

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231664265>

Improving Optical and Charge Separation Properties of Nanocrystalline TiO₂ by Surface Modification with Vitamin C

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY B · APRIL 1999

Impact Factor: 3.3 · DOI: 10.1021/jp9901904

CITATIONS

210

READS

20

5 AUTHORS, INCLUDING:



Tijana Rajh

Argonne National Laboratory

176 PUBLICATIONS 7,406 CITATIONS

SEE PROFILE



Lin X. Chen

Northwestern University

416 PUBLICATIONS 8,346 CITATIONS

SEE PROFILE



Oleg G Poluektov

Argonne National Laboratory

86 PUBLICATIONS 1,394 CITATIONS

SEE PROFILE



Marion Charlotte Thurnauer

Argonne National Laboratory

148 PUBLICATIONS 6,230 CITATIONS

SEE PROFILE

Improving Optical and Charge Separation Properties of Nanocrystalline TiO₂ by Surface Modification with Vitamin C

T. Rajh,* J. M. Nedeljkovic, L. X. Chen, O. Poluektov, and M. C. Thurnauer

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Received: January 14, 1999; In Final Form: March 11, 1999

The structural and electrochemical properties of nanoparticles were found to be different from those of the corresponding bulk semiconductors. Due to the specific binding of modifiers to “corner defects”, the optical properties of small titania particles were red shifted 1.6 eV compared to unmodified nanocrystallites. It was found using electron paramagnetic resonance (EPR) that, as with organic charge transfer superconductors, these novel nanocrystallites operate with a charge-transfer mechanism, and exhibit semiconducting properties through both constituents (large band gap semiconductor and organic modifier). The EPR spectra were consistent with hole trapping on the surface modifier and electron trapping on shallow interstitial and partially delocalized Ti sites. These systems have an important feature in that charge pairs are instantaneously separated into two phases—the holes on the donating organic modifier and the electrons in the conduction band of TiO₂.

Control of surface chemistry, particle shape, and particle organization of nanocrystalline materials (metals, semiconductors, or dielectrics) have gained considerable attention, primarily because of the resulting unique chemistry (enhanced chemical reactivity, specific syntheses, enhanced catalytic activity, hardening of materials, specific bindings). Titanium dioxide is the photocatalytic material which has been studied most extensively over the past 10 years because it is inexpensive, nontoxic, and photostable.¹ However, the use of TiO₂ for photocatalytic applications driven by solar light is limited because TiO₂ has a wide band gap ($E = 3.2$ eV) and thus absorbs less than 5% of the available photons of the solar spectrum. There has been tremendous interest in recent years in developing dye sensitization for photoexcitation of TiO₂ in the visible region via photoinduced interfacial electron transfer.²

In this letter we present a new approach to improving the optical properties of nanocrystalline TiO₂ which involves a charge transfer from surface modifiers into the conduction band of nanocrystalline TiO₂ particles. The present method consists of adjusting the electronic properties of nanocrystalline particles by adsorption of electron-donating bidentate ligands. Our previous work has shown that bidentate binding of α -substituted surface modifiers results in the formation of a five-membered ring at surface titanium atoms.³ These conformations of ligands involve significant enhancement of the dipole moment at the surface.^{4,5} The binding is exclusively characteristic of small particle colloids in the nanocrystalline domain. To understand the unique bindings to TiO₂ nanoparticles, the coordination environment of surface Ti atoms of particles having different sizes was studied using X-ray absorption near-edge spectroscopy (XANES)(Figure 1). We have previously reported that reduction of the particle size results in changes in the relative intensities and peak positions in the preedge features of the Ti K-edge spectrum.⁶ In this work we report that XANES results suggest that the coordination of Ti surface atoms changes from six coordinate (octahedral) in 500 Å particles to pentacoordinate (square-pyramidal) in small 20 ± 3.2 Å particle colloids. The

intensity of the A₂ preedge peak increases approximately two times, and the A₂ peak shifts to a lower energy by approximately 1 eV for 20 Å particles compared to 500 Å particles. These results are consistent with a change in the coordination number of surface Ti atoms.⁷ Extended X-ray absorption fine structure (EXAFS) results confirm the existence of shorter Ti–O bond lengths in 20 Å particles (1.79 Å) as compared to bulk anatase TiO₂ (1.96 Å).⁷ Distortion of the bond length accounts for the large curvature of small particles and converts surface sites into more reactive “corner defects”.

