# Fundamental Reactions in Illuminated Titanium Dioxide Nanocrystallite Layers Studied by Pulsed Laser

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Titanium dioxide layers, composed of 5 nm diameter closely packed nanocrystallites prepared by spin coating of concentrated TiO₂ sols (titanium isopropoxide hydrolysis), were exposed to pulsed laser photolysis, in the presence as well as in the absence of added reactants. Time profiles in the range 390−700 nm have been studied in the nanosecond time range. TiO₂ layers immersed in liquids (acidic or alkaline water, CCl₄, CCl₄/CBr₄ mixture, cyclohexane) show the same absorption vs time profiles as the dry layers. Iodide ions (0.5−7.6 M in water) convert the holes to I₂⁻ within less than 10 ns (quantum yield approaching unity is observed at the highest concentration). The absorption of I₂⁻ (peaking at 390 nm) is relatively stable during the first 4 μs, in contrast to the decay of the electron absorption which is only slightly different than in iodide-free solutions. This result is unexpected if the decay of the electron absorption is because of electron−hole recombination. Alcohols (methanol and 2-propanol) at high concentrations unexpectedly reduce the initially observed electron absorption (time resolution 10 ns) by up to 4-fold, without affecting the shape of the nanosecond time profile. The alcohol effect is assigned to formation of an alcoholic positive ion radical which is more reactive in recombination with conduction band electrons than the original hole. The electron scavenger H₂O₂ reduces the initial electron absorption without affecting the shape of the nanosecond time profile. It is concluded that (a) the decay of the visible absorption in the nanosecond time range is largely because of gradual electron trapping, with only a partial contribution of electron−hole recombination; (b) reactions with scavengers are important in the femtosecond−picosecond time range (reactions of $h_{vb}^+$ and $e_{cb}^-$) and in the microseconds or longer time (reactions of the respective trapped species), but the absorbance changes in the nanosecond time range are not affected by scavengers; (c) even in the absence of hole scavengers, trapping of the electron competes successfully with recombination when no more than one electron−hole pair is produced in a nanocrystallite. Most electrons still exist after several microseconds.
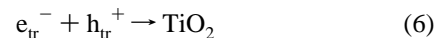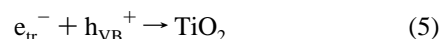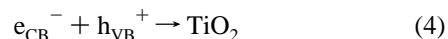
## Introduction

Interest in the detailed mechanism of illuminated TiO₂ reactions arises from the intensive use of aqueous TiO₂ in photocatalytic organic reactions and its application for complete mineralization of pollutants from wastewaters.[1−19] The primary step in the reaction mechanism is the photogeneration of pairs of electrons and holes in the TiO₂ particles (reaction 1). Trapping of the electrons (reaction 2) and holes (reaction 3) occurs within less than 30 ps.[20−25]

$$TiO_2 \xrightarrow{h\nu} h_{VB}^+ + e_{CB}^- \tag{1}$$

$$e_{CB}^- \rightarrow e_{tr}^- \tag{2}$$

$$h_{VB}^+ \rightarrow h_{tr}^+ \tag{3}$$

Second-order decay in the picosecond time range has been attributed to fast electron−hole recombination at high laser intensities (reaction 4).[26] A broad visible band peaking at 620 nm ($\epsilon = 1200$ M⁻¹ cm⁻¹)[21] in acidic solutionsand peaking at 780 nm ($\epsilon = 800$ M⁻¹ cm⁻¹)[27] in alkaline solutions has been

assigned to the trapped electrons.[20,21,27−30] At high laser intensities, most of this absorption decays within less than 1 ns. When an average of less than one electron−hole pair per nanocrystallite remains, absorbance changes extend to the nanosecond−microsecond time range. These have been attributed to reaction of trapped electrons with mobile or trapped holes (reactions 5 and 6).[21,22]

$$e_{CB}^- + h_{VB}^+ \rightarrow TiO_2 \tag{4}$$

$$e_{tr}^- + h_{VB}^+ \rightarrow TiO_2 \tag{5}$$

$$e_{tr}^- + h_{tr}^+ \rightarrow TiO_2 \tag{6}$$

Reaction 5 has been invoked because the absorption of trapped electrons in the time range 5−100 ns decreases faster than the absorption at shorter wavelength,[21,23,31] the latter attributed to trapped holes. This has been taken as indication that holes created by the light may have longer lifetime (≈250 ns) before they are trapped. Existence of two types of trapped holes, one of which in thermal equilibrium with the valence band hole, has been recently invoked in order to account for the time-dependent electron−hole combined spectrum.[31] The nanosecond time range is still considered highly significant for both

