Spectroscopic and Excited-State Properties of Titanium Dioxide Gels

Felix N. Castellano, Jeremy M. Stipkala, Lee A. Friedman, and Gerald J. Meyer*
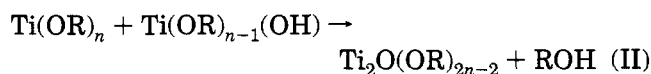
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Received June 10, 1994. Revised Manuscript Received August 4, 1994[®]

The optical and excited-state properties of sol–gel processed monolithic titanium dioxide (TiO_2) gels are reported. An important conclusion of this study is that amorphous polymeric TiO_2 gels display a band structure similar to crystalline materials rich in defect sites. This band structure manifests itself in a fundamental absorption edge, band-edge photoluminescence, and excited-state redox chemistry from the valence and conduction bands. The generation of long-lived electrons by ultraviolet light excitation proceeds with a quantum efficiency of 1%. Room-temperature absorption and electron paramagnetic resonance measurements indicate that the electrons are trapped at Ti(IV) sites. The electrons can be freed from the solid through interfacial electron transfer to acceptors located within the gel intrapore space producing mobile electron shuttles capable of doing external work.

Titanium dioxide is undoubtedly the most well-studied inorganic photocatalytic solid.[1] Much of the impetus for this research is the pioneering studies of Fujishima and Honda.[2] These workers first realized that bandgap excitation of TiO_2 single crystal electrodes, operating in a conventional aqueous photoelectrochemical cell, produces a sustained photocurrent. The product of the photocurrent is oxygen evolution at the TiO_2 anode and hydrogen production at the platinum cathode. Since that time, research has focused on understanding molecular level water-splitting mechanisms, increasing efficiencies, and sensitizing the process to visible light in single crystals, polycrystalline films, and colloidal solutions.[1] In addition, the oxidation of a large variety of organic compounds[3] and pollutants[4] have been explored. These studies have generated new classes of materials with interesting photocatalytic, electronic, and optical properties.

Recently, there has been growing interest in the preparation of materials by the sol–gel process.[5] The sol–gel process involves the hydrolysis (I) and condensation (II) of metal alkoxides to form macromolecular metal oxide networks. In general, the chemistry is far more complicated than that depicted in reactions I and

$$Ti(OR)_n + H_2O \rightarrow Ti(OR)_{n-1}(OH) + ROH \quad (I)$$

$$Ti(OR)_n + Ti(OR)_{n-1}(OH) \rightarrow$$
$$Ti_2O(OR)_{2n-2} + ROH \quad (II)$$

sation (II) of metal alkoxides to form macromolecular metal oxide networks. In general, the chemistry is far more complicated than that depicted in reactions I and

II. Most titanium alkoxides do not exist as individual molecular species in fluid solution, for example.[6] Furthermore, the hard Ti(IV) center is highly reactive, making the chemistry difficult to control. An observation which has emerged from extensive studies of transition metal sol–gel chemistry is that fast hydrolysis followed by slow condensation rates generally leads to the formation of polymeric gels.[6] A gel is a substance which contains a continuous solid skeleton enclosing a continuous liquid phase.[5e] A technologically important point is that gels can be formed into any desired shape or configuration. Gels also have the ability to shrink or swell in response to chemical or electrical stimuli and may form the basis of a new class of "soft" machines.[7]

Despite the fact that titanium dioxide gels have long been known,[8] their photophysical properties have not been previously reported. In this paper, we report the rapid preparation, redox, and photophysical properties of large (monolithic) TiO_2 gels with high visible transparency. The titania gels possess unique electronic and optical properties which may be useful for photonic materials applications.

Experimental Section

Materials. All chemicals and solvents were of commercially available reagent grade unless otherwise stated. HCl (Baker, reagent grade), $TiCl_3$ (Aldrich, 99%); methylviologen, MV^{2+}, 1,1'-dimethyl-4,4'-bipyridine dichloride (Aldrich, 98%), tetrabutylammonium perchlorate (TBAP, Fluka; electronic grade), and N,N'-tetramethylene-2,2'-bipyridine (TV^{2+}) dibromide (Sigma, 98%) were used without further purification. Ti(OEt)₄

® Abstract published in *Advance ACS Abstracts*, October 1, 1994.

(1) Finklea, H. O. *Studies in Physical and Theoretical Chemistry: Semiconductor Electrodes*; Elsevier: Amsterdam, 1988; p 43.

(2) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.

(3) Fox, M. A. *Top. Curr. Chem.* **1987**, *142*, 71 and references therein.

(4) Ollis, D.; Al-Ekabi, H. *Photocatalytic Purification and Treatment of Water and Air*; Elsevier: Amsterdam, 1993.

(5) For recent reviews of sol–gel processing, see: (a) Roy, R. *Science* **1987**, *238*, 1664. (b) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33. (c) Hench, L. L.; Vasconcelos, W. *Annu. Rev. Mater. Sci.* **1990**, *20*, 269. (d) Dutton, G. F. *Science* **1990**, *249*, 627. (e) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science*, Academic Press: New York, 1991. (f) Martin, J. E.; Adolf, D. *Annu. Rev. Phys. Chem.* **1991**, *42*, 311. (g) Lee, G. R.; Crayston, J. A. *Adv. Mater.* **1993**, *5*, 434. (h) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.

(6) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, *18*, 259.

(7) Osada, Y.; Ross-Murphy, S. B. *Sci. Am.* **1993**, *268*, 82.