In contrast to large particles and flat surfaces we have found using FTIR spectroscopy that under-coordinated “corner defects” in small-particle colloids bind ascorbic acid as bidentate ligands through both of the ortho-substituted hydroxyl groups of the furane ring. As shown in Figure 2, after modification of the small-particle colloids, the stretching vibrations of surface OH groups bound to surface Ti atoms at 3600 cm⁻¹ vanished, indicating replacement of surface OH groups with ascorbic acid. In the vibrational spectrum of ascorbic acid, on the other hand, the four stretching vibrations of the OH groups that belong to the 2,3 enediol group in ascorbate in the region 3000–3500 cm⁻¹ have disappeared. At the same time, the intensities of the lactone C=O group stretch (1780 cm⁻¹) and ring C=C stretch (1650 cm⁻¹) were not affected although their positions were slightly shifted toward lower energies after the adsorption, indicating a decrease in their electron densities. The more complex semicircle stretch mode (1380 cm⁻¹), where the top half of the ring stretches with the bottom half contracting,⁸ shows a slight increase in the energy of vibration. This is consistent with bidentate binding that results in the formation of a five-membered ring around the surface Ti atoms (Scheme 1) having a favorable conformation of bond angles and distances for octahedrally coordinated surface Ti atoms. XANES reveals that surface modification with ascorbic acid restores the preedge features of octahedrally coordinated Ti in the anatase crystal environment, while EXAFS studies indicate restoration of the Ti–O bond distance found in the bulk anatase geometry.⁹ This indicates that bidentate binding of ascorbic acid helps to reestablish the octahedral coordination of the nanocrystalline

* Corresponding author.

