

# Photoinduced Changes of Adsorbed Water on a TiO<sub>2</sub> Photocatalytic Film As Studied by <sup>1</sup>H NMR Spectroscopy

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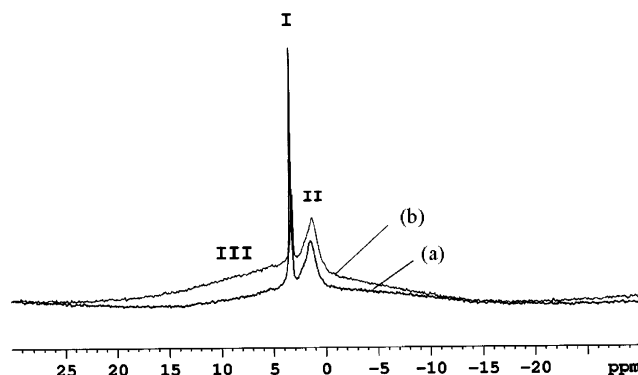
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The enhancement of the signal intensity of water molecularly adsorbed on TiO<sub>2</sub> films could be observed on UV irradiation by <sup>1</sup>H NMR spectroscopy, which has been difficult to elucidate so far with alternative spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and infrared reflection absorption spectroscopy (IRAS). It was also confirmed that the enhanced NMR signals resulted from the photoinduced hydrophilic conversion of the film surface decreased back to the original state with the recovery to the less hydrophilic state of the TiO<sub>2</sub> film surface when the film was kept in the dark.

TiO<sub>2</sub> photocatalysts have been intensively investigated because of their practical functions such as strong oxidation power, chemical inertness, and detoxification.<sup>1,2</sup> Besides, the UV irradiation of TiO<sub>2</sub> produces a highly hydrophilic surface.<sup>3–11</sup> This hydrophilic property has been widely applied to practical use such as antifogging and self-cleaning. To improve this property and develop new applications, the importance to establish appropriate methods for the quantitative evaluation of the hydrophilic conversion properties has been acknowledged.<sup>11</sup> <sup>1</sup>H NMR spectroscopy has been utilized as one of the most effective techniques to investigate adsorbed water. Recently, we observed proton NMR signals of adsorbed water on TiO<sub>2</sub> film prepared with a sol–gel method and found that the signals disappeared on UV irradiation in a closed system and recovered after the introduction of air but with a different spectral feature, possibly due to the photoinduced change of the TiO<sub>2</sub> surface environments.<sup>12</sup> In the present study, we prepared a TiO<sub>2</sub> film with a conventional sputtering method employed for actual practical applications and investigated the behavior of adsorbed water molecules on UV irradiation in an open system. The photoinduced effects on the water signals will be discussed in relation to the photoinduced hydrophilic properties of TiO<sub>2</sub>.

The TiO<sub>2</sub> film was prepared on SiO<sub>2</sub>-coated soda-lime glass by Ar ion sputtering with a Shimadzu HSM-752 apparatus at ambient temperature. The target materials for SiO<sub>2</sub> and TiO<sub>2</sub> were SiO<sub>2</sub> and Ti, respectively. The crystal structure was identified as anatase from the Raman scattering spectrum. The thickness of SiO<sub>2</sub> and TiO<sub>2</sub> layers were evaluated by SEM observation to be 64 and 180 nm, respectively. Two plates (4 × 20 mm) were placed in a 5 mm o.d. glass sample tube so as to direct the TiO<sub>2</sub>-coated surface of the plates back to back. The sample was UV irradiated outside the NMR probe in air (without a cap of the sample tube) with two cylindrical black-



**Figure 1.** <sup>1</sup>H NMR spectra measured at 800 MHz at 294 K: (a) an empty NMR sample tube; (b) TiO<sub>2</sub> film plates.

light lamps (20 W) from two sides. The excitation light intensity at the sample position was 2.2 mW/cm<sup>2</sup>. To avoid the photoinduced effect on an NMR glass tube, the film plates were placed in a different sample tube for NMR measurements. And to avoid the effect of the N<sub>2</sub> gas flow in the NMR probe, NMR measurements were carried out in a sample tube with a cap sealed with plastic films. <sup>1</sup>H NMR spectra were acquired at 800 MHz at 294 K on a Bruker Avance DRX 800 NMR spectrometer with 3 s recycle delay with a pulse duration of 9.6 μs. To eliminate the background signal of the NMR probe, the spectrum measured without a sample tube was subtracted from all the spectra. Chemical shifts were measured relative to DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) solution as an external reference.

