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Time-Resolved Raman Scattering Study of Adsorbed, Semioxidized Eosin Y Formed by Excited-State Electron Transfer into Colloidal TiO_2 Particles

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Abstract: Resonance Raman spectra of adsorbed, semioxidized eosin Y have been obtained following excitation of adsorbed eosin Y on colloidal TiO_2. In order to provide reference spectra for the surface photochemistry, solution photooxidation reactions yielding semioxidized eosin Y (E^+) have also been observed. In both cases, an initial 532-nm pulse excites eosin Y, and a time-delayed 448-nm pulse generates Raman spectra of E^+. The solution-phase E^+ spectra vary strongly with solvent composition in ethanol–water mixtures. The large relative intensity changes observed suggest that the sensitivity to solvent principally reflects changing solvation of the resonant E^+ excited state. The surface-adsorbed E^+ spectra on aqueous colloidal TiO_2 are different than aqueous E^+ spectra. The observed changes suggest a protonated surface species in a less polar local environment.

In this paper we attempt to characterize, using time-resolved Raman scattering, an adsorbed molecular species created by excited-state electron transfer to a colloidal TiO_2 particle. We wish to chemically identify the intermediate species made by this surface reaction and to explore the local environment and possible molecular distortion at those surface "sites" where electron exchange with the solid is kinetically feasible.

Above band gap optical excitation of a semiconductor produces a mobile hole h^+ and electron e^- that may oxidize or reduce a surface chemical species, as schematically shown in Figure 1a. In a recent paper labeled I we studied four examples of such photosensitized redox reactions occurring on the surfaces of TiO_2 and CdS aqueous colloidal particles.[1] The Raman spectra of the initial chemical intermediates showed no evidence of distortion due to prior adsorption of the precursor. In these examples the molecular precursor was itself soluble in the aqueous phase and adsorbed by electrostatic attraction, or was bound to the surface by adsorption of a long hydrophobic hydrocarbon side chain.

We now study the reverse process illustrated schematically in Figure 1b:

$$E_0 + h\nu \rightarrow E^* \rightarrow E^+ + e^-_{CB}(TiO_2) \qquad (1)$$

A photon insufficiently energetic to excite the semiconductor is absorbed by a surface adsorbed dye molecule E_0. The excited molecule E^* injects an electron into the semiconductor, leaving an oxidized species E^+ on the surface. Such sensitized photoinjection has long been pursued in order to extend the wavelength response of semiconductor electrodes in photoelectrochemical cells.[2-4] Our example eosin Y on colloidal TiO_2 at acid pH, has the added feature that the ground electronic-state precursor is not soluble in water and thus should be moderately strongly adsorbed. To our knowledge this is the first study of sensitized photoinjection using time-resolved Raman spectroscopy. Moser and Grätzel,[5] using transient absorption spectroscopy, have established that excited-state e^- transfer does occur in this system.

Through independent homogeneous photochemical oxidation experiments, we find that the resonance Raman spectra of semioxidized eosin Y, which have not previously been reported, are sensitive to solvation and protonation. The spectra are thus a useful probe of the local environment in the surface photochemical process.

Experimental Section

Our apparatus and techniques have been recently described.[6,7] In summary, there are two independent Nd:YAG lasers operating at 10 Hz with pulse widths on the order of 12 ns. The optical pulse from one is adjusted to a precise time delay with respect to that of the other. Pulses of 532 nm are generated as the second harmonic of the Nd:YAG fundamental at 1.064 μm. Pulses of 448 nm are obtained as the second stimulated Raman Stokes shift of the Nd:YAG third harmonic (355 nm) in high-pressure CH_4 gas. We perform a pump-probe experiment, with an initial 532-nm pulse creating the excited state and a delayed 448-nm pulse generating Raman spectra. The spectra are recorded with a triple spectrograph and a Reticon multichannel optical analyzer. The Reticon is gated in time to the 448-nm pulse, so that scattering from the sample is only collected during illumination by this pulse. The solution flows through the optical interaction region so that a fresh solution is illuminated by each pulse pair.