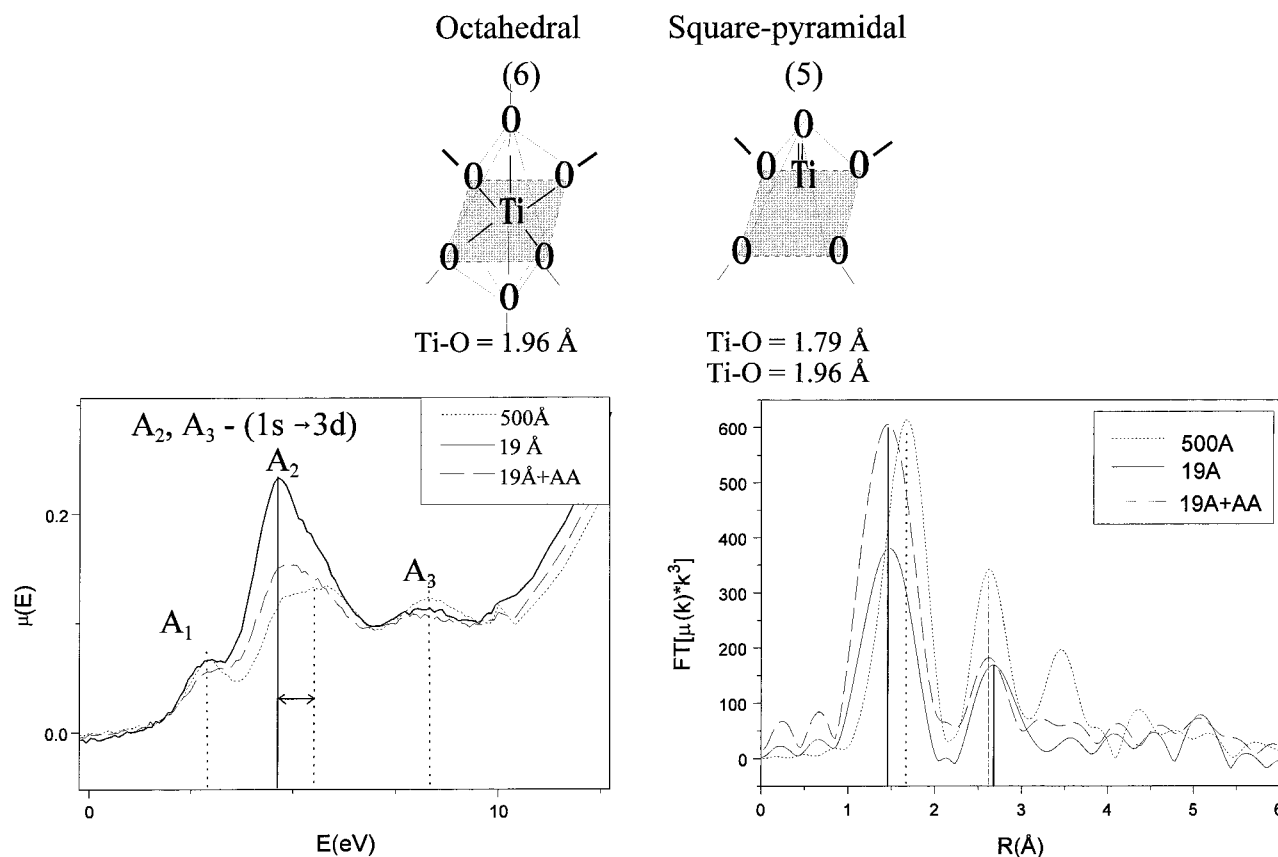


Figure 1. (Top) Schematic presentation of the coordination environment in flat surface and small-particle ($D = 20 \text{ Å}$) colloids derived from investigation of (bottom left) XANES studies of the preedge Ti K-edge ($E = 4.966 \text{ keV}$) structure and (bottom right) EXAFS spectra of Ti atoms in different size TiO_2 particles before and after surface modification.

surface, relaxing the surface Ti atoms to their original anatase environment (Figure 1).

Due to this specific binding of ascorbate to "corner defects", the optical properties of small titania particles change and the onset of absorption shifts by 1.6 eV to the red, compared to unmodified nanocrystallites. (The threshold of absorption is at 730 nm, compared with 380 nm for unmodified TiO_2 , Figure 3.) This is consistent with a shift of photoinduced luminescence of $\sim 350 \text{ nm}$ occurring at 736 nm. The unique bidentate bindings at the surface results in new hybrid properties of the surface-modified nanoparticle colloids that are between ligand-to-metal charge-transfer (CT) complexes and semiconductor properties. As in organic CT superconductors, in which metallic properties are obtained with charge transfer between non metal atoms,¹⁰ these novel nanocrystallites operate with a charge-transfer mechanism, and exhibit semiconducting properties between both constituents. These surface-modified TiO_2 particles exhibit charge-transfer properties that are manifested by a significant red shift of the onset of absorption toward the visible range of the light spectrum, and the optical properties of a semiconductor (continuous rise of absorption) due to the crystalline environment of the metal. Thus, these novel charge-transfer semiconducting materials exhibit unique electronic properties distinct from their constituents and can be qualified as CT nanocrystallites. It should be noted that monodentate binding on large surfaces does not induce a change in the optical properties.

Surface modification of titania colloidal particles with 6-palmitate ascorbic acid (6-PAA) also leads to the formation of a charge-transfer complex between the surface modifier and nanocrystalline TiO_2 .¹¹ Due to the increased hydrophobic character of the particles in this case, modification allows

extraction of TiO_2 nanocrystalline particles from an aqueous into an organic phase (3-methyl pentane, toluene, hexane, ether, or xylol). The optical properties of a charge-transfer complex with 6-PAA in the organic phase are identical to those obtained by surface modification with ascorbic acid in aqueous phase. These particles (6-PAA modified) have the property of organizing into transparent films that can be redispersed in a variety of organic solvents. It should be noted that modification with gluconic-acid- γ -lactone or dehydroascorbic acid (absence of 2,3 enediol $\text{C}=\text{C}$ group) did not lead to CT formation.

The appearance of absorption in the visible region by surface modification provides an alternative method for light sensitization of large band gap semiconductors. These newly developed systems have an important feature in that charge pairs are *instantaneously separated* into two phases following photoexcitation. Electron paramagnetic resonance spectroscopy (EPR) was used to obtain a molecular understanding of the origin of the charge transfer complex and the corresponding electron-accepting and -donating sites. Contrary to optical measurements, EPR spectroscopy has the ability to unambiguously identify the species involved in the charge separation processes. It was found using EPR that excitation with visible light, $\lambda > 500 \text{ nm}$ of the charge-transfer complex of 40 Å TiO_2 nanoparticles with ascorbic acid (or 6-PAA analog), resulted in low-temperature *reversible* charge separation in which an electron was excited from a donor to the acceptor site. This was manifest by the appearance of two signals in the continuous light photoinduced CW EPR spectrum, (i) a very narrow peak with $g = 1.988$ and, $\Delta H_{pp} = 2.5 \text{ G}$ associated with a broader signal at $g = 1.958$, and (ii) a signal at $g = 2.004$, $\Delta H_{pp} = 11 \text{ G}$ with small hyperfine coupling (Figure 4). Under the same conditions, no EPR signals