As shown in Figure 1, the NMR sample tube (empty tube) presents water signals adsorbed on the glass materials. The spectrum consists of two sharp peaks (I and II) and one broad peak (III). On placing two substrate glass plates (4 × 20 mm) in the sample tube a substantial increase in the signal intensities of peak II and peak III was observed. On placing two TiO<sub>2</sub> film plates (4 × 20 mm) in the sample tube, a further increase in intensities in peaks II and III was observed. Thus, Figure 1

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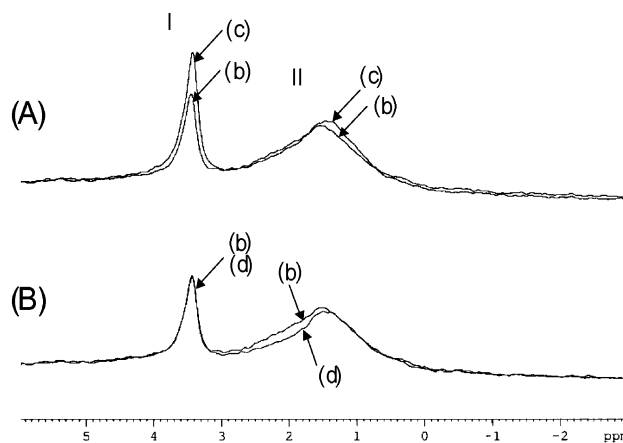
clearly indicates that substantially larger amounts of water molecules are adsorbed on the  $\text{TiO}_2$  film surface. The line widths at a half-peak height for peaks I–III of the  $\text{TiO}_2$  film were about 120 Hz, 600 Hz, and 13 kHz, respectively. Three NMR peaks indicate the presence of three distinct  $\text{H}_2\text{O}$  species. When the line width is determined mainly by the spin–spin relaxation rate of water proton, the mobility of the three different water species could be roughly estimated from the line widths. Taking into account that the line width becomes sharper with an increase of mobility, the molecular mobility of water would be higher in the order peak I > peak II > peak III. The mobility of peak I would be roughly estimated to be several times larger than that of peak II and about two magnitude of order larger than that of peak III. Because peak I was readily suppressed by  $\text{N}_2$  gas flow as compared with peaks II and III, peak I would correspond to the most mobile water species located in the most outer phase of the photocatalysts. The water species of peak II that are several times less mobile than those of peak I would be located at the inner phase of the water layer at the surface of photocatalyst. The water species of peak III whose mobility is most restricted would locate at the most inner surface region of the  $\text{TiO}_2$ . Peak I decreased in intensity upon becoming somewhat broader when substrate plates and  $\text{TiO}_2$  film plates were placed in a sample tube. This phenomenon could be attributed to the change in magnetic inhomogeneity caused by placing the sample plates in the tube because the sharpest signal is the most sensitive to the magnetic inhomogeneity. Further change was not observed in the NMR probe without photo-irradiation.

Previously we observed water NMR signals of various  $\text{TiO}_2$  in powder form with magic angle spinning with solid-state NMR. Because samples were packed in the  $\text{ZrO}_2$  sample tube without any vacant space in the sample tube, peak I was not observed.<sup>13</sup> This fact also strongly supports that peak I is weakly adsorbed water on the outermost surface of the film, exchanging slowly with gaseous water in the space.

