

## Quantitative Evaluation of the Photoinduced Hydrophilic Conversion Properties of TiO<sub>2</sub> Thin Film Surfaces by the Reciprocal of Contact Angle

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Kinetics on the photoinduced hydrophilic conversion processes of the TiO<sub>2</sub> surface was investigated. First, we show that there exist linear relationships between the reciprocal of the contact angle and the UV irradiation time and use the slope of this straight line as the hydrophilic conversion rate, which is independent of the initial value of the contact angle. Second, we examine the relationships between the reciprocal of the contact angle and the reconstruction of the surface hydroxyl groups and show that the reciprocal of the contact angle corresponds to the density of the surface hydroxyl groups reconstructed by UV irradiation. Finally, the dependence of the hydrophilic conversion on various parameters such as the incident UV intensity, the wavelength of irradiated light, and the concentration of the hole scavenger are quantitatively investigated with the proposed hydrophilic conversion rate. These results show that the photoinduced hydrophilic conversion proceeds competitively with the photocatalytic oxidation process on the TiO<sub>2</sub> surface under UV irradiation. The comparison of the hydrophilic conversion rate with the rate for the reverse process clarifies that the critical contact angle is obtained when the reconstruction of the surface hydroxyl groups and their relaxation process are equilibrated under UV irradiation.

### Introduction

In recent years, we have reported the photoinduced wettability conversion of TiO<sub>2</sub> surface.<sup>1–13</sup> Although a TiO<sub>2</sub> surface is originally less hydrophilic, it becomes highly hydrophilic by its band-gap excitation via UV light irradiation and gradually reverts to originally less hydrophilic in the dark. The highly hydrophilic property gives new applications of TiO<sub>2</sub> coatings such as anti-fogging and self-cleaning.<sup>1</sup> For example, TiO<sub>2</sub>-coated side mirrors of automobiles give a clear view even on a rainy day, and stains adsorbed on TiO<sub>2</sub>-coated wall tiles can be easily washed off by rainwater.

In addition, we have investigated the mechanism for the generation of such a highly hydrophilic surface. Considering the behaviors of the wettability changes under UV irradiation and in the dark, it had seemed that the highly hydrophilic surface could be achieved by the decomposition of adsorbed organic species, because of its conventional photocatalytic oxidation process by the photogenerated holes.<sup>14–25</sup> However, various experimental results relating to this phenomenon, e.g., sonication in pure water,<sup>4</sup> the hydrophilicity change of SrTiO<sub>3</sub>,<sup>7</sup> and the treatment of a TiO<sub>2</sub> surface with a warm concentrated NaOH solution,<sup>11</sup> have shown that alternate mechanism for the wettability conversion exists other than the removal of organic species adsorbed on the surface. From the results of XPS, FT-

IR, and the electrochemical experiments, we have concluded that the increase of the hydrophilicity is attributed to the increase of the surface hydroxyl groups on the TiO<sub>2</sub> surface, which is formed by the involvement of the photogenerated holes.<sup>12</sup>

On the basis of this mechanism, we have tried to enhance the hydrophilic conversion property and to obtain materials that can become highly hydrophilic state even under very weak UV irradiation. For example, we have developed a novel TiO<sub>2</sub> film on which the amorphous tungsten oxide is deposited.<sup>10</sup> The combined band structure of the WO<sub>3</sub>/TiO<sub>2</sub> film increases the charge separation efficiency to utilize the photogenerated holes for inducing the surface hydrophilic conversion efficiently. Consequently, a highly hydrophilic surface was obtained with very weak UV irradiation whose intensity is 1  $\mu$ W/cm<sup>2</sup>, the same as that from the fluorescent lamp. The development of such materials expands the application region of the highly hydrophilic surface to the inside area, with very weak intensity of UV light.