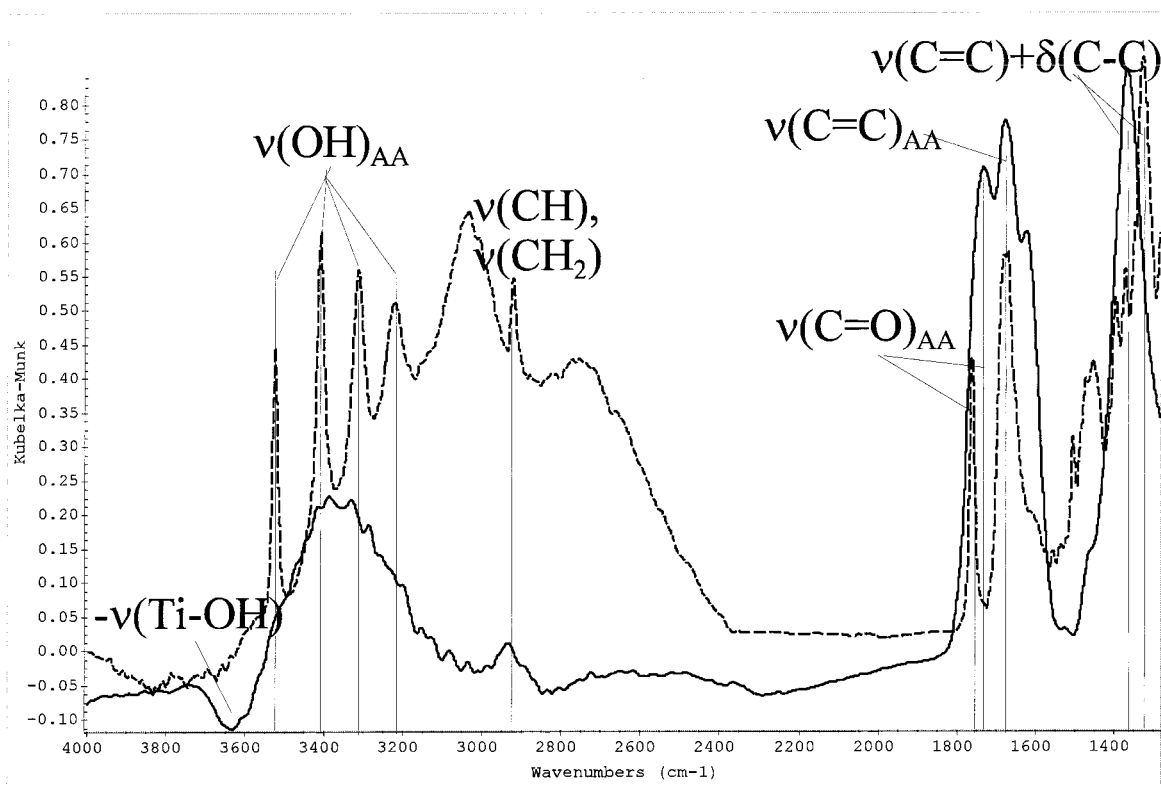
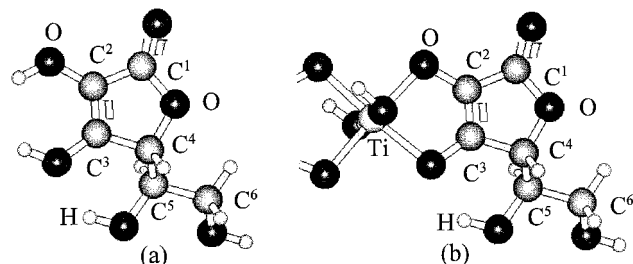


Figure 2. Ascorbic acid adsorption on 42 Å TiO_2 colloid. Infrared spectra of dried samples of ascorbic acid at pH 4 (---); 0.3 M TiO_2 colloid at pH 4 containing 0.1 M ascorbic acid dried and thoroughly washed with CH_3OH (—), the spectrum of dried TiO_2 colloid was subtracted.