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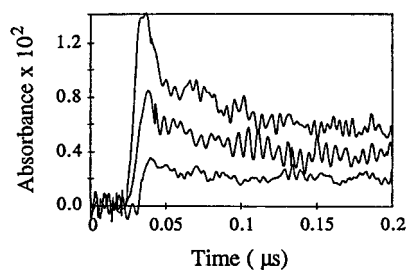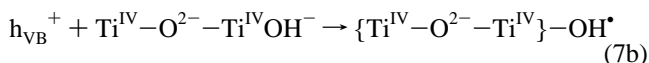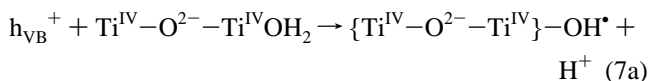**1690** *J. Phys. Chem. B, Vol. 102, No. 10, 1998*

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**Figure 1.** Typical nanosecond time profiles in the absence of added scavenger. "Dry" alkaline form of $TiO_2$. Measured at 600 nm. Each trace represents an average of 40 laser pulses. Intensities: $1.8 \times 10^{-9}$, $7.1 \times 10^{-9}$, and $2.9 \times 10^{-8}$ einstein/pulse, respectively (of which 92% is absorbed by the layer).

trapped electron–hole recombination and for photocatalyzed redox chemistry,[22] although there is evidence that hole transfer to scavengers successfully competes with mobile electron–hole recombination.[25,32,33]

The trapped positive hole, $h_{tr}^+$, has been assumed to be a surface bound OH radical, produced by oxidation of surface water or $OH^-$ ions (reaction 7a or 7b, respectively).

$$h_{VB}^+ + Ti^{IV}-O^{2-}-Ti^{IV}OH_2 \rightarrow \{Ti^{IV}-O^{2-}-Ti^{IV}\}-OH^\bullet + H^+ \quad (7a)$$

$$h_{VB}^+ + Ti^{IV}-O^{2-}-Ti^{IV}OH^- \rightarrow \{Ti^{IV}-O^{2-}-Ti^{IV}\}-OH^\bullet \quad (7b)$$

Diffusion of OH radicals to the bulk has also been suggested.[7] Evidence supporting one or another form of OH radicals (surface OH or free OH) as the active species include detection of hydroxylated intermediates,[2,3,6–8,11,13,34–38] distribution of the hydroxylation products,[2,34,35,39] competition kinetics,[34,35] kinetic isotope effect,[40] and spin trapping with subsequent ESR detection.[41] Pulse radiolysis showed that OH radicals react with $TiO_2$ colloid particles at a diffusion-controlled rate. The product was identified as a trapped hole at the particle surface or bound OH radical.[42] Popular electron scavengers are viologens,[38,43–48] oxygen, and hydrogen peroxide. Oxygen[49] and hydrogen peroxide[50–52] have been reported to increase the yield of reacting holes.

It has been shown that different methods of preparation of $TiO_2$ may induce different behavior under otherwise identical conditions.[28,22,53] This might introduce uncertainty when a unifying interpretation is based on results of different preparations. On the other hand, the picosecond decays of the electron signal in $TiO_2$ dry powders and in aqueous colloids of Q-particles are quite similar.[25,26]

The present paper concerns nanosecond kinetics in dry $TiO_2$ layers, as well as in layers immersed in various solutions. Earlier studies of a similar kind were carried out in colloid solutions and powders. There are inherent differences between laser photolysis of layers and solutions; the most pronounced one is the high local concentrations of reactive species compared to normally applied solute concentrations. Thus, depletion of scavengers, if present at low concentrations, may be more important than in solution. On the other hand, very high concentrations of scavengers could be used at any desired pH without changing the nature of the visibly totally transparent layers. The discussion of our results is based in part on comparison to previous work, which was mostly carried out using different $TiO_2$ preparation methods. As will be seen later, the nanosecond time profiles in the present work, even in the dry state (Figure 1), are very similar to other $TiO_2$ preparations,

e.g., colloid solutions prepared by hydrolysis of $TiCl_4$. In the absence of evidence to the contrary, a reasonable working assumption is that different $TiO_2$ preparations are qualitatively similar.

## Experimental Section

**The Pulsed Laser System.** The third harmonic light from a Lumonix YM-800 Q-switched Nd:YAG Laser was used for excitation. The output power was 160 mJ/pulse at maximum with a duration of 7ns in fwhm; however, it was necessary to detune the crystals to lower the output power. Light signal was monitored by a Hamamatsu R1913 photomultipler with five dinodes through a Ritsu-Oyo-Koken MC-10N monochromator. A SA-200E xenon flash lamp from Eagle Shoji Co. Ltd. and a PS-300 300 W CW xenon lamp from Ewig Shokai were used as monitoring light sources. The transient signals were recorded using a Tektronix TDS520 digital oscilloscope with an Epson PC286VG computer, averaging up to 120 pulses (usually 20–40 pulses were required for a good average) depending on the pulse intensity used. In some cases, when the absorbance change was sufficiently large, single pulses were taken. No effect of the number of accumulated pulses was observed.

