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Authors

Staniszewski, Aaron
Ardo, Shane
Sun, Yali
et al.

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Slow Cation Transfer Follows Sensitizer Regeneration at Anatase TiO_2 Interfaces

Aaron Staniszewski,[†] Shane Ardo,[†] Yali Sun,[‡] Felix N. Castellano,*[,‡] and Gerald J. Meyer*[,†]

Departments of Chemistry and Materials Science and Engineering, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218 and Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

Received May 16, 2008; E-mail: castell@bgnet.bgsu.edu; meyer@jhu.edu

In 1991, Grätzel and O'Regan first reported that the efficiency of dye-sensitized solar cells was dependent on the nature of cations present in the electrolyte.[1] Lewis acidic Li^+ cations gave the highest efficiencies, and the champion Grätzel cells of today still require them.[2] Since that time, it has been shown that Li^+ cations affect all of the desired electron-transfer processes in the solar cell: (1) excited-state injection,[3] (2) transport of the injected electron, $TiO_2(e^-)$, through the sensitized film,[4] and (3) reduction of the oxidized sensitizer by iodide.[5,6] Here we communicate that the third step, often referred to as sensitizer regeneration, does not in fact produce the sensitizer that was initially photoexcited. Instead, slow (μs to ms) cation transfer follows regeneration to yield the initial sensitizer. This behavior has been observed with all Ru(II) sensitizers investigated in our laboratories and is now apparent in previously published spectral data.[7,8]

Figure 1 shows the absorption and photoluminescence (PL) spectra of $[Ru(dtb)_2(dcb)](PF_6)_2$, where dtb is 4,4′-$(C(CH_3)_3)_2$-2,2′-bipyridine and dcb is 4,4′-$(COOH)_2$-2,2′-bipyridine, anchored to a mesoporous, nanocrystalline TiO_2 (anatase) thin film that was first immersed in 0.1 M $LiClO_4$ acetonitrile and then in neat acetonitrile. In the presence of Li^+, both maxima red-shifted and their intensity decreased relative to neat acetonitrile. The dramatic quenching of the PL intensity results from enhanced excited-state electron injection into TiO_2. Comparable absorption shifts were observed in acetonitrile upon addition of Li^+ to the deprotonated form of $[Ru(dtb)_2(dcb)](PF_6)_2$ indicating that TiO_2 is not required for said spectral changes. Similar, although less pronounced, cation-induced absorption and PL changes have previously been reported for $Ru(dcb)(bpy)_2/TiO_2$.[9] This effect is not limited to Li^+ and has been observed with other alkali and alkaline earth cations with a magnitude inversely related to the cation's size-to-charge ratio.[9] Interestingly, polarizing the sensitized electrode cathodically in 0.1 M $LiClO_4$ electrolyte resulted in $Ru(dcb)(bpy)_2/TiO_2$ absorption spectra like that observed in neat acetonitrile.

Pulsed 532 nm excitation of $Ru(dtb)_2(dcb)/TiO_2$ in a 0.1 M $LiClO_4$/0.5 M tetrabutylammonium iodide (TBAI) acetonitrile solution resulted in the microsecond absorption difference spectrum shown in Figure 2. Under such conditions, one would expect to observe an injected electron in TiO_2 and oxidized iodide products, I_3^-. The absorption features characteristic of I_3^- (λ < 420 nm) along with weak contributions from the injected electron (λ > 560 nm)[10,11] were indeed observed. However, the absorption band centered at 460 nm and the bleach at 510 nm could not be assigned to the electron transfer products expected.

