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Acceleration of secondary dark reactions of intermediates derived from adsorbed dyes on irradiated TiO_2 powders

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Abstract

Time-resolved diffuse reflectance flash photolysis has been used to characterize the kinetic behaviors of transients derived from several dyes (eosin Y, thionine, oxazine 725, and nile blue A) adsorbed on titanium dioxide powder (Degussa P-25) suspended in aqueous solutions of various pH. Secondary reaction rates on these powders were compared with those observed on analogous colloidal TiO_2 suspensions. Faster secondary reaction rates were observed on the powders, where the reaction surface is pseudo-two dimensional. Neither first nor second order decays were observed; instead, the observed kinetics depended on size distribution of the powder. With *N,N,N′,N′*-tetraphenylenediamine (TMPD), the decay rate of the singly oxidized cation radical $TMPD^{+\bullet}$ was found to depend on water concentration, thus implicating both direct electron transfer (ET) and OH-radical mediated oxidation pathways and complicating the observed kinetics.

Keywords: TiO_2; Secondary dark reactants

1. Introduction

The interfacial electron transfer (ET) to adsorbates present on the surface of titanium dioxide (TiO_2) semiconductor (SC) colloids and powders is a key step in photoelectrochemical reactions. The surface-mediated electron exchange initiates the process by which irradiated TiO_2 particles effect both complete mineralization of organic pollutants and the chemical transformation of many organic functional groups by pathways different from those observed in bulk solution [1]. In these photocatalytic conversions, light is absorbed by the suspended TiO_2 photocatalyst, producing an electron (e^-)/hole (h^+) pair, which is trapped at the surface by single electron transfer across the interface. Either oxidation or reduction of a redox-active adsorbate then result [2]. Extensive work in many laboratories over the last decade has shown this step to be crucial for efficient photocatalysis.

Little information is available, however, on kinetic differences encountered in the equally important secondary dark reactions that take place on these colloids and powders after the primary photochemical event. These processes, which determine the ultimate chemical fate of a given reagent, are undoubtedly influenced by the diffusion of the photogenerated transients along the surface of the particle [3–5], and are accordingly sensitive to surface composition and particle size. The role of surface dimensionality on kinetics in nonhomogeneous media, however, is not well-defined for solid-liquid interfaces. Such effects have been explored most extensively for micelles, both experimentally and theoretically [6]. For example, the reduction of diffusion dimensionality on the surface of a micelle has been shown to enhance the observed intramicellar rates of reaction of Br_2^- ion with several coadsorbates [7]. The relative importance of surface diffusion, surface stabilization of adsorbed ions, and adsorbate concentration as determinants of competing reaction pathways on TiO_2 is still unknown. Nonetheless, preliminary observations suggest that each of these variables may exert significant influence on partitioning among possible secondary reaction pathways. For example, Draper and coworkers have reported that photogenerated $(SCN)_2^{-\bullet}$ decays on colloidal TiO_2 by a second-order process, whereas $(SCN)_2^{-\bullet}$ produced photocatalytically on TiO_2 powder decays by a first-order process. These kinetic differences were rationalized by the local pseudo-planarity of the TiO_2 powder surface [8]. Furthermore, the reported effects of variable light and dark intervals on the quantum yields of several photoelectrochemical conversions [9,10] argue for studying secondary dark reactions, if the ultimate fate of organic oxidants under photocatalytic conditions is to be understood.

The opacity of a TiO_2 powder suspension necessitates diffuse reflectance as a means for its flash photolytic characterization [8–11], and this technique has been used extensively

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to study both oxidation and reduction reactions. In contrast, standard flash photolysis employing transmitted light can be used to characterize reaction rates on optically transparent semiconductor colloids. We present here a comparison of the rates of decay of transients derived from several highly absorptive dyes on colloidal and powdered TiO_2 surfaces. In practice, the detection of transients by this method is limited to those species with extinction coefficients greater than about 10 000 M^{-1} cm^{-1}. The probe substrates used in this study met this requirement and were chosen because their absorption spectra, as well as those of transients derived from them, had been previously well characterized. With *N,N,N′,N′*-tetramethylphenylenediamine (TMPD), the decay of the radical cation was also studied as a function of water concentration as a means to distinguish between direct electron transfer and OH-radical mediated pathways.

2. Experimental section

2.1. General

Titanium dioxide powder (Degussa P-25, primarily anatase, BET = 50 m^2 g^{-1}, average particle size = 30 nm, isoelectric point = pH 6.6) was dried overnight in a vacuum oven. Tetramethylphenylenediamine (Aldrich) was recrystallized twice from hot ethanol. Oxazine 725 (Exciton, 99%) and nile blue A (Aldrich, 99%) were used as received. Thionine (Aldrich) and eosin Y, disodium salt (Kodak) were purified by column chromatography on neutral Al_2O_3. The protonated form of eosin Y was prepared by acidifying with HCl.

The TiO_2 powder (50–200 mg) was suspended in 100 ml of a 10^{-5} M dye solution prepared in Millipore purified water (pH adjusted to 5.5). The pH (21 °C ± 1°) of the solution was adjusted with dilute NaOH or H_2SO_4 and measured using a pH meter. The resulting mixture was ultrasonically agitated for about 5 min to obtain a uniform dispersion.

Steady state irradiations were performed in a Rayonet photochemical reactor equipped with a circular array of phosphor-coated low pressure Hg lamps blazed at 350 (±20) nm. Each suspension was stirred during the irradiation, having been purged with N_2 (dried through a $CaCl_2$ tube) prior to exposure to the excitation light. The pH of each suspension, measured at the end of each experiment, was unchanged. After irradiation, the suspension was filtered under N_2 through a Millipore filter to remove the catalyst. The depletion of the dye from the filtrate was then monitored spectrophotometrically on a Hewlett-Packard 5719 spectrophotometer.

2.2. Flash photolysis

Flash photolysis experiments employed a Q-switched frequency-doubled (λ 532 nm) Nd:YAG laser (Quantel YG 581). The pulse width was 10 ns, and the energy delivered was 17 mJ per pulse. Diffuse reflectance measurements employed the third and second harmonics (355 and 532 nm, respectively) of a Quantel YG 581 Q-switched Nd:YAG laser for excitation in a previously described apparatus [8,9]. The excitation energy was varied using calcite Glan-Laser polarizers, with energies less than 17 mJ $pulse^{-1}$ being used for the diffuse reflectance measurements. In the transmission experiments, the analyzing lamp, sample, monochromator, and photomultiplier tube all lie on the same axis at 90° to the excitation beam. In the diffuse reflectance experiments, the optical rail holding the sample and analyzing lamp roughly bisects a 90° angle formed by the laser, sample, and monochromator to prevent specular reflection of the laser light from the cuvette's front face from entering the entrance slit of the monochromator. In the diffuse reflectance experiments, the area irradiated on the cuvette's front face was approximately 1 cm^2.

The diffusely reflected analyzing light from a 150 W Xe arc lamp was collected by a focusing lens (15 cm focal length) and directed through a Spex Minimate grating monochromator with a slit width of 5 mm to a Hamamatsu R928 photomultiplier tube. The signal from the photomultiplier tube was terminated across a 50 W load before being sent to a Biomation 8100 transient digitizer. A DEC PDP 11/70 computer was used to control the laser firing, shutter opening and closing, and operation of the lamp and digitizer and to analyze the collected data. Although the ΔJ values obtained in diffuse reflectance experiments have no direct absolute relationship to transient concentrations or absorptivity, the signal intensity was found to be proportional to transient concentrations at low laser power [9].

