

LETTERS

Semiconductor-Based Interfacial Electron-Transfer Reactivity: Decoupling Kinetics from pH-Dependent Band Energetics in a Dye-Sensitized Titanium Dioxide/Aqueous Solution System

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Hexaphosphonation of $\text{Ru}(\text{bpy})_3^{2+}$ provides a basis for surface attachment to nanocrystalline TiO_2 in film (electrode) or colloidal form and for subsequent retention of the molecule over an extraordinarily wide pH range. Visible excitation of the surface-attached complex leads to rapid injection of an electron into the semiconductor. Return electron transfer, monitored by transient absorbance spectroscopy, is biphasic with a slow component that can be reversibly eliminated by adjusting the potential of the dark electrode to a value close to the conduction-band edge (E_{CB}). Evaluation of the fast component yields a back-electron-transfer rate constant of $5(\pm 0.5) \times 10^7 \text{ s}^{-1}$ that is invariant between $\text{pH} = 11$ and $H_0 = -8$, despite a greater than 1 eV change in E_{CB} (i.e., the nominal free energy of the electron in the electrode). The observed insensitivity to large changes in band-edge energetics stands in marked contrast to the behavior expected from a straightforward application of conventional interfacial electron-transfer theory and calls into question the existing interpretation of these types of reactions as simple inverted region processes.

Introduction

Surface modification of wide-bandgap semiconductors via attachment of redox-active dyes offers a means of sensitizing these materials for visible-region photoelectrochemical applications.¹ It also creates a convenient framework for interrogating interfacial electron-transfer reaction kinetics. Among the most attractive systems for both applications are those based on carboxylate-functionalized ruthenium bipyridyl complexes together with high-area nanocrystalline titanium dioxide films.^{2,3} As with other semiconductor/molecular dye assemblies, these work by electron injection from a photoexcited state of the dye into the conduction band or surface states of the semiconductor. One of the key distinguishing features of the nanocrystalline TiO_2 /dye system is relatively slow back electron transfer ($\tau \approx 100 \text{ ns}$) after forward electron injection. Sluggish back electron transfer (ET) is advantageous in photoelectrochemical (photo-

voltaic) applications because it permits (a) capture of the dye-localized oxidizing equivalent by a solution-phase redox species, (b) conduction-band transport of the injected electron to an external circuit, (c) return of the electron to solution via a second (dark) electrode (i.e., turnover of the redox species), and therefore (d) relatively efficient sustained conversion of light to electrical energy.⁴

The prevailing wisdom suggests that back ET is uniquely (or nearly uniquely) slow in $\text{TiO}_2/\text{RuL}_3$ assemblies because the reaction occurs in the Marcus inverted region, where the reaction driving force (ca. -2 eV) is defined as the difference between the conduction band-edge energy ($\sim -0.7 \text{ V}$ at $\text{pH} = 3$) and the formal reduction potential of the oxidized dye (ca. $+1.3 \text{ V}$ for $\text{Ru}^{\text{III}}\text{L}_3$).⁵ We reasoned that the apparent driving force could be altered and the general hypothesis examined by taking advantage of the well-known Nernstian dependence of the conduction band edge energy (E_{CB}) on pH (Figure 1).⁶ Using this strategy, we have examined back ET to a highly adherent

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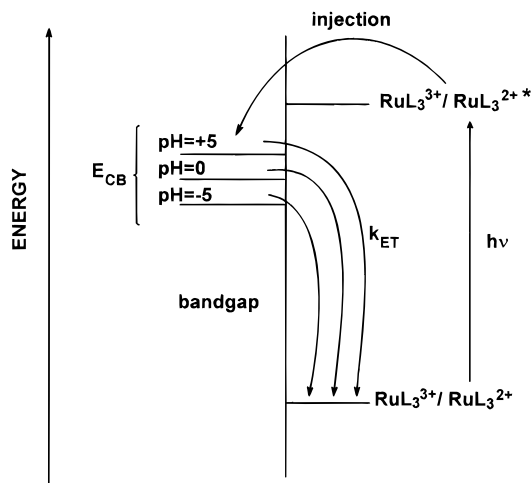


Figure 1. Schematic representation of pH-dependent energetics for forward electron transfer (dye injection) and back electron transfer.

form of the ruthenium dye over a nearly 20 pH unit range (i.e., greater than 1 eV change in overall reaction driving force). These measurements have been augmented with time-resolved luminescence measurements, transient absorbance spectral measurements and independent laser reflectance assessments of E_{CB} . We find that the combined results differ tremendously from the predictions of the simplest treatments of metal oxide semiconductor/solution reactivity and point to the need for new models for ET reactivity at these interfaces.