The TiO_2 colloid was prepared by hydrolysis of $TiCl_4$ in the manner described by Moser and Grätzel.[8] The solution pH was raised to pH $\simeq$ 2.5 via dialysis, and then $\simeq$0.07% PVA ($M_r \simeq 10000$, Aldrich No. 18 463-2) was dissolved to prevent colloid coagulation upon further adjustment of pH with NaOH. Colloids of TiO_2 concentration both 0.7 g/L and 1.5 g/L were used with identical results. The data are independent of colloid age and of prior degassing with bubbling Ar. The TiO_2 particles are reported to be polydisperse with an average diameter of 90 Å.[8] At this effective size, the concentration of crystallites is $\simeq 5 \times 10^{-7}$ M. The colloid is perfectly clear (non-scattering) to the eye and shows no color. The above band gap optical absorption of colloidal TiO_2 begins near 350 nm.

Results

(A) Homogeneous Solutions. In order to provide reference spectra for the surface photochemistry we have investigated solution-phase photochemical reactions yielding E^+.

Excited singlet eosin Y in water at neutral pH has a 0.19-ns lifetime controlled by intersystem crossing to the triplet, which has an intense optical absorption near 580 nm.[9-12] The long-lived triplet is quenched by ground-state eosin Y (E_0), with a small fraction of such quenching events yielding semioxidized (E^+) and semireduced (E^-) eosin Y absorbing at 460 and 410 nm, respectively. Kasche and Lindquist[10] showed that E^+ could be obtained in high yield by electron-transfer quenching of the triplet with $Fe(CN)_6{}^{3-}$.

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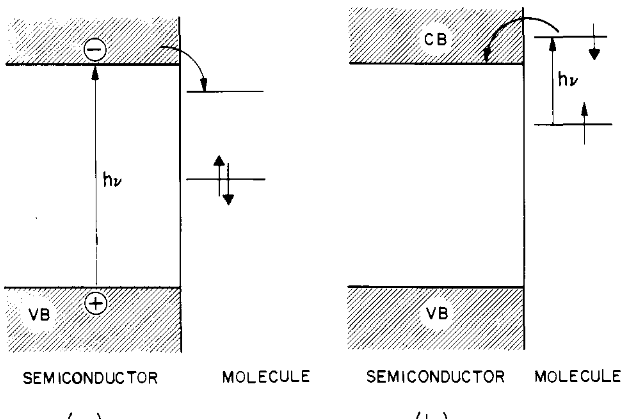

Figure 1. Schematic diagrams of (a) optical excitation of a semiconductor followed by e⁻ transfer to a surface adsorbed molecule and (b) optical excitation of a surface adsorbed molecule followed by e⁻ transfer to the semiconductor conduction band.

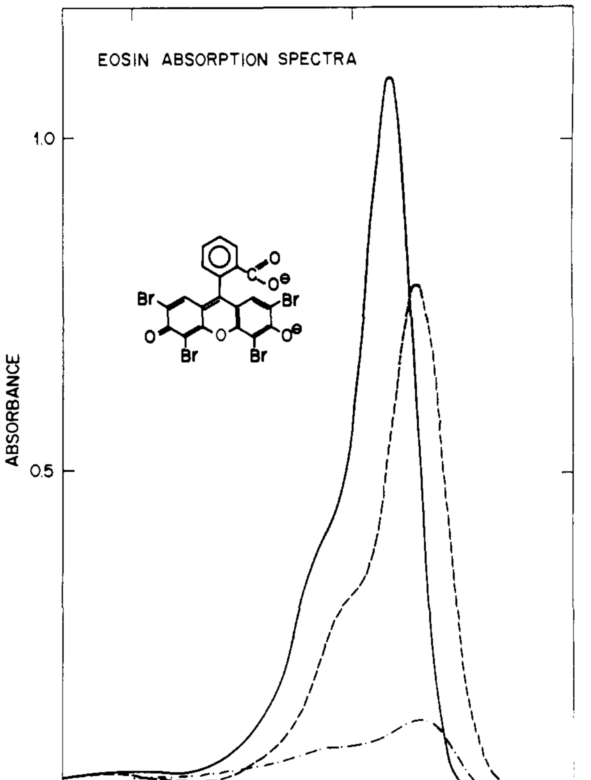

Figure 2. Absorption spectra (2-mm path length) of eosin Y at 6 × 10^{-5} M. Solid line: aqueous solution at pH 5.8. Dashed line: adsorbed on TiO_2 in a colloidal solution at pH 3. Dot-dash line: stabilized by 0.1% PVA in aqueous solution at pH 3 (no TiO_2).

