Investigation of Water Structure at the TiO2/Aqueous Interface

Sho Kataoka, Marc C. Gurau, Fernando Albertorio, Matthew A. Holden, Soon-Mi Lim, Richard D. Yang, and Paul S. Cremer*

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

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TiO2 thin films coated on SiO2 substrates were prepared for the investigation of water structure at the TiO2/aqueous interface by vibrational sum-frequency spectroscopy (VSFS). The films were first characterized by X-ray photoelectron spectroscopy, ellipsometry, and atomic force microscopy. Film thickness could be readily varied between 0.9 and 5.9 nm with the thinnest film displaying the least degree of surface roughness. The 0.9 nm films were employed in the VSFS investigations and showed characteristic 3200 and 3400 cm−1 OH stretch frequencies of highly aligned interfacial water. Such peaks were reminiscent of those known from SiO2/aqueous interfaces; however, the chemistry at TiO2/aqueous interfaces was significantly richer. In the presence of Cl anions, the surface had an isoelectric point near pH 5.5 and showed the least degree of water organization near this pH. Almost equally strong 3200 cm−1 features could be produced at pH 2.0 and 12.0. On the other hand, the spectra were dramatically altered in the presence of phosphate-buffered saline. The phosphate ions specifically bound to the substrate surface and shifted the isoelectric point of the interface to pH 2.0. In this case, the intensity of the 3400 cm−1 peak was significantly increased in comparison with the Cl ion data at both neutral and acidic pH values. This is presumably because of a lack of sites directly adjacent to the oxide for forming tetrahedrally coordinated water when phosphate ions are present.

Introduction

Titanium dioxide (TiO2) draws significant interest from researchers in a wide range of disciplines including catalysis, optics, and electrochemistry.1–4 Additionally, titanium metal is commonly employed in artificial implants due to the biocompatibility of the thin TiO2 layer at its surface.5–7 Studies of TiO2 interfaces, which are essential for understanding these applications, have greatly intensified with the development of modern analytical techniques such as scanning tunneling microscopy (STM),4,13 atomic force microscopy (AFM),14 X-ray photoelectron spectroscopy (XPS),15 Fourier transform infrared (FTIR) spectroscopy,16 and vibrational sum-frequency spectroscopy (VSFS).17–21

Of interest herein is the elucidation of water structure at the TiO2/aqueous interface. Obtaining such information may ultimately prove crucial for understanding the adsorption, displacement, and spreading of protein molecules at nascently formed artificial/biological interfaces.22,23 At present, little is known about the basic interfacial structure of water on titanium dioxide. In fact, the vast majority of VSFS studies of water structure at liquid/solid interfaces have been performed at the SiO2/aqueous interface.24–31 There are good reasons to suspect, however, that the behavior of water may be different on titanium dioxide surfaces. TiO2 has its isoelectric point much closer to neutral pH in the presence of simple salt solutions than does SiO2 (pH 5.5 vs 2.3).32–37 and TiO2;
becomes positively charged below pH 5.5. Also, TiO2 can specifically adsorb certain inorganic anions such as phosphate, which significantly shift the isoelectric point at the interface.32,33 SiO2, which has an isoelectric point near pH 2.3, does not seem to display similar behavior.39 VSFS has recently grown to be a powerful source of surface specific vibrational information under ambient conditions. The basic principles have been discussed elsewhere.44–47 Briefly, VSFS provides vibrational information on molecules at interfaces even in the presence of an overwhelming bulk contribution. As an optical technique, it has been exploited for investigating vapor–liquid, solid/liquid, and liquid/liquid interfaces. While VSFS has yet to be applied to the TiO2/aqueous interface, studies have been conducted at other solid/aqueous interfaces including the SiO2/water,24–27 Al2O3/water,48 and CaF2/water interfaces.45,46 TiO2/aqueous interfaces have been observed, however, by second harmonic generation (SHG).47,48 Furthermore, a cathodic complex has been made on colloidal TiO2 particles and a surface charge-transfer process was directly observed by SHG in aqueous solution in its presence.49,50 In terms of nonaqueous titanium dioxide interfaces, VSFS has recently been exploited for information on molecules at interfaces even in the presence of high concentrations of organic anions. VSFS has recently been used to study the adsorption of terephthalic acid on TiO2.20 Also, the presence of trace hydrocarbon species has been monitored on nanoparticulate TiO2 surfaces in the presence and absence of UV illumination.21

Herein we report on the preparation and investigation of ultrathin TiO2 films on SiO2 substrates. The surfaces were characterized by AFM, XPS, and ellipsometry. VSFS data were collected at the TiO2/aqueous interface in the presence of chloride and phosphate anions over a range of pH values. The results are directly compared to the SiO2/aqueous interface. The data reveal that water structure at titanium dioxide is highly dependent upon both the pH of the aqueous solution and the specific nature of the anions present.