The distribution of sized particles was estimated by a model developed originally for micelles by Albery and coworkers [12–15] with two adjustable parameters, an average rate constant (k_{av}) and a Gaussian distribution parameter (γ). The average value of γ for these data is 2.3, with a standard deviation of ±0.1. This very useful and general model has been successfully applied to heterogeneous powders [8a], and its use for powder suspensions has been fully justified elsewhere [8b]. Two types of photoreactions of adsorbed dyes have been studied: (1) spectral sensitization in which interfacial electron transfer is initiated from an excited state on the dye, e.g. eosin Y; and (2) direct band gap excitation of TiO_2 powder, producing a surface-confined electron-hole pair which is trapped by interfacial electron transfer from the ground state of the adsorbed dye, e.g., thionines, oxazines, nile blue and tetraalkylphenylenediamines.

3. Results and discussion

3.1. Photoreactions on TiO_2

Ultraviolet irradiation of TiO_2 suspended in pH 1 water produces an electronhole pair, with the conduction band edge at −0.1 V and a valence band edge at +3.1 V vs. SCE [2]. The holes are driven toward the particle surface by band bending in the large particle, (where they participate in oxidation reactions), whereas the electrons are forced into the bulk of the particle and may later be transferred to adsorbed reductants. In contrast, spectral sensitization involves the transfer of an electron to or from a photoexcited dye molecule adsorbed on the surface of the semiconductor so that the same net charge separation transpires with a quite different action spectrum. In this study, we have focused on reagents that have been reduced or oxidized previously on colloidal TiO_2 [9,15–17]. By using these dyes, we can compare our observed kinetic data on TiO_2 powders with that reported earlier for colloidal TiO_2.

3.2. Eosin Y

Eosin Y (EO, 10^{-5} M) exists as a dianion at pH 13, with an intense visible absorption at 515 nm and a shoulder ($\epsilon = 9.7 \times 10^4$ M^{-1} cm^{-1}) at 480 nm, Fig. 1. In acid, the absorption maximum is red-shifted: to 519 nm at pH 4 and to 539 nm at pH 2. The diffuse reflectance absorption spectrum of eosin Y adsorbed on TiO_2 powder in contact with a solution held at pH 3 shows a maximum absorbance at about 530 nm (Fig. 1, inset), which is similar to a previous report for this dye adsorbed on a single crystalline TiO_2 electrode [18].

Photolysis at 350 nm of a N_2-purged homogeneous EO solution at pH 4 produces a change in the absorption spectrum indicative of ground-state bleaching and triplet (T_1) formation at 530 nm, [19,20] Fig. 2. Excitation of EO in this region leads to the triplet state of EO [17], from which electron transfer takes place [18]. Under these conditions, >90% of the dye is adsorbed, even at the lowest concentration of photocatalyst, as determined by measuring the amount of dye present in the filtrate after the filtered removal of TiO_2 particles from the suspension. Thus, the transients observed are dominantly derived from adsorbed species.

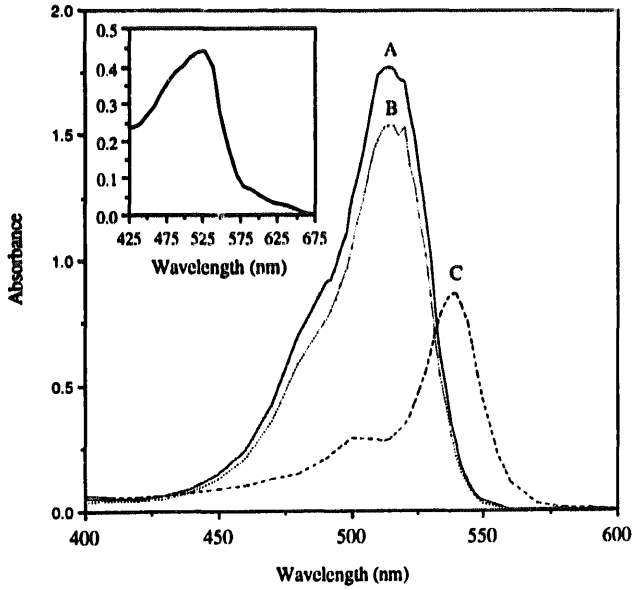


Fig. 1. Dependence of the absorption spectra of a solution of eosin Y on pH: (A) pH 10; (B) pH 4; (C) pH 2. Inset: absorption diffuse reflectance spectrum of TiO_2 powder with adsorbed eosin Y at pH 3; λ_{max} 530 nm. Reference: barium sulfate.

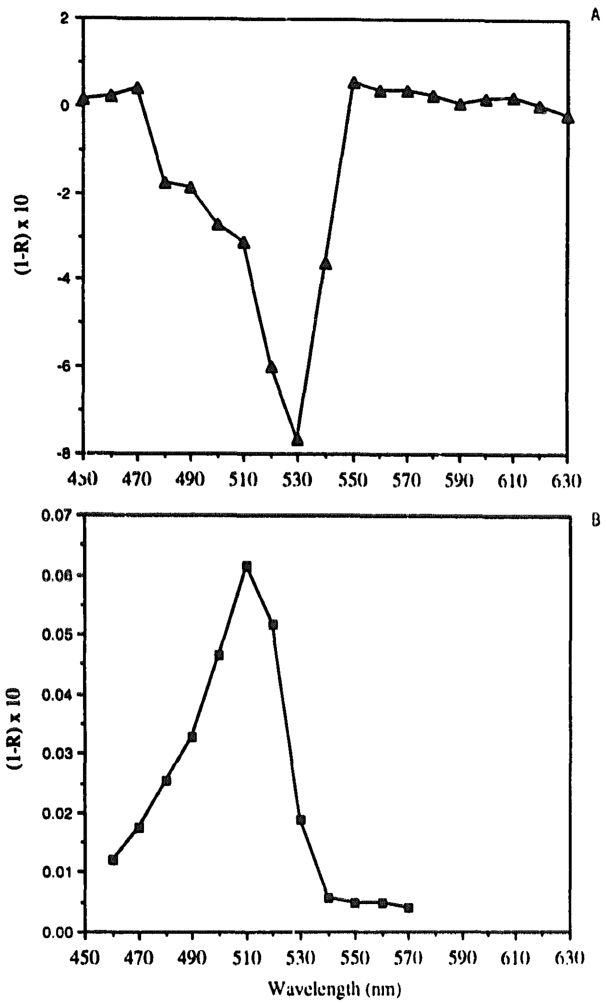


Fig. 2. Transient absorption spectra of ground state bleaching of eosin Y induced by laser flash photolysis (λ_{max} = 532 nm, 10 mJ $pulse^{-1}$, 10 ns pulse width) as 10^{-5} M solution in deaerated water, pH 4: (A) recorded 11.5 μs after the laser pulse; (B) as in spectrum A but corrected for ground state bleaching.

Table 1
Half-lives for the production and disappearance of transients produced by flash excitation (532 nm, 10 mJ/pulse laser energy, 10 ns pulse width) of a homogeneous 10^{-5} M aqueous solution of eosin Y at pH 4

	τ (μs)	
	O_2-Saturated	N_2-Saturated
Recovery from photobleaching	0.48 (±0.01)	250 (±5)
Triplet decay	0.55 (±0.01)	190 (±5)
Radical cation appearance	[a]	1000 (±10)
Radical cation disappearance	[a]	60 (±5)

[a] Too weak to be observed.