SCHEME 1. Molecular Structure of Ascorbic Acid before (a) and after (b) Binding to the Surface of Nanocrystalline TiO_2



were observed from 20 Å TiO_2 particles modified with ascorbate, probably because of the fast recombination rate due to the short charge separation distance (≤ 10 Å).

The narrow EPR signal at $g = 1.988$ accompanied with two low-intensity signals at $g = 1.958$ and $g = 1.961$ are characteristic of a radical in which the unpaired electron occupies the d-orbitals of Ti atoms having a strong component of angular momentum. It is generally assumed that Ti ions are found in a tetragonally distorted octahedral crystal field.¹² The g -factor of the EPR signal will depend on the extent of tetragonal distortion. In the small TiO_2 particles, Ti(III) centers are coordinated either^{13,14} (i) with anatase lattice oxygen atoms only, having little tetragonal distortion (interstitial Ti centers, $g_{\perp} = 1.988$, $g_{\parallel} = 1.958$, the shape or position of these signals is not affected by the surface modifier or solvent), (ii) with surface bound oxygen atoms from the surface modifier and having a higher extent of tetragonal distortion (two signals found $g_{\perp A} = 1.955$, $g_{\perp B} = 1.934$, $g_{\parallel A \text{ and } B} = 1.885$), or (iii) with surface OH groups or H_2O , having the highest extent of tetragonal distortion (surface Ti centers, $g_{\perp} = 1.924$, $g_{\parallel} = 1.885$). The g -factor for Ti(III) centers is consequently dependent on the separations of

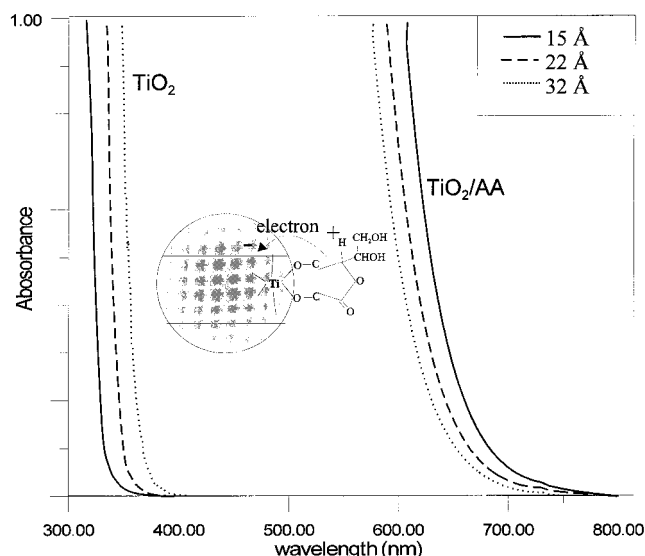


Figure 3. Absorption spectra and surface structure of 0.05 M TiO_2 nanoparticles with different sizes before (TiO_2) and after surface modification with ascorbic acid (0.05 M TiO_2).

orbital energies due to the tetragonal and octahedral components and a spin-orbit coupling constant.

Before surface modification of 42 Å TiO_2 the EPR spectrum obtained upon illumination with UV light was composed of two signals: one sharp component at $g_{\perp} = 1.988$, previously assigned to Ti(III) centers in anatase TiO_2 formed by electron trapping in the particle interior (i.e., lattice, $\text{Ti(III)}_{\text{latt}}$), and a broad signal with $g_{\perp} = 1.924$, previously assigned to Ti(III) centers formed by electron trapping at the particle surface.^{13,14} After modification with ascorbate or 6-PAA, no EPR signals associated with the surface components were observed, indicating that ascorbate (6-PAA) ligands raise the energy of the