### Experimental Section

#### TiO2 Thin Film Preparation and Characterization.

Recently, several methods have been developed for the preparation of TiO2 thin films.51–54 These methods were modified to fit the present studies as follows: round SiO2 substrates (1 in. diameter, 1/8 in. thick IR grade fused quartz; Quartz Plus Inc., Brookline, NH) were cleaned and subsequently annealed in a kiln at 500 °C for 6 h. Each disk was then soaked in concentrated sulfuric acid (EM Science, Gibbstown, NJ) for 5 h following by rinsing with copious amounts of water and methanol in order to hasten the interface. Next, the disks were exposed to titanium(IV) isopropoxide (Ti(OPr)4; Aldrich, Milwaukee, WI) in a closed environment for time periods ranging from 10 to 120 min at room temperature (see Figure 1), which allowed Ti(OPr)4 vapor (vapor pressure, 10 mmHg at 14 °C) to react with the surface silanol groups. The time period of exposure dictated the ultimate thickness of the film that could be achieved. Afterward, the disks were washed with water and acetone before a final calcination at 500 °C for 6 h.

The TiO2 films were characterized by XPS to determine their chemical composition. Ellipsometry measurements were made to access film thickness, and AFM was performed to provide topographical information about film thickness.

### Figure 1

Schematic diagram of the preparation of TiO2 thin films on a SiO2 disk: (left) a SiO2 disk was hydroxylated with H2SO4, (middle) then exposed to the Ti(OPr)4 precursor in a Petri dish, and (right) finally washed with water and acetone to remove excess isopropoxide.
through an optical parametric generation/amplification (OPG/OPA) stage (Laser Vision, Bellevue, WA) to produce a tunable IR beam between 2700 and 3700 cm\(^{-1}\) as well as fixed frequency radiation at 532 nm. The polarization combination used in these experiments was SSP, referring to the sum frequency, visible, and infrared beams, respectively.

The experimental setup, including a homemade Teflon flow cell for taking data, has been described in previous publications.\(^{28-31}\) A TiO\(_2\)-coated SiO\(_2\) disk was fitted onto the cell so that the coated side faced inward toward the water solution (Figure 2). The input laser beams were transmitted through the coated substrate and focused at the TiO\(_2\)/aqueous interface. All aqueous solutions were prepared with water obtained from a NANOpure Ultrapure Water System (Barnstead, Dubuque, IA). Several solutions at various pH values (2.0, 4.0, 6.0, 8.0, 10.0, and 12.0) were flowed through the system. The pH of the solutions was controlled by the addition of either NaOH or HCl (EM Science), while the total ionic strength of a given solution was maintained at 30 mM by the addition of NaCl (EM Science). Additional data were taken in the presence of phosphate ions. In this case, 30 mM phosphate-buffered saline (PBS) solutions were prepared using the appropriate quantity of sodium phosphate with the addition of NaOH or HCl to control the pH. The spectra collected at each pH value were averaged and normalized to spectra taken from a piece of Y-cut crystalline quartz.

**Results and Discussion**

**Film Preparation and Characterization.** After deposition of a titanium dioxide film onto a SiO\(_2\) substrate, XPS was used to characterize the chemical composition of the surface. Figure 3 shows both a survey and a high-resolution XPS spectrum for a TiO\(_2\) film made from a 10 min exposure to the Ti(O\(_i\)Pr)\(_4\) precursor. The survey scan contained noticeable peaks for Ti, O, C, and Si. The Ti 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks had binding energies of 458.9 and 465.0 eV, which are expected for Ti existing in the form of TiO\(_2\).\(^{12}\) The atomic fractions of all elements were constant over different regions of the film at least down to the size of the X-ray beam spot profile (200 \(\times\) 200 \(\mu\)m\(^2\)). As noted, the XPS survey spectrum contained a small but noticeable carbon peak (C 1s), which is believed to arise from atmospheric exposure of the film rather than as a consequence of the use of the Ti(O\(_i\)Pr)\(_4\) precursor since the organic should be completely oxidized to carbon dioxide during the film calcination process.