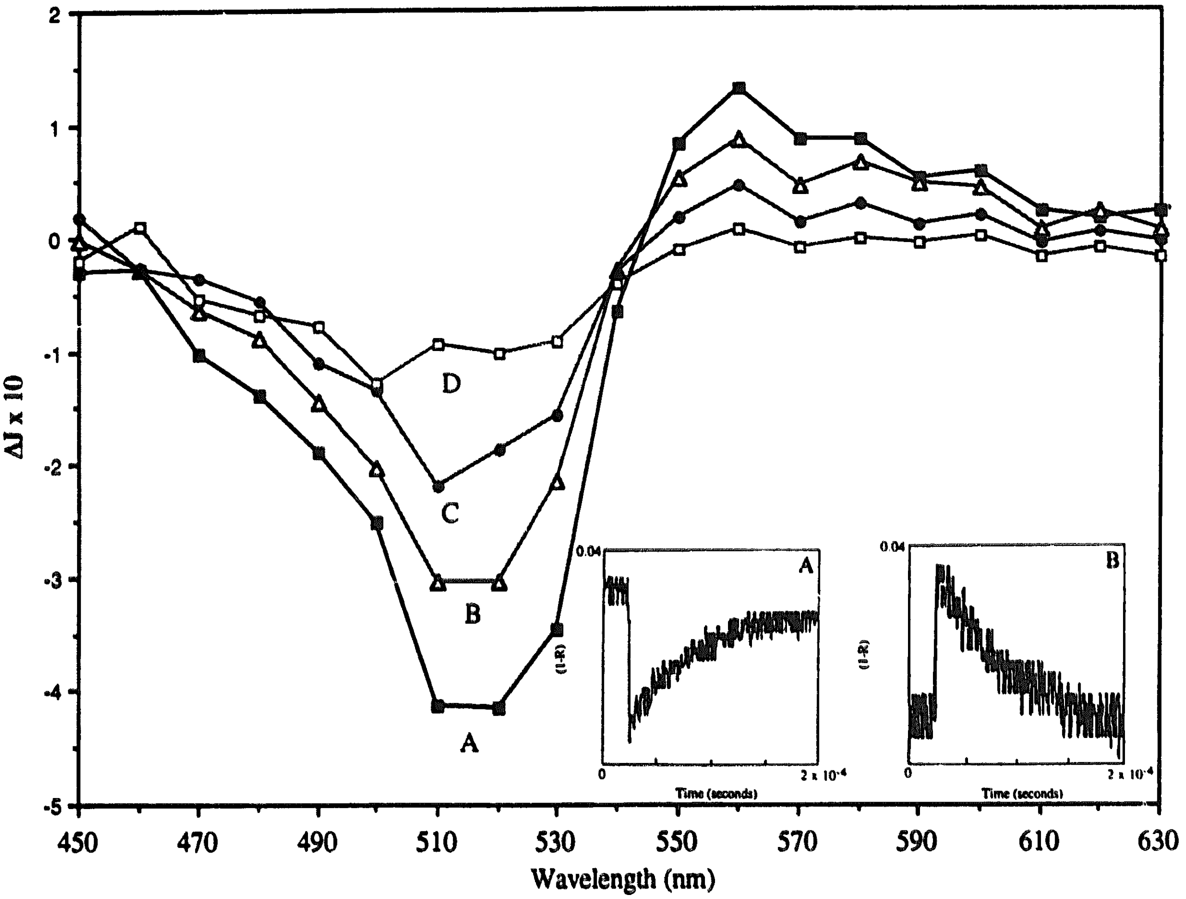


Fig. 3. Transient diffuse reflectance absorption spectra of eosin Y induced by laser flash photolysis (λ_{max} = 532 nm, 10 mJ pulse^{-1}, 10 ns pulse width) as a N_2-saturated 10^{-5} M aqueous suspension of TiO_2 (1 g l^{-1}) at pH 2.7 at various times after excitation: (A) 12 μs, (B) 35 μs, (C) 77 μs, (D) 150 μs. Insets: (A) bleaching recovery at 520 nm, $k_{av} = 5.0 \times 10^5$ s^{-1}, $g = 2.2$ and (B) decay at 600 nm, $k_{av} = 4.8 \times 10^3$ s^{-1}, $g = 2.3$.

The decay of EO(T_1), monitored at 620 nm where there is minimum overlap between the triplet absorption and the ground state absorption bands, shows first-order decay, Table 1. In O_2-saturated solution, the triplet is quenched to regenerate the ground state dye [21–26]. No absorptions attributable to the singly oxidized EO could be observed in O_2-saturated solution; it has been shown previously [24,25] that the singly oxidized intermediate is converted by reaction with O_2 to a product that does not absorb in the same region as ground state eosin.

Transient diffuse reflectance absorption spectra observed after photoexcitation at 532 nm of N_2-bubbled suspensions of TiO_2 powder (1 g l^{-1}) containing 10^{-5} M EO at pH 2.7 and 4 are shown in Figs. 3 and 4. Photobleaching at around 515 nm is accompanied by the appearance of a transient with an absorbance maximum at 560 nm. Subtraction of the contribution of the EO(T_1) state (l_{max} = 530 nm, Fig. 2(b)) from the observed absorption spectrum corrects the apparent photobleaching maximum to 535 nm. Photosensitized single electron oxidation of the excited state of an adsorbed EO molecule takes place within the 10 ns laser pulse. Unfortunately, the absorption peak at $EO^{+\bullet}$ was too weak to be observed, partly because of experimental limitations of the diffuse reflectance measurement and because of the low extinction coefficient. Hence, indirect evidence for the formation and decay of $EO^{+\bullet}$ relies on measurements of triplet decay and ground state bleaching. The triplet state of EO decays back to the ground state with a reaction rate of 1.3×10^9 M^{-1} s^{-1} in bulk aqueous solution [17]. We do not observe this reaction pathway in our diffuse reflectance experiments. Instead, a much slower decay is observed, Fig. 3(b).

As the data in Table 2 show, increasing the solution pH of a suspension of TiO_2 (1 g l^{-1}) in 10^{-5} M EO led to an increase in the lifetime of the triplet state, a slight decrease in the average particle size (from $\gamma = 2.3$ to 2.1), and a decrease in the rate constant for recovery of bleaching. No effect on the triplet lifetimes (average ±20 ms) could be found upon variation of the TiO_2 concentration at pH 4.

The formation of $EO^{+\bullet}$ on irradiated TiO_2 powder has been attributed to electron injection from an electronically excited state into the conduction band of the TiO_2 particle [14,18]. Both the singlet and triplet [27] states are of an appropriate energy for this injection to be thermodynamically permissible, Eq. (1).

