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Interfacial Water Structure at As-Prepared and UV-Induced Hydrophilic TiO₂ Surfaces Studied by Sum Frequency Generation Spectroscopy and Quartz Crystal Microbalance

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The interfacial water structures at surfaces of an as-prepared TiO₂ and of the TiO₂ after UV irradiation were investigated by sum frequency generation (SFG) spectroscopy and quartz crystal microbalance (QCM). It was shown that UV illumination led to an increase in the amount not only of adsorbed water as a whole but also of the ordered adsorbed water on the TiO₂ surface, confirming the increase of hydrophilicity of the surface.

Introduction

Titanium dioxide (TiO₂) is one of the most studied photo-electrodes[1,2] and the most important photocatalyst[3,4] and has attracted much attention from both industrial and fundamental research groups. The recent finding that the TiO₂ surface becomes hydrophilic by UV irradiation in the presence of ambient water has widened its application.[5−7] For a further understanding of the mechanism of the photocatalytic reactions and UV-induced surface hydrophilicity, information regarding the molecular structure of the adsorbates, water in particular, on the TiO₂ surface under illumination is essential.

Although a large number of investigations on the catalyst surface in an ultrahigh vacuum have been carried out, only a few investigations for the determination of the molecular structure during the photocatalytic reactions using in situ techniques such as ¹H NMR[8,9] and surface-enhanced IR adsorption (SEIRA)[10] have been carried out. These techniques are not necessarily surface sensitive. Sum frequency generation (SFG) vibrational spectroscopy is an interface-selective probe and has been applied to many systems including air/water,[11,12] water/quartz,[13,14] organic liquid/water,[15,16] and electrolyte/electrode[17,18] interfaces. SFG was also applied to study the structure of adsorbed water layer on mica in relation to humidity.[19]

SFG spectroscopy has been already applied to the TiO₂ surface by Shultz and her colleagues.[20−22] They observed surface the hydroxyl group on the TiO₂ surface under vacuum by SFG spectroscopy for the first time.[20] They also characterized the TiO₂ surface using methanol as a molecular probe and proposed a mechanism for photoinduced conversion of the surface nature to hydrophilic.[21,22] It is, however, not yet clear how the structure of adsorbed water on the TiO₂ surface changes with UV irradiation.

Here, we employed SFG spectroscopy together with a quartz crystal microbalance (QCM), which provides in situ information of a surface mass change in nanogram order, to investigate the interfacial water structures at the surfaces of an as-prepared TiO₂ and of the TiO₂ after UV irradiation. It was proved that the TiO₂ surface became hydrophilic by UV illumination, leading to not only an increase in the amount of adsorbed water but also ordering of the adsorbed water layer.

Experimental Section

A fused quartz prism (IR grade, hemi cylindrical shaped) and gold-coated quartz crystals[23] were used as substrates for the SFG and the QCM measurements, respectively. A 2-propanol solution of 25 mM titanium tetraisopropoxide was sprayed on the substrates (0.4 mL/spray for 10 times), which was being rotated at 2000 rpm, and then the sample was calcinated in air at 500 °C for 5 h to obtain a transparent TiO₂ film.[24] Light from a high-pressure Hg lamp (Ushio UIV-570) through a band-pass filter (Toshiba UV-D33S, 240−400 nm) was used for the UV irradiation.

The SFG system used in the present study was based on a picosecond Nd:YAG laser and an OPG/DFG system and was described in detail elsewhere.[14,25] A flow cell made of poly-chlorotrifluoroethylene was used for the SFG measurements so that gases and liquids contacting the TiO₂ film surface could be changed without any shifts in the sample position and optical alignment. The polarization combination was p, p, and p for the SFG, visible, and infrared light, respectively.

The resonant frequency of the quartz crystal, which was oscillated by a homemade oscillation circuit,[26] was monitored by a frequency counter (Hewlett-Packard, HP53131A). The mass change, Δm, was estimated from the resonant frequency shift, Δf, on the basis of the Sauerbrey equation:[27]

$$\Delta m/A = -S\Delta f \qquad (1)$$

where A is the surface area of the QCM and S is the mass sensitivity for the 5 MHz QCM used in the present study of 17.7 ng/Hz/cm².

Results and Discussion

Figure 1 shows the SFG spectra in the OH stretching vibration region of the TiO₂ film under various conditions.

