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pH-Dependent Redox Potential Induced in a Sensitizing Dye by Adsorption onto TiO₂

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The oxidation potential of a ruthenium(II)–polypyridine sensitizing dye is independent of pH when the dye is dissolved in solution. However, when the dye is adsorbed onto nanocrystalline TiO₂, its oxidation potential becomes pH-dependent, decreasing 53 mV per unit pH. This is approximately the same pH-dependence as followed by the flatband potential of the TiO₂. Therefore, the driving forces for both forward and back electron transfer reactions are practically independent of pH. This may explain the pH-independent rate of back electron transfer recently observed by Yan and Hupp (*J. Phys. Chem.* **1996**, *100*, 6867). To our knowledge, the induction of a pH-dependent redox potential upon adsorption of an otherwise pH-independent dye has not been previously reported.

Introduction

The photosensitization of high band gap semiconductor electrodes by adsorbed sensitizing dyes has been studied for a number of years.^{1–3} However, the solar energy conversion efficiency of the original systems was limited by the small amount of light absorbed by a monolayer of dye. With the advent of high-surface-area (or nanocrystalline) TiO₂ electrodes by Grätzel et al.,^{4–6} this limitation was overcome and the conversion efficiencies became high enough to elicit general interest in this type of solar cell. A number of recent studies have appeared concerning the sensitization of nanocrystalline TiO₂,^{7–11} the sensitization of other high-surface-area semiconductors such as SnO₂,^{12,13} and ZnO,^{13,14} and several solid state versions of dye-sensitized cells.^{15–17}

Despite the high level of activity, a comprehensive fundamental understanding is lacking and unexpected results are still being encountered. One such result was recently reported by Yan and Hupp¹⁸ who measured the rate of recombination between the electron in the TiO₂ and the oxidized dye as a function of pH. Since the conduction band potential of the TiO₂ is known to have a Nernstian dependence on pH,^{18–20} while the potentials of the usual family of ruthenium-based sensitizing dyes show little or no pH dependence in solution, it was assumed that varying the pH would vary the driving force for the recombination reaction. Surprisingly, the rate of the electron transfer reaction was independent of pH over a range where it was expected to change by many orders of magnitude.¹⁸

We report here measurements on a similar dye and show that, although its oxidation potential is independent of pH when the dye is dissolved in solution, its potential becomes pH-dependent when it is adsorbed on the TiO₂. Thus, the difference in potential between an electron in the TiO₂ and the oxidized dye is approximately independent of pH. This may explain the lack of pH-dependence of the recombination rate observed by Yan and Hupp. Such a change in pH-dependent behavior of a sensitizing dye upon adsorption has not been previously reported to our knowledge. Indeed, Sonntag and Spitler²¹ showed that a weakly adsorbed carbocyanine-type sensitizing dye exhibited a clear pH threshold for electron injection into single crystal SrTiO₃. In this case, the potential of the dye did not become pH-dependent upon adsorption. The different behavior of the carbocyanine dye and the ruthenium-based dye may be related

to the differences in binding energy and/or electronic coupling between the dye and the semiconductor in the two systems.

Experimental Section

TiO₂ Colloid. A volume of 37 mL of titanium(IV) isopropoxide (Aldrich, 99.9%) in 10 mL of 2-propanol was slowly dripped over 30 min into a stirred mixture of 80 mL of glacial acetic acid and 250 mL of deionized water at 0 °C. The resulting solution was heated to 80 °C for 8 h. It was then heated to 230 °C for 12 h in a titanium autoclave (Parr). Upon removal from the autoclave, the solution was sonicated for 5 min with a cell disrupter with an approximate power of 250 W. The solution was then concentrated to 150 g/L. A 4 g sample of Carbowax was added and it was stirred overnight.

Electrodes. Conductive glass substrates (Libby Owens Ford, 10 Ω/square SnO₂) were cleaned by overnight immersion in a solution of KOH in 2-propanol, rinsed with deionized water, and dried in a nitrogen stream. The TiO₂ colloid was spread over the substrate with a glass rod using adhesive tape as spacers. The films were fired at 450 °C for 45 min in air, resulting in an almost transparent 5 μm thick film. The dye was adsorbed by immersing the electrodes overnight in an aqueous 0.5 mM solution of the dye at pH 2.5.

Dye. The dye Ru^{II}LL'CN (shown in the inset of Figure 1), where L = 4'-phosphonic acid-2,2':6'2''-terpyridine and L' = 1,2-bis(4'-methyl-2,2'-bipyridyl-4-yl)ethane, was available from experiments related to the photo-oxidation of water that will be reported separately. The pendant bipyridine group of the L' ligand has no effect on the present experiments; identical results were obtained when it was coordinated to RuO₂. The dye was synthesized by a modification of literature methods that will be reported in detail later. The purity of the final complex was confirmed by ¹H NMR and cyclic voltammetry.

Electrochemical measurements were performed with a PAR 173 potentiostat in a three-electrode arrangement. Potentials are reported vs SCE. Absorption spectra were measured with a HP 8452 spectrophotometer using an undyed nanocrystalline TiO₂ electrode as a reference.

