

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231645047>

Shallow Electron Trap, Interfacial Water, and Outer-Sphere Adsorbed Oxalate IR Absorptions Correlate during UV Irradiation of Photocatalytic TiO₂ Films in Aqueous Solution†

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · JULY 2010

Impact Factor: 4.77 · DOI: 10.1021/jp102723u

CITATIONS

12

READS

24

3 AUTHORS:



David Michael Savory

University of Otago

4 PUBLICATIONS 38 CITATIONS

SEE PROFILE



David S. Warren

University of Otago

7 PUBLICATIONS 166 CITATIONS

SEE PROFILE



Alexander James Mcquillan

University of Otago

122 PUBLICATIONS 6,074 CITATIONS

SEE PROFILE

Shallow Electron Trap, Interfacial Water, and Outer-Sphere Adsorbed Oxalate IR Absorptions Correlate during UV Irradiation of Photocatalytic TiO₂ Films in Aqueous Solution[†]

David M. Savory, David S. Warren, and A. James McQuillan*

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand

Received: March 25, 2010; Revised Manuscript Received: May 23, 2010

IR spectroscopic analysis of thin particle film anatase-containing TiO₂ systems during UV irradiation and when immersed in acidic anoxic aqueous solution reveals a striking broad asymmetric IR peak $\sim 880\text{ cm}^{-1}$ extending to over 2000 cm^{-1} , which has been previously attributed to electron excitations from a shallow trap level. The observations of this broad IR absorption in quasi-vacuum conditions or in aqueous solutions appear contradictory but are explained by the absence of electron scavengers or hole scavengers, respectively. The broad IR absorption associated with the shallow electron trap becomes more pronounced with a decrease in pH from 5 to 2 and is greatly enhanced in the presence of adsorbed oxalate. Oxalate ion adsorption/desorption kinetics has been followed with IR spectroscopy during UV irradiation to show that the shallow trap IR absorption correlates with that of outer-sphere adsorbed oxalate acting as a hole scavenger. The IR spectra indicate the involvement of interfacial water in the electron trapping, probably via bridged hydroxyl groups which are more prevalent under acidic solution conditions.

Introduction

In spite of considerable research effort to understand the complexities of photocatalytic processes at ‘dry’ and water-immersed TiO₂ surfaces,^{1,2} there remain many unanswered questions. In situ spectroscopic analysis of working photocatalytic systems has offered hope of revealing mechanistic details not readily obtained from macroscopic measurements. However, the occurrence of reduction and oxidation processes in concert at particle surfaces presents difficulties in attributing spectroscopic observations to specific reactions.

There have been many in situ spectroscopic studies of photocatalytic systems, including those by UV–vis absorption and EPR spectroscopies^{1,3} but relatively few infrared spectroscopic investigations.^{4–8} When attenuated total reflectance infrared (ATR-IR) spectroscopy was utilized to monitor the oxidation of adsorbed glyoxylic acid to adsorbed oxalate during TiO₂ photocatalytic processes in aqueous acidic solution, Ekström & McQuillan⁹ observed a broad asymmetric absorption peaking at $\sim 880\text{ cm}^{-1}$, which was tentatively attributed to a surface peroxo species. Nakamura et al.¹⁰ also used ATR-IR to study anatase TiO₂ under aqueous alkaline photocatalysis conditions and attributed an asymmetric band peaking at 943 cm^{-1} to a Ti–(O–O) surface peroxo species. Subsequent transmission IR work on TiO₂ in quasi-vacuum conditions by Yamakata et al.,¹¹ Szczepankiewicz et al.,¹² in which a similar broad absorption was observed, suggested an origin from intraconduction band or shallow trap electron excitations. Warren & McQuillan¹³ confirmed the shallow trap explanation using ATR-IR spectroscopy and suggested that the $\sim 880\text{ cm}^{-1}$ peak corresponds to the shallow trap excitation threshold. More recent work by Panayotov & Yates¹⁴ has shown that a similar broad IR absorption is observed when atomic hydrogen is introduced to TiO₂ at low pressure in the absence of UV

irradiation. Thus, it seems paradoxical that the broad asymmetric IR absorption, probably related to shallow electron traps, is observed both under aqueous solution conditions, and in quasi-vacuum conditions where the removal of water is observed to increase the IR absorption intensity¹³ and presence of water diminishes it.¹²

In this report, we have used in situ IR spectroscopy to monitor the absorptions corresponding to the presence of shallow electron traps, interfacial water, and of adsorbed oxalate species on UV-irradiated TiO₂ particle films immersed in aqueous solutions. The relationships demonstrated in this study between shallow electron traps, adsorbed oxalate species, TiO₂ surface groups, and interfacial water provide new insights into interfacial photocatalytic processes and opportunities for further such studies.