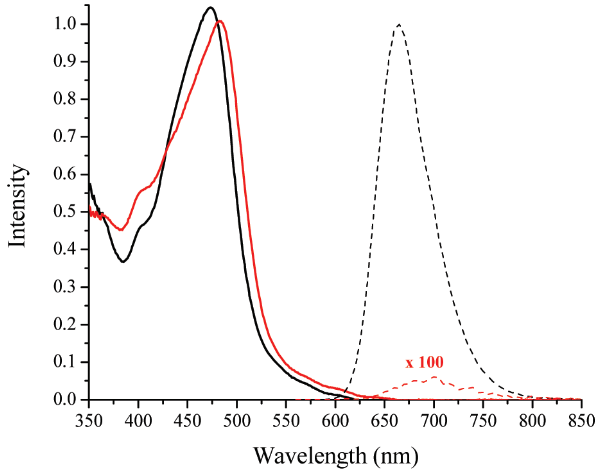

Figure 1. Absorption and photoluminescence spectra of $Ru(dtb)_2(dcb)/TiO_2$ in 0.1 M $LiClO_4$ acetonitrile (red) and in neat acetonitrile after removal of the $LiClO_4$ by 10 acetonitrile washings (black).

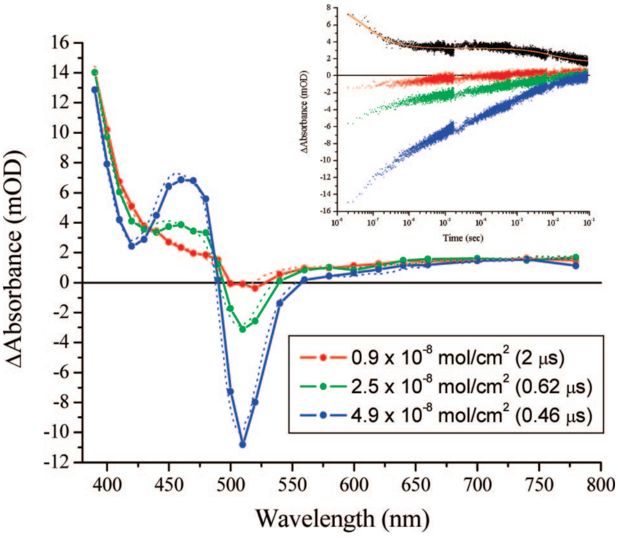

Figure 2. Transient absorption difference spectra of three $Ru(dtb)_2(dcb)/TiO_2$ thin films at the indicated surface coverages and delay times measured after pulsed 532 nm excitation in 0.1 M $LiClO_4$/0.5 M TBAI acetonitrile solution. Overlaid in dashed lines are simulations of the data. The inset shows absorption transients monitored at 510 nm for each surface coverage, which corresponds to cation transfer, and a single absorption change measured at 433 nm (- -), assigned to $TiO_2(e^-)s + I_3^-$ recombination.

Spectral modeling studies indicated that the absorption features at 460 and 510 nm resulted from Ru(II) sensitizers that were regenerated in an environment depleted of Li^+. In other words, the sensitizer that was initially photoexcited has an absorption spectrum shown in red while that which was observed after

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[†] Johns Hopkins University.
[‡] Bowling Green State University.

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regeneration was that shown in black, Figure 1. Overlaid on the data in Figure 2 are simulations based on the weighted addition of (1) the absorption spectrum of I_3^-, (2) the $TiO_2(e^-)$ absorption spectrum, and (3) the difference in the absorption spectra of $Ru(dtb)_2(dcb)/TiO_2$ in the absence minus the presence of Li^+. Likewise, similar absorption features due to Ru(II) were observed with the neutral, organic donor phenothiazine (PTZ) in place of iodide. The excellent agreement between observed and simulated data provides compelling evidence that Ru(II) is regenerated in an environment that lacks outer-sphere Li^+ interaction(s). Similar but less pronounced absorption features were observed after pulsed-light excitation of $Ru(dcb)(bpy)_2/TiO_2$ and $Ru(dcbq)(bpy)_2/TiO_2$, where dcbq is 4,4′-$(COOH)_2$-2,2′-biquinoline, in a 0.5 M iodide solution as well as in the published literature for *cis*-$Ru(dcb)_2(NCS)_2/TiO_2$ (i.e., $N3/TiO_2$) and $Ru(dcb)(bpy)_2/SnO_2$ (see Supporting Information).[7,8] In all cases, absorption features were observed that were due to neither oxidized iodide products nor $TiO_2(e^-)$s and could reasonably be described as sensitizer regeneration in a Li^+-deficient milieu.