**Actinometry and Determination of Quantum Yields.** Actinometry was carried out applying air-saturated $5 \times 10^{-3}$ M $Ru(bpy)_3^{2+}$ solution between two glass plates spaced at 0.021 cm. Absorbance at 355 nm, the excitation wavelength, was 0.593. Bleaching due to excitation was measured at 480 nm, and calculation of photon flux was carried out using $\Delta\epsilon_{480} = \epsilon_{480}(Ru(bpy)_3^{2+}) - \epsilon_{480}(Ru(bpy)_3^{2+*}) = 3430$ $M^{-1}$ $cm^{-1}$. Actinometry was carried out at 25% of the maximum pulse intensity used in this work. At this intensity, biphoton reaction did not occur, as the concentration of the $Ru(bpy)_3^{2+*}$ triplet was small compared to the ground state. This was verified by the absence of any transient absorbance change at 510 nm, typical of Ru(I), which is produced at the highest intensity because of biphoton formation of hydrated electrons, which subsequently reduce $Ru(bpy)_3^{2+}$.

The highest laser pulse intensity under our conditions was $3.0 \times 10^{-8}$ einstein/$cm^2$ per pulse; 92% of it has been typically absorbed by the $TiO_2$ layers. Unless otherwise stated, this intensity has been used in the reported experiments. Light losses because of scattering were negligible. Lower pulse intensities obtained by introducing appropriate $NiSO_4$ solutions between the laser source and the samples were calculated from the apparent absorbance of the $NiSO_4$ solutions (spectrophotometrically measured vs air). No bleaching of the $NiSO_4$ absorbance by the laser pulse is expected because of the high concentrations employed. Quantum yields of $I_2^-$ have been determined by comparison of the absorbance change at 390 nm ($\epsilon_{390}(I_2^-) = 9400$ $mol^{-1}$ $cm^2$).

**Materials.** $TiO_2$ layers were prepared on ITO surface (Geomatec's, 10 ohm/square) using $TiO_2$ nanocrystallites dispersed in water at pH 2.5 (300 g/L, containing 1 wt % Triton x-100) by successive spin coatings followed by heating at 450 °C. Accumulated $TiO_2$ amounted to approximately 1 mg/$cm^2$, with absorbance of 1.1 at 355 nm. $TiO_2$ was prepared by hydrolysis of the respective propoxide at acid pH. The ITO plate carrying the $TiO_2$ layers, with the dimensions $0.85 \times 5$ cm, was coupled with a bare plate of similar dimensions. The two plates where separated by a thin Teflon spacer and tightly held together by means of an appropriate slit at the Teflon base at the bottom of a four-window plastic cell. A specially fitted cover held the two plates tightly together at the top. The cell was flushed with Ar gas for at least 20 min prior to photolysis;
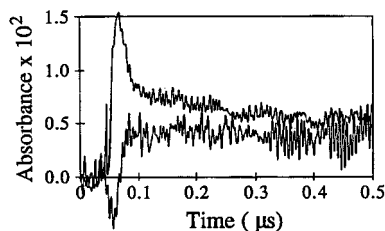
Titanium Dioxide Nanocrystalline Layers

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**Figure 2.** Absorption vs time profiles in the presence of 7 M NaClO$_4$: upper, 600 nm; lower, 390 nm.
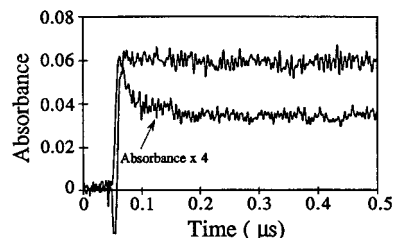


**Figure 3.** Effect of concentrated iodide on the time profiles at 390 and 600 nm. TiO$_2$ layer in the basic form. In contact with 5.3 M KI solution (neutral, not buffered). Upper, 390 nm; lower, 600 nm, vertical scale amplified ×4.
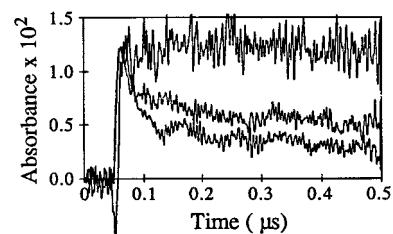


**Figure 4.** Effect of moderate iodide concentrations on the absorption vs time profiles. Acidic TiO$_2$ layer. Upper: 0.53 M iodide, 390 nm. Absorption normalized to initial signal at 600 nm dividing by a factor of 2.5. Middle: 0.53 M iodide, 600 nm. Lower: 600 nm, no iodide.