Eosin Y at neutral pH is a dianion with an intense visible absorption of 515 nm as shown in Figure 2.[11] We excite ground-state E_0 at 532 nm and probe for E^+ with a blue shifted pulse at 448 nm. The value of 448 nm is close to the reported absorption maximum of E^+ ($\epsilon_m(460) \simeq 6 \times 10^4$ M^{-1} cm^{-1}),[12] and absorption by E_0 itself is weak here. In general, we depend upon the Raman cross-section enhancement which occurs in resonance with an electronic transition in order to experimentally detect a transient species at very low concentration.

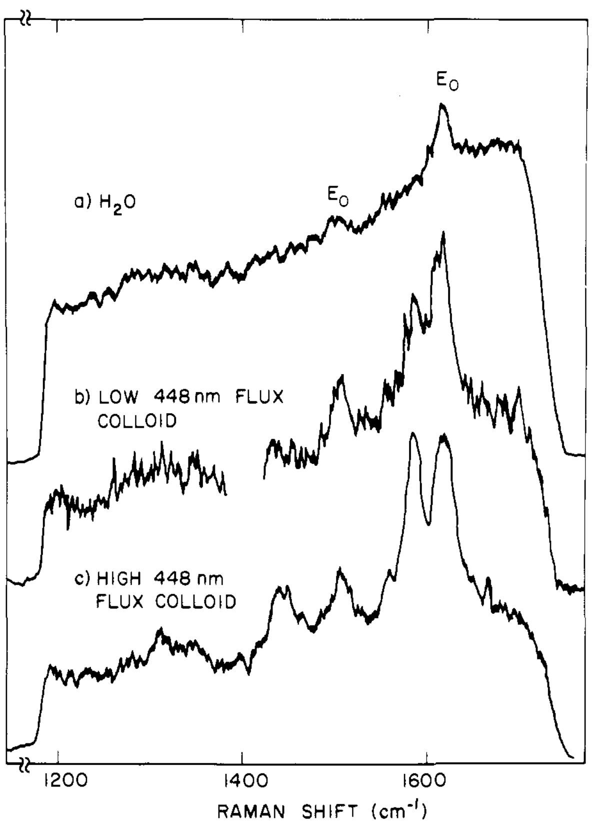

Figure 3. Single pulse Raman spectra at 448 nm: (a) 2 × 10^{-4} eosin Y in water at pH 6 (b) 5 × 10^{-6} M eosin Y adsorbed on TiO_2 at pH 3; 448-nm fluence ≃0.3 mJ/pulse; (c) as in (b) with 448-nm fluence =1 mJ/pulse. The two colloidal spectra contain lines from both ground-state and semioxidied eosin Y, as discussed in the text.

Table I. Raman Spectra[a]

E_0, H_2O	E_0, TiO_2	E^+, H_2O	E^+, ethanol	E^+, TiO_2
1625 (3)	1623 (3)	1618 (10)	1619 (2)	1619 ± 4 (2–3)
		1591 (10)	1593 (10)	1590 (10)
1515 ± 4 (1)	1515 (1)			
		1456[b] (6)	1456[b] (3)	≃1450[b] (3)
		1446[b] (6)	1446[b] (3)	
		1322 (3)	~1315 (1)	1320 ± 4 (1)
		1289 (15)	~1287 (0.5)	

[a] In cm^{-1}. Estimated relative intensities in parentheses. Accuracy is ±2 cm^{-1} unless otherwise noted for very weak lines. [b] Indicates two overlapping lines.

In Figure 3a we show the 448-nm Raman spectrum of a 2 × 10^{-4} M E_0 aqueous solution (pH 6) taken *without* a prior 532-nm pulse. Two weak E_0 lines at 1624 and 1515 cm^{-1} are observed on top of moderately strong continuous luminescence that results from (weak) excitation of E_0 itself at 448 nm. As seen in the figure, noise associated with this luminescence[13] limits our Raman detection sensitivity for E_0 (and possible transient species) under these conditions.