(8) (a) Klosky, S.; Marzona, C. *J. Phys. Chem.* **1925**, *29*, 1125. (b) Klosky, S. *J. Phys. Chem.* **1925**, *30*, 1125. (c) Hurd, C. B.; Jacober, W. J.; Godfry, D. W. *J. Am. Chem. Soc.* **1941**, *63*, 723. (d) Woodhead, J. L. *Sci. Ceram.* **1977**, *9*, 29. (e) Ragai, J.; Sing, K. S. W. *J. Colloid Interface Sci.* **1984**, *101*, 369. (f) Quinson, J. F.; Tchipkam, N.; Dumas, J.; Bovier, C.; Serughetti, J.; Guizard, A.; Larbot, A.; Cot, L. *J. Non-Cryst. Solids* **1988**, *99*, 151. (g) Yoldas, B. E. *J. Mater. Sci.* **1986**, *21*, 1087. (h) Doeuff, S.; Henry, M.; Sanchez, C.; Livage, J. *J. Non-Cryst. Solids* **1987**, *89*, 206. (i) Chee, Y. H.; Cooney, R. P.; Howe, R. F.; van der Heide, P. A. W. *J. Raman Spectrosc.* **1992**, *23*, 161.

(Gelest, 20−21% Ti) was distilled at 1.0 ± 0.5 mmHg, 122 °C and stored under dry argon. Absolute ethanol was dried over 3 Å molecular sieves for several days prior to distillation over activated Mg turnings under argon. Water was deionized with a Barnstead Nanopure system. Polystyrene cuvettes were purchased from Fisher Scientific. Quartz EPR tubes with a 2.8 mm inner diameter were obtained from Wilmad Glass. Optically transparent indium doped tin oxide (8 Ω/cm^2) was obtained from Libby-Owens-Ford. Parafilm M (American National Can) was used as received.

1-Methyl-4,4'-bipyridine (PF₆, monoquat (MQ⁺)) was prepared, purified, and characterized by literature methods.[9]

Materials Preparation. *Sol−Gel Processing.* To a stirred EtOH/HCl solution (170 mmol, 2.42 mmol), in a 50 mL polypropylene beaker, Ti(OEt)₄ (12.1 mmol) was added. Once the solution was well mixed, water (44 mmol) was added and stirring continued for 5 s. This solution was then transferred via pipets to polystyrene cuvettes, capped, and sealed with Parafilm wax. For 10 mm path length cuvettes, 3 mL was added to each cuvette and for 4 mm cuvettes 700 μL were cast in each cuvette. Gelation took place within 5 min yielding optically transparent sol−gel monoliths. These materials were aged for 3 days, during which time they became detached from the polystyrene cuvette walls, before being placed in argon saturated alcohol baths for spectroscopic measurements. In some experiments, the gels were prepared and aged in a nitrogen-filled Vacuum Atmospheres drybox. Gels were doped with Ti(III) by dissolving TiCl₃ in the water reactant of reaction III. Gels were doped with TBAP by dissolving it in the ethanol reactant of reaction III. The gel density was determined by drying alcogels of known initial volume at 80 °C for 8 h and weighing them.

Preparation of Xerogels. Gels were first prepared as stated above and were allowed to age in the dark for 2 weeks. After 2 weeks, a pinhole was made in the cuvette cover which allowed the liquid phase to slowly evaporate. After 2 months, the gels shrunk to a final volume about 2.7% of the original size. The xerogels are optically transparent and can be cut and handled in the ambient.

Spectroscopic Characterization. *X-ray Scattering.* X-ray scattering of TiO₂ xerogels was performed with a Philips MDP 1880 X-ray diffraction system operating equipped with a PW 1820 goniometer. The instrument was operated using ADP 1700 software for automatic powder diffraction. Both thin slices and finely ground powders of TiO₂ xerogels were examined.

Absorption Spectra. Absorption spectra were obtained on a Hewlett-Packard 8451A Diode Array, a Shimadzu UV 160U, or a Cary 14 spectrophotometer. In many instances, a 385 nm long-pass filter was placed in the optical path to prevent direct excitation of the gel material. The reference sample was either ethanol or an unphotolyzed TiO₂ gel. Polystyrene or quartz cuvettes with path lengths of 4 or 10 mm were employed.

Yield and Molar Absorptivity for Trapped Electrons. The extinction coefficient for accumulated electrons was calculated by employing a spectrophotometric redox titration with the electron acceptor MV²⁺. The methyl viologen radical, MV˙⁺, has a pH-independent redox potential (−0.44 V vs NHE), with an extremely well-known extinction coefficient,[10] ϵ = 13 800 ± 300 M⁻¹ cm⁻¹ at 611 nm in EtOH. An argon-saturated TiO₂ gel was irradiated with 360 nm light from a 150 W Xe lamp equipped with a holographic grating. The output from the monochromator was collimated and focused such that a 1 cm² area on the sample was illuminated. Absorbance measurements before and after photolysis afford the spectrum of the accumulated electrons. Addition of MV²⁺ induces the complete loss of the accumulated electrons and appearance of the characteristic MV˙⁺ absorption. Assuming the electron transfer quantum yield to be unity, the accumulated electron extinction coefficient was quantitated. The quantum yield for electron accumulation was measured in the same way, except

the illumination time, light intensity, and illuminated volume were measured. The irradiance of the excitation source was measured with a calibrated Si photodiode from UDT Technologies. Chemical actinometry[11] with 0.15 M ferrioxylate resulted in light intensities within 5% of those measured with the calibrated diode. Incident quantum yield was calculated as (moles of accumulated electrons/moles of incident photons), without correcting for scattered or unabsorbed light.

Photobleaching Studies. Attempts to bleach the absorption from the trapped electrons were performed. Typically, an argon saturated TiO₂ alcogel was illuminated with UV light until the optical density at 582 nm was >1. The gel was then irradiated with a 457.9, 488.0, or 514.5 nm line from a Coherent Innova 70A Ar⁺ laser for periods of 5 min. The laser beam was passed through a bandpass filter prior to incidence on the sample and incident irradiances from 500 mW/cm² to 1 W/cm² were employed. After laser irradiation, the sample was visually inspected and the absorption spectrum taken. Spectra before and after laser excitation were completely superimposable.