Although various materials are proposed to enhance the hydrophilic conversion property, no quantitative evaluation methods have been proposed for the hydrophilic conversion properties, which can be determined by the hydrophilic conversion rate under UV irradiation, the rate for the reverse process in the dark, and the critical contact angle (the lowest value of the contact angle under UV irradiation). For example, although it seems that the hydrophilic conversion rate is defined by the slope of the plots between the contact angle and the UV irradiation time, it is often difficult to compare the hydrophilic conversion rate among samples if the initial values of the contact angle are different each other, because of different surface energy<sup>26</sup> and/or different surface roughness.<sup>27</sup> Therefore, it is necessary to propose the hydrophilic conversion rate, which is independent of the initial value of the contact angle. In addition,

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the absence of the quantitative hydrophilic conversion rate does not allow the kinetic analysis for the photoinduced hydrophilic conversion of TiO<sub>2</sub> surfaces, whereas the kinetic studies of the photocatalytic oxidation reaction have been reported significantly.<sup>28–36</sup>

In the present paper, we have examined the relationships between the changes of the contact angle and the changes of surface hydroxyl groups under UV irradiation by various physical and chemical methods in order to obtain the quantitative evaluation method of the hydrophilic conversion rate. Then we have applied it to various situations. We have also examined the other parameters for the hydrophilic conversion property: the rate for the reverse process and the critical contact angle.

### Experimental Section

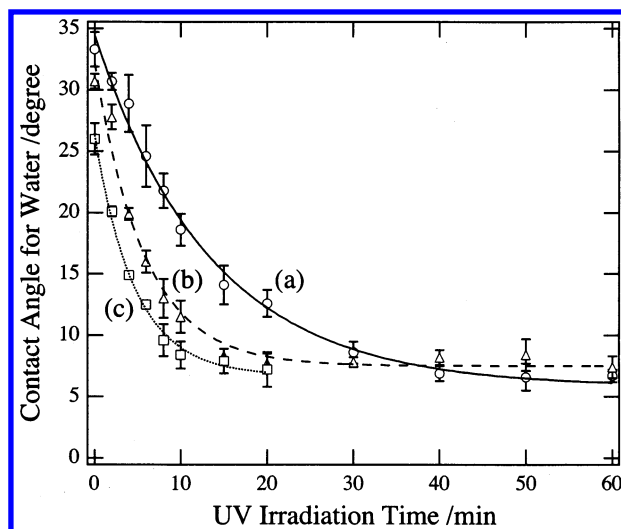
TiO<sub>2</sub> films were prepared using a dip-coating method. The glass substrates coated with SiO<sub>2</sub> thin film (thickness 100 nm) were dip-coated in the titanium tetraisopropoxide solution (Type NDH-510C, Nippon Soda). A withdrawal rate of 15 cm min<sup>-1</sup> was used for all samples. The samples were dried in a furnace for 40 min at 120 °C and sintered at 500 °C for 30 min in air, which resulted in polycrystalline TiO<sub>2</sub> (anatase) films. The above dip-coating procedure was repeated three times to produce a TiO<sub>2</sub> film with its thickness of 240 nm, which was estimated based on both the interference oscillations in UV–vis absorption spectra and the focused laser microscopic observation. The surface roughness,  $R_a$ , was estimated by the atomic force microscopic (AFM) observations to be ca. 1.3 nm, which shows the relatively flat surface. Si wafers (001) and SnO<sub>2</sub>-coated glass plates were used as the substrates for the TDS experiments and the electrochemical experiments, respectively.

A cylindrical black-light lamp (BLB) and a Hg–Xe lamp with a UV filter (UV-D36B, Toshiba) were employed as the excitation source. The excitation light intensity was measured using a commercial UV radiometer (UVR-2, TOPCON) at the sample position. The hydrophilicity of the surface was evaluated by the contact angle measurement by use of a commercial contact angle meter (CA-X, Kyowa Interface Science, Japan). The contact angle was measured at least 6 times with the same sample in an ambient air, and the average value was used.

X-ray photoelectron spectra (XPS) were acquired in an ultrahigh vacuum system with a Perkin-Elmer model 5600 X-ray photoelectron spectrometer. Mg K $\alpha$  radiation was used to generate the spectra, and the photoelectrons were collected at a takeoff angle of 45° with respect to the film surfaces. The base pressure of the UHV system was at the level of 10<sup>-10</sup> Torr, and the base pressure in the prevacuum chamber was 10<sup>-7</sup>–10<sup>-8</sup> Torr.