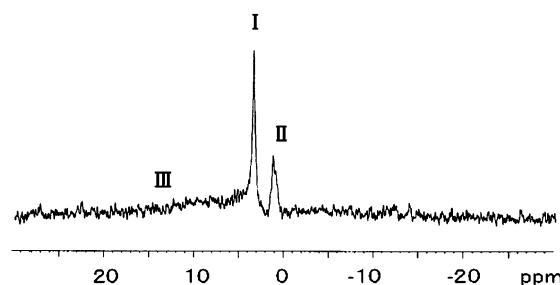
Thus, the water molecules adsorbed on the  $\text{TiO}_2$  films in the present case would be categorized into three states: (I) very mobile and weakly adsorbed water located in the outermost layer of  $\text{TiO}_2$  surface; (II) less mobile water in the inner layer; (III) very rigid water with restricted mobility near the solid surface and/or chemically bound OH groups on the surface.

It has been reported that a  $\text{TiO}_2$  surface becomes highly hydrophilic on UV light irradiation and gradually reverts to the originally less hydrophilic state in the dark.<sup>3–11</sup>  $\text{TiO}_2$  film prepared in the present study showed a water contact angle of  $6.5^\circ$  before UV irradiation. After 30 min UV irradiation, water droplets spread out on the film, resulting in a contact angle of  $0^\circ$ . And the contact angle came back to  $4.7^\circ$  after the sample was kept in the dark for 2 h. These changes of hydrophilicity of the film surface were found to be quite well correlated with the changes of the NMR signal intensities.

On 30 min UV irradiation, a substantial amount of increase in the intensities of peaks I and II was observed for  $\text{TiO}_2$  film plates (Figure 2A (c) and Figure 3). From the difference spectrum between the spectra before and after UV irradiation (Figure 3), a slight increase in the intensity in peak III could also be recognized. When the sample was kept in the dark for 2 h in air, the signal intensities of peaks I–III decreased back to the original state. Peak I reverted completely to the original state in 2 h whereas peak II presented a different signal feature and the signal intensity was slightly decreased (Figure 2B). Because the line shape of peak II of the substrate plates was affected by UV irradiation for some reason (data are not shown),



**Figure 2.**  $^1\text{H}$  NMR spectra of  $\text{TiO}_2$  film plates measured at 800 MHz at 294 K: (A) (b) before and (c) just after 30 min UV irradiation in air; (B) (b) before (same as (b) in (A)) and (d) 2 h (stored in the dark) after 30 min UV irradiation in air.

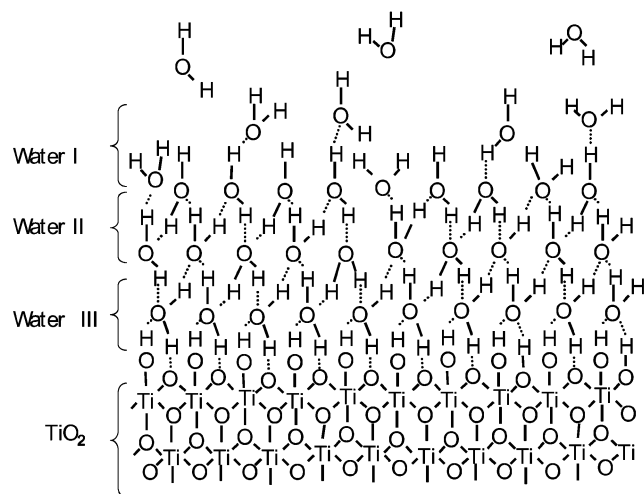


**Figure 3.** Difference spectrum between the spectra before and just after 30 min UV irradiation measured at 800 MHz at 294 K (subtraction of (b) from (c) in Figure 2A).

we could not conclude whether the signal change of peak II after UV irradiation arises from the photoinduced effect on the substrate glass or from the chemical environmental change around the physisorbed water near the  $\text{TiO}_2$  surface resulting from the photoinduced surface structural change.<sup>11</sup> However, for the substrate glass plates, on UV irradiation, peaks I and III were not affected and no signal enhancement was observed for all the peaks. Therefore, this enhancement must be specific to the  $\text{TiO}_2$  film. We carried out the same experiments several times, which provided highly reproducible results.

