Chemisorbed and Physisorbed Water at the TiO$_2$/Water Interface

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Supporting Information

ABSTRACT: The interfacial structure of water in contact with TiO$_2$ is the key to understand the mechanism of photocatalytic water dissociation as well as photoinduced superhydrophilicity. We investigate the interfacial molecular structure of water at the surface of anatase TiO$_2$, using phase-sensitive sum frequency generation spectroscopy together with spectra simulation using $ab$ initio molecular dynamic trajectories. We identify two oppositely oriented, weakly and strongly hydrogen-bonded subensembles of O–H groups at the superhydrophilic UV irradiated TiO$_2$ surface. The water molecules with weakly hydrogen-bonded O–H groups are chemisorbed, i.e. form hydroxyl groups, at the TiO$_2$ surface with their hydrogen atoms pointing toward bulk water. The strongly hydrogen-bonded O–H groups interact with the oxygen atom of the chemisorbed water. Their hydrogen atoms point toward the TiO$_2$. This strong interaction between physisorbed and chemisorbed water molecules causes superhydrophilicity.

Owing to its photoinduced superhydrophilicity as well as the photocatalytic activity, TiO$_2$ finds unique applications in self-cleaning surfaces and hydrogen generation through photocatalytic water dissociation. For these applications, the adsorption and arrangement of water molecules on the TiO$_2$ surface is crucial. Therefore, water organization and dissociation on single crystalline TiO$_2$ surfaces have been intensively examined with a variety of techniques such as X-ray photoelectron spectroscopy (XPS), scanning tunneling microscope (STM), nuclear magnetic resonance (NMR), and contact angle measurements.3–9 These studies typically focus on adsorption of thin water layers on TiO$_2$ at low water vapor pressure and at low temperatures (typically 170 K or less). However, these experimental conditions are far from the atmospheric pressure and room temperature conditions under which TiO$_2$ is commercially used. Moreover, the properties of a thin water layer are different from those of bulk water.7,10–12 It is thus desirable to determine the properties of interfacial water on TiO$_2$ in contact with bulk water.

In many experimental methods used in studying bulk water in contact with TiO$_2$, a limiting factor is the overwhelming signal of bulk water compared to the signal from water at the interface. By contrast, vibrational sum frequency generation (SFG) spectroscopy, owing to its selection rules, is an inherently surface sensitive tool, allowing for studying water molecules at the interface between TiO$_2$ and bulk water with no bulk signal contribution. In particular, the O–H stretching region of a SFG spectrum constitutes an ideal local probe for the strength of hydrogen bonding of the interfacial water molecules, since the O–H stretch frequency is sensitive to the hydrogen-bonding strength. Conventional SFG has revealed the pH dependence of the water configuration near the TiO$_2$ surface as well as the effect of the UV illumination on the degree of ordering of water at the TiO$_2$ surface.16 However, the microscopic structure of the UV illuminated TiO$_2$/water interface such as the orientation of the interfacial water molecules and their hydrogen-bond strength has not been clarified.

Molecular dynamics (MD) simulation has been used as a powerful tool to investigate the microscopic structure of water molecules in contact with TiO$_2$.10,11,17–20 The interfacial water structure has been shown to depend, using force field MD simulations, on the number of hydroxyl groups at the surface, which can be modified by pH or UV irradiation.17 Recently, $ab$ initio MD (AIMD) simulation, where the atomic forces are calculated within the density functional theory, was used to study the water configuration near TiO$_2$ surfaces and its pH dependence.18,19 For example, AIMD simulation proposed that water molecules adsorb molecularly or dissociatively on specific binding sites at the anatase TiO$_2$ surface.20 Although the conformational energies of the molecular versus dissociated state of water molecules with their optimized structures have been discussed in the $ab$ initio calculation,21,25,26 the MD technique allows us to explore the possible conformation at finite temperature. As such, AIMD provides the microscopic picture under the thermal fluctuation. Nevertheless, AIMD results have not been well examined through comparison with experiments at the TiO$_2$/water interface.