Thermal desorption spectra (TDS) were acquired using a commercial thermal desorption spectrometer (EMD-WA1000S, ESCO Ltd.) equipped with a mass spectrometer (QMS-421). The temperature was controlled at the sample surface and/or the stage surface. The heating rate used during TDS experiments was 60 °C/min. The signals for the M/z = 18 were recorded to follow the desorption of H<sub>2</sub>O. The background pressure was on the order of 10<sup>-9</sup> Torr.

Electrochemical analyses for the surface structure in aqueous solutions were carried out in conventional three-electrode cells with a potentiostat and an X–Y recorder coupled with a function generator (HSV-100, Hokuto Denko). The polycrystalline TiO<sub>2</sub> thin film electrode, whose preparation method is reported elsewhere,<sup>12</sup> served as the working electrode. The counter and the reference electrodes were platinum wire and Ag/AgCl/saturated KCl(aq), respectively. A standard buffer solution (pH 6.86) containing 0.2 mol dm<sup>-3</sup> sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) was



**Figure 1.** Changes of the contact angle of the TiO<sub>2</sub> thin film surface under UV irradiation with its intensity of (a) 0.2, (b) 0.7, and (c) 1.0 mW/cm<sup>2</sup>.

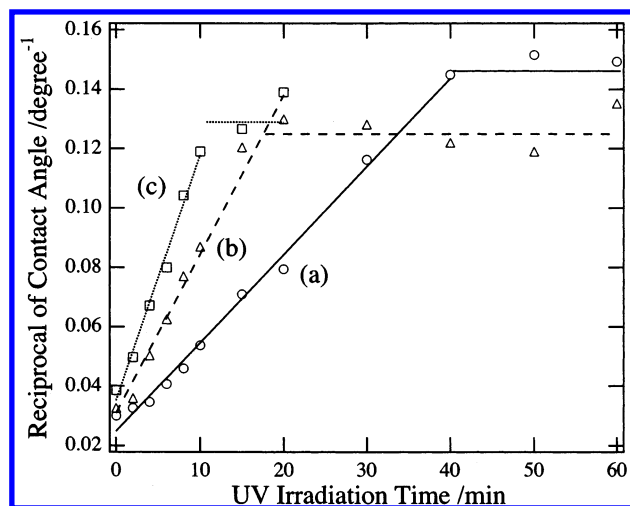
employed as the supporting electrolyte after being deaerated by bubbling with N<sub>2</sub>. All potentials in aqueous media are further referred to the Ag/AgCl electrode in the following.

### Results and Discussion

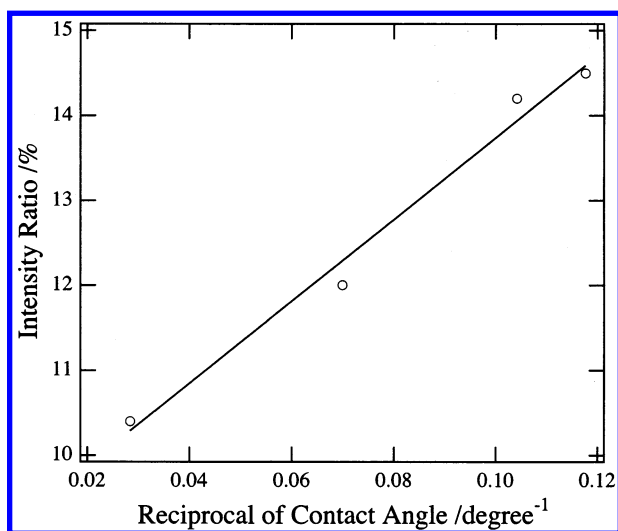
**Definition of the Hydrophilic Conversion Rate.** The changes of the contact angle under various intensities of UV light were examined, as shown in Figure 1. The initial values of the contact angle were (a) 33.3 ± 1.4°, (b) 30.7 ± 0.6°, and (c) 26.0 ± 1.3°. The difference of the initial values of the contact angle is considered to be due to the difference of the dark storage time after the highly hydrophilic state produced by UV irradiation: (a) 24, (b) 17, and (c) 8 days. The contact angle on all of the samples decreased with UV irradiation time, but the hydrophilic conversion rate seems to be different than each other. Although the rate can be defined by the slope of the plots in the initial region of UV irradiation, it does not give a constant value even in the same condition of UV irradiation because it depends on the initial value of the contact angle. It is, therefore, necessary to define the hydrophilic conversion rate, which is independent of the initial value of the contact angle.