The thickness of the TiO\(_2\) films varied with the amount of time a given disk was exposed to Ti(O\(_i\)Pr)\(_4\). The results of ellipsometric measurements are shown as a function of the exposure time, along with the atomic fraction of Si and Ti obtained from the XPS spectra (Figure 4). The film thickness increased roughly linearly with increasing exposure time. As expected, the atomic fraction of Si detected by XPS was highest for the thinnest film and decreased with film thickness. On the other hand, Ti showed the opposite behavior. The Si peak is expected to be present for all exposure times even for uniformly covered surfaces since the escape depth of the photoelectrons is at least as large as the thickness of the films in the present study.\(^{57}\)

The films were next characterized by AFM. Figure 5 shows images taken of (a) a bare SiO\(_2\) disk, (b) a 0.9 nm film, (c) a 1.6 nm film, and (d) a 3.2 nm film. All images were acquired in tapping mode with a scan area of 200 \(\times\) 200 nm\(^2\). The 0.9 nm thick TiO\(_2\) film was not noticeably rougher than the one obtained from bare SiO\(_2\), indicating that no "islandlike" film deposition occurred. Indeed, the root-mean-square (rms) roughness of the film was 0.057 nm over a 200 \(\times\) 200 nm\(^2\) scan area as compared to 0.055 nm for bare SiO\(_2\). The surface became somewhat rougher for the thicker films: the rms roughness was 0.128 nm for the 1.6 nm film and 0.172 nm for the 3.2 nm film. These are still rather smooth films; however, the increase may reflect an insufficient number of OH termini on top of the growing TiO\(_2\) film. This in turn may limit subsequent uniform attack by the Ti(O\(_i\)Pr)\(_4\) precursor from the vapor phase. No particulate deposition was detected for any of

the films. Based on the above ellipsometry, XPS, and AFM results, it is reasonable to conclude that the TiO$_2$ film covered the vast majority of the SiO$_2$ substrates. Indeed, even the thinnest film showed little evidence for nonuniform surface coverage over scales ranging from hundreds of microns (XPS) to nearly one nanometer (AFM).

**VSFS Spectra: pH Effects.** Because of its relative smoothness and good uniformity, the 0.9 nm film was employed in the VSFS experiments presented below.$^{38}$ All VSFS investigations were undertaken at both the SiO$_2$/aqueous and TiO$_2$/aqueous interfaces. For reference, VSFS data were recorded between 2700 and 3700 cm$^{-1}$ at the bare SiO$_2$/aqueous interface over a pH range from 2.0 to 12.0. The results are shown in Figure 6a. The spectra were dominated by two broad and prominent features at 3200 and 3400 cm$^{-1}$, consistent with previous studies of this interface.$^{24-26,41,43,59-61}$ The 3200 cm$^{-1}$ peak is indicative of water with tetrahedral bonding. Its strength is largely determined by the magnitude of the electric field emanating from the negatively charged deprotonated silanols at the interface. The strength of this peak increases almost monotonically as the bulk pH is raised because a continually greater fraction of the silanols exist near the isoelectric point and this interface is in contrast to that of SiO$_2$, which only reaches its isoelectric point around pH 5.5 based on zeta potential measurements.$^{32-37}$