$$EO(T_1) \longrightarrow EO^{+\bullet} + e_{CB}^{-}(TiO_2) \qquad (1)$$

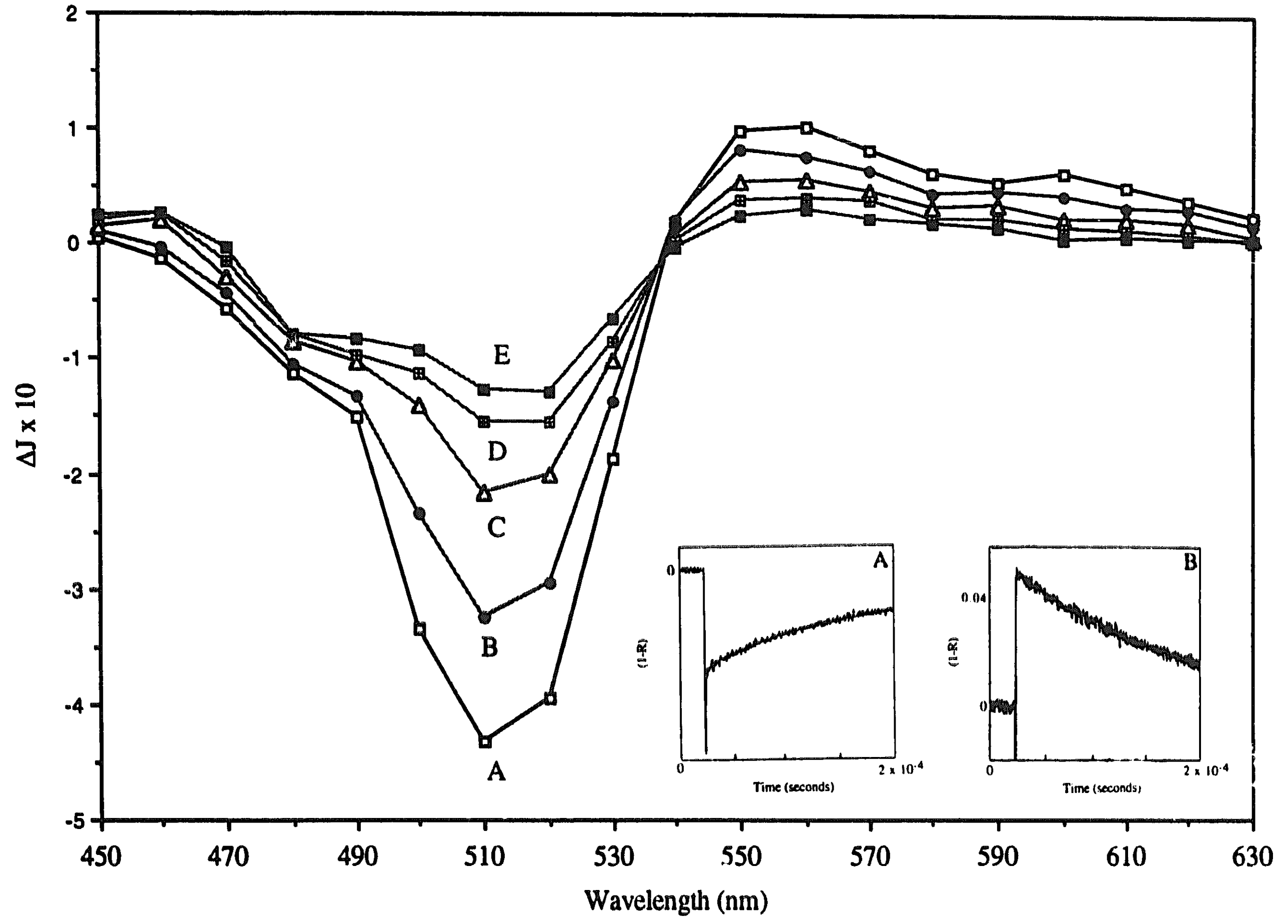


Fig. 4. Transient diffuse reflectance absorption spectra of eosin Y induced by laser flash photolysis (λ_{max} = 532 nm, 10 mJ pulse^{-1}, 10 ns pulse width) as a N_2-saturated 10^{-5} M aqueous suspension of TiO_2 (1 g l^{-1}) at pH 4.0 at various times after excitation: (A) 12 μs, (B) 35 μs, (C) 77 μs, (D) 110 μs, (E) 150 μs. Insets: (A) bleaching recovery at 520 nm, $k_{av} = 2.4 \times 10^5$ s^{-1}, g = 2.0 and (B) decay at 600 nm, $k_{av} = 6.5 \times 10^3$ s^{-1}, g = 2.2.

Table 2
Effect of pH on the half-life of the excited triplet of eosin Y produced by flash excitation (532 nm, 10 mJ/pulse laser energy, 10 ns pulse width) of a N_2-saturated 10^{-5} aqueous solution of eosin Y containing 1 g/L TiO_2 powder

pH	τ (μs, ±20 μs)	γ [a]
4.0	100	2.3
5.0	170	2.0
11.5	210	2.1

[a] Albery particle size distribution function.

Table 3
Effect of pH on the half-life of recovery of ground state bleaching of eosin Y produced by flash excitation (532 nm, 10 mJ/pulse laser energy, 10 ns pulse width) of a N_2-saturated 10^{-5} M aqueous solution of eosin Y containing 1 g/L TiO_2 powder

pH	k_{av} (s^{-1}) [a]	τ (μs) [a]	γ
4.0	2.4×10^5	4.1	2.0
10.0	5.7×10^3	180	2.1
11.5	6.0×10^3	170	2.3

[a] The values of k_{av} and τ have errors of ± approx. 25%.

At pH values below the point of zero charge (6.3), TiO_2 particles are positively charged (Eq. (2)), and above this pH, they are negatively charged (Eq. (3)) [28]

$$-TiOH_2^+ \rightleftharpoons -TiOH + H^+,\ pK_a = 4.95 \qquad (2)$$

$$-TiOH \rightleftharpoons -TiO^- + H^+,\ pK_a = 7.8 \qquad (3)$$

Although there is a sufficient driving force for the required interfacial electron transfer under alkaline conditions, this driving force is overwhelmed by the electrostatic repulsion between the EO dianion and the negatively charged TiO_2 surface that exists under basic conditions. In contrast, in acidic suspensions the semiconductor surface is positively charged and Coulombic attraction of the dianionic dye to the semiconductor surface effects strong adsorption. Such pre-adsorption is required if interfacial ET is to compete with other channels of excited state deactivation, such as intersystem crossing and nonradiative deactivation.

In powder suspensions at pH 4, excitation of the dye on the semiconductor surface was followed by ground state recovery within 4.1 μs, in a pH-dependent process, Table 3. This is significantly faster than the ground state recovery observed in homogeneous solution (247 μs) or on colloidal suspensions (95 μs) at the same pH. This faster ground state recovery on TiO_2 powder is consistent with previous reports [8,9] that bimolecular dark reactions are accelerated on solid catalytic surfaces because of enhanced collisional diffusion.

The kinetics observed for EO sensitization of TiO_2 powder are consistent with those previously reported for sensitization of a TiO_2 single-crystal electrode in pH 6 water, where triplet decay was faster on the semiconductor surface (compared with homogeneous solution or colloidal suspension): partial ground-state recovery occurred in less than 0.1 μs. As on the single crystal electrode, the photocatalytic oxidation of excited EO on powdered TiO_2 appears to occur via electron injection from EO to TiO_2 rather by triplet-triplet dismutation on the surface of the semiconductor [29]. If concentration quenching by this triplet-triplet dismutation mechanism were significant, increasing the TiO_2 concentration in the suspension should lead to a decrease in the average proximity of EO molecules adsorbed onto a given TiO_2 particle and, hence, in the average value for the decay rate constant for the EO triplet. The lack of concentration dependence of suspended TiO_2 indicates that this is not the case. Furthermore, from an analysis of the kinetics of diffusional motion on the surface of a spherical aggregate, Hatlee et al. [6] have estimated the average time between encounters on a 110 Å size TiO_2 particle to be between 0.07–1.5 μs. This timescale is incompatible with the observation of $EO^{+\bullet}$ formation within the 10-ns laser pulse. Since concentration quenching does not play a significant role when EO is strongly adsorbed to TiO_2 powder, a second pathway for excited state deactivation must prevail.

3.3. Thionine

An absorption spectrum reflecting the effect of pH on the ground-state absorption of neutral thionine (TH) is presented in Fig. 5 [30]. For solutions with a pH between 1–5, the absorption maximum is at 600 nm. The protonated form of TH could not be observed, even at pH 1. The absorption spectrum, however, does shift significantly at basic pH (8 and 11): the absorption band at 600 nm has decreased in intensity, and another band appears near 500 nm.