The SFG spectrum of as-prepared TiO₂ (Figure 1a) has no characteristic peaks except for a small peak at 3760 cm⁻¹ and a broad one around 2900 cm⁻¹. The former peak may be assigned to the free OH mode of the adsorbed water molecule or the hydroxyl group on the TiO₂ surface. It is well-known

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Letters

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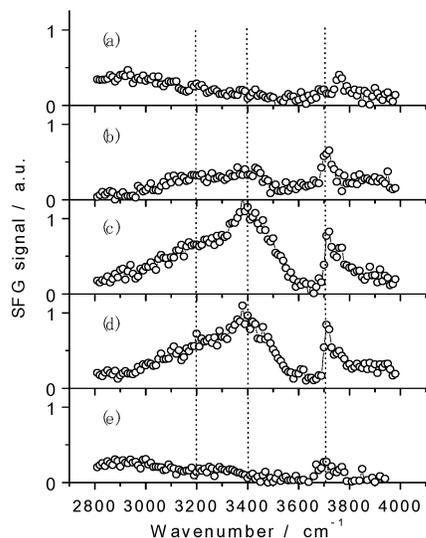
Figure 1. SFG spectra in the OH stretching vibration region of the TiO$_2$ film (a) immediately after the calcination under the flow of pure Ar, (b) under the flow of water-vapor-saturated Ar after the measurement (a), (c) under the flow of water-vapor-saturated Ar and the UV illumination after a 30 min UV illumination, (d) under the flow of water-vapor-saturated Ar after being kept in the dark for 1 h after the measurement in (c), and (e) under the flow of pure Ar after the measurement in (d).

Figure 2. Frequency change of the QCM coated with TiO$_2$ film corresponding to the change of Ar flow and water vapor flow (a) before and (b) after UV irradiation.

that there is adsorbed water on an oxide surface except for under high vacuum conditions, but because there is no peak in the hydrogen-bonded OH stretching vibration region in Figure 1a, one can conclude no liquid water layer but isolated water molecules exist on the surface in the present case. Thus, the small peak at 3760 cm^{-1} is originated not from the surface hydroxyl group but from water molecules, which are adsorbed on the TiO$_2$ surface without forming a liquid layer. The latter may be related to the C−H vibration of the unreacted reactant, reaction intermediate, and/or surface contaminants. The size of these peaks varied from sample to sample.

After the flow of water vapor, the intensity in the central region of the SFG spectrum, i.e., hydrogen-bonded OH stretching vibration region, slightly increased, and a sharp peak appeared at 3700 cm^{-1}, as shown in Figure 1b. The presence of these peaks suggests that the presence of a multilayer of liquid water.[19] The position of the latter peak is slightly different from the one observed in Figure 1a (3760 cm^{-1}) and can be assigned to the OH stretching of the non-hydrogen-bonded water at the air/adsorbed water interface, as the position and shape of the peak are in agreement with those observed for air/water interfaces and octadecylsilane monolayer/water.[11,28] This also confirms that the 3760 cm^{-1} peak observed in Figure 1a is not due to OH stretching of water at the air/ water interface and the absence of a liquid water layer on the TiO$_2$ surface when Figure 1a was obtained.

The SFG intensity in the OH stretching vibration region drastically increased after the TiO$_2$ film was irradiated with UV light for 30 min, as shown in Figure 1c. A broad band with a peak at 3400 cm^{-1} and a shoulder at 3200 cm^{-1} was observed. The shoulder at 3200 cm^{-1} is known to be of "ice-like water", representing the symmetric OH stretching (ν_1) of tetrahedrally coordinated water molecules.[11,28] The broad peak around 3400 cm^{-1} is known to be of "liquid-like water", representing the asymmetric OH stretching (ν_3) of water molecules in a more random arrangement.[11,28] An increase in these bands corresponding to the hydrogen-bonded OH bands clearly demonstrates that the number of ordered water molecules at the TiO$_2$
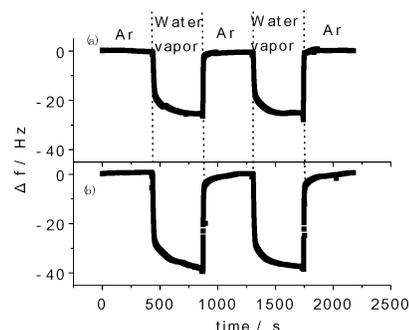
surface increased. Observation of these broad bands associated with hydrogen-bonded water indicates that the TiO$_2$ film after UV irradiation was covered with water in the condensed phase, i.e., liquid water. The intensity of the sharp peak at 3700 cm^{-1} corresponding to an OH stretching of non-hydrogen-bonded water at the air/adsorbed water layer interface also increased but less significantly. Although the SFG spectra contain contributions from both the air/adsorbed water layer and the adsorbed water layer/TiO$_2$ interfaces, the increase in a broad band with a peak at 3400 cm^{-1} and a shoulder at 3200 cm^{-1} after UV irradiation should be due to the contribution from the adsorbed water layer/TiO$_2$ interface because it is very difficult to think the UV irradiation would affect the nature of the water surface.