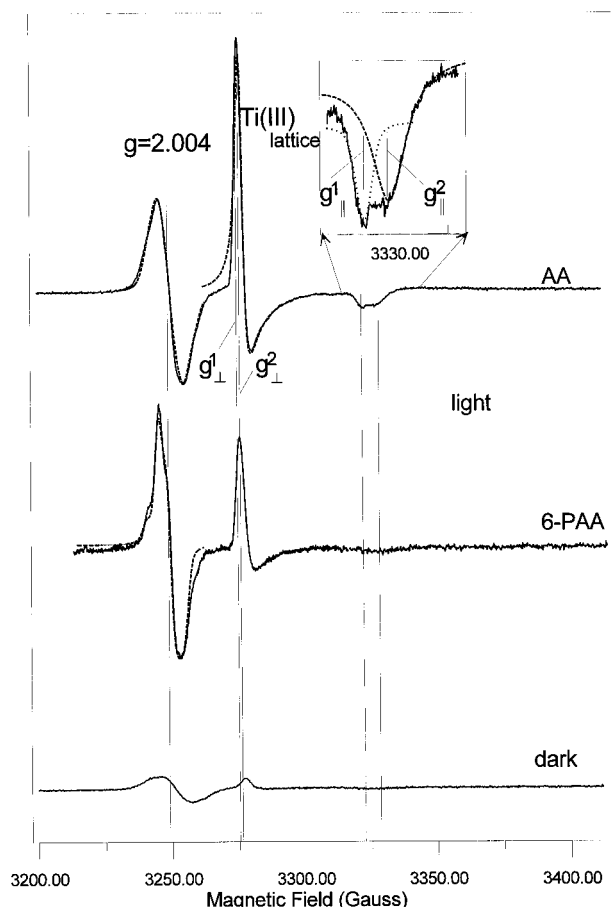


Figure 4. Light-induced EPR (X-band) spectra of degassed aqueous TiO_2 colloids (0.3 M) modified with (top) ascorbic acid (0.1 M) or (middle) 6-palmitate ascorbic acid, irradiated with white light (cut off filter 400 nm) at 4.2 K. In the dark after illumination at 4.2 K (bottom) residual irreversible component. The spectra at $g = 2.004$ were simulated²¹ (dashed lines) assuming hyperfine interaction with two equivalent spin 1/2 nuclei (presumably 4-CH and 5-CH) and one spin 1/2 nucleus with smaller coupling constant (probably 5-COH). The Gaussian line widths used for simulation were 5 G in the case of surface modification with ascorbate in water and 2.5 G for surface modification with 6-PAA in toluene. Axial g anisotropy ($g_x = g_y = 2.0040$ and $g_z = 2.0000$) was included in the simulation. Ti sites were simulated assuming axial g anisotropy of two signals, one with $g_{\perp}^1 = 1.9885$ and $g_{\parallel}^1 = 1.9615$ both having 0.8/0.2 ratio of Lorentzian/Gaussian line width of 2 G (dotted line), and second with $g_{\perp}^2 = 1.9880$ having pure Lorentzian line width 3 G and $g_{\parallel}^2 = 1.9581$ having Lorentzian line width of 5 G (dashed line).

surface trapping sites. Furthermore, the signal for the interior Ti(III) becomes more intense and narrow, and the parallel component is composed of two signals ($g_{\parallel}^1 = 1.961$ and $g_{\parallel}^2 = 1.958$). The splitting of the parallel component indicates that there are two paramagnetic Ti(III) centers contributing to the overall signal. The higher field component is identical to one previously assigned to the parallel component of an electron localized on interstitial Ti atoms (shallow defects).¹³ Meanwhile the narrower component at 1.961 can be associated with a signal motionally narrowed by electron hopping from center to center (delocalized electrons).¹⁵ A similar signal has been observed from partially reduced rutile TiO_2 and attributed to electrons loosely bound to interstitial titanium atoms or completely delocalized electrons (A center).¹⁶ Future work with high field and transient EPR will be carried out in order to better resolve the spectral features and gain more insight into their nature. Preliminary femtosecond transient optical absorption measure-

ments show a continuous rise of absorption toward the IR that forms within the laser pulse (<150 fs) and confirms the existence of loosely bound electrons to interstitial titanium atoms.¹⁷