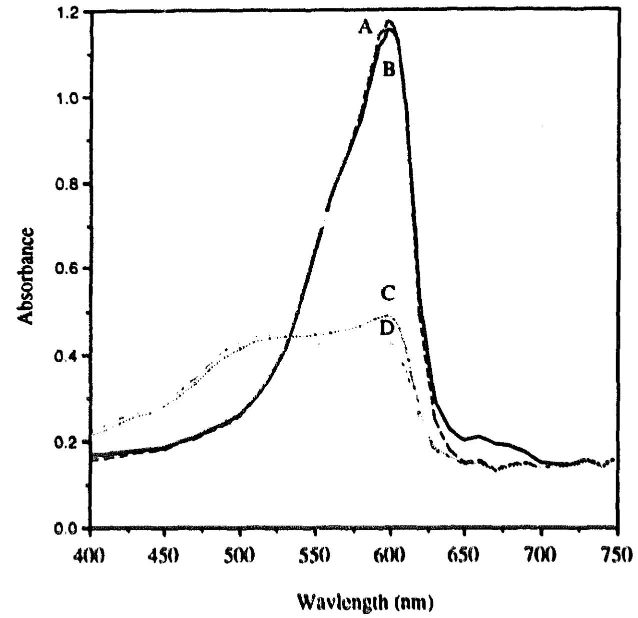


Fig. 5. Absorption spectra of 10^{-5} M thionine in water at different pH: (A) pH 3, (B) pH 5, (C) pH 8, (D) pH 11.

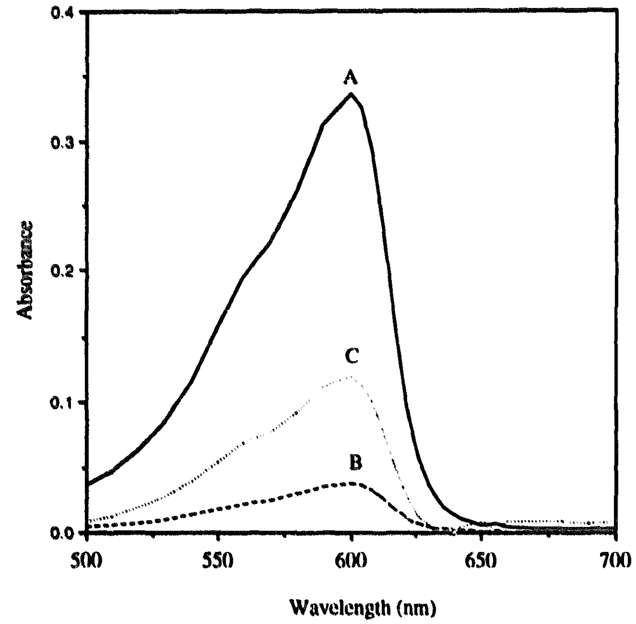
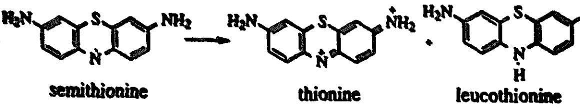


Fig. 6. Absorption spectra of a partially deaerated solution of 10^{-5} M thionine on TiO_2 (1 g l^{-1}) after removal of powder from the suspension: (A) before steady-state photolysis; (B) following steady-state photolysis; (C) 5 min after cessation of photolysis. The suspension was irradiated at 350 nm in a Rayonet photochemical reactor, with the solid TiO_2 photocatalyst having been removed by filtration before the spectroscopic measurements.

The ease of reduction of TH (0.064 V vs. NHE [13]) provides a substantial driving force for trapping a conduction band electron at the TiO_2 surface, leading to bleaching of TH. Accordingly, an absorption spectrum of semithionine is observed after a 4 min irradiation at 350 nm in a Rayonet photochemical reactor of a partially deaerated aqueous suspension of TiO_2 powder (1 g l^{-1}) containing 10^{-5} M TH, Fig. 6(b). Partial recovery of TH is observed 5 min after cessation of irradiation (Fig. 6(c)), presumably by the disproportionation equilibration shown in Eq. (4). (No evidence for significant differences between adsorption during excitation and in the dark could be found.) A similar spectrum of semithionine has been reported upon excitation of a dispersion of colloidal TiO_2 in the presence of the methyl viologen dication [16].



(4)

The transient diffuse reflectance absorption spectrum of semithionine (ϵ_{420} = 12 000 M^{-1} cm^{-1}) [15,26,30] was obtained by excitation of a suspension of TiO_2 powder (1 g

