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

Susan G. Yan and Joseph T. Hupp*

Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60208

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Hexaphosphonation of Ru(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($\times 10^7$ s$^{-1}$) that is invariant between pH 11 and pH 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. 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. 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 ($\tau \approx 100$ 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.

The prevailing wisdom suggests that back ET is uniquely (or nearly uniquely) slow in TiO$_2$/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 ($\sim -0.7$ V at pH = 3) and the formal reduction potential of the oxidized dye (ca. +1.3 V for Ru$^{III}$/L$_3$). 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). Using this strategy, we have examined back ET to a highly adherent
Experimental Section

Preparation of TiO2 Sols and Films. Colloidal TiO2 sols were prepared by published methods. High-surface-area films were prepared via the following modification of the method of Nazeeruddin et al.: 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. Reflectance spectroelectrochemistry was carried out by using a PAR 273 potentiostat in conjunction with a 786 nm diode laser (Diolite). 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(OCH2CH2)2)2-2,2’-bipyridine (=L, 1) was prepared by refluxing 4-bromomethyl-2,2’-bipyridine10 in freshly distilled triethylphosphate (Aldrich) for 4–6 h. The solvent was removed by distillation. The dark product 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 phosphate 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 calc. (found) for [RuL3](PF6)2, m/e 1616 (parent compound – PF6), 1415 (–2(PF6), –2(C2H4)), 1359 (–2(PF6), –4(C2H4)), 1335 (–4(PF6), –10(C2H4)), 1279 (–PF6, –12(C2H4)), 1247 (–2(PF6), –8(C2H4)). 1H NMR (D2O) δ 1.3 (H1, t, J = 10.6 Hz, 3H), 4.1 (H2, q, J = 8.8 Hz, 2H), 3.5 (H3, 2s, 12H), 8.2 (H5, s, 6H), 8.7 (H6, s, 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 λmax = 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 (H0 = +1 to −8, H0 is the Hammett acidity parameter) were prepared by diluting concentrated H2SO4.

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
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 ≈ 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). 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 state). 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 absorbance; its absence clearly is consistent with the contention that the electron instead has been injected into the semiconductor.

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. Changing the applied potential changes the Fermi level and 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. The absorbance onset was followed by diode laser reflectance measurements as described elsewhere. From reflectance measurements at several pH’s, the flatband potential or conduction band edge (in volts vs SSCE) can be written as

$$E_{CB} = -0.5 - 0.06(pH)$$

These values are roughly 0.1 V more negative than literature values for unmodified TiO₂, 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. 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. Figure 4 illustrates the remarkable result that the first-order rate constant, $k_{ET}$, is invariant over a 19 pH unit range. 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 ECB (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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References and Notes

(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.
(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 M⁻¹ cm⁻¹ at 780 nm (trapped electron))²¹ versus the coordinated radical anion (~2400 M⁻¹ 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 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 ± 2 ns) over the available pH range but decreased by ca. 50% when the dark assembly was potentiostatted near ECB. Fits to a more complex function (two exponentials plus a constant) also yielded a pH invariant fast component.
(22) See also: Redmond, G.; Fitzmaurice, D. J. Phys. Chem. 1993, 97, 4931.
(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 (~100 ns) when bound to TiO₂ 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 prototypical dye, Ru(4,4’-carboxylate-2,2’-bipyridine)²⁻, 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 but were complicated by desorption at extreme pH’s. 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 but were complicated by desorption at extreme pH’s.
(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 Spitzer (J. Phys. Chem. 1985, 89, 1453) which shows that dye-sensitized photovoltaic reactivity for single-crystal SrTiO₃ can be turned on and off via pH changes. In view of the present findings, transient studies of this system could be very informative.