The 3200 cm$^{-1}$ peak is accompanied by a comparable 3400 cm$^{-1}$ peak. However, the strength of these features reached a minimum near pH 4.0 and 6.0. It then showed a marked increase as the pH was lowered to 2.0. This increase in VSFS intensity under acidic conditions stems directly from the nature of TiO$_2$ surface chemistry. The TiO$_2$ interfacial layer is hydroxylated (i.e., forms TiOH$^\text{+}$) in a manner analogous to silanol formation on SiO$_2$.$^{39,44,64}$ However, the Ti$^{4+}$--OH groups, which have an isoelectric point around pH 5.5, become positively charged under more acidic conditions. This behavior is in contrast to that of SiO$_2$, which only reaches its isoelectric point near pH 2.3.$^{29}$ In the case of TiO$_2$, there is probably a mixture of TiO$_2$$^\text{2+}$, TiOH$^\text{2+}$, and TiOH$_2$$^\text{3+}$ moieties that exist near the isoelectric point and this interface becomes continuously more positively charged as the pH is lowered.$^{37}$ Since the sign of the charge of the TiO$_2$/aqueous interface changes as the pH is lowered through the isoelectric point, the water dipoles almost certainly flip as a result.$^{27}$ In other words, the oxygen end of the water molecules most likely points downward at low pH, while the protons face the surface under basic conditions.

**VSFS Spectra: Phosphate Ion Effects.** In the next set of experiments, phosphate-buffered saline was introduced at the SiO$_2$/aqueous and TiO$_2$/aqueous interfaces. In this case, 30 mM PBS was employed and the pH was adjusted to the desired value. Spectra for the SiO$_2$/aqueous interface between pH 2.0 and 12.0 are shown in Figure 7a. The intensity and width of the 3200 and 3400 cm$^{-1}$ peaks are almost identical to those shown in Figure 6a, and the presence of phosphate ions in the buffer seems to

![Figure 5](image.png)  
**Figure 5.** AFM images of TiO$_2$ thin films on a SiO$_2$ disk over a 200 × 200 nm$^2$ region: (a) a bare SiO$_2$ surface, (b) a 0.9 nm film, (c) a 1.6 nm film, and (d) a 3.2 nm film.

![Figure 6](image.png)  
**Figure 6.** VSFS spectra of (a) the SiO$_2$/aqueous and (b) TiO$_2$/aqueous interfaces as a function of pH. Solutions were made with only HCl, NaOH, and NaCl.

This was especially noticeable at pH values of 8.0 and 10.0. The intensity of the 3400 cm\(^{-1}\) peak was quite small at pH 2.0 relative to more basic values. Such zeta potential results in combination with the phosphate adsorbate makes it more difficult to obtain the requisite registry for tetrahedral water coordination in the first water monolayer. This causes an increase in the number of water molecules directly adjacent to the surface without a full complement of hydrogen bonds and hence increases the 3400 cm\(^{-1}\) signal.

**Outlook.** Investigations of water structure at the TiO2/aqueous interface clearly demonstrate some similarities and some differences of this oxide with silica. The door is now open to exploring TiO2 films in the presence of various polymer, protein, and surfactant adsorbates. A key question for future studies will be to ascertain whether the molecular level details of water organization can be correlated with biofouling processes. This is especially important in light of the fact that TiO2 can be used in implants. From a molecular point of view, it will be key to determine if water molecules either directly adjacent to the substrate (associated with the 3400 cm\(^{-1}\) peak) or those aligned by the interfacial electric field (associated with the 3200 cm\(^{-1}\) peak) can signify resistance or enhancement of macromolecular adsorption.

**Conclusions**

Herein we have developed a simple procedure for creating TiO2 ultrathin films on SiO2 substrates suitable for the investigation of water structure using VSFS. Characterization of these films by XPS, ellipsometry, and AFM suggested that 0.9 nm thick films were uniform both chemically and topologically. The method could be used to control layer thickness, although thicker films suffered from slightly greater roughness. VSFS spectra of films at the solid/aqueous interface revealed the presence of ordered water structure reminiscent of that seen from the SiO2/aqueous interface. The TiO2 films, however, proved to have far richer chemistry. In the presence of simple salt solutions (NaCl), the water peaks displayed a minimum in intensity near pH 4.0 and 6.0. This is quite close to the system’s known isoelectric point of pH 5.5. The intensity of the 3200 cm\(^{-1}\) feature was dramatically increased at pH values above and below this point. On the other hand, adding phosphate anions to the solution shifted the isoelectric point down near pH 2.0 due to their strong adsorption on the surface of TiO2. This caused the 3200 cm\(^{-1}\) peak intensity to obey roughly the same behavior as a function of pH as that seen at the SiO2/aqueous interface. The 3400 cm\(^{-1}\) peak was strengthened in relation to the 3200 cm\(^{-1}\) feature by the presence of phosphate ions.

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