however, flushing for 15 h gave identical results. Wet surface was obtained upon addition of air free 150 $\mu$L solution with which the TiO$_2$ had been equilibrated before. The laser light was absorbed by the TiO$_2$ before reaching the solution between the plates. The liquid filled the space between the plates due to capillary forces. Equilibration with an electron or hole scavenger was carried out by shaking with 3 cm$^3$ of appropriate scavenger solution at pH 2 (HClO$_4$, in the following "acidic form") or at pH 7.2 (2 mM phosphate buffer) or pH 10.5−12 (NaOH), "basic form". Nafion has been adsorbed to the TiO$_2$ by shaking 48 h with a polymer solution (0.9% Nafion or 1% poly(vinyl alcohol)). Pure solvents and concentrated solutions (alcohols, CCl$_4$, CCl$_4$/CBr$_4$, H$_2$O$_2$) were shaken for a few minutes after preequilibration with acid or base. All the materials were of the highest available purity and were used as received.

**Results and Discussion**

We measured absorption vs time profiles in the ranges 390−750 nm and 10−3600 ns. Typical results using dry TiO$_2$ layers in the absence of scavenger are shown in Figure 1. These results are very similar to earlier observations in colloid solutions prepared by hydrolysis of TiCl$_4$.[21,31] In the absence of scavengers, the traces in both dry and wet TiO$_2$ are very similar. Both initial absorbances and time profiles are unaffected by variation of the pH (between 2.5 and 12), although this has a remarkable effect on the TiO$_2$ surface charge. Adsorption of the negatively charged Nafion from acidic solutions, immersion in concentrated NaClO$_4$ solution (up to 7.6 M, see Figure 2), or removing the water at 450 °C (16 h) and then applying pure dried (by CaCl$_2$) CCl$_4$ or 1:1 w/w CBr$_4$ in CCl$_4$ has no observable effect. These results imply that, in the absence of reactive scavengers, the initial absorption and decay kinetics of the visible absorption in the given time range is not affected by the state of the TiO$_2$ surface. The pronounced effects (which will be shown later) of hydrogen peroxide, iodide, and alcohols must be attributed to chemical reactions. Note that steady-state photolysis shows that CCl$_4$ and CBr$_4$ undergo dehalogenation by TiO$_2$ electrons.[54] The yields are apparently too small to affect the electron time profiles under our conditions.

In contrast to the decay at 600 nm (Figures 1 and 2), the absorbance at 390 nm is stable at least in the range 40−3600 ns (see Figure 2). This is in line with the earlier observations in the time range 5−100 ns, showing faster decay at longer wavelengths.[21,31] The contrast between the UV and visible time profiles suggests that at least part of the above nanosecond decay of the electron absorption in the visible range does not represent reaction with holes (absorbing light at 390 nm). Nevertheless, the nanosecond time range is commonly believed to be highly significant both for recombination of holes with trapped electrons and for the photocatalyzed redox chemistry.[21,22,31] In view of this we studied the effect of high iodide concentrations which replace the holes with the less reactive I$_2^-$ ion radicals.

Moreover, the latter have very strong absorption at 390 nm, which makes it easy to compare the time profiles of the electron and the new surface hole. This will be described in the following section.

**The Iodide Scavenger.** Considerable work has been carried out using iodide ions,[29,38,48,55−57] mostly in colloid solutions where precipitation limits the iodide ion concentration. The study of transparent porous layers does not have this limitation. Earlier works show contradictory results: Henglein[29] reported a quantum yield $\Phi(I_2^{\bullet-}) = 0.16$ at 2 M iodide in strong acid (flocculation probably took place during experiments). Moser and Graetzel[55] reported a higher (limiting) yield, $\Phi(I_2^{\bullet-}) = 0.42$ in 0.7 M NaI at pH 2, while Grabner and Quint[48] reported a limiting yield $\Phi(I_2^{\bullet-}) = 0.20$ in 0.1 M KI at pH 1. Fitzmaurice, Frei, and their co-workers[56,57] observed the formation and decay of I$_2^{\bullet-}$ ion radicals by their 750 nm absorption band in photosensitized TiO$_2$ sols. Bimolecular decay of the I$_2^{\bullet-}$ ion radical takes place in the millisecond time range.