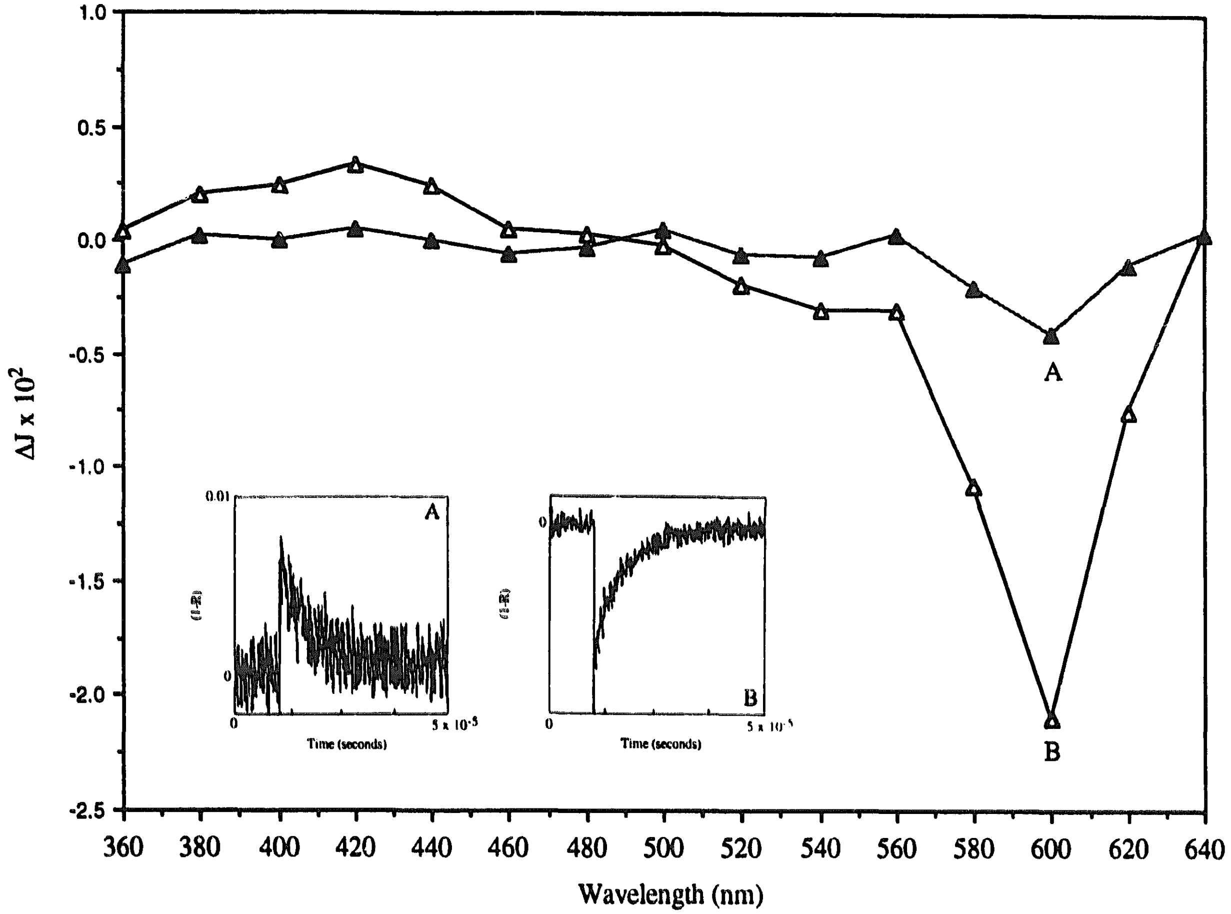


Fig. 7. Diffuse reflectance absorption spectra attributed to semithionine generated by flash excitation (λ_{max} = 355 nm, 8–10 mJ pulse^{-1}, 10 ns pulse width) of a TiO_2 powder (1 g l^{-1}) suspended in 3×10^{-5} M aqueous thionine (N_2-saturated, pH 4.8): (A) 5.1 μs and (B) 39.3 μs after the flash. Insets: (A) decay of reduced TH monitored at 420 nm: $k_{av} = 1.5 \times 10^5$ s^{-1}, $g = 2.5$ and (B) decay at 600 nm: $k_{av} = 1.5 \times 10^5$ s^{-1}, $g = 2.6$.

l^{-1}) in N_2-saturated aqueous TH (3×10^{-5} M) at pH 4.8, Fig. 7. The decay of this transient, monitored at its absorption maximum at 420 nm, is complete within 39 μs. The appearance of semithionine was prompt: interfacial electron transfer takes place within the laser pulse. The decay was analyzed using the Albery model, with $k_{av} = 1.5 \times 10^5$ s^{-1}. In the photobleaching of thionine on colloidal TiO_2 at pH 3 (flocculation became a problem when the pH was adjusted above pH 3), the rate of disproportionation of semithionine on colloidal TiO_2 ($k_{av} = 10^3$ s^{-1}) [16] is more than an order of magnitude lower than that observed on TiO_2 powder, again consistent with faster reaction rates on the powder than in solution or colloidal suspensions.

The effect of pH on the decay of semithionine monitored at 420 nm is shown in Table 4. Increasing the solution pH leads to a small increase in the rate of recovery of photobleaching, with the size of the increase becoming larger in base. The reduction potential of thionine is pH independent [16], but the conduction band edge of TiO_2 ($E_{CB} = -0.10$ V vs. NHE at pH 1) shifts negative by 59 mV per pH unit as the pH is increased [31]. As a result, a greater driving force for thionine reduction exists at higher suspension pH. We observe that as the pH of the suspension is increased, the rate of decay (k_{av}) of semithionine increases. This effect is similar to that observed in the pH-dependent reduction of the methyl viologen dication on TiO_2 suspensions [32]. The absence of growth of the semithionine absorbance after pulse excitation, however, rules out diffusion-limited electron transfer to free dye molecules in solution as a source of the observed reduction product, in contrast with previous reductions of methyl viologen on colloidal TiO_2 [32–33].

3.4. Oxazine 725 and Nile Blue A

The photobleaching and thermal recovery of oxazine 725 (OX) and nile blue A (NBA) is observed after steady-state irradiation at 350 nm in a Rayonet photochemical reactor of a partially deaerated aqueous TiO_2 powder (1 g l^{-1}) suspension, containing 10^{-6} M OX or 10^{-5} M NBA, Figs. 8 and 9, respectively. The steady-state irradiation of these suspensions for 4 min at 350 nm led to bleaching of the dyes, which have negligible absorption at the irradiation wavelength. Partial bleaching recovery of the dyes in the presence of oxygen is observed several minutes after the irradiation is stopped (Figs. 8 and 9, curves C). Photochemical bleaching of both OX and NBA on illuminated TiO_2 powders is consistent with

Table 4
Effect of pH on the decay of semithionine produced by a N_2-saturated suspension of 1 g/L TiO_2 powder in a 3 ± 10^{-5} M thionine solution ($\lambda_{exc}=355$ nm, 8–10 mJ/pulse, 10 ns pulse width)

pH	k_{av} (s^{-1}) (±10%) [a]	γ
2.6	1.3×10^5	2.6
3.3	1.5×10^5	2.4
4.8	1.9×10^5	2.4
6.6	5.1×10^5	2.4
9.7	5.8×10^6	2.8
11	7.3×10^6	2.4

[a] The k_{av} values have an error of approx. ±25%.

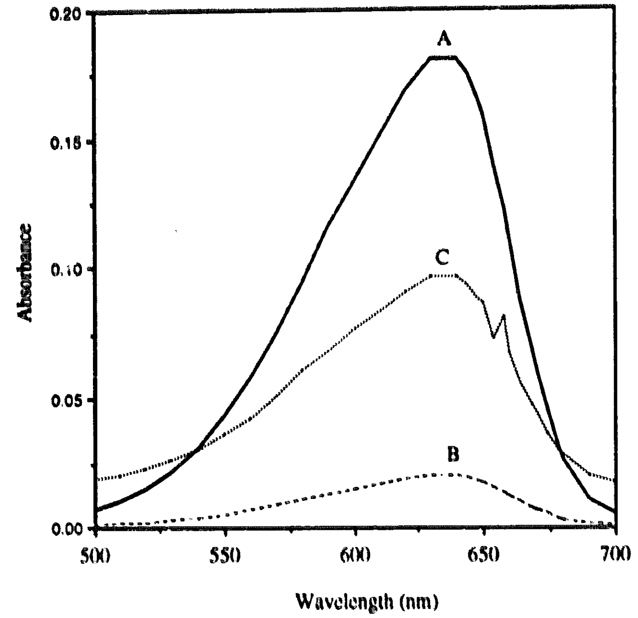


Fig. 8. Absorption spectra of a partially deaerated solution of 10^{-5} M nile blue A containing TiO_2 (1 g l^{-1}): (A) before steady-state photolysis; (B) following steady-state photolysis; (C) 5 min after cessation of photolysis. The suspension was irradiated at 350 nm in a Rayonet photochemical reactor, with the solid TiO_2 photocatalyst having been removed by filtration before the spectroscopic measurements.

previous reports of analogous bleaching on irradiated colloidal TiO_2 dispersions in acetonitrile [16], where absorption spectra showed the presence of long-lived transients in the 400–420 nm region ($\tau>70$ μs) that were attributed to one-electron reduction of the dyes.

The photobleaching of OX and NBA could also be induced by flash excitation at 355 nm (Nd-YAG laser, 7 mJ $pulse^{-1}$) of a N_2-saturated solution of the dyes (10^{-5} M) in anhydrous CH_3CN containing suspended TiO_2 powder (1 g l^{-1}). Upon exposure to atmospheric O_2, gradual recovery of the dye (over 2 min) was observed. In neither case could photobleaching be detected by diffuse reflectance. Although the energetics are similarly favorable for conduction band electron trapping by OX and NBA (−0.02 V for OX and −0.12 V for NBA, both vs. NHE in CH_3CN [16]), we have been unable to observe the single electron reduction products of these dyes by diffuse reflectance spectroscopy. Our ability to observe bleaching, but no such transients, on powdered TiO_2 under conditions which did produce such intermediates of colloidal TiO_2 implies that disproportionation to the leuco dye must occur within the 10 ns laser pulse on the powder. This, again, is consistent to a much more rapid secondary reactions on powders than on colloidal TiO_2.