The EPR signal at $g = 2.004$ has line width and g -value consistent with a carbon-centered radical. As electrons are involved in the reduction of Ti, this signal can be reasonably assigned to the reversible trap for photogenerated holes. The signal obtained from oxidation of ascorbic acid in aqueous solution consists of a doublet of triplets having small splittings (doublet of 1.7 G and triplet of 0.17 G).¹⁸ The signal has been interpreted as a radical centered on an oxygen of one of the 2,3 enediol groups. These small couplings, or low spin density on the carbon framework, contrast with the signal with 11 G line width observed at $g = 2.004$ for ascorbic acid bound to the surface of nanocrystalline TiO_2 . This suggests that oxidation (hole trapping) of bound ascorbate involves a different mechanism than the one observed for oxidation of ascorbic acid in solution. In the case of ascorbate bound to TiO_2 the enediol groups are not available for hole trapping due to the bidentate binding of the oxygens as suggested from the IR data presented above (Scheme 1). Oxidation of dihydrofurans (DHF),¹⁹ which have the furane ring without hydroxyl groups at the 2 and 3 carbon positions, gives rise to allylic radicals. We suggest that in the ascorbate-modified TiO_2 , the hole is trapped at the 2, 3 double bond of bound ascorbate, producing a radical on the carbon framework. The fact that the trapping is reversible suggests that oxidation is not followed by proton loss forming an allylic radical as in DHF. Thus, we attribute the reversible signal at 2.004 to the radical cation of the ascorbic acid bound to the surface of TiO_2 . The number of holes trapped on the ascorbic acid was roughly equal to the number of trapped electrons (4×10^{13} to 1×10^{15} spins cm^{-1} in the systems containing 1×10^{14} to 5×10^{15} TiO_2 particles cm^{-1}) as determined by comparison to a calibrated sample.²⁰

A similar signal having more pronounced structure at $g = 2.004$ was observed when 6-PAA was used as modifier and irradiated in frozen organic solvents. Narrowing of the line width in this case is consistent with the absence of inhomogeneous broadening caused by the presence of water molecules. Reasonable simulations of both signals that are consistent with trapping at the 2,3 double bond could be attained. These required two protons having approximately equivalent hyperfine couplings (possibly 4-CH and 5-CH), and one proton having smaller hyperfine coupling. A small axial g -anisotropy, consistent with the presence of the oxygen atom in the furane ring, was assumed in these preliminary simulations. Future work involving deuteration of the ascorbic acid and the use of higher frequency and transient EPR will help clarify the details of the hole trapping process. Preliminary experiments show that the system can undergo further chemical reaction leading to stable charge separation.

In conclusion, nanosize TiO_2 particles experience an adjustment in the coordination geometry of the Ti atoms near the particle surface from octahedral to square-pyramidal in order to accommodate the large surface curvature. XANES reveals that surface modification with ascorbic acid restores the preedge features of octahedrally coordinated Ti in the anatase crystal environment. Specific binding of the ascorbate modifier to surface "corner defects" induces a 1.6 eV shift in the onset of absorption, compared to unmodified nanocrystallites. As with CT salts, the red shift of absorption is explained by a charge-transfer mechanism. EPR was used in order to obtain a molecular understanding of the origin of the charge-transfer

complex and the corresponding accepting and donating sites. It was found that the donating site in the CT complex is the ascorbate modifier, while the accepting site is the conduction band of TiO₂.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-31-109-Eng-38. The authors acknowledge the insights gained from discussions with D. Tiede, A. Trifunac, and S. Wasserman. We thank W. Jäger for assisting in data acquisition.