We have found that the reciprocal of the contact angle plotted against the UV irradiation time gives the straight line in the regions before the contact angle reaches the minimum value, as shown in Figure 2. The correlation coefficients of the regression straight line were estimated to be (a) 0.997, (b) 0.989, and (c) 0.995, which indicate the good linearity. These slopes of the straight line can be defined as the hydrophilic conversion rate ( $k_f$ ), which is independent of the initial value of the contact angle. The values of the  $k_f$  were estimated to be (a) 3.0 × 10<sup>-3</sup>, (b) 5.4 × 10<sup>-3</sup>, and (c) 8.3 × 10<sup>-3</sup> degree<sup>-1</sup> min<sup>-1</sup>. This is, to our best knowledge, the first example that makes it possible to evaluate the hydrophilic conversion rate quantitatively.

**Spectroscopic Investigation on Surface OH Groups.** The structural changes of the TiO<sub>2</sub> surface were investigated by XPS in detail. As we previously reported,<sup>4,6</sup> no change was observed in Ti 2p XPS spectra before and after UV irradiation, whereas the shoulder peak in O 1s XPS spectra increased with UV irradiation. This shoulder band can be fitted to two bands which are 1.5 and 2.6 eV higher than the O 1s main band, corresponding to dissociative water (hydroxyl groups) adsorption<sup>37,38</sup> and molecular water adsorption,<sup>39</sup> respectively. The integrated intensity of the dissociative water was examined on the TiO<sub>2</sub>



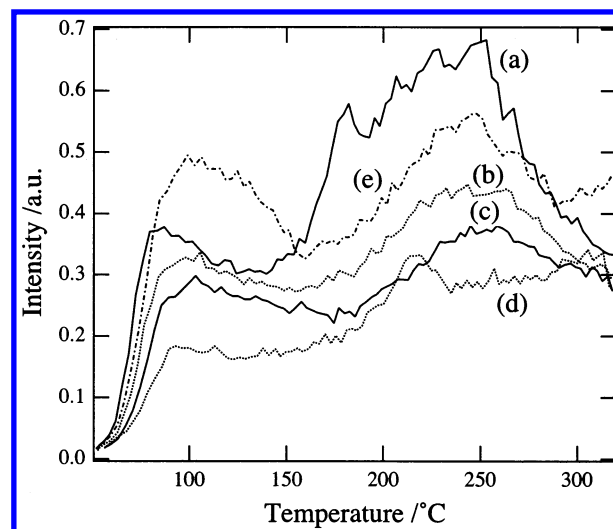
**Figure 2.** Reciprocal of the contact angle plotted against the UV irradiation time. The annotations are the same as in Figure 1. Each line is the regression straight line for each plot.



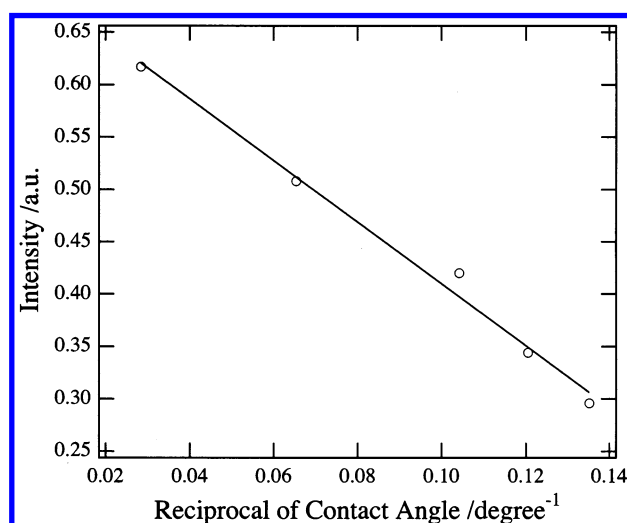
**Figure 3.** Intensity ratio of the surface hydroxyl groups to the O 1s band plotted against the reciprocal of the contact angle. The solid line is the regression straight line with its correlation coefficient of 0.993.

film surface with various values of the contact angle. To compare the XPS results with the contact angle, the intensity ratio of the dissociative water to the O 1s band was plotted against the reciprocal of the contact angle, as shown in Figure 3. The correlation coefficient of the regression straight line was estimated to be 0.993, which shows the strong positive correlation between the increase amount of the surface hydroxyl groups and the change of the reciprocal of the contact angle.