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In this study, by combining phase-sensitive (heterodyne-detected) SFG measurements with AIMD-SFG simulation, we connect the microscopic structure of the TiO$_2$/water interface to SFG features. Our results reveal that the superhydrophilic nature of anatase TiO$_2$ arises from the chemisorbed hydroxyl groups on the TiO$_2$ surface having weakly donating H-bonds. By contrast, the physisorbed water molecules at the topmost layer are strongly H-bonded to the anatase TiO$_2$ surface.

A polycrystalline TiO$_2$ film with a thickness of 1.5 μm was deposited on a precleaned CaF$_2$ window by spin coating. The Raman spectrum of the deposited TiO$_2$ sample after calcination at 500 °C, presented in Figure 1a, contains peaks at ~399 cm$^{-1}$, ~518 cm$^{-1}$, and ~639 cm$^{-1}$, indicating the formation of anatase TiO$_2$. The scanning electron microscope (SEM) image of the sample presented in Figure S1a shows that the TiO$_2$ layer consists of 50--200 nm globular particles. Before each SFG measurement, the TiO$_2$-coated CaF$_2$ was cleaned in an UV-ozone cleaner for 20 min and immediately put in contact with a 2 mm thick water layer (with selected H$_2$O:D$_2$O ratio) in a homemade cell, which was sealed using another CaF$_2$ window (Figure 2a). The TiO$_2$ surface shows hydrophobic nature before UV irradiation (contact angle ~54°), while it becomes superhydrophilic afterward (contact angle ~0°), as seen in Figure 1b,c. All SFG measurements are performed on the UV irradiated surface. The cleanliness of the TiO$_2$ surface after UV-ozone cleaning was examined by SFG measurements in the C=H stretching region; no spectral signature for hydrocarbon contamination was observed (Figure S1b).

To study the water orientation and H-bonding strength, we measured SFG spectra of water in contact with TiO$_2$. As neat water SFG spectra in the O–H stretching region are quite complicated due to the presence of inter- and intra- molecular couplings, we performed SFG measurements for neat as well as isotopic diluted water. In isotopic diluted water, the coupling effects are reduced. Details of the SFG setup are provided in the Supporting Information. The obtained spectra from the TiO$_2$/water interface were normalized to the SFG signal from a gold-coated CaF$_2$ window located at the same position as the sample. Figure 2b displays measured conventional (homoodyne-detected) SFG spectra obtained from the TiO$_2$/water interface for pure H$_2$O, pure D$_2$O and mixtures of H$_2$O and D$_2$O. The data were corrected for isotope-dependent Fresnel factors, following ref 29 (see Supporting Information). The spectrum of pure H$_2$O (black curve in Figure 2b) exhibits two spectral features centered at ~3200 cm$^{-1}$ and ~3450 cm$^{-1}$. Upon decreasing the H$_2$O:D$_2$O ratio, the shape of the spectra changes dramatically, i.e., the lower frequency peak is blue-shifted and the intensity of both peaks is lowered. Such changes in the SFG spectra upon isotopic dilution indicate a strong coupling between O–H groups of interfacial water molecules. Similar shifts to higher frequency has been observed in an ATR-FTIR experiment of isotopic diluted water adsorbed on a TiO$_2$ film.

To obtain information about the orientation of water molecules at the TiO$_2$/water interface, we performed phase-resolved SFG measurements on 100% H$_2$O and 50% H$_2$O:50% D$_2$O (hereafter referred to as 50% H$_2$O) in contact with TiO$_2$. Analysis of the 50% H$_2$O case is simpler as inter- and intramolecular couplings are reduced. Phase resolved SFG allows for determination of the Re[χ$^{(2)}$] (solid lines) and Im[χ$^{(2)}$] (dots) for 100% H$_2$O and 50% H$_2$O. (d) Experimentally measured conventional SFG spectra (dot-lines) versus the intensity spectra reconstructed from the phase-resolved measurements (solid lines), both measured under identical circumstances in the phase resolved setup.