FTIR Spectra. Infrared spectra were recorded on a Mattson Instruments 4030 FTIR (±4 cm⁻¹, 32 scans). Xerogels were ground into powders and pressed into KBr pellets. Liquids and alcogels were measured on NaCl plates.

EPR Measurements. Room-temperature electron paramagnetic resonance (EPR) spectra were obtained with a Varian E-12 spectrometer operating at 9.3 GHz. The g factors were calibrated by reference to a powder sample of 1,1-diphenyl-2-picrylhydrazyl (DPPH, g = 2.0037 ±. 0.0002).[12] EPR samples were prepared under anaerobic conditions and transferred to quartz EPR tubes under argon prior to gelation. Samples were photolyzed by sunlight or UV light from a 150 W Xe lamp with a 305 nm long-pass and water solution filter. Subsequent to the excitation, the samples were transferred to the EPR spectrometer for analysis.

Photoluminescence Measurements. Steady-state and time-resolved photoluminescence measurements were performed with an apparatus which has been previously described.[13]

Excited-State Absorption Spectroscopy. The experimental apparatus has been described previously,[34b] with a frequency-tripled Continuum Surelite Nd:YAG laser (355 nm, 4−6 ns fwhm, 1−5 mJ/pulse) as the excitation source. The instrument response function of the apparatus is 20 ns. The probe beam was a pulsed 150 W Applied Photophysics Xe lamp appropriately filtered with a 400 nm long-pass filter to prevent direct excitation of the TiO₂ gels. The 355 nm pump beam is completely absorbed by the gel at the surface. To compensate for this, the pump and probe beams were incident on the same corner of the sample, normal to each other.

Electrochemical Studies. *Sample Preparation.* A two-electrode cell containing a TiO₂ gel sandwiched between two indium-doped tin oxide electrodes was prepared as follows: the tin oxide electrodes were cut into 60 mm × 6 mm strips, washed with ethanol, and placed in a polystyrene cuvette with the conductive sides facing in. The TiO₂ gel solution was prepared, as described above, and poured into the cuvette before gelation occurred. The gel was then sealed with Parafilm, secured with a rubber band, and aged for 3 days. Prior to electrochemical measurements, the Parafilm and rubber band were removed, and a few drops of ethanol were added to the gel to prevent drying and cracking.

Photoelectrochemical Measurements. A Princeton Applied Research Model 173 Potentiostat or a Bioanalytical Systems CV-27 voltammogram was used in conjunction with the HP 8451A Diode Array spectrometer. The gel sandwich cell was placed in the spectrometer and connected with alligator clips to the potentiostat. An external bias of 0.0 V across the gel was used as the spectrometer reference. Absorption measurements were then made as a function of applied potential. In

(9) (a) Yonemoto, E. H.; Riley, R. L.; Kim Y.; Atherton, S. J.; Schmehl, R. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 8081. (b) Curtis, J. C.; Sullivan B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.
(10) Watanabe T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(11) Calvert, J. G.; Pitts, J. N. Jr. *Photochemistry*; John Wiley & Sons: New York, 1966; p 784.
(12) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; Chapman and Hall: London, 1986.
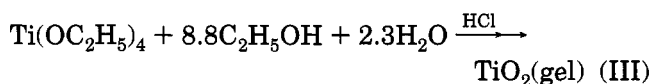(13) Castellano, F. N.; Heimer, T. A.; Tandhasetti, M.; Meyer, G. J. *Chem. Mater.* **1994**, *6*, 1041.

some cases, absorption measurements were taken as a function of time after a potential jump.

Results

Reaction III produces gels which are both transparent and possess good mechanical stability. To avoid TiO$_2$

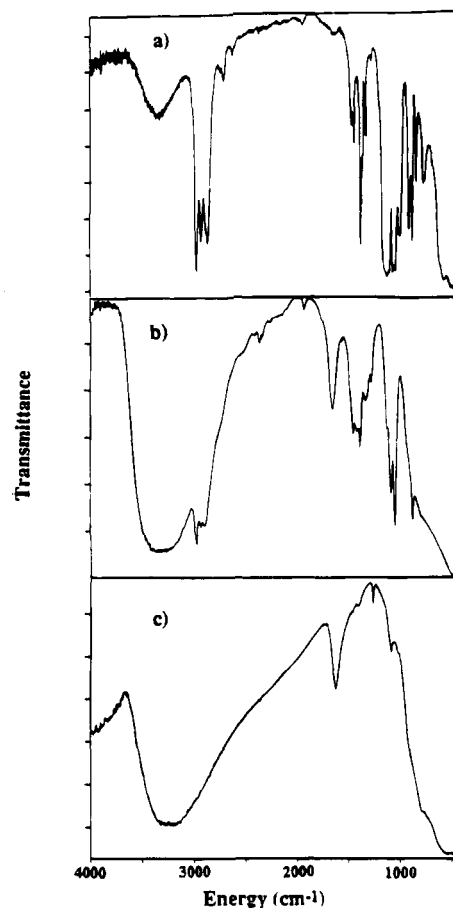$$Ti(OC_2H_5)_4 + 8.8C_2H_5OH + 2.3H_2O \xrightarrow{HCl}$$
$$TiO_2(gel) \quad (III)$$

precipitation, it is important to add water to the reaction mixture last. Generally, the titanium ethoxide and ethanol were distilled before use; however, similar results were obtained with as-received reagents. Gelation occurs within 5 min in covered polystyrene cuvettes. Syneresis, or shrinkage, after 3 days of aging is minimal and yields freestanding solids with typical dimensions of ~1 cm × 1 cm × 3 cm. The gels are stable in ethanol, isopropyl alcohol, acetone, acetonitrile, dichloromethane, diethyl ether, and in a dry ice/ethanol bath. However, the gels do slowly dissolve in water or methanol. The main focus of this report is for TiO$_2$ gels placed in either ethanol or isopropyl alcohol, collectively termed alcogels, which display no measurable decomposition for periods of months. Gels prepared at higher hydrolysis ratios are also optically transparent; however, they do not detach from the polystyrene cuvette walls after several weeks. Alcogels dried by slow evaporation yield xerogels ~2.7% of their original volume.