To further study the nature of the visible decay in the nanosecond time range, we immersed TiO$_2$ layers in solutions containing iodide ions at concentrations up to 8 M (nearly saturated NaI). We monitored the absorption of I$_2^{\bullet-}$ at 390 nm, $\epsilon = 9400$ M$^{-1}$ cm$^{-1}$, and compared it with the time profile of the electron at 600 nm, where I$_2^-$ has only a small absorption ($\epsilon = 230$ M$^{-1}$ cm$^{-1}$).[58] The effect of 0.5−7.6 M iodide has been studied at both wavelengths (Figures 3 and 4). Unlike in colloid solution,[29] both acid and basic forms of TiO$_2$ (prepared by equilibration of the layer with 0.01 M HClO$_4$ or NaOH, respectively, washing excess acid or base with water) show similar results. At the highest laser pulse intensities used, the absorbance measured in the acid pH was somewhat higher (0.074 compared to 0.065 using the basic TiO$_2$). In all iodide systems the I$_2^{\bullet-}$ absorption at 390 nm shows only relatively little or no change up to 3.6 $\mu$s, in contrast with the 600 nm absorption. The initial absorption at 600 nm (after applying 25% correction for the contribution of I$_2^-$) and its decay profile were only little affected by the iodide. At all iodide concentrations the oxidation to I$_2^{\bullet-}$ is completed within the time resolution of the measurements (10 ns). Thus, if any TiO$_2$ holes are left

after 10 ns, they do not react with iodide ions, at least within the first 3.6 $\mu$s when the absorption of $I_2^-$ remains unchanged.

Quantum yields were determined by comparing the $I_2^-$ absorption to the bleaching of $Ru(bpy)_3^{2+}$ absorption at 480 nm using $\epsilon_{480}(Ru(bpy)_3^{2+}) - \epsilon_{480}(Ru(bpy)_3^{2+*}) = 3430$ M$^{-1}$ cm$^{-1}$. As expected, the quantum yield of $I_2^{\bullet-}$ decreases with increasing the pulse intensity. In 7.6 M iodide, the quantum yield decreases from 0.90 at $(0.5-1) \times 10^{-9}$ einstein/cm$^2$ per pulse to only 0.3 at $3 \times 10^{-8}$ einstein/cm$^2$ per pulse. (The latter is the highest intensity used; 92% of the photons are absorbed by the $TiO_2$.) Similarly, in 1 M iodide, the quantum yield decreases from 0.45 at $(0.5-1) \times 10^{-9}$ einstein/cm$^2$ per pulse to 0.16 at $3 \times 10^{-8}$ einstein/cm$^2$ per pulse. These results show that the iodide ion reacted with valence band hole within our resolution time and not with trapped holes. Had trapped holes been reactive toward iodide in the studied time range, an additional, relatively slower buildup of absorbance would have been observed. It may be argued that the additional buildup is not observed because it is superimposed with $I_2^{\bullet-}$ decay or, alternatively, that trapped holes react extremely fast with iodide, so that such reaction is completed during the laser pulse. The first argument can be ruled out because coincidental superposition may account for one specific iodide concentration at which the rate of formation and decay happen to be the same. We observe no significant change in $I_2^{\bullet-}$ absorbance after the end of the laser pulse in the entire range 0.5 M > $I^-$ > 7.6 M. The second argument is ruled out since it does not explain the observation that hole scavenging is completed by the end of the laser pulse while the $I_2^{\bullet-}$ absorbance increases strongly with iodide concentration without a parallel increase of the electron absorption at 600 nm. Thus, reaction of mobile holes with iodide as well as trapping of mobile holes must take place within the first 10 ns, in agreement with previous work.[22] At high iodide concentrations, such as in Figure 3, it is possible to achieve oxidation quantum yield of nearly unity (although at lower intensities), and therefore the only transients remaining at the end of the laser pulse are $I_2^{\bullet-}$ and electrons. Thus, the partial decay of the 600 nm absorbance cannot be largely due to reaction of electron with hole, because there is no hole other than $I_2^{\bullet-}$, and the latter is stable in the relevant time range (no comparable decay at 390 nm). We suggest that the partial decay of absorbance at 600 nm at high iodide concentration represents changes in electron trapping energy as deeper traps are being filled. The initial 600 nm absorbance in the presence of high iodide concentration at the highest pulse intensity is about 20% higher than in the iodide-free system. This small effect is surprising, because conversion of $TiO_2$ holes into the relatively unreactive $I_2^-$ radical ions is expected to increase the yield of electrons that escape recombination. Moreover, if the initial absorption is corrected for the absorption of $I_2^-$ at 600 nm (see above), the result is that iodide has hardly an effect on the initial electron yield observed after 10 ns. The fraction of absorbance decaying within the first 200 ns is 40% higher in the absence of iodide, but when corrected for the absorption of $I_2^-$, the respective ratio is only $\approx$1.2. Thus, comparison of the decay of the 600 nm absorption in the absence and presence of iodide suggests that even in the absence of iodide, electron–hole recombination is not the predominant process in the nanosecond time range. The lack of significant increase of the initial electron absorption at high iodide concentration means that under our conditions, when there is only one electron–hole pair per nanocrystallite, trapping of the electron proceeds with a quantum yield not much lower than unity. At higher electron and hole concentrations, fast
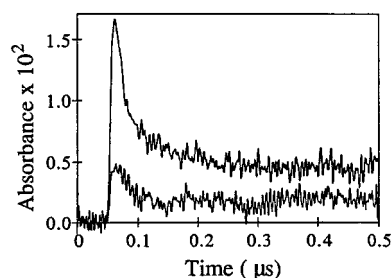
**Figure 5.** Effect of 100% 2-propanol on the transient absorption at 600 nm. $TiO_2$ layer was in the acidic form. Upper trace: no 2-propanol (dry layer, result identical with water-wet layer). Lower trace: layer equilibrated with 100% 2-propanol was in contact with 2-propanol during experiment.
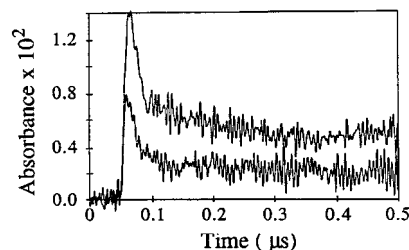
**Figure 6.** Effect of aqueous methanol on the transient 600 nm absorbance. $TiO_2$ layer in the acidic form. Upper trace, no methanol; lower trace, 20% (v/v) methanol present.