If this solution undergoes prior excitation at 532 nm, the spectrum is unchanged.[14] However, if $K_3Fe(CN)_6$ is added, new Raman lines develop identical with those shown in Figure 4a. At 10^{-2} M $K_3Fe(CN)_6$ these lines have reached their maximum intensity at a time delay of 50 ns, and are an order of magnitude more intense than E_0 Raman lines. This new spectrum shows no change in shape or decay in intensity for delays out to several

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(13) This luminescence, in the 480-nm region, is blue shifted from the vibrationally relaxed dye fluorescence near 530 nm. We apparently observe "hot luminescence" emitted during relaxation of the dye.

(14) Excitation at 532 nm creates triplet eosin Y via intersystem crossing from the short-lived singlet. The triplet, with a transient absorption peaking at 580 nm, must have a low Raman cross section at 448 nm.

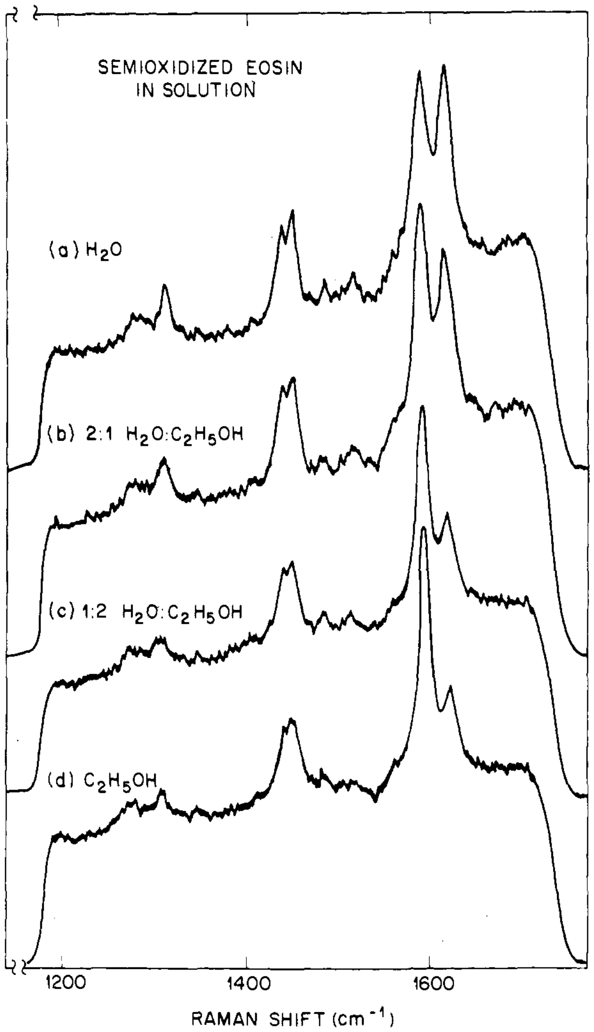

Figure 4. Time-resolved Raman spectra of solution-phase semioxidized eosin Y as a function of solvent at neutral pH. In each case the solution contains 2×10^{-4} M eosin Y and 10^{-2} M *p*-benzoquinone. Excitation at 532 nm (4 mJ/pulse) is followed 50 ns later by a Raman generating probe pulse at 448 nm ($\simeq$0.3 mJ/pulse).

microseconds, and is independent of pH in the range 5–11. The signal is saturated with respect to 532-nm fluence above $\simeq$1 mJ/pulse; at these flux levels every eosin Y is excited during the 532-nm pulse. We observe exactly the same behavior at pH 6 if *p*-benzoquinone, also a good electron acceptor with $E_0[BQ/BQ^-]$ = +0.1 V vs. NHE,[15] is added instead of $K_3Fe(CN)_6$.

In view of these observations and the previous transient absorption experiments, we assign this spectrum to semioxidized eosin Y E^+. The detected Raman transitions are listed in Table I; we searched the region 700–1800 cm^{-1}. As is typical for a π–π^* resonance on an aromatic system, there are strong transitions in the regions of the C—C, C=C, and C=O characteristic frequencies.

This 448-nm E^+ resonance Raman spectrum shows a strong dependence on solvent. As shown in Figure 4 and Table I, there are major changes in relative intensities. For example, the ratio *R* of the intensities of the two strong lines at 1590 and 1618 cm^{-1} changes radically in ethanol–water mixtures. In water at neutral and basic pH $R = 1$, and in ethanol $R \simeq 0.2$. Changes in frequencies are very small, with the exception of a minor band at 1322 cm^{-1} that shifts about 7 cm^{-1} to lower frequency in ethanol. Similar relative intensity variations are observed in mixed acetone–water solvents.