The IR spectra of the starting Ti alkoxide (a), a TiO$_2$ alcogel (b), and a TiO$_2$ xerogel (c) are shown in Figure 1. Figure 1a exhibits sharp bands around 2980−2800 and 1470−1320 cm^{-1} corresponding respectively to the stretching and bending vibrations of the aliphatic CH$_2$ and CH$_3$ groups. Ti−O−C vibrations of the ethoxy groups directly bonded to titanium are assigned to the manifold of broad bands between 1130 and 1040 cm^{-1}.[8h,14] Figure 1b shows the large OH vibrational contribution in the high-energy region between 3700 and 3100 and at 1622 cm^{-1}. The low-frequency band and contributing shoulders in Figure 1c are assigned to an envelope of Ti−O−Ti bonds,[14] which are the most dominant features in the spectrum.

X-ray scattering measurements reveal an amorphous gel structure. Alcogels have an initial density of 0.079 g/cm^3 which increases to 1.9 ± 0.1 g/cm^3 as xerogels. The gels are sufficiently porous that methyl viologen radical can diffuse through the gel structure and can be easily monitored by eye. The uniformity of the incorporated radicals was examined by cutting the gels in half with a razor blade and visually inspecting the homogeneity of the color. The characteristic blue MV$^{•+}$ is evenly distributed through the gel.

The electronic spectrum of processed TiO$_2$ alcogels is dominated by a fundamental absorption at short wavelength which tails into the visible region (Figure 2). Excitation into the fundamental absorption results in room-temperature photoluminescence, PL (Figure 2). The excited state lifetime is too short to be measured by our current apparatus, τ < 1 ns. The TiO$_2$ gel absorption and PL spectra are unchanged in an ethanol

(14) (a) McDevitt, N. T.; Baun, W. L. *Spectrochim. Acta.* **1964**, *20*, 799. (b) Thiele, K.-H.; Panse, M. *Z. Anorg. Allg. Chem.* **1978**, *441*, 23.

Figure 1. Infrared spectrum of (a) Ti(OCH$_2$CH$_3$)$_4$ in NaCl plates, (b) a TiO$_2$ alcogel sandwiched between NaCl plates, and (c) a TiO$_2$ xerogel in a KBr pellet. The data are an average of 32 scans with a resolution of ±4 cm^{-1}.
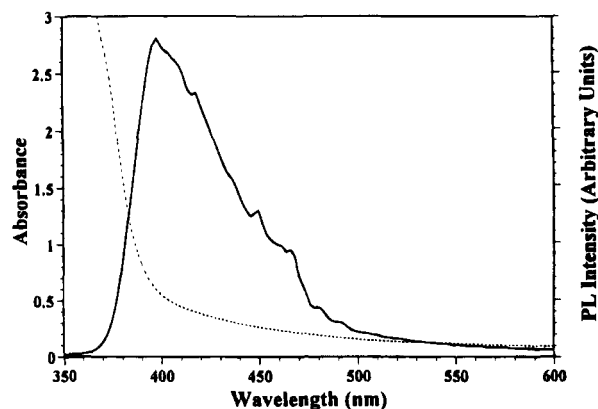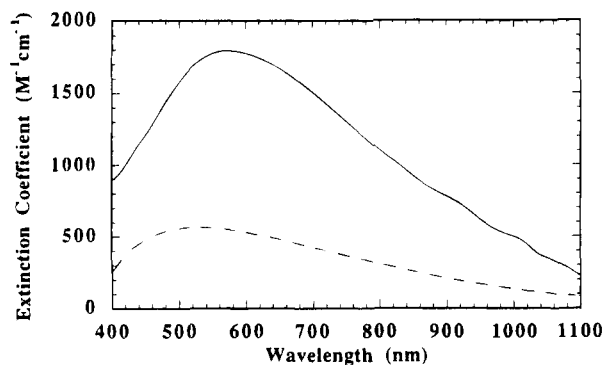

Figure 2. Visible absorbance (dashed line) and the corrected steady-state photoluminescence (solid line) spectra of a sol−gel processed titanium dioxide monolithic gel in absolute ethanol. The photoluminescence spectrum was obtained by excitation with 325 nm light.

or an isopropyl alcohol bath for periods of months after an initial 3 days of aging. The absorption spectrum shifts ~8 nm toward longer wavelength as the temperature is increased from 20 to 70 °C. Cooling the gel restores the initial absorption spectrum.

Ultra-bandgap excitation of TiO$_2$ gels produces a surface-localized blue-black color, whose spectrum is shown in Figure 3. For comparison, the absorption spectrum of a gel doped with TiCl$_3$ is also presented. Attempts to bleach this broad absorption with visible laser excitation have been unsuccessful. The absorption

Figure 3. Absorbance spectrum (solid line) of a sol—gel processed TiO_2 monolithic gel after irradiation with diffuse sunlight. The lower spectrum (dashed line) is a sol—gel processed TiO_2 gel doped with Ti(III). The absorbance spectra were obtained in an absolute ethanol bath with an unphotolyzed gel as a reference.
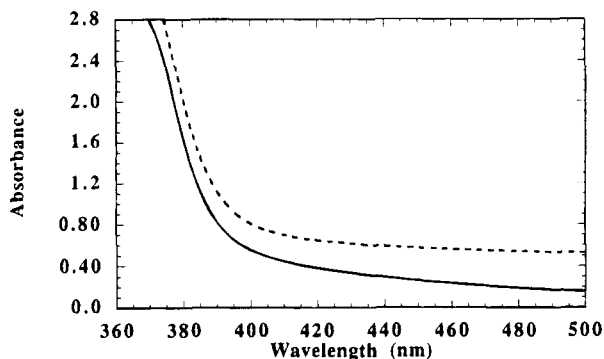
Figure 4. Absorption spectrum of a sol—gel processed TiO_2 monolithic gel before (solid line) and after irradiation (dashed line) with diffuse sunlight. The absorbance spectra were obtained in an absolute ethanol bath with an ethanol reference.

spectra is extremely stable and is independent of temperature from 10 to 70 °C. Photolyzed samples sealed in EPR tubes under nitrogen have maintained their black color and EPR spectrum for over 1 year. If the TiO_2 gel is photolyzed in an isopropyl alcohol bath, the absorption spectrum is similar but shifted to the blue by ~4 nm. Excited state absorption measurements demonstrate that the electrons are produced within a 4—6 ns 355 nm laser pulse. Figure 4 shows that the fundamental absorption edge shifts to lower energy by ~8 nm with bandgap excitation.