recombination channels of electrons and holes are opened, with which neither trapping nor iodide effectively competes.

The nearly plateau absorbance reached after about 100 ns in the presence of high iodide concentration represents electrons with $\epsilon_{600} = 8 \times 10^5$ mol$^{-1}$ cm$^2$ (corrected for $I_2^-$ absorption), in fair agreement with Kolle, Moser, and Graetzel.[27]

The earlier assignment of the visible decay in the nanosecond time range to electron–hole recombination was affected by the observation that the overall decay of the electron absorption is much more pronounced than the time-dependent spectral shift. However, gradual trapping of the electrons into deeper traps may be associated with a gradual decrease in extinction coefficient, although a decrease larger than 2-fold is not expected.[59] Additional contribution to the decay may include some electron–hole recombination, and besides, the decay may be affected by parallel formation of species that have little or no absorption in the visible, such as $Ti^{3+}$ centers.

Comparison of the results in the presence and absence of iodide shows that, under conditions where less than one electron–hole pair is produced in a nanocrystallite, most electrons escape recombination with holes even in the absence of iodide. At the highest laser pulse intensity used in this work the yield of electrons escaping recombination is $\Phi \approx 0.3$ after 100 ns. Recombination in the subnanosecond time range becomes increasingly important when the number of electron–hole pairs is increased.

**Alcohols**. Both in the pure state and in concentrated aqueous solution, alcohols have a remarkable effect on the visible absorption as demonstrated in Figures 5 and 6. Thus, pure alcohols, and to lesser degree alcohol–water mixtures, eliminate a substantial fraction of the initial absorption. To the best of our knowledge, no such observation has been reported so far. The remaining absorbance decays in a way comparable to the absence of alcohol. These results are in contrast with the increase in initial electron absorption signal which is expected if holes are removed by the alcohol. Moreover, no building up of absorbance as a result of electron injection from an alcohol

radical takes place up to at least 10 $\mu$s after the laser pulse. We noticed a very fast decay of the electron absorption during the laser pulse which is not always observed because of resolution limitation.

The $TiO_2$ layer became quickly damaged (probably because of dissolution) under the influence of repetitive laser pulses. No such effect is observed in the absence of alcohol. Figures 5 and 6 represent results before $TiO_2$ deterioration could be noticed.

According to Lawless, Serpone, and Meisel,[42] holes have no absorption at all in the visible, although Bahnemann et al.[30] have reported in platinized $TiO_2$ a broad band of hole absorption peaking at 450 nm with a significant contribution at 600 nm ($\epsilon_{600}/\epsilon_{390} = 0.55$). In any case, since we find that the ratio of the absorbance at 390 nm to the initial absorbance at 600 nm in the absence of scavengers, $D_{390}/D^0_{600}$, is only 0.25, one must conclude that the contribution of holes to the 600 nm absorption is <13% of the initial absorption. Thus, elimination of holes can have only a marginal direct effect on the absorption at 600 nm. Since alcohols are inert even toward the hydrated electron, one must consider an indirect alcohol effect.