In water the highest pK_a value, corresponding to protonation of the carboxylic group, is 4.47.[11] This pK_a shifts to higher values

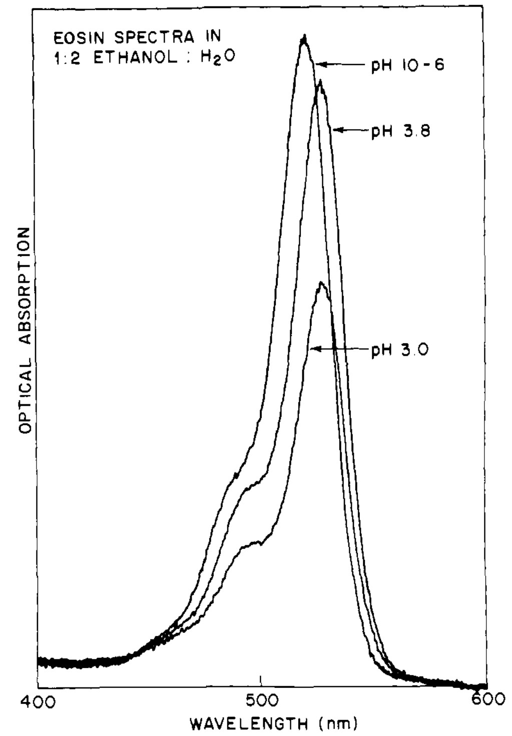

Figure 5. Absorption spectra of 10^{-4} M eosin Y in 1:2 ethanol:water at the indicated pH values.

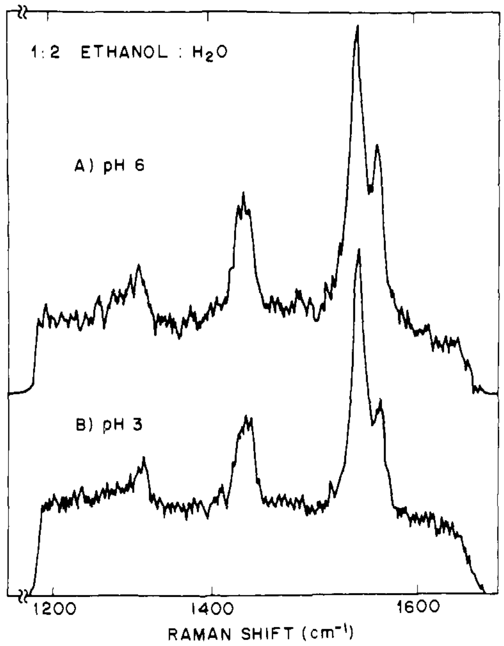

Figure 6. Time-resolved Raman spectra of semioxidized eosin Y as a function of pH in 1:2 ethanol:water.

in aqueous mixtures and in alcohols. The four solutions in Figure 4 are sufficiently basic that eosin Y is present as the dianion in each case, as determined by electronic absorption spectra.

If aqueous eosin Y is acidified, precipitation occurs.[9] The dianion is protonated,[11] and the singly charged organic anion is apparently not soluble in water. We observe that 10^{-4} M eosin Y in 1:2 ethanol:water does not precipitate when acidified. The optical spectrum is constant in the pH range 6–10; it changes below pH $\simeq$4, as expected for carboxylic protonation,[11] as shown in Figure 5. Thus, protonated eosin Y at pH 3 is soluble in 1:2 ethanol:water. If 10^{-2} M $K_3Fe(CN)_6$ is added and the 532–448-nm photooxidation experiment is performed, the E^+ resonance Raman spectrum in Figure 6B is observed. This spectrum is different than the previously discussed pH 6 spectrum in Figures

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4 and 6A. The ratio *R* drops from ≃0.55 at pH 6 to ≃0.3 at pH 3; *R* is independent of delay time at both pH values. A large change in the Raman spectrum is not observed as the xanthene chromophore itself is not protonated. We conclude that at pH 3 we observe the Raman spectrum of protonated semioxidized E^+, and that E^+ remains protonated on a microsecond time scale at pH 3.