The absorption changes that correspond to cation transfer were found to be nonexponential but could be satisfactorily fit to the Kohlrausch−Williams−Watts function, $A(t) = A_o \exp[-(t/\tau)^\beta]$ where $0 < \beta < 1$, which has been widely used to model electron transport in these materials.[12,13] Values for $\tau = 4.1\ (\pm 2.5) \times 10^{-5}$ s and $\beta = 0.16 \pm 0.01$ were found. The low β value corresponds to a broad Levy distribution of rate constants. Tens of microseconds to even milliseconds were required for completion of the cation transfer at high surface coverage. While the bulky tertiary butyl groups may inhibit cation motion, we have observed cation transport on similar time scales with $Ru(dcb)(bpy)_2/TiO_2$ and $N3/TiO_2$ where sterics are expected to be less significant. The time scale for cation transfer was in itself remarkable considering that the sensitized film was immersed in 0.1 M Li^+-containing electrolyte. This also highlights the locality of said effect. Even though the sensitizer surface coverage is high, only a small concentration of sensitizers, approximately equal to that of $TiO_2(e^-)$s, are found to be in this Li^+-deficient environment, i.e. the effect is local in nature rather than macroscopic.

On nanosecond and longer time scales, the magnitude of the cation effect was found to be strongly dependent on sensitizer surface coverage: nearly absent at low coverage but clearly observed at saturation surface coverage and with the expected stoichiometry. One hypothesis is that *all* of the Ru(II) regenerated after iodide (or PTZ) oxidation was initially present in a unique ionic environment with some subnanosecond cation motion at lower surface coverages.

Cation transfer occurs on time scales similar to that of $TiO_2(e^-)$s + I_3^- recombination, Figure 2 inset. For these measurements, the laser irradiance was controlled so that approximately the same number of excited states and initial concentrations of I_3^- and $TiO_2(e^-)$s were generated. The decrease in the concentration of I_3^- was also nonexponential and followed a kinetic mechanism similar to that previously proposed: a fast recombination with $TiO_2(e^-)$s and a slower diffusional process.[14,15] However, there was a negligible surface-coverage dependence on the rate of I_3^- reduction which was not the case with cation motion.

The spectral data indicate that Li^+ transfer away from the sensitizer occurs in <10 ns. In the absence of donor molecules, there was no clear evidence for cation-induced spectral changes during the back reaction of $TiO_2(e-)$s with Ru(III) (data not shown).[16] Furube et al.[17] reported time-resolved infrared data consistent with picosecond Li^+ transfer after excited-state injection by coumarin sensitizers, behavior attributed to Coulombic repulsion between the oxidized coumarin and Li^+. Also, cations are required for charge compensation of the injected electron which could also induce Li^+ to migrate away from the oxidized sensitizer. Indeed, intercalation of Li^+ into anatase TiO_2 is known to occur in batteries[18] and is consistent with quartz crystal microbalance studies.[19] In this regard, the finding that the same Ru(II) spectral changes can be observed by partial electrochemical reduction of the TiO_2, when no oxidized sensitizer was present, indicates that charge compensation also plays a role.

In summary, after fast photoinduced electron injection into TiO_2 and iodide regeneration, sensitizers are present in an environment distinctly different from that prior to light absorption. Significantly, the newly generated sensitizer is in an environment that is known to be less favorable for excited-state electron injection.[9] Under air mass 1.5, 1 sun irradiation, the slow (μs−ms) cation transfer discovered is not expected to limit the efficiency of Grätzel solar cells as a typical Ru(II) sensitizer absorbs light approximately once every second. However, at higher irradiances or at planar TiO_2 surfaces this effect may limit light-to-electrical power conversion efficiency. In all cases, the operative sensitization mechanism put forth in review-type articles, where a Ru(II) sensitizer is regenerated to its *initial* state within 10 ns, needs to be modified.[20,21] The oxidized sensitizer may be reduced in ~10 ns, but it is not brought back to the environment prior to light absorption until slow (μs−ms) cation transfer has taken place.

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Supporting Information Available: Simulations of spectra from refs 7 and 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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