Experimental Section

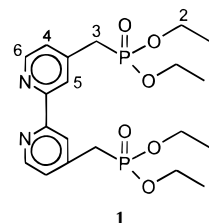
Preparation of TiO₂ Sols and Films. Colloidal TiO₂ sols were prepared by published methods.⁷ High-surface-area films were prepared via the following modification of the method of Nazeeruddin et al.^{2b} TiO₂ (P25, Degussa, 3 g) was ground in a mortar with 2 mL of 2-methoxyethanol. The viscous paste was slowly diluted by addition of 2-methoxyethanol (6 mL) with continuous grinding. A surfactant (0.1 mL of Triton X-100, Aldrich) was added to facilitate colloid spreading. The TiO₂ colloid was then cast by spin-coating onto conductive glass (Asahi fluorine-doped SnO₂) that was masked with Teflon tape. The electrode was fired for 1 h at 450 °C in air. Dye was adsorbed by immersing the TiO₂ electrode in an aqueous solution (pH = 2.45, adjusted with HNO₃) of hydrolyzed RuL₃ (see below) for 24 h.

Measurements. Transient absorbance experiments were initiated by using the frequency-doubled (532 nm) output of a short-cavity, Q-switched Nd:YAG laser (2.5 ns pulse) as a pump beam. The probe beam was generated with a pulsed 75 W xenon arc lamp (0.2 ms pulse)⁸ positioned normal to the laser input. For ET kinetics studies, the sample was probed at the dye ground-state absorbance maximum (464 nm) and detection was accomplished with a fast (5-stage) photomultiplier tube. Data were collected on either a LeCroy 9400 digital oscilloscope or a LeCroy 6880 digitizer, and an average of 1000 shots was recorded. Time-resolved emission studies (ca. 6 ns resolution) were carried out with a N₂-pumped dye laser (PRA Models LN1000 and LN102) with detection at right angles via a monochromator, fast PMT, and digitizer or digital oscilloscope. Ground state UV-vis absorbance spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer.

Variable potential experiments were performed with a PAR 264A potentiostat in a three-electrode cell comprised of the TiO₂/SnO₂ working electrode, a Pt wire counter electrode and a saturated sodium calomel (SSCE) reference electrode. Laser reflectance spectroelectrochemistry was carried out by using a

PAR 273 potentiostat in conjunction with a 786 nm diode laser (Diolite).⁹ The detector was a fast photodiode (Thor Labs). Photodiode voltage versus potential signals were recorded on a Houston 2000 X-Y recorder.

Materials. The chelating ligand, 4,4'-(CH₂PO(OCH₂CH₃)₂)₂-2,2'-bipyridine (=L, **1**) was prepared by refluxing bis-4,4'-



bromomethyl-2,2'-bipyridine¹⁰ in freshly distilled triethylphosphite (Aldrich) for 4–6 h. The solvent was removed by distillation. The dark product was cooled, washed with ether, and collected by filtration. This preparation is a modification of literature methods.^{11,12} ¹H NMR (CDCl₃) δ 1.3 (H₁, t, *J* = 9.3 Hz, 12H), 4.1 (H₂, q, *J* = 7.5 Hz, 8H), 3.2, 3.3 (H₃, s, 4H), 7.3 (H₄, d, 2H), 8.3 (H₅, s, 2H), 8.6 (H₆, d, *J* = 9 Hz, 2H).