Protonated semioxidized eosin Y has a net charge of zero and should be less strongly solvated than E^+ at pH 6. It is perhaps not surprising then that the Raman spectra shift in the same manner as for E^+ in less polar solvents (i.e., pure ethanol).

Resonance Raman spectra combine aspects of both electronic absorption spectra and ordinary Raman spectra. The Raman shifts are the vibrational frequencies of the ground electronic state, as in ordinary Raman spectroscopy. However, the selection and relative intensity of modes in the spectra are determined by the resonant excited electronic state. In our present case, we see a relative intensity change without a frequency shift in the strongest lines. This result indicates that the resonance process is varying with solvation and protonation.

The fact that the E^+ resonance Raman spectrum is especially sensitive to environment and protonation suggests that eosin Y may be a useful probe when adsorbed on the TiO_2 surface.

(B) Eosin Y on Colloidal TiO_2. As previously described, if neutral aqueous eosin Y is acidified (HCl) to pH ≃3.5, precipitation occurs.[9] If 6×10^{-5} M eosin Y is dissolved in pH 6 PVA stabilized TiO_2 colloid, essentially the same electronic spectrum is observed as in pure water. Eosin Y resides principally in the aqueous phase. If this solution is acidified to pH 3, the eosin Y spectrum red shifts (Figure 2) without precipitation. In principle, the eosin Y is either adsorbed on the PVA stabilized TiO_2 particles or complexed with PVA at some distance from TiO_2 particles.

Eosin Y (6×10^{-5} M) in a 0.1% PVA aqueous solution (i.e., without TiO_2) can also be acidified to pH 3 without precipitation. However, this acidic spectrum (Figure 2) is markedly different than the corresponding acidic spectrum in TiO_2 colloidal solution. We conclude that, in the colloid, the eosin Y is actually adsorbed on the TiO_2 surface, perhaps with nearby PVA. If it were simply complexed to PVA, at some distance from the TiO_2 these two absorption spectra should have been the same.

The absorption spectrum change which accompanies adsorption on TiO_2 at pH 3 in Figure 2 is very similar to the spectral change accompanying protonation in 1:2 ethanol:water in Figure 6. This observation is circumstantial, yet not conclusive, evidence that eosin Y is protonated on the TiO_2 surface.[16]

In Figure 3, the 448-nm Raman spectrum, *without* prior 532-nm excitation, of surface adsorbed eosin Y is observed to change as a function of 448-nm fluence. At the lowest fluence (≃0.2 mJ/pulse) at which we can record Raman spectra, two lines at 1624 and 1515 cm^{-1} (previously assigned to E_0) are observed. At a factor of ≃5 higher fluence, three additional lines (1590, 1447, and 1318 cm^{-1}) previously assigned to E^+ grow in intensity relative to the E_0 lines.[17] The intial E_0 line at 1624 cm^{-1} also broadens and shifts 2–3 cm^{-1} to lower frequency.

As 448-nm light is (weakly) absorbed by eosin Y, a 448-nm pulse can both photolyze E_0 to E^+ and generate E^+ Raman spectra. This sequence requires two 448-nm photons, and thus the E^+ spectra will grow in relative intensity at higher fluences (assuming that the photolysis step does not saturate).

In colloidal experiments involving time sequenced 532- and 448-nm pulses, we keep the 448-nm fluence at 0.2 mJ/pulse in order to minimize photochemistry generated by this pulse. Raman spectra generated by this pulse can thus provide a true record of the time evolution of transients created by a prior, more intense 532-nm pulse.

One further aspect of Figure 3 deserves mention. The intensity ratio of E_0 Raman spectra to underlying continuous luminescence is lower for adsorbed eosin Y than for dissolved eosin Y dianion at pH 6. This implies that eosin Y luminescence has been partially quenched on the TiO_2 surface.