3.5. N,N,N',N'-Tetramethylphenylenediamine (TMPD)

Photoexcitation of an O_2-saturated suspension of TiO_2 powder (1 g l^{-1}) in a 9×10^{-4} M solution of TMPD in anhydrous acetonitrile, Fig. 10, led to the absorption spectrum of the radical cation of TMPD ($\epsilon_{420}=20\,000$ M^{-1} cm^{-1}) [8] by direct electron transfer to a photogenerated hole since the transient is present immediately after the excitation pulse (10 ns pulse width), Eq. (5).

$$h^+ + TMPD \underset{k_{bet}}{\overset{k_{inj}}{\rightleftharpoons}} TMPD^{+\bullet} \qquad (5)$$

The decay of the radical cation, when monitored at $\lambda_{max}=570$ nm, was complete within 27 μs. In contrast, $TMPD^{+\bullet}$ was found to be stable for over 50 μs when produced on colloidal TiO_2 [8].

The addition of water to an O_2-saturated TiO_2 powder (1 g l^{-1}) suspended in acetonitrile has a significant effect on the rate of decay of $TMPD^{+\bullet}$, Table 5 and Fig. 11. Increasing the water content (10, 20 and 50%) leads to a significant decrease in the rate of disappearance of the transient at 570 nm, indicating an appreciable increase in either the lifetime

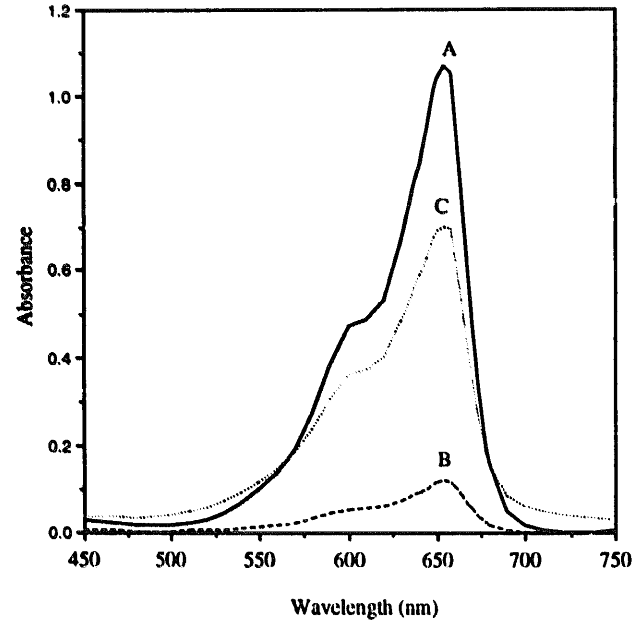


Fig. 9. Absorption spectra of a partially deaerated solution (pH 6.6) of 10^{-6} M oxazine 725 containing TiO_2 (1 g l^{-1}): (A) before steady-state photolysis; (B) following steady-state photolysis; (C) 7 min after cessation of photolysis. The suspension was irradiated at 350 nm in a Rayonet photochemical reactor, with the solid TiO_2 photocatalyst having been removed by filtration before the spectroscopic measurements.

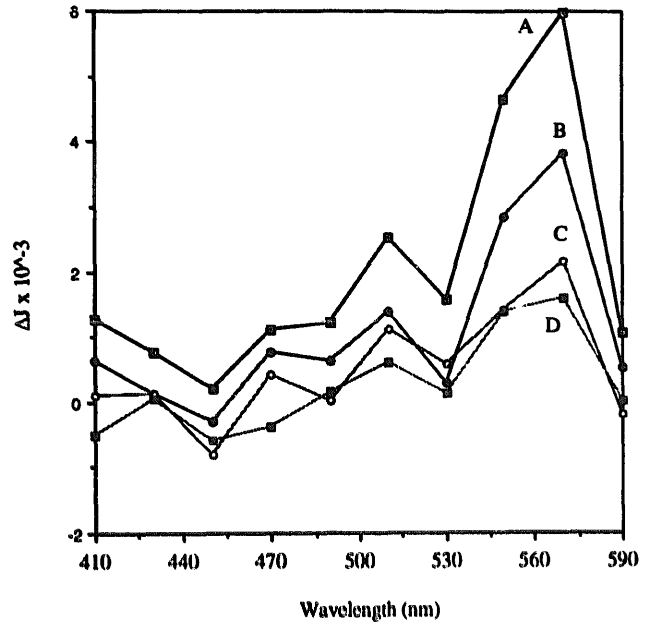


Fig. 10. Diffuse reflectance absorption spectra attributed to $TMPD^{+\bullet}$ generated by flash excitation (λ_{max} = 355 nm, 8–10 mJ $pulse^{-1}$, 10 ns pulse width) of a TiO_2 powder (1 g l^{-1}) suspended in 10^{-3} M TMPD in O_2-saturated anhydrous acetonitrile: (A) 2.5 μs, (B) 8.4 μs, (C) 14 μs, (D) 17 μs.

of the radical cation or of another species absorbing in the same region.

In the photoexcited suspensions of TiO_2 powder in aqueous acetonitrile, an additional mechanism for $TMPD^{+\bullet}$ formation can be envisioned involving an OH radical formed by water oxidation on TiO_2, Eq. (6) [34].

$$TiO_2(h_{VB}^+) + H_2O \longrightarrow {}^\bullet OH + H^+ \qquad (6)$$

Hydroxyl radicals, which can also be generated via reaction of the hole with surface OH^- groups, Eq. (7) [35], have been implicated as key reactive intermediates in the semiconductor-photosensitized degradation of many organic compounds in water [35–41]. The hydroxy radical adduct has a maximum absorption identical to that of the radical cation of TMPD, and no changes in the spectral shapes were observed with time.

(7)

Such hydroxy radicals can then attack adsorbed TMPD either at the aromatic ring or to the amino group, forming one of several possible ˙OH-TMPD adducts [43]. Secondary loss of OH^- can lead to the formation of $TMPD^{+\bullet}$, Eq. (8).

$${}^\bullet OH + TMPD \longrightarrow {}^\bullet OH\text{-}TMPD \longrightarrow OH^- + TMPD^{+\bullet} \qquad (8)$$

Thus, indirect water oxidation can compete with direct substrate oxidation by hole scavenging, initiating a sequence by which surface-bound OH radicals reversibly add to the adsorbate or abstract an electron, ultimately producing $TMPD^{+\bullet}$. This latter route can account for the 'growing-in' portion of the transient profiles, especially for the case where the suspension contains 50% (v/v) water. Thus, the absorption at 570 nm cannot be unambiguously assigned to $TMPD^{+\bullet}$ in the presence of water, since the OH radical adduct of TMPD (TMPD-OH) also has a characteristic absorption maximum at 570 nm [8].

Table 5
Dependence on water concentration of the decay rate of $TMPD^{+\bullet}$ produced by flash excitation (λ_{max} = 355 nm, 8 mJ/pulse, pulse width = 10 ns) of an O_2-saturated suspension of 1 TiO_2 powder g/L in a 9 × 10^{-4} M solution of TMPD [a]

H_2O (% v/v)	k_{av} (s^{-1}) [b]	γ
0	1.03×10^6	2.8
10	1.30×10^4	3.2
20	1.20×10^4	3.0
50	2.50×10^3	2.7

[a] The $TMPD^{+\bullet}$ concentration was monitored at 570 nm.
[b] The values of k_{av} have errors of ± approx. 25%.