[RuL₃](PF₆)₂ was prepared from RuCl₃ (Aesar) and L by literature methods,¹³ except that 2-methoxyethanol was used as solvent. (Attempts to isolate the compound from “standard” solvents such as DMF and ethylene glycol were unsuccessful.) After partial removal of solvent and addition of water, the crude compound was precipitated via addition of aqueous NH₄PF₆ and subjected to rapid, short-column chromatography. It should be noted that the coordinated ligand is relatively easily hydrolyzed in aqueous solutions. (Partial hydrolysis was established by NMR.) This ultimately was not a concern, however, since the complex is subsequently intentionally hydrolyzed in acid (6 M HCl) to facilitate surface attachment, presumably via phosphonate chelation of Ti(IV). Nevertheless, partial hydrolysis complicates isolation from water and renders elemental analysis, while satisfactory, relatively uninformative. Supporting evidence for the proposed formulation was obtained, therefore, from mass spectrometry and other methods. Elemental analysis calcd (found) for {RuL₃(PF₆)₂·2(NH₄PF₆)–2(C₂H₄)} (=C₅₆H₉₀N₈O₁₈–P₁₀F₂₄Ru): C: 33.50 (33.13), H: 4.45 (4.47), N: 5.84 (5.52). (Note that for the calculated elemental analysis, protons were assumed to be present for ligand charge compensation.) FAB mass spectrometry for [RuL₃](PF₆)₂, *m/e* 1616 (parent compound – PF₆), 1415 (–2(PF₆), –2(C₂H₄)), 1359 (–2(PF₆), –4(C₂H₄)), 1335 (–PF₆, –10(C₂H₄)), 1279 (–PF₆, –12(C₂H₄)), 1247 (–2(PF₆), –8(C₂H₄)). ¹H NMR (D₂O) δ 1.3 (H₁, t, *J* = 10.6 Hz, 30H), 4.1 (H₂, q, *J* = 8.8 Hz, 20H), 3.5 (H₃, 2s, 12H), 8.2 (H₅, s, 6H), 8.7 (H₆, d, 6H). The ¹H NMR spectrum for the intentionally hydrolyzed complex displayed a loss of the peaks at 1.3 and 4.1, confirming loss of the ethyl groups. The compound exhibits an intense metal-to-ligand charge-transfer absorbance with λ_{max} = 464 nm (ε = 12 600 M^{–1} cm^{–1}). The Ru(II/III) formal potential (prior to intentional hydrolysis) was 1.24 V vs SSCE in acetonitrile containing 0.1 M tetrabutylammonium perchlorate.

Desired buffer solutions were prepared from appropriate combinations of KH₂PO₄ and NaOH in water. Solutions of extreme acidity (*H*₀ = +1 to –8, *H*₀ is the Hammett acidity parameter)¹⁴ were prepared by diluting concentrated H₂SO₄.¹⁵

Results and Discussion

Transient absorbance signals (464 nm probe; Figure 2) are characterized by an instrument-limited bleach (MLCT excitation and rapid injection) and a biphasic recovery (back ET) whose

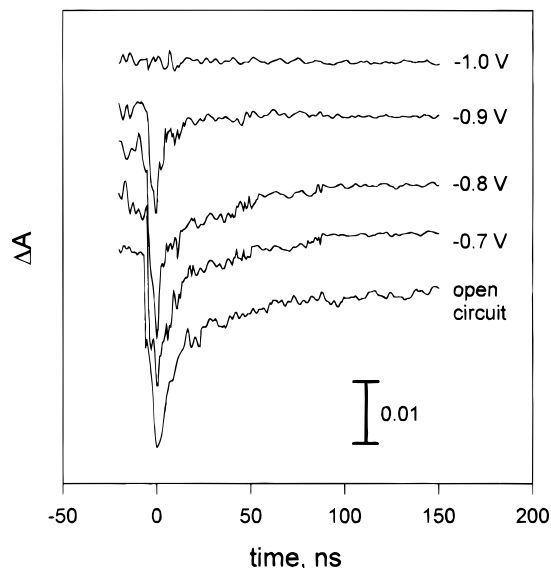


Figure 2. Transient absorbance decay data (464 nm probe wavelength) for RuL₃ on TiO₂ (film on conductive glass) as a function of applied potential. For clarity, curves are offset along the absorbance axis.

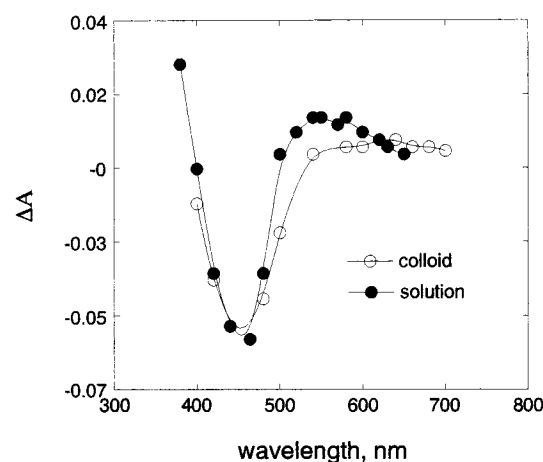


Figure 3. Transient absorbance spectra ($t = 0$) for free RuL₃ (4×10^{-5} M; filled circles; corrected for residual red luminescence) and RuL₃ adsorbed on colloidal TiO₂ (open circles), both in aqueous solutions.