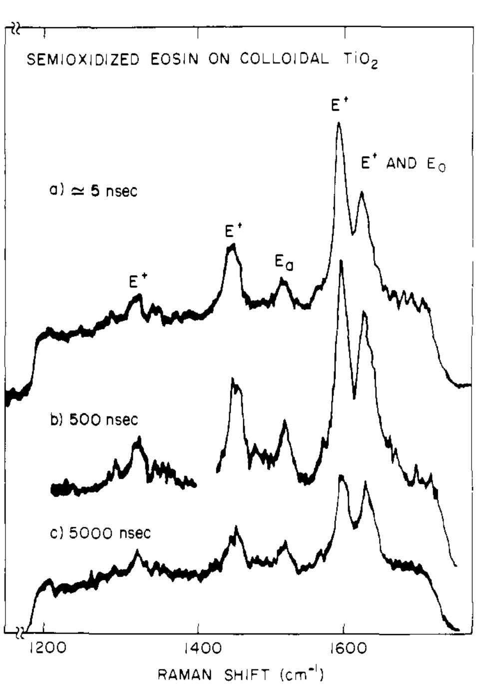

Figure 7. Time-resolved Raman spectra of surface adsorbed semioxidized eosin Y as a function of delay time. Excitation at 532 nm (≃4 mJ/pulse) followed by Raman probe pulse at 448 nm (≃0.3 mJ/pulse).

Figure 7 shows the Raman spectra observed in two-pulse (532 and 448 nm) experiments as a function of time delay. These spectra can be interpreted as a superposition of E^+ and E_0 spectra. The E^+ signal is created by the 532-nm pulse, appears without measurable rise time (≤5 ns), and decays on a microsecond time scale.

A comparison of 448-nm spectra with and without a prior 532-nm pulse shows that the absolute magnitude of the E_0 contribution to the spectra is essentially unchanged. Thus, the prior 532-nm pulse, which creates E^+, actually converts a negligible fraction of E_0 to E^+ under our conditions. The intensity of the E^+ signal as a function of 532-nm fluence saturates at about ≃0.5–1.0 mJ/pulse. Because of the very large eosin Y absorption cross section, all ground-state molecules are excited at these fluence levels. A smaller fraction are converted to E^+ than in the previously described homogeneous solution oxidation processes, as judged by a comparison of E^+ and E_0 intensities.

The absolute magnitude of the Raman signals in Figure 7 are extremely weak. These spectra are an average of 6000 pulse pairs; on the strongest E^+ peak at 1590 cm^{-1} the Reticon count rate is 0.15 counts/(pulse·channel). The modest signal-to-noise ratio achieved limits our ability to detect possible subtle line-shape modifications in the E^+ spectra.

Nevertheless $R = I(1590)/I(1615)$ is clearly not 1, as observed for oxidation of the aqueous dianion at pH 6 (Figure 3a). In Figure 7 the apparent ratio *R* appears to change with time. We believe this occurs because the peak at 1590 cm^{-1} is entirely E^+, while the peak in the neighborhood of 1615 cm^{-1} is a superposition of both E^+ and E_0 peaks. A direct subtraction of a 448-nm E_0 spectrum from Figure 3a yields a E^+ spectrum with a small peak at 1619 cm^{-1}, with $R \simeq 0.25$. This spectrum is close in shape to the E^+ spectrum in pure ethanol (Figure 4d) and to the protonated E^+ spectrum at pH 3 in 1:2 ethanol:water (Figure 6B). There is no evidence, at our present modest signal-to-noise ratio, that the E^+ spectrum itself changes shape as it decays in time.

The e^{-1} decay time is about 2–4 μs. In Figure 7, at a delay of 5 μs, about two-thirds of the observed E^+ is created by the 532-nm pulse and perhaps one-third by direct 448-nm photolysis, as in Figure 3b. The signal-to-noise ratio is not adequate to follow E^+ kinetics on longer time scales.

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(16) The TiO_2 surface has a net positive charge at pH 3, and the eosin Y pK_a should be lower on the surface than in aqueous solution.

(17) Although the signal to noise in Figure 3 is not high, this difference between low-fluence and high-fluence spectra was systematically observed in repeated experiments.

Experiments with a 461-nm probe wavelength show very similar kinetics and spectra to those reported here at 448 nm. Experiments with a 395-nm probe pulse yielded no detectable transients. The results are consistent with the reported transient absorption of E^+, which peaks at 460 nm.

Discussion

At 5×10^{-5} M adsorbed E_0 we calculate that there is a substantial fraction of a monolayer coverage on the TiO_2 particles. There are $\simeq 100$ E_0 per particle assuming an average diameter of $\simeq 90$ Å. We excite every E_0 with the 532-nm pulses and find a low net quantum yield of charge injection into TiO_2.