Ultra-bandgap excitation of TiO_2 gels yields a room temperature EPR spectrum (Figure 5). No EPR signal is observed in the absence of UV excitation under these conditions. Chemically doping the gel with Ti(III) produces an identical EPR spectrum. The obtained g value ($g = 1.906$) for the paramagnetic species was independent of the gelation time and age of the sample in both the Ti(III)-doped and the photolyzed gels. The main source of the paramagnetic signal comes from electrons localized on ^{46}Ti, ^{48}Ti, and ^{50}Ti isotopes where the nuclear spin (I) is 0. In the absence of nuclear spin, the unpaired electron will give rise to a singlet. The ^{47}Ti and ^{49}Ti isotopes have I = $^5/_2$ and $^7/_2$ which gives rise to a six-line and eight-line spectrum, respectively, when one unpaired electron is coupled to those nuclei. An interesting fact is that ^{47}Ti and ^{49}Ti have almost the same magnetogyric ratios;[12] thus, the hyperfine splittings for each isotope will be approximately the same. Our spectra demonstrate the superposition of these
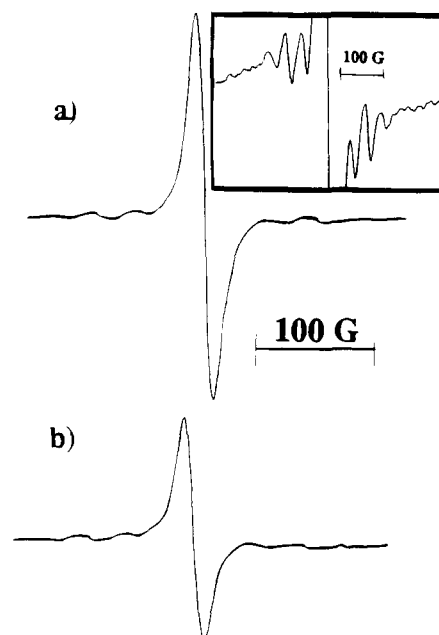

Figure 5. Room-temperature electron paramagnetic resonance spectra of (a) a TiO_2 alcogel irradiated with ultraviolet light and (b) a TiO_2 alcogel doped with 1 mM $TiCl_3$. The inset displays the hyperfine electron paramagnetic resonance spectrum of a TiO_2 alcogel irradiated with 360 nm light.

hyperfine lines as the outer pair of lines is weak with only ^{49}Ti, a 5.51% natural abundance, contributions and the inner lines show contributions from both ^{47}Ti (7.75% natural abundance) and ^{49}Ti. The center line contains contributions from all five isotopes.

The intentional addition of the electron acceptors O_2 or MV^{2+} to the ethanol bath surrounding the gel results in the rapid loss of the trapped electrons. These interfacial electron transfer events occur for photolyzed gels and those doped with Ti(III). The addition of MQ^+ or TV^{2+} does not effect the absorption spectra of the trapped electrons. In the case of MV^{2+} addition, the characteristic spectrum of the methyl viologen radical, $MV^{•+}$, is observed. Assuming interfacial electron transfer occurs with a quantum yield of unity, an estimate of the trapped electrons' extinction coefficient and the quantum yield for their formation, $\phi = 0.01 \pm 0.005$, has been made. After prolonged photolysis, $MV^{•+}$ diffuses to the solution external to the gel matrix.

Titania solutions were gelled between two optically transparent conductive electrodes. These sandwich cells are transparent in a transmission mode and the absorption spectra at the open circuit potential is essentially superimposable on those prepared in the absence of the electrodes. However, absorption measurements below ~370 nm were not possible due to absorption from the electrodes and the polystyrene cuvettes. Application of a voltage more negative than ~−3.3 V produces a black color which reaches its maximum absorptivity within 2 min (Figure 6). The color change is localized near the cathode and can be removed by switching the field to potentials more positive of 0.0 V. Negligible color change is observed when an ethanol—H_2O—HCl solution is placed between two tin oxide electrodes and biased in a similar manner. The time required for removal of the color is typically 10 min. Gels can be switched from black to transparent at least 10 times; however, con-

Titanium Dioxide Gels

Chem. Mater., Vol. 6, No. 11, 1994 2127
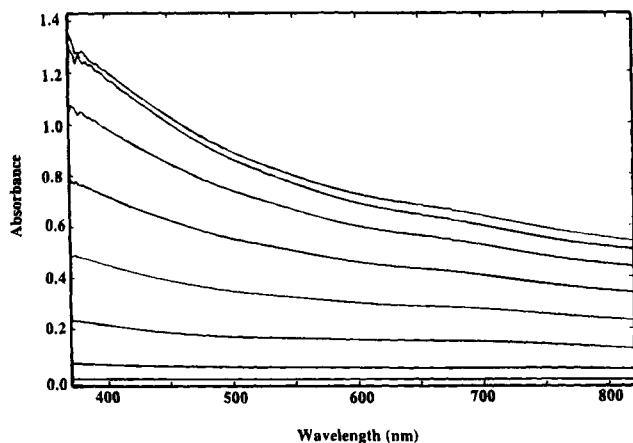
Figure 6. The absorption spectrum of a sol–gel processed TiO$_2$ monolithic gel as a function of applied potential. The reference spectrum was obtained at 0.0 V. From bottom to top: 0.0, −3.2, −3.3, −3.4, −3.5, −3.6, −3.8, and −4.0 V.

tinued switching often requires increasingly more positive potentials to remove the black color.