Experimental Section

Materials and Film Preparation. TiO₂ powders were used as received to prepare aqueous suspensions of 1 mg mL^{-1} concentration for film creation. Suspensions were prepared using deionized water (Millipore, Milli-Q, resistivity $18\text{ M}\Omega\text{ cm}$) and were sonicated for a duration of 30 min prior to film creation (Bandelin Sonorex). Thin films were prepared by depositing $10\text{ }\mu\text{L}$ of the suspension on the ATR prism, followed by 15 min drying under a diaphragm pump vacuum ($\sim 10^3\text{ Pa}$). Prior to preparation of TiO₂ thin films the diamond-surfaced ATR prism surface was cleaned by polishing with $0.015\text{ }\mu\text{m}$ γ -alumina aqueous slurry on a Buehler microcloth. Chemicals used in the flow experiments or for the purposes of adsorption: glyoxylic acid monohydrate (Merck, >97%), sodium oxalate (BDH, 99.5%), glycolic acid (DuPont, 99%), sodium chloride (LR grade), sodium hydroxide (AR grade), and hydrochloric acid (AR grade) were used for solution pH adjustments. Solution sparging was performed with nitrogen (BOC, oxygen-free).

Infrared Analysis. ATR-IR spectroscopy facilitates the spectroscopic monitoring of thin particle film surface chemistry

[†] Part of the “Alfons Baiker Festschrift”.

* To whom correspondence should be addressed. E-mail: jmcquillan@chemistry.otago.ac.nz. Phone: +64-3-479-7928. Fax: +64-3-479-7906.

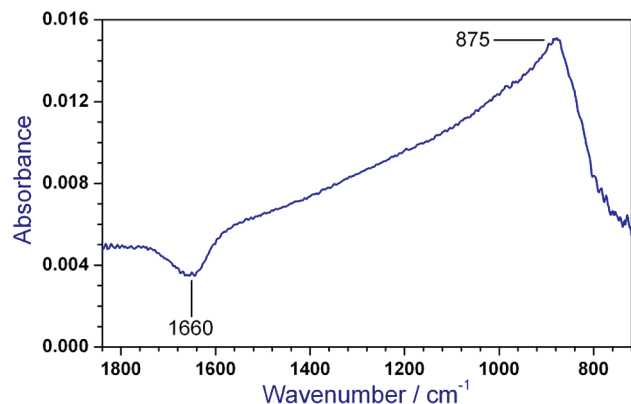


Figure 1. IR spectrum collected during initial 80 s UV irradiation of 400 nm anatase particle film immersed in pH 2.3 HCl aqueous solution. Background spectrum from system prior to UV irradiation.

concomitant with UV irradiation. A DuraSamplIR 3 mm diameter diamond-faced 3 reflection ZnSe prism (ASI sensIR Technologies) was used for this purpose. This accessory has a chemically inert diamond surface, which is effective in isolating any influence of the ZnSe on the TiO₂ during band gap irradiation. Films were immersed under a solution flow using a flow cell setup (Supporting Information) at a flow rate of ~ 2 mL min⁻¹ achieved with a peristaltic pump (Cole Parmer, Masterflex C/L). It was established that preliminary cleaning of the TiO₂ films with an alkaline washing procedure⁹ had little influence on the observed results so was not always employed. ATR-IR spectra were collected at 22 °C over 64 scans using a Digilab Excalibur Series FTS4000 at a resolution of 4 cm⁻¹. With this spectrometer and the ATR prism a lower frequency spectral cutoff of 650 cm⁻¹ is observed. UV irradiation of films was achieved using a 2.5 mW 375 nm light-emitting diode at an applied current of 10 mA, producing a light intensity of ~ 1 mW cm⁻². See Supporting Information for full experimental details.

Results and Discussion

In the present study, thin TiO₂ particle films were created from TiO₂ powders to monitor under aqueous conditions the IR spectroscopic behavior during 375 nm UV irradiation. Various TiO₂ samples ranged from the widely studied industrial photocatalyst, Degussa P25 ($\sim 75\%$ anatase, $\sim 25\%$ rutile) to large and small particle anatase and rutile polymorphs. The immersion of a large particle anatase film (~ 400 nm) in nitrogen-sparged flowing pH 2.3 HCl aqueous solution, and subsequent UV irradiation via a glass-covered flow cell, immediately produced a prominent IR absorption peaking at ~ 875 cm⁻¹ having an attendant broad, almost featureless absorption tailing to above 2000 cm⁻¹ (Figure 1) and a concomitant absorption loss peaking about 1660 cm⁻¹. The absorption at ~ 875 cm⁻¹ is consistent with electronic excitation from a shallow trap to a continuum of states in the conduction band,¹¹ although intraconduction band transitions may also contribute to this absorption.¹¹

Previously, similar broad IR absorptions have been observed under dry conditions at the solid/gas interface,^{11,12} and indeed as a result of deliberate removal of surface water,¹³ thus observation of this shallow trap related absorption under aqueous conditions is unexpected. It has been established that the hydration of TiO₂ particles significantly affects electron and hole trapping and that anhydrous conditions do not often exhibit behavior relevant to aqueous media.¹⁵ The absorption loss at