The oxidation experiments were carried out as follows. A series of identical dye-coated TiO₂ films were prepared. The absorption spectrum of a film was measured before oxidation. Then the film was immersed in a 20 mM aqueous solution of Br₂ at the specified pH for 15 min. The film was removed, rinsed with water, and dried in a nitrogen stream. A second

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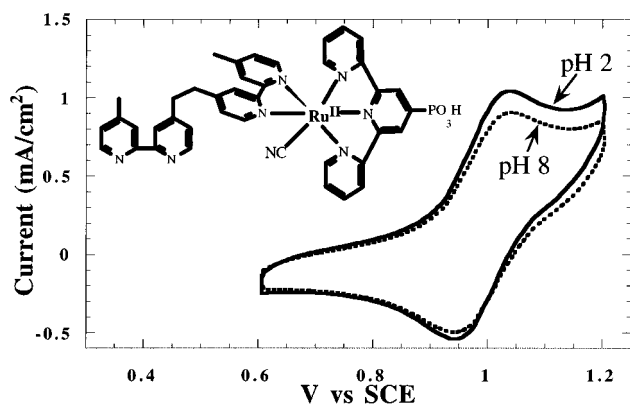
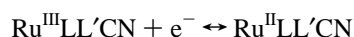


Figure 1. Cyclic voltammograms at a glassy carbon electrode of 1 mM Ru^{III}LL'CN in water at pH 2 and pH 8. The scan rate was 50 mV/s. The structure of the dye is shown in the inset.

absorption spectrum was measured. Then the film was reduced with triethylamine and its spectrum measured a final time. This procedure was repeated with a fresh film for each data point over the range pH 2.5–8. The amount of Br₂ in the solution was 10⁴ times higher than the amount of dye on the film, so the change in potential of the Br₂ solution resulting from oxidation of the dye was negligible. The potential of the Br₂ solution was 1.02 ± 0.02 V vs SCE, independent of the pH in the range of these experiments. A stock solution of Br₂/HClO₄ was made at pH 2.5; the pH was adjusted by addition of NaOH, and the solutions were used immediately to avoid changes in potential resulting from the slow oxidation of water by Br₂ at higher pH. The ionic strength was approximately 10 mM throughout the pH range. The concentration of Br⁻ produced from Br₂ by oxidation of the dye was never greater than 0.3% of the ClO₄⁻ concentration. Therefore, changes in electrolyte composition near the interface resulting from the electrostatic charge on the TiO₂ surface did not significantly change the ratio Br⁻/Br₂ at the interface. Furthermore, experiments at pH 6.9 showed no change in the fraction of oxidized dye with increasing ionic strength up to 200 mM.

Results and Discussion

Cyclic voltammograms of the dye in solution at pH 2 and pH 8 are shown in Figure 1. The electron transfer process



is kinetically facile, and the dye is chemically stable in both oxidation states. The formal potential in solution, $E^{\circ} = 0.99$ V vs SCE, is independent of pH over the range of our experiments.

Once adsorbed to the nanocrystalline TiO₂ film, the dye remained strongly bound in aqueous solutions below pH 8.5. Above this value it desorbed. Thus, our experimental window was limited to values less than pH 8. The absorption spectra of the dye-sensitized films at different degrees of oxidation are shown in Figure 2. Curve a in Figure 2 shows the spectrum of the dye-sensitized film before oxidation. Curve b shows the absorbance of the film after immersion in aqueous Br₂ solution at pH 7.7 for 15 min. By comparison with the original spectrum (curve a) and with the spectrum of the fully oxidized dye (curve d), it is apparent that the dye was approximately half oxidized at pH 7.7. Exposure of the partially oxidized film to triethylamine results in the rereduction of the dye (curve c). The spectrum after rereduction was almost the same as the original spectrum, showing that the dye neither desorbed nor decomposed during the experiment. The film could not be completely

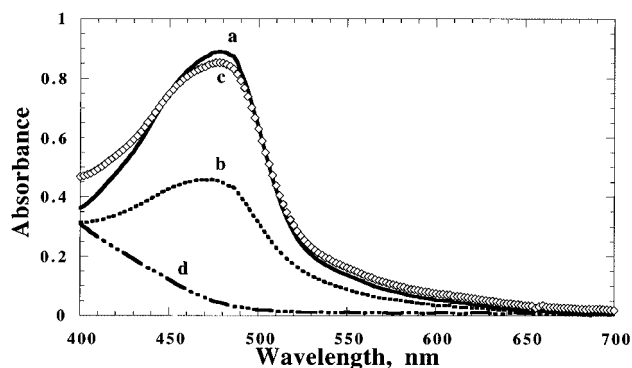


Figure 2. Typical absorption spectra of the adsorbed dye: (a) initial spectrum before oxidation; (b) after partial oxidation with aqueous bromine at pH 7.7; (c) after rereduction of the dye with triethylamine; (d) after complete oxidation with Ce^{IV} at pH 0.