Discussion

The rapid preparation of titania gels with high visible transparency has been achieved. A general observation in the preparation of a large number of gels is that rapid condensation reactions produce opaque gels or precipitated powders. To avoid this, we have experimentally found that at a given hydrolysis ratio (mole H$_2$O/mole Ti), condensation reactions can be inhibited by either using a high concentration of ethanol or hydrochloric acid. Very high ethanol concentrations lead to the formation of transparent gels which are extremely fragile and difficult to handle and too much acid produces solutions which do not gel for periods of months. Unlike SiO$_2$ gels,[15] acid addition increases the gelation time. The stoichiometry given in reaction III produces gels with the combined highest stability and optical transparency in the visible. These gels are stable in most organic solvents and can be cut into thin slices.

Slow evaporation of solvent converts the titania alcogels to xerogels. Solvent evaporation is accompanied by shrinkage (syneresis) of the gel to ~2.7% of their initial volume and a final density of 1.9 ± 0.1 g/cm^3. Syneresis occurs through reactions IV and V, with

$$||-Ti-OH + HO-Ti-|| \rightarrow ||-Ti-O-Ti-|| + H_2O$$
(IV)

$$||-Ti-OH + RO-Ti-|| \rightarrow ||-Ti-O-Ti-|| + ROH$$
(V)
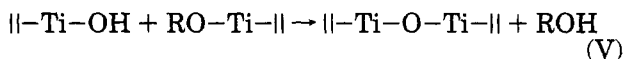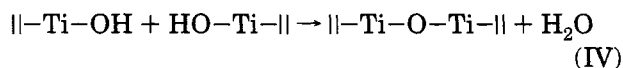
reaction V being particularly important as only 2.3 equiv of water are added for each mole of titanium. These reactions are conveniently monitored by IR spectroscopy. The processed xerogels maintain their optical transparency and are stable toward cracking in the laboratory ambient. The instability of the gels in water and methanol is a likely indication that the condensation reactions are reversible.

Gels are generally classified by two extremes termed "particulate" and "polymeric". Polymeric gels can be

crudely thought of as a collection of "worms", while particulate gels are more similar to a collection of "tumble weeds".[5e] Titania gels are generally regarded as polymeric, although the structures are not exactly known and depend highly on experimental conditions. The dramatic syneresis and stability in high ionic strength solutions suggests that the titania alcogels studied here are also polymeric in nature. More studies are necessary to better understand the molecular structure of these gels; however, they do display interesting optical and electron-transfer properties discussed below.

The fundamental absorption of the titania gels is observed in the ultraviolet region. Excitation of the gels with ultra-bandgap light leads to a deep blue photoluminescence. The high-energy side of the corrected photoluminescence spectrum is edge emission, due to recombination of electrons in the conduction band with holes in the valence band,[16] and the onset energy is approximately equal to the bandgap, $E_g \sim 3.35 \pm 0.05$ eV. The estimated energy gap is slightly larger than that measured for anatase TiO$_2$ materials[1] and may be a signature of quantum confinement.[17] Photoluminescence has been previously observed from TiO$_2$ materials,[18] but the reported emission energy is always equal to or less than 3.2 eV. The broad emission and absorption (Urbach) tail are indicative of intra-bandgap states within the TiO$_2$ gel.[16,19]

Ultra-bandgap excitation produces a surface localized blue-black color which we attribute to trapped electrons. This assignment is based on the similarity of the spectroscopic features with those observed previously in irradiated TiO$_2$ colloids[20] and their potent reducing ability, as discussed below. The appearance of the trapped electrons is also accompanied by an apparent red shift in the fundamental absorption edge. Our preliminary hypothesis is that a charge-transfer band associated with the accumulated electrons appears at high energy which overlaps the gel fundamental absorption edge resulting in the observed spectra. Charge-transfer bands are well-known for Ti(III) compounds, Ti(H$_2$O)$_6^{3+}$ for example.[21] It is interesting to note that the injection of excess charge into TiO$_2$ and other semiconductor quantum particles shifts the fundamental absorption edge toward higher energy.[17]

The electron absorption spectrum is extremely stable, and there are no significant spectral changes during the decay process. The decay process presumably involves the reduction of trace impurities, such as O$_2$, or electron recombination with trapped holes. The optical spectrum

(15) Pope, E. J. A.; MacKenzie, J. D. *J. Non-Cryst. Solids* **1986**, *87*, 185.

(16) (a) Pankove, J. I. *Optical Processes in Semiconductors*; Dover Publications: New York, 1971; p 34.

(17) Henglein, A. *Top. Curr. Chem.* **1988**, *143*, 149.

(18) (a) Nakato, Y.; Tsumura, A.; Tsubomura, H. *J. Phys. Chem.* **1983**, *87*, 2402. (b) Chandrasekaran, K.; Thomas, J. K. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1163. (c) Anpo, M.; Aikawa, N.; Kubokawa, Y.; Che, M.; Louis, C.; Giamello, E. *J. Phys. Chem.* **1985**, *89*, 5017.

(19) Mott, N. F.; Davis, E. A. *Electronic Processes in Non-Crystalline Materials*; Clarendon Press: Oxford, 1979; p 238.