One possibility is that reaction of an alcohol molecule with a hole does not "remove" the hole but converts it to adsorbed $ROH^+$ (reaction 8),

$$h^+ + ROH \rightarrow ROH^+ \qquad (8)$$

which is just another kind of hole. According to this hypothesis, $ROH^+$ reacts with the $TiO_2$ electron during the laser pulse, faster than does the original hole. Consequently, the initial observed electron absorption is lower in the presence of alcohol. This ultrafast back-reaction and lack of electron injection from the alcohol radical to the $TiO_2$ (at least before any surface damage is noticed) is in contrast with the clear evidence for electron injection from 2-propanol radicals, reported by Henglein.[29] The apparent contradiction can be resolved if one considers that the $ROH^+$ radical ion is produced according to reaction 8 at high alcohol concentration, while the $CH_3COHCH_3$ radical is obtained in moderate alcohol concentrations upon abstraction of hydrogen by the OH radical. Different hole reactions at low and high substrate concentrations have been previously noticed in the phenol system.[49] While electron abstraction with ultimate formation of a positive ion radical takes place at high phenol concentrations, OH additions to the aromatic ring occur at low concentrations. This has been attributed to competition between the substrate (phenol) and surface water for the $TiO_2$ hole oxidation. In the present case, $ROH^+$ and $CH_3COHCH_3$ produced by electron and hydrogen abstraction by mobile holes and adsorbed OH radicals, respectively, are expected to show a remarkable difference with respect to electron injection: $CH_3COHCH_3$ with the radical on the $\alpha$ carbon is a powerful reducing radical. Reaction of this radical with an electron is unlikely because the immediate product is an unstable carbanion. This is not the case for $ROH^+$, which regenerates the stable alcohol molecule upon reaction with an electron. When $ROH^+$ loses its proton, the product is the RO (radical on the oxygen), which is an oxidizing radical and cannot be involved in electron injection but is not an efficient electron scavenger either. (It reacts very slowly even with hydrated electrons.[60]) Thus, the proposed very fast recombination reaction must involve $ROH^+$ ion radicals and not RO. Since precisely the same results are obtained with both acidic and basic forms of $TiO_2$, the back-reaction between $ROH^+$ and the electron must be sufficiently fast as to successfully compete with deprotonation of $ROH^+$.
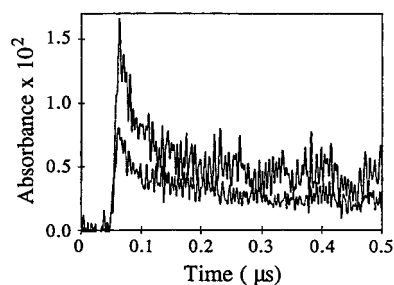


**Figure 7.** Effect of hydrogen peroxide on the 600 nm absorbance vs time profile. Acidic form of the $TiO_2$. Upper, no $H_2O_2$; lower, 0.27−4.4 M $H_2O_2$ (superimposed).

Suppression of the electron yield by elimination of electron traps at the $TiO_2$ surface (as a result of replacement of surface water by alcohol) is not likely to be the cause of the pronounced suppression of the electron absorption. As stated above, we failed to observe any effect on the initial electron absorption and its decay profile in the presence of chemically inert absorbants as well as when using dry $TiO_2$ surface. Note that 25% of the initially observed electron absorption that remains at the end of the laser pulse in the presence of 2-propanol decays with a time profile similar to that in the absence of alcohol. This is expected if the role of the alcohol is related to its chemistry, as opposed to indirectly a microenvironmental surface effect.

**Effect of $H_2O_2$.** The effect of hydrogen peroxide is shown in Figure 7. The initial absorption at 600 nm decreases by 50% in 0.27 M $H_2O_2$. No further decrease is observed at higher concentrations (up to at least 4.4 M). At the same time the initial absorbance change at 390 nm (about 0.005) is unchanged (0.9 M peroxide has been tested), although a partial decay with $\tau \approx 0.5$ $\mu$s is observed, compared to the plateau in the absence of peroxide. Only the acidic form of $TiO_2$ has been studied. (The basic form catalyzes $H_2O_2$ decomposition.) The effect of $H_2O_2$ is attributed to electron scavenging, taking place during the laser pulse. There is no effect of $H_2O_2$ on the electron decay profiles, suggesting reaction 9a between $H_2O_2$ and the conduction band electrons, while reaction 9b with trapped electrons is not observed under our conditions.