The SFG spectrum of the TiO$_2$ film being kept in the dark for 1 h after the UV illumination was terminated (Figure 1d) is essentially the same as that obtained under illumination (Figure 1c), showing the adsorption state of the water layer on the TiO$_2$ surface was maintained for at least 1 h in the flow of water vapor without UV irradiation.

The SFG spectrum of the TiO$_2$ film under the flow of Ar, which was obtained after Figure 1d was measured, is shown in Figure 1e. The SFG signal due to adsorbed liquid water was essentially absent, although a small peak corresponding to the free OH peak was still observed around 3700−3760 cm^{-1}.

The increase of the intensity of the hydrogen-bonded OH band by UV irradiation can be due to the increase of either the amount of adsorbed water on the TiO$_2$ surface or the orientational order of the adsorbed water layer as the SFG intensity is proportional to the absolute square of the macroscopic second-order nonlinear susceptibility, $\chi^{(2)}$, which depends on the density of surface molecules (N) and the molecular hyperpolarizability (β) averaged over all molecular orientations on the surface.

Figure 2 shows the frequency change at the TiO$_2$-coated QCM (a) before and (b) after UV irradiation, corresponding to the change between the flow of Ar and water vapor.

When water vapor flowed, the frequency decreased by 25 and 37 Hz for the samples before and after the UV irradiation, respectively. These frequency changes correspond to the increase of 14 and 21 adsorbed water layers on the TiO$_2$ surface before and after UV irradiation, respectively, upon contact with water vapor, according to eq 1. This result clearly shows that a significant amount of water layers existed on the TiO$_2$ surface even before the UV irradiation. This is in good agreement with the result of SFG measurement that the OH stretching of the non-hydrogen-bonded water, i.e., the multilayer of liquid water, was present even before the UV irradiation. However, although the amount of adsorbed water/TiO$_2$ interface changed only by 50% according to the QCM measurement, the UV-induced SFG
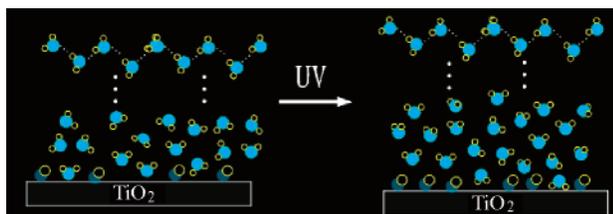
Figure 3. Schematic model of the interfacial structure of adsorbed water layer before and after UV irradiation.

intensity change was much more significant. Thus, the UV irradiation seemed to induce a structure ordering of the water layer at the adsorbed water/TiO$_2$ interface, which may be associated with an increase in the surface OH group as suggested by previous studies.[4,10,20,30,31] Recently, White et al. suggested that a contamination layer is responsible for the surface wettability switch of TiO$_2$ on the basis of temperature program desorption (TPD) measurement.[32] The contamination layer certainly plays an important role in controlling the hydrophilicity of the surface, but the present results show that the removal of the surface contamination layer is not the sole reason for the UV-induced hydrophilic TiO$_2$ surface. In conclusion, the combination of SFG spectroscopy and QCM measurements provided detailed information on the UV-induced interfacial structure of adsorbed water layer on TiO$_2$ surface and the schematic models of the interfacial structure of adsorbed water layer on TiO$_2$ surface before and after UV illumination are shown in Figure 3.

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