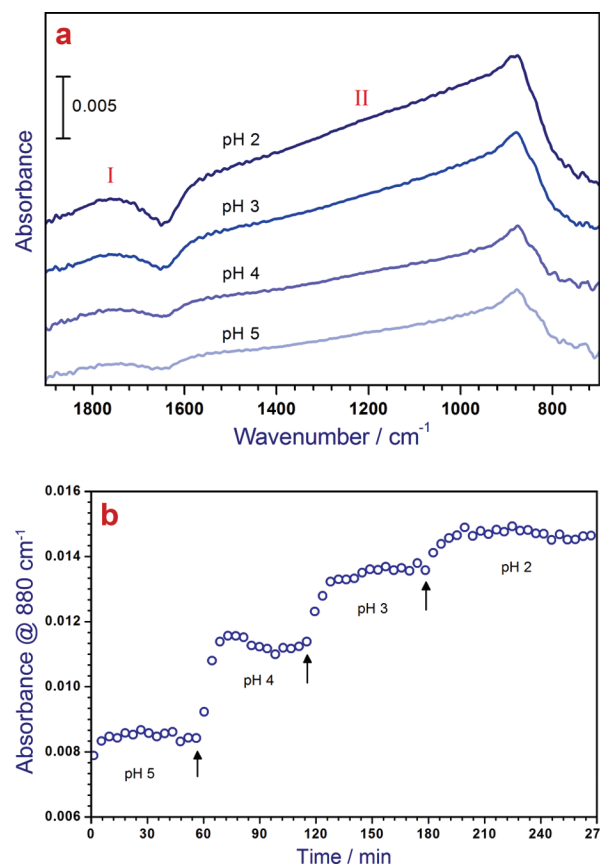


Figure 2. (a) Spectra showing the variation in shallow trap-related absorption at ~ 880 cm⁻¹ over time during flowed immersion of a 400 nm anatase film in different pH HCl solutions. Background spectrum for these measurements was at pH 6 before UV irradiation. Numerals I–II indicate the spectral features attributed to H₃O⁺. Spectra are offset but on the same absorbance scale. The film was immersed in pH 6 solution followed by stepwise pH decreases. All solutions were at a constant ionic strength of 1×10^{-2} M, adjusted using NaCl. (b) Plot of the temporal variation of absorbance of the peak at ~ 880 cm⁻¹ during immersion in consecutively lower pH solutions. Arrows indicate times at which the pH was changed.

1660 cm⁻¹ occurs on initiation of UV irradiation and is most likely due to reaction of a water-related TiO₂ surface species, as the peak wavenumber of the bending mode vibration of bulk water is about 1635 cm⁻¹.¹⁶

The pH dependence of the appearance of the shallow trap IR absorption was evaluated for the ~ 400 nm anatase thin films. The intensity of the ~ 880 cm⁻¹ absorption during flowed immersion in consecutively lower pH solutions was recorded and the data is presented in Figure 2. These experiments showed that the IR band could be observed with acidic media (pH ≤ 5) but was diminished at pH > 6 and absent at pH > 8 . This observation suggests that a modification of TiO₂ under acidic conditions favors the population of the electron trap state. Part a of Figure 2 shows the spectral changes associated with stepwise decreasing pH and the significant enhancements of both shallow trap absorption and water loss at 1660 cm⁻¹. Part b of Figure 2 illustrates how the absorbance at 880 cm⁻¹ changes with solution flow time and clearly shows a pronounced and rapid response to pH changes. Additionally, there appears to be a small absorption centered at ~ 1750 cm⁻¹ (I of part a of Figure 2) and a weak, broad absorption centered at ~ 1200 cm⁻¹ (II of part a of Figure 2), which are typical of H₃O⁺.¹⁷

The absorption loss at 1660 cm⁻¹ (Figure 1) is at a greater wavenumber than that of bulk water and must correspond to

strongly hydrogen-bonded interfacial water.¹⁸ The frequency of this vibration is lower than what would be expected for an H_3O^+ -like species.^{16,19,20} There is little corresponding absorption loss in the O–H stretching region centered at $\sim 3200\text{ cm}^{-1}$ (not shown). Furthermore, the absorbance loss at 1660 cm^{-1} correlates with and is proportional to the absorbance increase at 875 cm^{-1} . The loss of this water species absorption could therefore result from the formation of the trap state itself. These water absorption changes may be explained by the conversion of an interfacial water species to an interfacial hydroxyl group.

A comparable experiment involving a particle film of Degussa P25 immersed in acidic aqueous solution gave insignificant spectral changes with UV irradiation. Degussa P25 contains a mixture of rutile ($\sim 85\text{ nm}$) and anatase ($\sim 30\text{ nm}$).²¹ Similar observations were obtained with small particle ($\sim 18\text{ nm}$) anatase, $\sim 40\text{ nm}$ rutile, and $\sim 300\text{ nm}$ rutile particle films. However, the UV irradiation of Degussa P25 particle films in $10^{-3}\text{ mol L}^{-1}$ sodium oxalate aqueous solution at pH 2.3 resulted in the appearance of an intense shallow trap IR absorption. Similar observations were made with P25 in corresponding solutions of glyoxylic and glycolic acid. The addition of oxalate ion to the solution in the 400 nm anatase particle film experiment resulted in significant enhancement of the broad band IR absorption. Small particle anatase also displayed this absorption in the presence of adsorbed oxalate, while both rutile TiO_2 samples did not.