References and Notes

- (1) For comprehensive reviews see: Hoffman, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69–98; Hagfeldt, A.; Gratzel, M. *Chem. Rev.* **1995**, *95*, 49; Mills, A.; LeHunte, S. J. *Photochem. Photobiol. A* **1997**, *108*, 1–35, and references therein.
- (2) Rehm, J. M.; McLendon, G. L.; Nagasawa, Y.; Yoshihara, K.; Moser, J.; Gratzel, M. *J. Phys. Chem.* **1996**, *100*, 9577; Nasr, C.; Liu, D.; Hotchandani, S.; Kamat, P. *J. Phys. Chem.* **1996**, *100*, 11054; Burfeindt, B.; Hannappel, T.; Stork, W.; Willig, F. *J. Phys. Chem.* **1996**, *100*, 16463; Mayer, G. J. *J. Chem. Educ.* **1997**, *74*, 652; Martini, I.; Hodak, J.; Hartland, G. V.; Kamat, P. V. *J. Chem. Phys.* **1997**, *107*, 8064; Huang, S. Y.; Schlichthorl, G.; Nozik, A. J.; Gratzel, M.; Frank, A. J. *J. Phys. Chem. B* **1997**, *101*, 2576; Ellingson, R. J.; Asbury, J. B.; Ferrere, S.; Ghosh, H. N.; Sprague, J. R.; Lian, T. Q.; Nozik, A. J. *J. Phys. Chem. B* **1998**, *102*, 6455.
- (3) Rajh, T.; Tiede, D. M.; Thurnauer, M. C. *J. Non-Cryst. Solids* **1996**, *207*, 815–820; Rajh, T.; Tiede, D. M.; Thurnauer, M. C. *Acta Chem. Scand.* **1997**, *51*, 610.
- (4) Dipole moment calculations were performed with HyperChem software, a product of Hypercube Inc. using the ZINDO/1 semiempirical method for determining the structures of complexes containing transition metals (titanium) in a single point calculation. The program was tested with molecules of known dipole moments. The conformations of the modifier that were used for calculations were the ones suggested by IR studies.⁵
- (5) Rajh, T.; Thurnauer, M.; Thiyagarajan, P.; Tiede, D. M. *J. Phys. Chem.* in press.
- (6) Chen, L. X.; Rajh, T.; Wang, Z.; Thurnauer, M. C. *J. Phys. Chem. B* **1997**, *101*, 10688.
- (7) Farges, F.; Brown, G. E., Jr; Rehr, J. J. *Geochim. Cosmochim. Acta* **1996**, *60*, 3023; Farges, F.; Brown, G. E., Jr; Rehr, J. J. *Phys. Rev. B* **1997**, *56*, 1809.
- (8) Lin-Viem, D.; Colthap, N. B.; Fateley, W. G.; Grasselli, J. G. In *Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: San Diego, 1991.
- (9) Chen, L. X.; Rajh, T.; Jäger, W.; Nedeljkovic, J.; Thurnauer, M. C. *J. Synchrotron Rad.*, in press.
- (10) Williams, J. M. *Organic superconductors (including fullerenes): synthesis, structure, properties, and theory*; Prentice Hall: Englewood Cliffs, NJ, 1992.
- (11) In a typical preparation a methanol solution of 6-PAA was added into an aqueous colloidal solution of 45 Å TiO₂ (obtained by the method described previously³) in the presence of ether (1 mL of 0.2 M 6-PAA added in 2 mL 0.3 M TiO₂ with a layer of 1 mL of ether). A thick reddish cloud was slowly separated in the top phase that was subsequently flushed by an excess of methanol. As a result of methanol addition an excess of nonbound 6-PAA was removed and a clear, dark-red ether solution containing surface-modified TiO₂ particles was easily separated from the rest of the aqueous solution.
- (12) Wertz, J. E.; Bolton, J. R. In *Electron Spin Resonance: Elementary Theory and Practical Applications*; McGraw-Hill Book Co.: New York, 1972; p 269; Watanabe, T.; Fujiwara, S. *J. Magn. Reson.* **1970**, *2*, 103.
- (13) Meriaudeau, P.; Che, M.; Jorgensen, C. K. *Chem. Phys. Lett.* **1970**, *5*, 131; Howe, R. F.; Gratzel, M. *J. Phys. Chem.* **1985**, *89*, 4495; Anpo, M.; Shima, T.; Fujii, T.; Suzuki, S.; Che, M. *Chem. Lett.* **1987**, 1997.
- (14) Rajh, T.; Ostafin, A. E.; Micic, O. I.; Tiede, D. M.; Thurnauer, M. C. *J. Phys. Chem.* **1996**, *100*, 4538.
- (15) Ohlsen, W. D.; Johnson, O. W. *J. Appl. Phys.* **1973**, *44*, 1927; Shen, L. N.; Johnson, O. W.; Ohlsen, W. D.; DeFord, J. W. *Phys. Rev.* **1974**, *B10*, 1823.
- (16) Kerssen, J.; Volger, J. *Physica* **1973**, *69*, 535; Yagi, E.; Hasiguti, R. R. *J. Phys. Soc. Jpn.* **1977**, *43*, 1998.
- (17) Rajh, T.; Nedeljkovic, J.; Wiederrecht, G.; Wasielewski, M.; Thurnauer, M. C. To be published.
- (18) Lagercrantz, C. *Acta Chem. Scand.* **1964**, *2*, 562.
- (19) Ko, S. E. W.; Ling, C. *J. Magn. Reson.* **1983**, *54*, 67.
- (20) The number of radicals was determined using calibrated weak pitch in KCl sample under the same conditions (1.15×10^{13} spins cm⁻¹, Bruker Instruments).
- (21) The spectra were simulated using commercial “Simfonia” simulation program, the product of Bruker Instruments Inc.