$$e_{CB}^- + H_2O_2 \rightarrow OH + OH^- \qquad (9a)$$

$$e_{tr}^- + H_2O_2 \rightarrow OH + OH^- \qquad (9b)$$
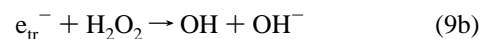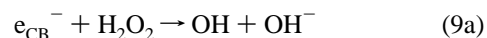
It may be of interest to compare our results with those reported by Sun and Bolton[50] although they used a different preparation of $TiO_2$. According to Sun and Bolton,[50] the limiting yield of OH radicals under steady-state illumination, 0.22, is reached at 0.018 M $H_2O_2$, compared to a yield of only 0.04 in the absence of $H_2O_2$. Over 50% of the limiting yield is reached already at 1 mM peroxide[50] compared to only 30% decrease of the initial electron absorption by as much as 90 mM $H_2O_2$ under our conditions. Thus, $H_2O_2$ is apparently by about 2 orders of magnitude more reactive under the steady-state conditions, although a higher limiting yield of 0.5 is obtained for electron scavenging under our conditions at much higher concentrations. It is possible to account for the pronounced difference by assuming that the different preparations of the $TiO_2$ powder[50] and layers (this work) somehow lead to very different results. An alternative explanation of this apparent discrepancy attributes the limiting yield of 0.22 to scavenging of trapped electrons at low hydrogen peroxide concentrations[50] (reaction 9b), as opposed to scavenging of conduction band electrons under our conditions.

Such an interpretation points to a problem of material balance in the steady-state work:  Since each electron reacting with $H_2O_2$ produces one OH radical, the yield of the trapped electrons under steady-state illumination must also be $\varphi = 0.22$.[50]  This yield is more than twice higher than in the respective $H_2O_2$ free system ($\varphi = 0.04$), while conversion of electrons to OH radicals by reaction with $H_2O_2$ is supposed to only double the yield. Note that the problem of material balance comes up irrespective of our results:  $H_2O_2$ reaction with conduction band electrons at concentrations as low as 1 mM has been invoked in order to account for the apparent lack of material balance.[50]  The unexpected plateau observed at $[H_2O_2] > 0.018$ M was attributed to reaction of $H_2O_2$ with OH.[50]  However, this interpretation is doubtful because $H_2O_2$ is known as a poor OH scavenger relative to methanol, while methanol was present at higher concentration,[50] making competition of $H_2O_2$ for OH unlikely.  In addition, competition is expected to lead to a maximum yield of formaldehyde (used as a measure for OH radicals), rather than a plateau.

If our suggestion that under the conditions of low $[H_2O_2]$ applied in the steady-state work[50] reaction 9b, and not reaction 9a, is responsible for electron scavenging is correct, material balance requires the existence of another kind of trapped holes ($\varphi = 0.18$), produced in parallel to OH ($\varphi = 0.04$) from the valence band holes.  These trapped holes may be $-Ti^{IV}-O^-$ (radical on the oxygen), reported in $TiO_2$ colloids at low temperature using EPR.[61]  The limiting yield of electron scavenging in this work may reflect saturation of the $TiO_2$ surface with $H_2O_2$.  More work related to material balance in different $TiO_2$ preparations is required.

## Conclusions

The most important conclusion of the present work is the high yield of electron trapping when only one electron−hole pair is produced in a given nanocrystallite and that most electrons are still present after several microseconds. The decay of absorption at 600 nm during the first 100 ns is assigned to changes of the spectrum as electrons migrate to lower traps, rather than electron−hole recombination.  This has been concluded on the basis of comparison between the visible (600 nm) and UV (390 nm) absorbance vs time profiles in the presence of high iodide concentrations and by comparing the 600 nm time profiles in the absence and presence of iodide.

In contrast to iodide ions, which protect the electrons by removing holes, high concentrations of organic compounds such as alcohols enhance electron−hole recombination by conversion of the holes into $ROH^+$ radical ions which presumably are more reactive with respect to recombination with electrons.

Another example of organic compounds that may be expected to react differently with OH and with holes are the carboxylates. OH radicals are expected to abstract $\alpha$ hydrogen, producing a free radical located on the carbon.  On the other hand, holes are likely to abstract a carboxy electron with subsequent decarboxylation.[62−66]  If the decarboxylation process competes effectively with $RCO_2$−electron recombination, the R radical produced by $RCO_2$ decomposition may give rise to further reduction rather than reoxidation of the $TiO_2$ electron.  This hypothesis may explain the very high decomposition yields that are observed in some of the carboxylate systems (e.g., degradation of dichloroacetate which proceeds with a quantum yield up to 0.6[67]), but it requires further study.

It may be argued that conclusions based on very high concentrations of scavengers may not apply to low concentrations.  Studies of systems in which the $TiO_2$ surface was changed by adsorption of chemically inert or nearly inert solutes, such as $H^+$, $OH^-$, Nafion, 7 M $NaClO_4$, dry $TiO_2$, and water-free $TiO_2$ in $CCl_4$, all show no affect on the time profile of the electron decay or on the initially observed absorption.  Moreover, the use of high bulk concentrations such as 0.5−7.6 M iodide, 20−100% alcohol, and 0.27−4.4 M $H_2O_2$ may at most saturate the surface.  The high bulk concentrations as such are meaningless under our conditions, as no reactions that could be attributed to scavenger molecules in the bulk have been observed.

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