(20) (a) Henglein, A. *Ber. Bunse-Ges. Phys. Chem.* **1982**, *86*, 241. (b) Duonghong, D.; Ramsden, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2977. (c) Moser, J.; Grätzel, M. *J. Am. Chem. Soc.* **1983**, *105*, 6547. (d) Bahnemann, D.; Henglein, A.; Lilie, J.; Spanhel, L. *J. Phys. Chem.* **1984**, *88*, 709. (e) Dimitrijevic, N. M.; Savic, D.; Micic, O. I.; Nozik, A. J. *J. Phys. Chem.* **1984**, *88*, 4278. (f) Bahnemann, D.; Henglein, A.; Spahnel, L. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 151. (g) Rothenberger, G.; Moser, J.; Grätzel, M.; Serpone, N.; Sharma, D. K. *J. Am. Chem. Soc.* **1985**, *107*, 8054. (h) Kolle, U.; Moser, J.; Grätzel, M. *Inorg. Chem.* **1985**, *24*, 2253. (i) Kormann, C.; Bahnemann, D. W.; Hoffman, M. R. *J. Phys. Chem.* **1988**, *92*, 5196.
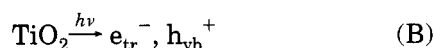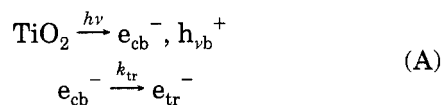
(21) Hartman, H. *Z. Anorg. Allg. Chem.* **1956**, *284*, 153.

of valence band holes has not been observed on nanosecond or longer time scales. Positive trapped holes with high extinction coefficients in the visible region have been previously observed in aqueous colloidal TiO$_2$ solutions.[20d] Our inability to observe such an absorption feature may be due to a lower extinction coefficient or rapid hole transfer to a surface site or solvent. Hole transfer could be facilitated by the gel matrix which has a composition rich in $-OH$ and $-OC_2H_5$. The possibility that solvent oxidation is facilitated through unhydrolyzed ethoxy groups[22] is particularly intriguing, as efficient hole transfer is generally regarded as the key to the preparation of practical artificial photosynthetic devices based on TiO$_2$.[23]

Addition of O$_2$ or MV^{2+} to the ethanol bath surrounding a photolyzed TiO$_2$ gel results in the complete symmetric loss of the electron absorption spectrum. Electron transfer to the viologens MQ$^+$ and TV^{2+} does not occur, which places the redox potential of the trapped electrons between -0.44 and -0.65 V vs NHE. In the case of methylviologen addition, the characteristic absorption spectrum of MV$^{•+}$ appears with a quantum yield of $0.010 + 0.005$. This yield is close to that estimated previously for TiO$_2$ quantum particles.[20i] Reduced methylviologen molecules could potentially serve as mobile electron shuttles capable of doing work in the external solution.[24]

The optical properties of electrons can provide information on the degree of electronic localization in the semiconductor. The molar absorptivity of a free moving electron increases with wavelength,[25,26] where a trapped electron displays an absorption maximum. The observed absorption spectrum is therefore indicative of trapped electrons. It remains uncertain whether electrons are (A) first excited to the conduction band and

$$TiO_2 \xrightarrow{h\nu} e_{cb}^-, h_{\nu b}^+$$
$$e_{cb}^- \xrightarrow{k_{tr}} e_{tr}^- \qquad\qquad (A)$$

$$TiO_2 \xrightarrow{h\nu} e_{tr}^-, h_{\nu b}^+ \qquad\qquad (B)$$

subsequently move to Ti(IV) trap site(s), or (B) directly excited to the trap site(s), or both. The high-energy emission onset indicates that some electrons are excited to the conduction band. Furthermore, visible excitation of the gels ($\lambda_{exc} > 400$ nm) does not result in electron trapping, making pathway (A) more likely. The average time of electron trapping in colloidal TiO$_2$ solutions has recently been estimated to be less than 100 fs.[27] If hole or electron trapping occurs within TiO$_2$ gels, it must be fast, $k_{tr} > 10^9$ s^{-1}, in order to efficiently compete with

excited-state decay.

There exists strong literature evidence that photogenerated electrons are trapped at Ti(IV) sites in aqueous TiO$_2$ colloidal solutions.[17] To evaluate this possibility for the gels studied here, the absorption spectrum of irradiated and Ti(III)-doped gels were compared and found to be very similar. Both spectra display a broad absorption feature with a maximum in the visible which extends into the near infrared. A single absorbance band is expected for a d^1 metal ion in an undistorted octahedral field, $t_{2g} \rightarrow e_g$. The broad structureless absorbance precludes further analysis of the Ti(III) coordination environment(s).[28] Room-temperature electron paramagnetic resonance measurements provide further evidence that the electrons are trapped at Ti-(IV) sites. Sharp superimposable room temperature spectra of the photolyzed and Ti(III)-doped titania gels are observed with $g = 1.906$. Interestingly, we observe hyperfine structure from Ti isotopes, $A = 36$ G, which to our knowledge has not been previously observed in TiO$_2$ materials.[29] Taken together, the spectroscopic results strongly suggest that photogenerated electrons are trapped at Ti(IV) sites.

A gray-black color can be electrochemically generated on the monolithic gel surface which is different from that generated with light. Specifically, electrochemically reduced gels do not display an absorption maximum but rather an increasing absorptivity toward the blue. The gels can be switched from gray-black to clear at least 10 times. The threshold voltage for coloration is -3.3 V and bleaching requires 0.0 V. While the short lifetime of these gels precludes any practical applications, we note that the conditions have not been optimized. In this regard, Livage and co-workers have recently prepared "all-gel" electrochromic devices which have been cycled over 10 000 times without failure.[30]

Conclusion

Amorphous titania gels exhibit photophysical properties very similar to single-crystal materials, suggesting related band structures. Band structure manifests itself in a fundamental absorption, edge emission, and redox chemistry from the valence and conduction bands. The spectroscopic data strongly suggest that photogenerated electrons in sol$-$gel processed TiO$_2$ gels are trapped at Ti(IV) sites. The remarkably long lifetime of trapped electrons is further evidence that soft gelatinous materials can respond to changes in electronic environment[7] and stabilize radicals.[31] Electron transfer to methylviologen acceptors located within the gel intrapore region

(22) Gas chromatographic analysis of photolyzed TiO$_2$ gels in 2-propanol demonstrates the formation of acetone. Although the identity of ethanol oxidation products remains uncertain, there exists ample literature precedence for ethanol photoinduced oxidation by TiO$_2$. See, for example: (a) Miyake, M.; Yoneyama, H.; Tamura, H. *Chem. Lett.* **1976**, 635. (b) Cunningham, J.; Hodnett, B. K. *J. Chem. Soc., Faraday Trans.1* **1981**, 77, 2777. (c) Finklea, H. O. *Semiconductor Electrodes*, Elsevier: New York, 1988; p 129.