A flow experiment under constant UV irradiation involving the initial adsorption to Degussa P25 TiO_2 of oxalate from a $10^{-3}\text{ mol L}^{-1}$, nitrogen-sparged HCl solution at pH 2.3, followed by the desorption of the adsorbed oxalate into the corresponding oxalate-free solution, was most revealing. Such experiments in the absence of UV light have recently been reported.²² The film was initially exposed to pH 2.3 HCl solution and the IR difference spectra in part a of Figure 3 show the time dependence of the response to oxalate adsorption. Initially there is a dramatic increase in the shallow trap absorption which dominates the spectral changes, as well as growth in superimposed adsorbed oxalate peaks at 1721, 1410, 1308, and 1256 cm^{-1} . The stronger peaks at 1721, 1410, and 1256 cm^{-1} correspond to inner-sphere coordinated oxalate while the weak peak at 1308 cm^{-1} is from outer-sphere adsorbed oxalate.^{22,23} The 1308 cm^{-1} peak is initially more prominent due to influence of the positive TiO_2 surface charge and diminishes as the coordinated oxalate becomes more dominant, thereby reducing the net surface charge.²⁴ Adsorption saturation under these conditions was rapidly reached (part a of Figure 3) and after 40 min the desorption phase was commenced (part b of Figure 3). It is noticeable that the peaks corresponding to the inner-sphere and outer-sphere adsorbed oxalate species have different absorbance decay rates as illustrated in Figure 4, which is consistent with the different adsorption affinities of the different adsorbed species.²² Here, it is clearly shown that the broad band IR absorption correlates closely with that of the outer-sphere adsorbed oxalate.

Oxalate ion is a hole scavenger and this behavior is expected to be more pronounced for outer-sphere adsorbed species than inner-sphere adsorbates, due to the altered redox behavior of solution oxalate ion when it becomes adsorbed by inner-sphere coordination to surface Ti(IV) ions. The coordinatively adsorbed oxalate reactant is more strongly adsorbed than the carbon dioxide product leading to the oxalate ion oxidation occurring at a more positive potential.²⁵ This consideration suggests that the diminution of the broad band IR absorption shown in part b of Figure 3 is the result of the reduction in efficacy of oxalate

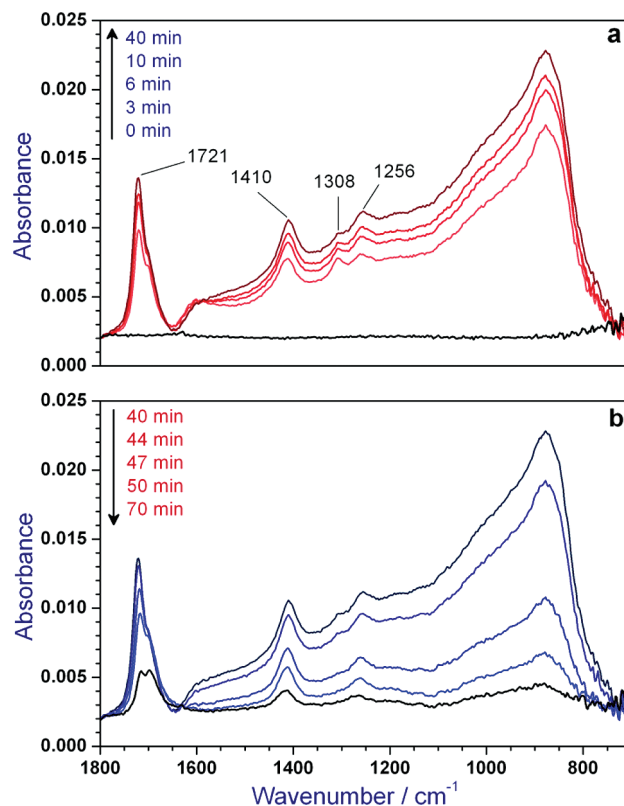


Figure 3. IR spectra of UV-irradiated Degussa P25 TiO_2 film collected during (a) adsorption from $10^{-3}\text{ mol L}^{-1}$ oxalate and (b) desorption. All solutions were adjusted to pH 2.3 with HCl. Background spectrum from UV-irradiated system prior to adsorption. All spectra given same absorbance at 1800 cm^{-1} .