In the previous studies for the  $\text{TiO}_2$  film piece prepared with a sol–gel method, the changes of the spectral feature of the water peak corresponding to peak III was clearly detected before and after UV irradiation in a closed system, which could be ascribed to the photoinduced structural change.<sup>12</sup> In the present measurements, as shown in Figure 3, the signal feature of peak III differs also before and after UV irradiation, reflecting the structural change of the solid surface although the change was not so clearly detected as the previous study because of the poor signal-to-noise ratio for  $\text{TiO}_2$  in the form of two thin film plates.

The characteristics of adsorbed water and surface hydroxyl groups have been extensively studied by temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS).<sup>14–27</sup> It was reported that the high hydrophilicity of  $\text{TiO}_2$  surfaces caused by UV irradiation arose from the dissociative adsorption of water on the photoinduced oxygen defects of  $\text{TiO}_2$  surfaces to form surface hydroxyl groups.<sup>3–11</sup> The photoinduced hydrophilic surface of  $\text{TiO}_2$  becomes less hydrophilic in an  $\text{O}_2$  atmosphere in the dark. It was confirmed by XPS studies that, on UV irradiation in air, the total amount of the surface hydroxyl groups increased, but the amount of



**Figure 4.** Plausible structure of water layers I–III at the idealized  $\text{TiO}_2$  surface, deduced from the  $^1\text{H}$  NMR observations.

the surface hydroxyl groups bound to oxygen vacancy was found to decrease with TPD experiments by Sakai et al.<sup>11</sup> Therefore, they suggested that UV irradiation should increase the amount of water, which could not be observed in their TPD experiments.<sup>11</sup> Actually, by the TPD observation started from the lower temperature, it was indicated that a substantial number of water molecules were desorbed from the  $\text{TiO}_2$  surface below room temperature under vacuum.<sup>27</sup> In addition, the photoadsorption of gaseous water on  $\text{TiO}_2$  surfaces was also reported by SEIRAS by Sato and co-workers.<sup>24</sup> On the basis of the fact that the water photoadsorbed on  $\text{TiO}_2$  was removed easily by  $\text{O}_2$ , they suggested that the photoadsorption of water should be rather weak.

The increase of the molecularly adsorbed water on UV irradiation was clearly evidenced in the present NMR study by the enhancement of intensities of peak I. The intensity of the water peak increased with the photoinduced hydrophilic conversion of the surface and decreased with the recovery of the less hydrophilic surface of the film in the dark resulting from the desorption of water from the surface. The fact that the chemical shift of peak I was unchanged before and after UV irradiation evidently indicates that the adsorption of this water is molecular but not dissociative.

Three kinds of water molecules represented by peaks I–III might stay in the outer, the intermediate, and the inner parts of the water layers adsorbed on the  $\text{TiO}_2$  surface, respectively, as illustrated in Figure 4, and exchange among three layers slowly on the NMR time scale. The strong interaction among different kinds of hydroxyl groups was also indicated by SEIRAS measurements.<sup>24</sup> Several plausible factors responsible for the photoinduced hydrophilicity on  $\text{TiO}_2$  films have been reported.<sup>3–11</sup> Although the photoinduced structural change on the  $\text{TiO}_2$  surface has not been completely elucidated, it must be one of the most important factors. The photoinduced change of the  $\text{TiO}_2$  surface environments (structures) would cause the change of the binding states of the surface hydroxyl groups and/or the change of the

structures of water associates in the inner layer near the solid surface, resulting in the enhancement of the hydrophilicity. This change would lead to the successive enhancement of the water contents of the intermediate and the outer layers, resulting in the observed large enhancement of NMR peaks I and II, because water molecules are considered to exchange slowly among three water layers. The present NMR results indicate a potential applicability of this technique to the quantitative evaluation of the wettability of  $\text{TiO}_2$  films prepared with various materials. Further investigation on the photoadsorption of water on  $\text{TiO}_2$  surfaces is in progress in our laboratory with different materials of  $\text{TiO}_2$  film, substrates, and glass tubes.

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