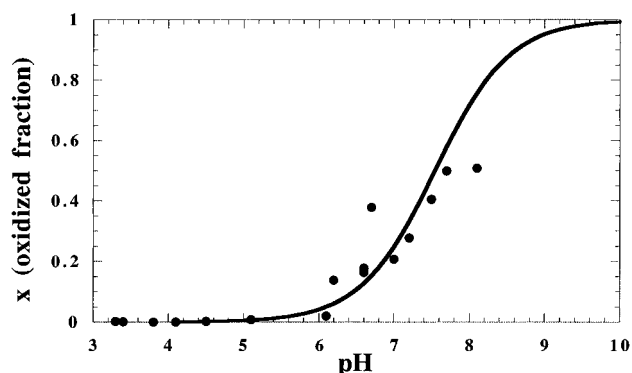


Figure 3. Fraction of oxidized dye, x , as a function of the pH of the bromine solution. The line is the fit to eq 2.

oxidized by Br₂ solution in the available pH range. Therefore, the spectrum of the completely oxidized dye (curve d) was obtained by immersing the film in a solution containing a large excess of Ce(IV) at pH 0.

The fraction, x , of the dye oxidized by the Br₂ solution at each pH was calculated from the absorption spectra according to

$$x = \frac{A_{\text{red}}^{\circ} - A'}{A_{\text{red}}^{\circ} - A_{\text{ox}}^{\circ}} \quad (1)$$

where A_{red}° and A_{ox}° are the absorbances at the monitored wavelength of the fully reduced and fully oxidized species, respectively, and A' is the absorbance of the partially oxidized film. The results shown in Figure 3 were calculated from the absorbances at 480 nm. The calculated values of x varied by less than 5% if other wavelengths were used.

The fraction of oxidized dye as a function of pH is shown in Figure 3. As the pH increases, an ever greater fraction of the dye becomes oxidized. To express the pH dependence of the dye's oxidation potential, we write the Nernst equation as

$$E = E^{\circ}_{(\text{pH}=0)} - Z \text{pH} + \frac{RT}{nF} \ln\left(\frac{x}{1-x}\right) \quad (2)$$

where $E^{\circ}_{(\text{pH}=0)}$ is the formal potential of the adsorbed dye at pH 0, and Z is the change in the dye's potential per unit pH. E is the potential of the Br₂ solution (1.02 ± 0.02 V). The data of Figure 3 were fit to eq 2, leading to values of $E^{\circ}_{(\text{pH}=0)} = 1.42 \pm 0.03$ V and $Z = 53 \pm 5$ mV/unit pH. The oxidation potential of the adsorbed Ru^{III}LL'CN at pH 0 was thus shifted 400 mV positive of its solution value. The value of Z is close to the 59 mV/unit pH expected theoretically for the flatband

potential of an oxide semiconductor.^{18–20} Therefore, in this system there is little or no change in the difference between the TiO₂ flatband potential and the Ru^{II}/Ru^{III} potential of the adsorbed dye over the range from pH 2.5 to pH 8.

We are attempting to extend these results to other dyes. However, we are limited by the potential of the available dyes, the pH window in which the dyes remain adsorbed, and the availability of pH-independent oxidants in the appropriate potential range. Some additional support for the results described above has been obtained with two dyes, *cis*-Ru^{II} (4-phosphonic acid-2,2'-bipyridine)₂CN₂ and Ru^{II} (4-phosphonic acid-2,2':6',2''-terpyridine)₂. Both dyes have oxidation potentials of approximately 1.15 V and can be partially oxidized by Ce^{IV}. Since Ce^{IV} is stable only in strongly acidic solution, we measured the oxidation of the dyes only over a range of 1.5 pH units. Qualitatively, the same trend was observed as for the Ru^{II}LL'CN dye detailed above. The formal potentials of both adsorbed dyes were shifted positively by at least 400 mV at pH 0 compared to their potentials when dissolved in solution.

The induced pH dependence of the oxidation potential in the ruthenium-based sensitizing dyes may explain the recent observation of a pH-independent rate of the recombination reaction between electrons in the TiO₂ and the oxidized dye.¹⁸ It also has implications for the design and optimization of dye-sensitized solar cells, especially those based on aqueous electrolytes. The mechanism of the induced pH dependence is not yet known. It may be related to the strong electronic coupling between the dye and the TiO₂ that is necessary to promote the high quantum efficiencies (>80%) for electron injection observed in these systems.^{4,5} In Sonntag and Spittler's system,²¹ where no pH dependence was induced in the dye, the adsorption was weaker and the quantum efficiency was substantially lower (1–2%). The electric field resulting from ions (H⁺ and OH⁻) adsorbed on the semiconductor surface may also have a greater influence on the potential of a specifically adsorbed dye than on a dye that interacts only weakly with the surface. Further experiments to clarify the mechanism are in progress.

Conclusions

The oxidation potential of Ru^{II}LL'CN becomes pH-dependent when adsorbed on nanocrystalline TiO₂, although it is not pH-dependent when dissolved in solution. The energetics of the electron transfer reactions between the dye and the TiO₂ are therefore approximately independent of pH. This may explain the recent observation of a pH-independent rate of the recom-

bination reaction between electrons in the TiO₂ and the oxidized dye. Attempts to modify the TiO₂ flatband potential to enhance cell performance should take this phenomenon into account.

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