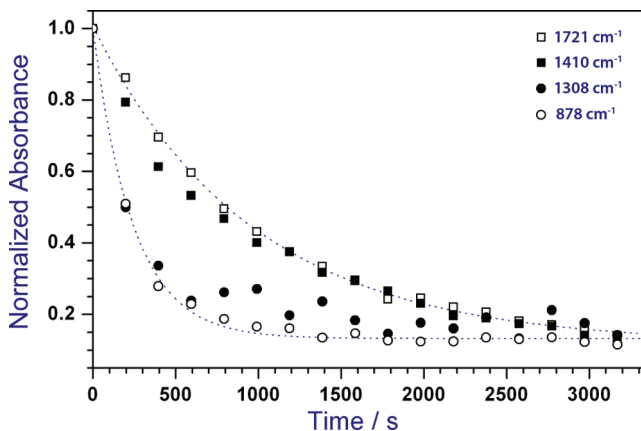


Figure 4. Temporal behavior of adsorbed oxalate peak intensities during the desorption phase (part b of Figure 3). Peak absorbances are normalized for comparison purposes and were derived from the observed spectra by subtraction of the broad shallow trap background. Dashed lines emphasize the different decay trends.

hole scavenging. At much lower oxalate concentrations where there is a greater predominance of inner-sphere adsorbed oxalate,²² albeit at a lower surface concentration, the shallow trap absorption is still present, indicating that both forms of adsorbed oxalate under these conditions may contribute to the appearance of the broad IR absorption.

The UV irradiation of TiO_2 creates electron and hole pairs, which readily recombine in the absence of local trap states and/or an electric field promoting their separation. In the above experiments, the presence of adsorbed oxalate provides a hole trapping pathway, which reduces surface recombination and

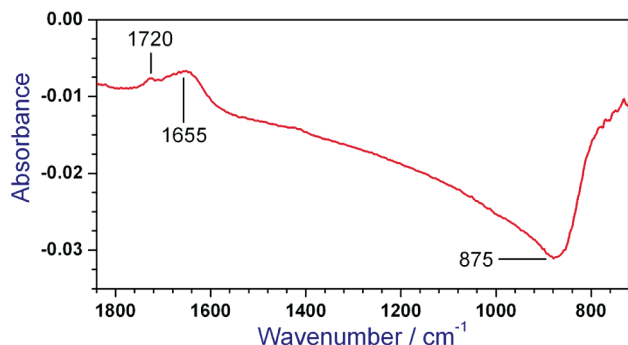
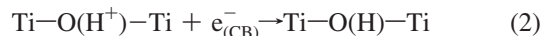
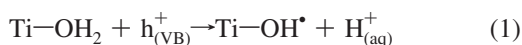


Figure 5. IR difference spectrum showing loss of the shallow trap IR absorption and regeneration of the $\sim 1660\text{ cm}^{-1}$ water related signal, as a result of introduction of oxygen to a flowed solution of $10^{-3}\text{ mol L}^{-1}$ oxalate at pH 2.3 under UV irradiation. The small peaks at 1720 and 1410 cm^{-1} arise from a change in the amount of adsorbed oxalate. Background spectrum from system immediately prior to O₂ introduction.

facilitates the persistence of electrons, allowing them to migrate to shallow traps of energy $\sim 0.1\text{ eV}$ below the CB edge. The observations on different TiO₂ polymorphs suggest the shallow trap is specific to anatase, while more significant shallow trap absorption on large particle anatase suggests bulk properties have an important influence. Given that larger particle size TiO₂ during UV irradiation has more extensive band-bending with a larger space-charge region,²⁶ recombination may be reduced in the 400 nm anatase allowing for significant shallow electron trapping in the absence of a hole scavenger. Additionally, if photogenerated holes are primarily trapped at surface sites²⁷ in mixed-phase TiO₂, rapid recombination with electrons trapped at surface-localized trap sites would be expected. In a repeated adsorption/desorption experiment, the switching to an oxygen-saturated solution resulted in rapid and complete loss of the shallow trap IR absorption with concomitant absorption gain in the water bending mode region, as shown in Figure 5. This observation appears to indicate that the $\sim 1660\text{ cm}^{-1}$ absorption gain is a direct consequence of the blocking of shallow electron trapping. Our several IR experiments with UV-irradiated TiO₂ have indicated that the 1660 cm^{-1} absorbance loss occurs at the same rate as the shallow trap absorbance gain.

Recently Panayotov and Yates¹⁴ showed that a similar broad IR absorption was observed with atomic hydrogen-treated Degussa P25 TiO₂ at 0.2 Torr H₂ pressure in the absence of UV irradiation. They attributed the IR absorption to electron excitations from shallow traps populated via the atomic hydrogen induced production of Ti–O(H)–Ti groups, which donate electrons to shallow traps, leaving Ti–O(H⁺)–Ti bridging hydroxyl groups. The pH dependence of the shallow trap related absorption observed in our experiments may indicate that electron trapping by Ti–O(H⁺)–Ti groups, only formed under acidic conditions, provides an alternative route to Ti–O(H)–Ti structures and ensuing population of the shallow electron trap state responsible for the broad IR absorption. The reduction of Ti–O(H⁺)–Ti by UV-generated CB electrons may therefore diminish the absorption of a water species associated with this charged surface group. Possible simple mechanisms for these observations under acidic aqueous conditions are presented in Figure 6.