shape is independent of pump power. Consistent with the rapid electron injection interpretation, luminescence from the interface-bound dye is undetectable. (In contrast, the dye in solution (pH $\approx$ 2.5) readily luminesces with a single-exponential decay time of 500 ns.) Additional evidence that interfacial electron transfer has occurred comes from excited-state/ground-state difference spectra (Figure 3).¹⁶ For the dye in solution the pertinent spectral features are the depletion of intensity in the MLCT region (400–500 nm) and the concurrent appearance of a coordinated ligand radical anion absorbance near 550 nm (expected for an MLCT excited state¹⁷). The corresponding spectrum for the dye on TiO₂ also shows the MLCT bleach, indicating transient formation of Ru(III). Lacking, however, is the ligand-based absorption; its absence clearly is consistent with the contention that the electron instead has been injected into the semiconductor.¹⁸

Returning to Figure 2, we find that the decay kinetics can be altered by applying an external potential. As the potential of the photoelectrode approaches the conduction band edge (–0.9 V at pH = 7; see below), the long component of the absorbance decay is lost and a roughly single-exponential decay remains.^{19,20} Changing the applied potential changes the Fermi level and

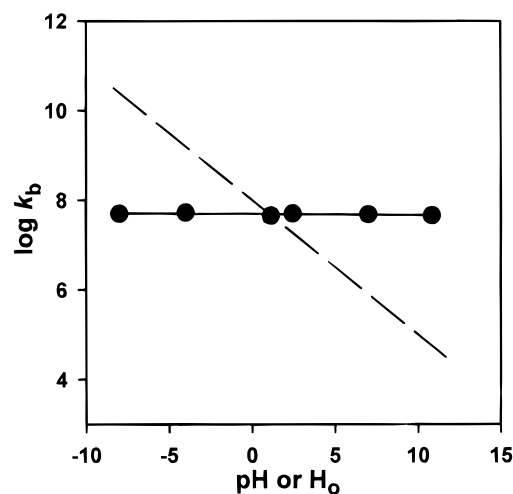


Figure 4. Dependence of back electron transfer rate constant (k_b) on solution pH or H_0 . Rate measurements were made at open circuit.²⁰ Dashed line is a hypothetical illustration (with arbitrary intercept) of anticipated inverted region behavior assuming a factor of 10 change in rate for a 0.2 eV change in conduction band-edge energy.

provides an external means of filling or emptying surface electronic states (where filled states would not be expected to participate in the ET processes). Loss of the long-decay component is interpreted, therefore, as an effect arising from reversible filling of subbandgap states.

Further shifts in potential lead to accumulation layer formation and the appearance of a near-infrared (ground state) absorbance.²¹ The absorbance onset was followed by diode laser reflectance measurements as described elsewhere.^{9,22} From reflectance measurements at several pH's, the flatband potential or conduction band edge (in volts vs SSCE) can be written as

$$E_{CB} = -0.5 - 0.06(\text{pH}) \quad (1)$$

These values are roughly 0.1 V more negative than literature values for unmodified TiO₂,⁶ an effect presumably related to the negative charge introduced on the molecular side of the interface by dye phosphonate groups.

Pump/probe measurements under accumulation conditions (Figure 2, top curve) are characterized by a complete loss of the transient absorbance signal. (Luminescence is also absent (or undetectably fast).) It would appear that injection either is prevented under these conditions or is followed by back electron transfer of such rapidity that no bleaching signal can be detected.²³ In any case, the potential dependent experiments permit a separation between those reactions that clearly involve subbandgap states and those that do not.

With these results in hand, we sought to examine the driving force dependence (pH dependence) of the short component of the back ET reaction.²⁴ Figure 4 illustrates the remarkable result that the first-order rate constant, k_{ET} ($=1/\tau_{\text{short}}$), is invariant over a 19 pH unit range.^{20,25} From eq 1 this corresponds to a greater than 1.1 eV change in the apparent free energy of the semiconductor-bound electron and should have resulted in an enormous variation in k_{ET} (i.e. several orders of magnitude variation based on conventional interfacial electron-transfer theories). We suggest two possibilities. First, back ET might be occurring from "special" surface states that are induced by dye binding and that are somehow decoupled from the energetic effects described by eq 1. The difficulties with this explanation are that (a) the most obvious surface states can be reversibly eliminated electrochemically (Figure 2) without tremendously altering the "fast" decay kinetics ("short" lifetime component) and (b) the chemical basis for elimination of the pH effect upon

the putative surface state energetics remains unelucidated. A second explanation focuses attention back upon the origin of the phenomenon described by eq 1. Recent electrochemical quartz crystal microbalance studies from our laboratory have shown unequivocally that electron accumulation layer formation is accompanied quantitatively by intercalation of charge compensating cations.⁹ If the cation is H^+ , then E_{CB} (effectively the onset potential for accumulation layer formation) unavoidably acquires a Nernstian pH dependence²⁶ and interfacial ET becomes a proton-coupled process. The detailed kinetics, however, could entail stepwise electron and proton transfer. If rate-determining ET preceded the proposed H^+ transfer, then the kinetically relevant driving force would differ from the overall reaction driving force and could conceivably lack a pH dependence.