The transient decay profiles for $TMPD^{+\bullet}$ in TiO_2 suspensions containing water are biphasic: that is, the decay profiles exhibit an apparent initial growth, followed by decay, especially in 1:1 (v/v) water: acetonitrile. The faster decay of $TMPD^{+\bullet}$ in pure acetonitrile and in acetonitrile containing a small amount of water is caused by rapid back electron transfer from TiO_2 to $TMPD^{+\bullet}$. Pulse radiolysis studies of TMPD in water have shown that the decay of TMPD-OH to $TMPD^{+\bullet}$ occurs with a rate constant of ca. 8.0×10^4 s^{-1} [8]. The observed rate constants for the decay of the 570 nm band listed in Table 5 for aqueous acetonitrile suspensions are in the same range. Thus, the decay of 570 nm band in an aqueous heterogeneous suspension can likely be attributed to decay of both TMPD-OH˙ and $TMPD^{+\bullet}$, complicating the interpretation of the observed kinetics. Thus, a determination of whether the same kinetic acceleration is observed with $TMPD^{+\bullet}$ on TiO_2 powder as on colloidal suspension is not possible because of this mechanistic complexity.

4. Conclusions

Photocatalyzed reaction were investigated by diffuse reflectance detection of transients produced by flash excitation of aqueous suspensions of TiO_2 powder. Such powders offer a practical advantage in that they permit the solution pH to be varied without the pH-dependent flocculation sometimes observed with colloidal TiO_2. This method allowed analysis of the kinetics of decay of surface-bound transients by the two-parameter kinetic model developed by Albery for heterogeneous systems. This model has been shown earlier to apply well to powder suspensions.

The photoredox reactions occur by direct electron transfer between the adsorbate and TiO_2 powder. The possible excep-

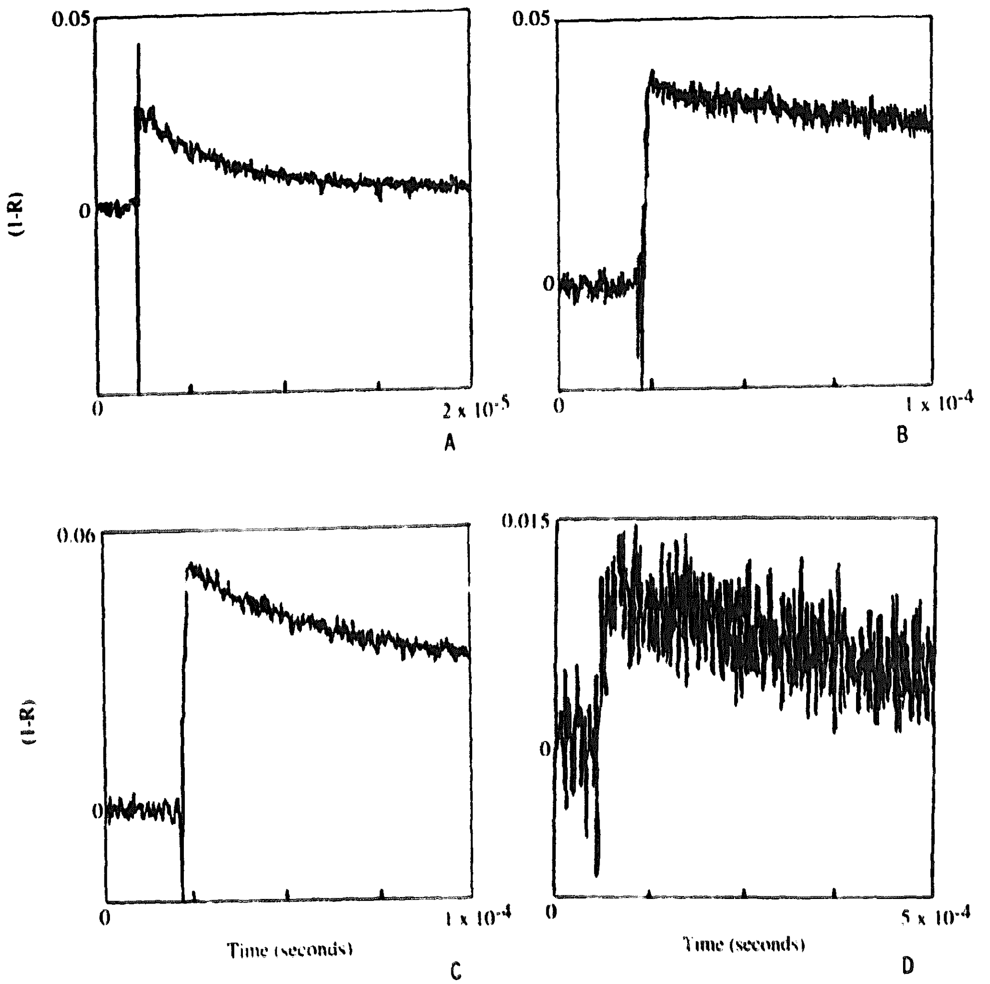


Fig. 11. Decay profiles for the transient attributed to TMPD$^{\bullet+}$ generated by flash excitation (λ_{max} = 355 nm, 8–10 mJ pulse^{-1}, 10 ns pulse width) of a TiO_2 powder (1 g l^{-1}) suspended in O_2-saturated 10^{-3} M TMPD containing: (A) no water, (B) 10% water, (C) 20% water, and (D) 50% water.

tion is the TiO_2 powder-catalyzed photo-oxidation of TMPD in aqueous solution. In this case, OH radical can attack TMPD to form TMPD-OH which expels OH^- to form TMPD$^{\bullet+}$. Sensitization of TiO_2 powder by eosin Y took place by single electron oxidation and the observed pH dependence of the observed efficiency of electron injection suggests that adsorption of eosin on the semiconductor surface is a prerequisite for successful photosensitization. One electron reduction reactions of xanthene dyes (i.e., OX, NBA, and TH) on photoexcited TiO_2 powder were followed by further disproportionation to yield colorless, stable leuco dyes.

The lifetimes of the transients formed on TiO_2 powder suspensions are significantly shorter than those observed on TiO_2 colloids. The recovery from photobleaching of EO on TiO_2 powder at pH 4 occurs within 4 μs, whereas ground state recovery on colloidal TiO_2 occurs after 200 μs [17]. Semithionine decays at a rates of 1.5×10^4 s^{-1} on colloidal TiO_2^{15} and of 3×10^5 s^{-1} on TiO_2 powder. The transient species formed in the reduction of OX and NBA on TiO_2 powder suspensions decay within the lifetime of the laser pulse (10 ns), whereas these species have lifetimes greater than 70 μs on colloidal TiO_2 [16]. The transient produced by flash photolysis of TMPD decays within 27 μs on aqueous TiO_2 powder suspensions, but persists for 20 μs on colloidal TiO_2 in acetonitrile. The observed kinetics are complicated by the concurrent presence of a hydroxy radical adduct in the aqueous experiments [9].

Reaction rate accelerations on TiO_2 powders may be attributed to the pseudo-two dimensionality of the powders, compared with the probable three-dimensionality of a surface-capped colloid. A pseudo two-dimensional surface is clearly advantageous for enhancing the efficiency of photoinduced electron transfer reactions taking place through several steps, either by minimizing the randomness of directional diffusion, by enhancing adsorptive binding of co-reactants in a proximate relationship that favors reaction, or by altering the intrinsic stability of the adsorbed ions.

We conclude that the rates of secondary dark reactions taking place on TiO_2 powder are significantly greater than the analogous reactions taking place on colloidal TiO_2. We attribute these kinetic effects to the local pseudo-planarity of the TiO_2 powder. Draper and Fox [8] have argued previously for this interpretation in the photooxidation of thiocyanate on TiO_2 powder by a process parallel to that described by Hatlee and coworkers [6] for the interaction of donor-acceptor pairs on the surface of micelles. This interpretation is also similar to that advanced by Brown and coworkers in their description of the dependence of distributed kinetics on particle size in heterogeneous photocatalysis [14].

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