Mechanism A represents a closed loop with charge conservation at the TiO₂ surface and introduction of h^+ and e^- generated by UV irradiation. Reactions 1 and 2 represent the formation of a bound hydroxyl radical via h^+ oxidation of adsorbed water and the electron trapping at bridging hydroxyl groups, respectively. Reaction 3 represents the net overall process occurring at the TiO₂ surface. Figure 6 also presents an alternative mechanism (B) with an equivalent outcome involving a second water molecule. Such a water molecule could facilitate electron transfer from the initial Ti–OH₂ hole capture site to the bridging hydroxyl group in a way similar to that proposed by Mattioli et al.,²⁷ in which a strongly hydrogen bonded bridging water molecule is involved. However, such behavior would require CB electron reduction of the nascent terminal Ti–OH[•] group immediately following hole capture by the Ti–OH₂ group initially involved. Such an occurrence is unlikely given that recombination would be the expected outcome.

With termination of UV irradiation the water species with IR absorption at 1660 cm^{-1} reappears, similarly to Figure 5. This band regenerates rapidly in pH 6 conditions, indicating that the associated species is probably not involved in the acidic conditions shallow electron trap requirement. It is apparent from the pH variation data (Figure 2) that there is an increase in surface-localized H₃O⁺, indicated by a hump at $\sim 1750\text{ cm}^{-1}$ and a broader absorption around 1200 cm^{-1} (part a of Figure 2, features I and II), both of which increase as pH is lowered, in agreement with the IR absorptions being associated with H₃O⁺.¹⁷ Although this will primarily come from the decreasing pH of flowed solution, similar but weaker absorptions are observed as a result of prolonged UV irradiation of 400 nm anatase films immersed in acidic solutions. The precise spectroscopic monitoring of a small decrease in surface pH is difficult due to the relatively weak absorptions of H₃O⁺ but is in agreement with the proposed mechanisms for trap formation. A similar broad absorption centered around 2000 cm^{-1} is apparent in the work of Panayotov and Yates.¹⁴ However, this is observed at higher

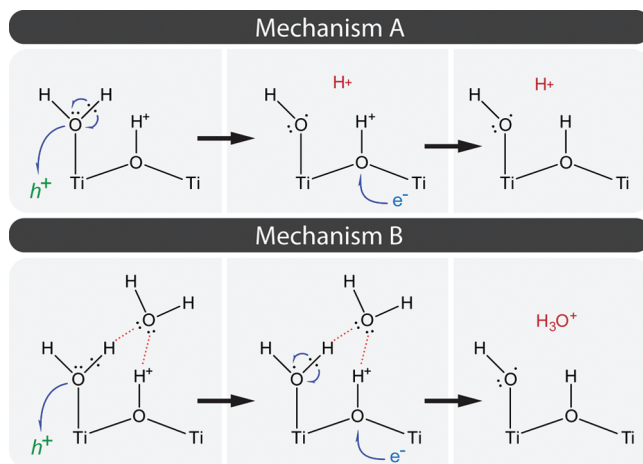


Figure 6. Schematic showing proposed mechanisms for the oxidation of an adsorbed water species to an adsorbed hydroxyl radical during the formation of the Ti–O(H)–Ti species responsible for population of the shallow trap state. The lower panel shows an alternative mechanism with an equivalent outcome involving a second water molecule during the formation of Ti–OH[•].

wavenumber than those in the present work and under non-aqueous conditions, so is undoubtedly from a different source. Detection of any such TiO₂/aqueous interface absorption in the present work is prevented by the strong absorption of the diamond prism in the $\sim 1850\text{--}2400\text{ cm}^{-1}$ range.

The apparent correlations between IR spectroscopic observations related to shallow electron traps, interfacial water, and adsorbed hole scavengers encourages interpretation of these observations in terms of the photocatalytic interfacial reactions. It is well established that the predominant (101) face of anatase is dominated by coordinatively unsaturated Ti(IV) sites (Ti—OH₂) and bridging oxygen sites that will readily adsorb molecular water,²⁹ with the latter becoming protonated under acidic conditions to form bridging hydroxyls.^{30,31} Because, under neutral pH conditions the species giving rise to IR absorption at $\sim 1660\text{ cm}^{-1}$ is able to be reformed, it is unlikely this species is a protonated hydroxyl group (Ti—OH₂) and hence the low pH requirement points to the involvement of protonated bridging oxygen groups.