As is evident from Figure 2c, for both 100% and 50% H$_2$O, Im[χ$^{(2)}$] is positive at the low frequency side of the spectrum, passes through zero around 3200 cm$^{-1}$, and becomes negative for higher frequency. The positive sign of Im[χ$^{(2)}$] at low frequencies indicates that strongly hydrogen-bonded O–H groups are pointing with their transition dipole moments away from the bulk water (i.e., with the H atom toward the TiO$_2$), while the negative sign of Im[χ$^{(2)}$] at higher frequencies shows that the transition dipole moments of weakly hydrogen-bonded O–H groups are aligned toward the bulk water. As shown in Figure 2d, reconstructed SFG intensity spectra (solid lines) from phase resolved measurements show perfect agreement with the conventional SFG spectra measured under identical circumstances (dotted curves).

Indeed, with a positive amplitude for the low frequency mode and a negative amplitude for the high frequency mode, all...
intensity SFG spectra of Figure 2b can be well described with the following equation:

\[ I_{\text{SF}} \propto A_{\text{NR}} e^{\varphi_{\text{NR}}} + \sum_{n} \frac{A_n}{\omega_n - \omega_{\text{IR}} + i\Gamma_n} \]  

\[ (1) \]

where \( A_{\text{NR}} \) and \( \varphi_{\text{NR}} \) represent magnitude and phase of the nonresonant susceptibility and \( A_n, \omega_n, \Gamma_n \) and \( \omega_{\text{IR}} \) are the amplitude, vibrational transition frequency, line width of mode \( n \), and the IR laser frequency, respectively. See the Supporting Information for details of fitting.

To relate the 3100 cm\(^{-1}\) positive and 3400 cm\(^{-1}\) negative SFG features to the microscopic structure of water, we ran AIMD simulations of water in contact with a nonhydroxylated anatase (101) surface with the CP2K software\(^{35}\) and simulated the SFG spectra at the BLYP/DZVP level of theory with the Grimme's van der Waals (D3) corrections.\(^{36}\) The choice of BLYP exchange and correlation functionals plus D3 correction arises from the fact that this combination can reproduce both the surface tension\(^{37}\) and SFG spectra\(^{38}\) accurately. Furthermore, the absorption energy calculation of water on rutile TiO\(_2\) surface demonstrated that the van der Waals corrections are essential for reproducing the water conformation (molecular vs dissociated state) on the TiO\(_2\) surface.\(^{39}\) We compared the (101) surface with the experimental polycrystalline film, as the (101) surface is thermodynamically the most stable facet.\(^{40}\) We simulated the SFG spectra with the autocorrelation function based on the velocity-velocity correlation function scheme.\(^{38}\) Details of the simulation protocols are given in the Supporting Information.

Depth-dependent SFG spectra of the O–H stretch chromophores near the nonhydroxylated surface are shown in Figure 3a, while Figure 3b displays a snapshot of the AIMD trajectory. The simulated SFG spectra show that the amplitude of \( \text{Im}[\chi(2)] \) is maximized when the O–H groups are within the first 4 Å from the topmost Ti layer. The TiO\(_2\) anatase surface generates a strong ordering of water O–H groups within the first 4 Å, with a net orientation toward TiO\(_2\). By contrast, including O–H groups located further away from the surface in the SFG response, the SFG amplitude is reduced. This manifests that the sequential water layers point to the bulk water, consistent with a previous simulation study.\(^{20}\) The spectra converge around 6 Å from the surface, illustrating that the topmost \( \sim 1 \) nm water layer contributes to the SFG signal, which is in agreement with a previous classical force field study.\(^{17}\) The dipole orientations are discussed in the Supporting Information.

