. Am. Chem. Soc.* **1999**, *121*, 1324.
(10) Liu, C.-Y.; Pan, H.-I.; Fox, M. A.; Bard, A. J. *Science* **1993**, *261*, 887.
(11) (a) O'Regan, B.; Moser, J.; Anderson, M.; Grätzel, M. *J. Phys. Chem.* **1990**, *94*, 8720. (b) Galoppini, E.; Guo, W.; Zhang, W.; Hoertz, P. G.; Qu, P.; Meyer, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 7801.
(12) Hoertz, P. G. Unpublished results.
(13) Kober, E.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1324.
(14) Qu, P.; Meyer, G. J. *Langmuir* **2001**, *17*, 6720.
(15) Kelly, C. A.; Farzad, F.; Meyer, G. J. *Langmuir* **1999**, *15*, 731.
(16) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 90.
(17) Rothenberger, G.; Fitzmaurice, D.; Grätzel, M. *J. Phys. Chem.* **1994**, *98*, 4133.
(18) We note that the acceptor states in TiO_2 may be localized rather than E_{cb}.
(19) (a) Heimer, T. A.; D'Arcangelis, S. T.; Farzad, F.; Stipkala, J. M.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 5319. (b) Bonhote, P.; Gogniat, E.; Tingry, S.; Barbe, C.; Vlachopoulos, N.; Lenzmann, F.; Comte, P.; Grätzel, M. *J. Phys. Chem. B* **1998**, *102*, 1498. (c) Trammell, S. A.; Meyer, T. J. *J. Phys. Chem. B* **1999**, *103*, 104.
(20) Prolonged excitation can lead to absorption spectra that differ from that observed on the sub-ms time scale and that expected for the CSS intermediate. Spectroelectrochemical analysis indicates that a fraction of M^{III}/TiO_2 is absent, presumably due to slow reduction by impurities.
(21) (a) Kelly, C. A.; Thompson, D. W.; Farzad, F.; Stipkala, J. M.; Meyer, G. J. *Langmuir* **1999**, *15*, 7047. (b) Thompson, D. W.; Kelly, C. A.; Farzad, F.; Meyer, G. J. *Langmuir* **1999**, *15*, 650.
(22) Gräztel, M. *Nature* **2001**, *414*, 338.

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