It is frequently considered that hole trapping readily occurs at Ti—OH groups, and likely at Ti—OH₂ groups, leading to an adsorbed hydroxyl radical Ti—OH[•],^{12,32–36} and this reaction could account for the reversible loss of the water absorption $\sim 1660\text{ cm}^{-1}$ with introduction of UV irradiation. Loss of water molecules is generally associated with an oxidation process rather than a reduction that is accompanying electron trapping. However, the breakage of surface bridging oxygen bonds as a consequence of UV irradiation, perhaps in a similar way to that proposed by Sakai et al.³⁷ for the photoinduced hydrophilic effect, and consequent formation of two terminal OH groups would also consume water, perhaps not reversibly, producing a net loss of water in proximity to the TiO₂ surface. Structural sensitivity in the dissociation of water molecules on TiO₂ surfaces has been observed,³⁸ and it may be that restriction of the shallow trap feature to anatase is a result interfacial water behavior not possible on the rutile surfaces exposed. This difference could be due to the significant corrugation of the anatase (101) surface, in comparison to rutile (110),³⁹ which causes a pronounced increase in the distance between Ti centers. This increased atomic spacing, in line with the mechanism proposed in Figure 6, may provide adequate separation of the hole and electron reaction sites, limiting recombination and hence allowing for extensive trapping at bridging hydroxyls.

The observation of the shallow trap related absorption in 'dry' film conditions in previous work,¹³ without an associated absorption loss at $\sim 1660\text{ cm}^{-1}$ suggests this loss occurs as a direct result of the electron trapping behavior but is not a requirement for formation of the shallow trap. Under aqueous conditions the water absorbance loss at $\sim 1660\text{ cm}^{-1}$ is proportional to the broad band IR absorbance gain (Figure 1), thus must occur as a direct consequence of shallow trap formation or is requisite to it. Although the exact nature of the shallow electron trap species remains elusive, the requirement for acidic conditions, which points to involvement of bridging hydroxyl groups, and the conversion of Ti—OH₂ to a Ti—OH group, suggests the involvement of a surface structure consisting of a bridging hydroxyl adjacent to the nascent terminal hydroxyl. A species similar to $\text{Ti}^{4+}\text{—O}^{\bullet}\text{—Ti}^{4+}\text{—OH}^-$, which is a surface or subsurface hole trap previously discussed,¹⁵ may be involved in the shallow trapping process responsible for the broad IR absorption. Yoshihara et al.⁴⁰ demonstrated a pH influence on the behavior of photogenerated holes and reported acidic conditions to alter the spectrum of these holes, whereas the spectrum of photoelectrons was unperturbed. Although here we

propose acidic conditions result in a greater concentration of shallow trap species, alterations to hole trapping pathways with decreasing pH may additionally affect the persistence of this shallow trap and perhaps parallel the effect of exogenous hole scavengers such as oxalate.

Henderson et al.⁴¹ concluded that the scavenging of electrons, which occurs via direct reaction of O₂ with electrons trapped at bridging hydroxyl groups. This may explain the apparent lack of any oxygen related spectral features in Figure 5 and would be consistent with bridging hydroxyl involvement in the behavior of the shallow trap species. The great enhancement of the shallow trap IR absorption by adsorption of oxalate ion is not yet fully understood. Adsorption of oxalate may cause structural changes on the TiO₂ surface that favor trap formation and persistence of trapped electrons. The hole scavenging ability of oxalate is the likely cause of the enhancement of shallow trapping of electrons; however the reactions occurring between inner- and outer-sphere oxalate, interfacial water species and bulk water have yet to be more fully elucidated.

Conclusions

We have shown with IR spectroscopy and adsorption/desorption kinetics that band gap UV excitation of anatase-containing TiO₂ thin particle films in acidic aqueous solution of hole-trapping outer-sphere adsorbing oxalate ion leads to population of shallow electron traps. This appears to be the first reported infrared spectroscopic analysis of TiO₂ photocatalysis in aqueous conditions in which hole- and electron-trapping-related processes have been observed and correlated. Additionally, the spectroscopic evidence points to the involvement of interfacial water and TiO₂ surface groups in the photocatalytic processes. The observed requirement for acidic conditions indicates an acidic surface species is necessary for persistence of the shallow trap and demonstrates that the nature of functional groups at TiO₂ surfaces under aqueous conditions has great influence on the photocatalytic behavior. Whereas the observation of the shallow trap IR absorption in quasi-vacuum or aqueous solution conditions may be explained in terms of absence of electron scavengers or presence of hole scavengers respectively, the role of interfacial water in these processes remains to be clarified. More extensive exploration of the system variables has considerable potential for further clarification of photocatalysis mechanisms.

Acknowledgment. We thank the Department of Chemistry, University of Otago for supporting this research.