However, the simulated \( \text{Im}[\chi(2)] \) spectrum at the nonhydroxylated TiO\(_2\)/water interface does not reproduce the experimentally obtained 3100 cm\(^{-1}\) positive and 3400 cm\(^{-1}\) negative SFG features (Figure 2c), demonstrating that the simulated nonhydroxylated TiO\(_2\) surface is not representative of the experimentally examined surface. In fact, previous studies have suggested that the TiO\(_2\) surface after UV irradiation exhibits a superhydrophilic nature, which was tentatively attributed to TiO\(_2\) hydroxylation upon UV irradiation or to the TiO\(_2\) mediated photo oxidation and removal of hydrocarbons.\(^{40,41,44,45}\) To assess whether surface hydroxyls can affect the SFG response we also simulated the hydroxylated TiO\(_2\) surface and calculated the contribution of the hydroxyl group and the surrounding O–H groups hydrogen bonded to the hydroxyl group to the \( \text{Im}[\chi(2)] \) SFG spectra.

The AIMD simulated spectra for water in contact with a hydroxylated anatase surface are shown in Figure 3c, while Figure 3d shows a snapshot of the hydroxylated TiO\(_2\)/water interface. The simulated spectrum evidence that the H-up water molecule H-bonded to the surface hydroxyl group (O–H···O\(_b\)) of physisorbed water molecules results in a positive SFG response at low frequency, while the H-down hydroxyl group (Ti\(_{5v}\)–O\(_b\)–H) of chemisorbed water molecules gives rise to a negative high frequency SFG feature. Note that the broad negative peak at high frequencies indicates that the Ti\(_{5v}\)–O\(_b\)–H group exhibits a very inhomogeneous, yet relatively weak donating H-bond interaction with other water molecules. The first layer of water molecules has strong H-bond donors as concluded from the low frequency of the O–H···O\(_b\) signal. The simulated spectra of the hydroxylated surface are in very good agreement with the experimentally measured SFG spectra. This similarity suggests that the effect of defects present in the TiO\(_2\) sample used in the experiments on water adsorption and structure is negligible. Our AIMD simulation indicates that the O–H groups of the physisorbed water molecules H-bonded to the chemisorbed water show a vibrational signature at \( \sim 3100 \) cm\(^{-1}\). This frequency is very low compared to the frequency of the H-bonded water at the water/air interface, which has its O–H stretch vibrational signature at \( \sim 3400 \) cm\(^{-1}\) for isotopically diluted water.\(^{47}\) This indicates that the interactions between the water molecules physisorbed to the Ti–OH groups is stronger than the water–water interaction in the bulk, driving the TiO\(_2\) surface superhydrophilicity.
In conclusion, phase-resolved SFG measurements at the superhydrophilic TiO\textsubscript{2}/water interface show both positive and negative features in the Im[\tilde{\chi}^{(2)}] signal in the O–H stretching region, indicating OH groups residing at the TiO\textsubscript{2} surface with opposite orientation of their dipole moments. The AIMD simulation on a hydroxylated surface revealed that the O–H groups of the physisorbed water molecules contribute to a positive SFG feature at 3100 \text{ cm}^{-1}, while the O–H groups of the chemisorbed water molecules contribute to a \sim 3500 \text{ cm}^{-1} negative SFG feature. These physisorbed water molecules are strongly H-bonded to the chemisorbed water molecules via the oxygen atom of these chemisorbed water molecules (O\textsubscript{3} atom). The superhydrophilicity of the TiO\textsubscript{2} surface thus arises from the strong H-bonding interaction between chemisorbed and physisorbed water molecules.

## ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b00564. Sample preparation and characterization, SFG setup, Fresnel factor correction procedure, phase-sensitive SFG measurements, phase correction procedure, fitting parameters, protocols of \textit{ab initio} molecular dynamics simulation, simulation protocol of SFG spectra, and water orientation near the TiO\textsubscript{2}/water surface (PDF)

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### Notes

The authors declare no competing financial interest.

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