(23) Brown, G. T.; Darwent, J. R. *J. Phys. Chem.* **1984**, 88, 4955.

(24) Slama-Schwok, A.; Ottolenghi, M.; Avnir, D. *Nature* **1992**, 355, 240.

(25) Seeger, K. *Semiconductor Physics: An Introduction* **1982**, Springer-Velag: Berlin, 1982; pp 343−356.

(26) Nenadovic, M. T.; Rajh, T.; Micic, O. I.; Nozik, A. J. *J. Phys. Chem.* **1984**, 88, 5827.

(27) Colombo, D. P. Jr.; Roussel, K. A.; Bowman, R. M. *Abstract 319 PHYS, 207th ACS National Meeting*, 1994, San Diego.

(28) (a) Iwamoto, N.; Hidaka, H.; Makino, Y. *J. Non-Cryst. Solids* **1983**, 58, 131. (b) Pizzini, S.; Nirducci, D.; Daverio, D.; Mari, C. M.; Marazzoni, F.; Gervasini, A. *J. Chem. Soc., Faraday Trans. 1* **1987**, 83, 705.

(29) (a) Huizinga, T.; Prins, R. *J. Phys. Chem.* **1981**, 85, 2156. (b) Howe, R. F.; Grätzel, M. *J. Phys. Chem.* **1985**, 89, 4495. (c) Howe, R. F.; Grätzel, M. *J. Phys. Chem.* **1987**, 91, 3906. (d) Howe, R. F.; Grätzel, M. *J. Phys. Chem.* **1990**, 94, 2566. (d) Micic, O. I.; Zhang, Y.; Cromack, K. R.; Trifunac, A. D.; Thurnauer, M. C. *J. Phys. Chem.* **1993**, 97, 7277. (e) Micic, O. I.; Zhang, Y.; Cromack, K. R.; Trifunac, A. D.; Thurnauer, M. C. *J. Phys. Chem.* **1993**, 97, 13284.

(30) (a) Judeinstein, P.; Livage, J.; Zarudiansky, A.; Rose, R. *Solid State Ionics* **1988**, 28, 1722. (b) Nabavi, M.; Doeuff, S.; Sanchez, C.; Livage, J. *J. Mater. Sci. Eng.* **1989**, B3, 203.

(31) (a) Symons, M. C. R. *Nature* **1987**, 325, 659. (b) Ragai, J. *Nature* **1987**, 325, 703.

Titanium Dioxide Gels

Chem. Mater., Vol. 6, No. 11, 1994 2129

provides a means of removing the photocreated redox energy from the gel network.

The amorphous gels can be compared to nanostructured TiO$_2$ films which are practically useful in photovoltaic devices.[32-35] These films are comprised of a porous interconnected anatase structure typically ~10 μm thick. In contrast to the gels studied here, the TiO$_2$ films are sintered to provide ohmic contact between the particles and an electron pathway. Electrochemical reduction of these films reportedly produces mainly free carriers and efficient conduction.[35] While carrier mobility may preclude the use of these titania gels in many electrooptical applications, they hold significant potential in photocatalysis, combining the high surface area of colloids and the ease in handling of bulk materials. In this regard, we note that efficient photodecomposition of organic pollutants over supercritically dried titania gels has recently been reported,[36] and efficient hydrogen evolution from heat-treated titania gels has long been known.[37] These and other applications are certainly forthcoming from this interesting class of TiO$_2$ materials.

(32) (a) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. *J. Am. Chem. Soc.* **1985**, *107*, 2988. (b) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 1216. (c) Liska, P.; Vlachopoulos, N.; Nazeeruddin, M. K.; Comte, P.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 3686. (d) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. *J. Am. Chem. Soc.* **1990**, *112*, 7099. (e) O'Regan, B.; Moser, J.; Anderson, M.; Grätzel, M. *J. Phys. Chem.* **1990**, *94*, 8720. (f) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. *J. Am. Chem. Soc.* **1990**, *94*, 8720. (g) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (h) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382. (i) Hay, A.; Grätzel, M. *J. Phys. Chem.* **1993**, *97*, 6272.

(33) (a) Eichberger, R.; Willig, F. *Chem. Phys.* **1990**, *141*, 159. (b) Schwarzburg, K.; Willig, F. *Appl. Phys. Lett.* **1991**, *58*, 2520.

(34) (a) Heimer, T. A.; Bignozzi, C. A.; Meyer, G. J. *J. Phys. Chem.* **1993**, *97*, 11987. (b) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.*, in press.

(35) (a) O'Regan, B.; Grätzel, M.; Fitzmaurice, D. *Chem. Phys. Lett.* **1991**, *183*, 89. (b) O'Regan, B.; Grätzel, M.; Fitzmaurice, D *J. Phys. Chem.* **1991**, *95*, 10525. (c) Rothenberger, G.; Grätzel, M.; Fitzmaurice, D *J. Phys. Chem.* **1992**, *96*, 5983. (d) Redmond, G.; Grätzel, M.; Fitzmaurice, D *J. Phys. Chem.* **1993**, *97*, 6951.

(36) Dagan, G.; Tomkiewicz, M. *J. Phys. Chem.* **1993**, *97*, 12651.

(37) Kruczynski, L.; Gesser, H. D.; Turner, C. W.; Speers, E. A. *Nature* **1981**, *291*, 399.