Supporting Information Available: Materials, experimental methods, and sample characterization details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Fujishima, A.; Zhang, X.; Tryk, D. *Surf. Sci. Rep.* **2008**, *63*, 515–582.
- (2) Thompson, T. L.; Yates, J. T., Jr. *Chem. Rev.* **2006**, *106*, 4428–4453.
- (3) Berger, T.; Sterrer, M.; Diwald, O.; Knözinger, E.; Panayotov, D.; Thompson, T. L.; Yates, J. T., Jr. *J. Phys. Chem. B* **2005**, *109*, 6061–6068.
- (4) Fan, J.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 4686–4692.
- (5) Yu, Z.; Chuang, S. *J. Catal.* **2007**, *246*, 118–126.
- (6) Dolamic, I.; Burgi, T. *J. Catal.* **2007**, *248*, 268–276.
- (7) Araujo, P.; Mendive, C.; Rodenas, L.; Morando, P.; Regazzoni, A.; Blesa, M.; Bahnemann, D. *Colloids Surf., A* **2005**, *265*, 73–80.
- (8) Stafford, U.; Gray, K. A.; Kamat, P. V.; Varma, A. *Chem. Phys. Lett.* **1993**, *205*, 55–61.
- (9) Ekström, G. N.; McQuillan, A. J. *J. Phys. Chem. B* **1999**, *103*, 10562–10565.

- (10) Nakamura, R.; Imanishi, A.; Murakoshi, K.; Nakato, Y. *J. Am. Chem. Soc.* **2003**, *125*, 7443–7450.
- (11) Yamakata, A.; Ishibashi, T.; Onishi, H. *Chem. Phys. Lett.* **2001**, *333*, 271–277.
- (12) Szczepankiewicz, S. H.; Colussi, A. J.; Hoffmann, M. R. *J. Phys. Chem. B* **2000**, *104*, 9842–9850.
- (13) McQuillan, A. J.; Warren, D. S. *J. Phys. Chem. B* **2004**, *108*, 19373–19379.
- (14) Panayotov, D. A.; Yates, J. T., Jr. *Chem. Phys. Lett.* **2007**, *436*, 204–208.
- (15) Howe, R. F.; Grätzel, M. *J. Phys. Chem.* **1987**, *91*, 3906–3909.
- (16) Kim, J.; Schmitt, U. W.; Gruetzmacher, J. A.; Voth, G. A.; Scherer, N. E. *J. Chem. Phys.* **2002**, *116*, 737.
- (17) Giguère, P. A.; Turrell, S. *Can. J. Chem.* **1976**, *54*, 3477–3482.
- (18) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; WH Freeman, 1960.
- (19) Downing, H. D.; Williams, D. *J. Phys. Chem.* **1976**, *80*, 1640–1641.
- (20) Falk, M.; Giguère, P. A. *Can. J. Chem.* **1957**, *35*, 1195–1204.
- (21) Ohno, T.; Sarukawa, K.; Tokieda, K.; Matsumura, M. *J. Catal.* **2001**, *203*, 82–86.
- (22) Young, A. G.; McQuillan, A. J. *Langmuir* **2009**, *25*, 3538–48.
- (23) Hug, S.; Bahnemann, D. *J. Electron Spectrosc. Relat. Phenom.* **2006**, *150*, 208–219.
- (24) Connor, P. A.; Dobson, K. D.; McQuillan, A. J. *Langmuir* **1999**, *15*, 2402–2408.
- (25) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 2001.
- (26) Tsong, T. *Surf. Sci.* **1979**, *81*, 28–42.
- (27) Hurum, D. C.; Gray, K. A.; Rajh, T.; Thurnauer, M. C. *J. Phys. Chem. B* **2005**, *109*, 977–980.
- (28) Mattioli, G.; Filippone, F.; Caminiti, R.; Bonapasta, A. A. *J. Phys. Chem. C* **2008**, *112*, 13579–13586.
- (29) Diebold, U.; Ruzycski, N.; Herman, G. S.; Selloni, A. *Catal. Today* **2003**, *85*, 93–100.
- (30) Zhang, Z.; Bondarchuk, O.; Kay, B. D.; White, J. M.; Dohnalek, Z. *J. Phys. Chem. B* **2006**, *110*, 21840–21845.
- (31) Boehm, H. P. *Discuss. Faraday Soc.* **1971**, *52*, 264.
- (32) Turchi, C. S.; Ollis, D. F. *J. Catal.* **1989**, *119*, 483–496.
- (33) Phillips, L. A.; Raupp, G. B. *J. Mol. Catal.* **1992**, *77*, 297–311.
- (34) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735–758.
- (35) Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. *Environ. Sci. Technol.* **1991**, *25*, 494–500.
- (36) Ollis, D. C. *R. Acad. Sci., Ser. IIc: Chim.* **2000**, *3*, 405–411.
- (37) Sakai, N.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Phys. Chem. B* **2001**, *105*, 3023–3026.
- (38) Henderson, M. A. *Langmuir* **1996**, *12*, 5093–5098.
- (39) Tilocca, A.; Selloni, A. *Langmuir* **2004**, *20*, 8379–8384.
- (40) Yoshihara, T.; Tamaki, Y.; Furube, A.; Murai, M.; Hara, K.; Katoh, R. *Chem. Phys. Lett.* **2007**, *438*, 268–273.
- (41) Henderson, M. A.; Epling, W. S.; Peden, C. H.; Perkins, C. L. *J. Phys. Chem. B* **2003**, *107*, 534–545.