A theoretical model of Gerischer and colleagues[18] predicts that the quantum yield of excited-state e^- transfer should be near unity under typical conditions. These authors call attention to the importance of sequential reverse e^- transfer in lowering apparent quantum yields. On small colloidal particles reverse transfer should be an important effect. If a substantial number of e^- were injected into a small TiO_2 particle, the electron–electron repulsion and the quantum localization energies would create a high redox potential for reverse transfer.[19] It may be that each TiO_2 particle is able to sustain (on a 10^{-9}-s and longer time scale) only a few surface E^+ molecules.

The 448-nm TiO_2 adsorbed E^+ spectrum is clearly distinguishable from the unprotonated E^+ spectrum in pure water. The surface spectrum is very similar to the protonated E^+ spectrum in the less polar solvent mixture 1:2 ethanol:water and to the unprotonated E^+ spectrum in pure ethanol. It is likely that the surface species we observe is protonated and that the effective environment is less polar than pure water. The surface E^+ spectrum does not evolve in shape, at our present level of signal to noise, as it decays on a 10^{-6}-s time scale. This result implies that this species remains adsorbed on the surface and decays by relatively slow back transfer of the e^- from TiO_2.

We do not observe significant E^+ Raman frequency shifts, as observed in SERS spectra of molecules on metal surfaces,[20] for example. The limited available Raman data in this manuscript and in I show no static distortion of ground-state E^+. As previously discussed, the change in R ratio implies a change in the excited-state resonance at 448 nm on the surface and in the mixed solvents. We conjecture that this change might be simply a shift in the E^+ excited-state energy with respect to the 448-nm laser frequency. The absorption spectra and excited-state photophysics of xanthene dyes are known to be especially sensitive to solvation.[21-23]

Chandrasekaran and Thomas[24] have recently observed that several aromatic hydrocarbons adsorbed on aqueous TiO_2 powder suspensions have significantly perturbed electronic absorption and emission spectra and excited-state lifetimes. Adsorbed pyrene shows no excimer emission, and there appears to be no surface mobility on the time scale of the excited-state lifetime. These observations indicate significant adsorption effects on excited states for the hydrophobic species investigated.

An interesting experiment of Gerischer and colleagues[25] bears on the question of the influence of the solvent on such adsorbed molecules. The similar xanthene dye rose bengal was adsorbed on a ZnO single-crystal electrode in a photoelectrochemical cell. The photocurrent action spectra were observed as a function of solvent composition and protonation in mixed water–ethanol solvents. The spectra changed with increasing ethanol component in much the same fashion as the dye absorption spectra did in homogeneous solution. Thus, adsorbed rose bengal under Gerischer's conditions remains sensitive to solvent composition.

In the present experiment, and in I, we observe adsorbed redox reaction products in "sites" where the molecular precursor was coupled to the surface sufficiently strongly to exchange electrons, as in Figure 1. The Raman spectra of semioxidized eosin Y are especially sensitive to varying solvation, and we have seen that the surface Raman spectra at pH 3 suggest a protonated species in a less polar environment than pure water. This is not an unreasonable result, and it is important to note that we have not observed a "unique" surface distortion that might suggest "specific" adsorption (chemisorption). In I, the redox reaction products had Raman spectra indistinguishable from the same species in pure water. These limited results appear consistent with electron exchange with the solid without loss of the molecular solvation shell in these cases where there presumably is a favorable alignment of the electronic energy levels.

Conclusions

The time-resolved 448-nm resonance Raman spectra of solution-phase semioxidized eosin Y E^+ have been observed following quenching of excited-state eosin Y by $Fe(CN)_6^{3-}$ or *p*-benzoquinone. The spectra are a strong function of solvent composition in ethanol–water mixtures.

E^+ adsorbed on aqueous colloidal TiO_2 has been observed following optical excitation of adsorbed eosin Y at an energy below the band gap of TiO_2. E^+ appears with a risetime ≤ 5 ns and decays on a 10^{-6}-s time scale. The E^+ spectra on TiO_2 show relative intensity changes with respect to aqueous E^+ spectra, in a direction suggesting a protonated species apparently in a less polar environment.

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Registry No. E_0, 17372-87-1; E^+, 90670-69-2; TiO_2, 13463-67-7.

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