Regardless of the ultimate explanation, the pH independence shown in Figure 4 raises important questions concerning fundamental interfacial reaction kinetics as well as design criteria for photoelectrochemical cell optimization.^{27,28} We hope to report shortly on additional experiments directed toward both questions.

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- (16) Because of the increased optical density available, the transient spectrum was obtained with a colloidal dispersion of the dye-coated semiconductor, rather than a thin film. The decay kinetics for colloid versus film samples were similar.
- (17) See, for example: Ohno, T.; Nozaki, K.; Ikeda, N.; Haga, M. *Adv. Chem. Ser.* **1991**, 228, 215.
- (18) The injected electron also is expected to absorb in the red portion of the spectrum. The comparatively small extinction coefficient for this species (ca. $600 \text{ M}^{-1} \text{ cm}^{-1}$ at 780 nm (trapped electron))²¹ versus the coordinated radical anion ($\sim 2400 \text{ M}^{-1} \text{ cm}^{-1}$), however, makes the former difficult to detect under the conditions of our experiment.
- (19) As expected, at lower pH the slow component is lost at less positive potentials (e.g., -0.7 V at $\text{pH} = 2.4$).
- (20) The admittedly complex transient signals were idealized via fits to an exponential decay (short component) plus a constant (long component; essentially invariant over first 400 ns). The open-circuit lifetime of the short component was unchanged ($20 \pm 2 \text{ ns}$) over the available pH range but decreased by ca. 50% when the dark assembly was potentiostatted near E_{CB} . Fits to a more complex function (two exponentials plus a constant) also yielded a pH invariant fast component.
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- (22) See also: Redmond, G.; Fitzmaurice, D. *J. Phys. Chem.* **1993**, 176, 493.
- (23) The absence of a transient bleaching signal implies the existence of a very rapid excited-state decay process, in addition to (or as an alternative to) elimination of injection. Although we can only speculate at present, a candidate reaction would be interfacial energy transfer. Interestingly, the analogous carboxylated dye reportedly displays a long-lived luminescence ($\sim 100 \text{ ns}$) when bound to TiO_2 under accumulation conditions (i.e., rapid quenching is absent; see: O'Regan, B.; Moser, J.; Anderson, M.; Grätzel, M. *J. Phys. Chem.* **1990**, 94, 8720).
- (24) Preliminary studies with the the prototypical dye, $\text{Ru}(4,4'\text{-carboxylate-2,2'-bipyridine})_3^{4+}$, were suggestive of behavior similar to that for the phosphonated dye but were complicated by desorption at extreme pH's.
- (25) A reviewer has pointed out that Degussa P25, while predominantly comprised of anatase, also contains rutile. Because the two differ slightly with respect to band-edge energetics, we also examined reactivity on a purely anatase electrode prepared from a colloidal dispersion that had been generated by hydrolyzing titanium isopropoxide. For the phosphonated dye on the pure anatase surface, we obtained open-circuit results similar to those shown in Figure 2, except that τ_{short} was ca. 45 ns. Consistent with results shown in Figure 4, the decay time proved to be pH independent over the range from 2 (the lowest pH examined) to 10 (the highest pH examined).
- (26) For alternative explanations of pH/E_{CB} correlations for TiO_2 see: Finklea, H., *Semiconductor Electrodes*; Elsevier, New York, 1988, Chapter 2.
- (27) At the suggestion of a reviewer, we also examined ET kinetics in the absence of solvent. (No attempt was made, however, to remove chemisorbed water.) Results similar to those shown in Figure 2 were obtained.
- (28) A reviewer has drawn our attention to a report by Sonntag and Spittler (*J. Phys. Chem.* **1985**, 89, 1453) which shows that dye-sensitized photovoltaic reactivity for single-crystal SrTiO_3 can be turned on and off via pH changes. In view of the present findings, transient studies of this system could be very informative.

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