Although the XPS experiments have revealed that the amount of the surface hydroxyl groups increases with the hydrophilic conversion of the  $\text{TiO}_2$  surface, it cannot clarify which type of the surface hydroxyl groups increases. The interaction of  $\text{H}_2\text{O}$  with  $\text{TiO}_2$  surfaces has been extensively studied by the temperature programmed desorption (TPD)<sup>37,40–43</sup> and infrared absorption spectroscopy (IRAS).<sup>41,44–51</sup> It can be summarized that there are three kinds of surface hydroxyl groups: (1) molecularly adsorbed  $\text{H}_2\text{O}$  whose thermal desorption peak is observed at 250–300 K and OH stretching frequency ( $\nu_{\text{OH}}$ ) is observed at 3300–3250  $\text{cm}^{-1}$ , (2) dissociatively adsorbed  $\text{H}_2\text{O}$  whose thermal desorption peak is observed at 375 K and OH stretching frequency ( $\nu_{\text{OH}}$ ) is observed at 3450–3400  $\text{cm}^{-1}$ , and (3) surface hydroxyl groups bound to oxygen vacancies whose



**Figure 4.** Thermal desorption spectra of  $\text{H}_2\text{O}$  from the  $\text{TiO}_2$  surface after pre-UV irradiation in air for (a) 0, (b) 10, (c) 30, and (d) 120 min. (e) is the same surface as (c) followed by the storage in the dark for 16 h.



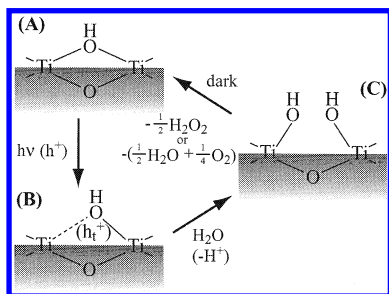
**Figure 5.** TDS integral in the temperature region in 200–270  $^{\circ}\text{C}$  plotted against the reciprocal of the contact angle. The solid line is the regression straight line with its correlation coefficient of 0.995.

thermal desorption peak is observed at 500 K and OH stretching frequency ( $\nu_{\text{OH}}$ ) is observed at 3700–3650  $\text{cm}^{-1}$ .

To obtain the information on the kind of the surface hydroxyl group, which has changed with the UV irradiation, the thermal desorption spectroscopy (TDS) was employed. In Figure 4 are shown the TD spectra ( $M/z = 18$ ) for the  $\text{TiO}_2$  films with different exposure times of UV irradiation in air. There are two desorption peaks around 100  $^{\circ}\text{C}$  and in the temperature region of 200–270  $^{\circ}\text{C}$ . It was observed that the latter desorption peak decreases with the decrease of the contact angle by UV irradiation and conversely increases with the increase of the contact angle, which had been made by the storage in the dark. It was also found that the TD integral for the latter peak strongly correlates with the reciprocal of the contact angle, as shown in Figure 5. The correlation coefficient of the regression straight line was estimated to be 0.995. It was therefore considered that the changes of the latter desorption peak integral strongly correlate to the changes in the wettability of the  $\text{TiO}_2$  surface.

According to the summary on the surface hydroxyl groups, which is shown above, it seems that the former desorption peak corresponds to the dissociatively adsorbed water and the latter



**SCHEME 1: Surface Structural Models for the TiO<sub>2</sub> Surface<sup>a</sup>**

<sup>a</sup> (A) (Before UV irradiation) the OH group is bound to oxygen vacancy, (B) (at the transition state) the photogenerated hole is trapped at the lattice oxygen, and (C) (after UV irradiation) new OH groups are formed.

the surface hydroxyl groups bound to oxygen vacancies. The assignment for the latter desorption peak was conducted to obtain the TD spectra before and after UV irradiation in ultrahigh vacuum (UHV). It was reported that the UV irradiation in UHV creates the lattice oxygen vacancies of TiO<sub>2</sub> surface<sup>52</sup> and the following water exposure heals them, producing the surface hydroxyl groups bound to oxygen vacancy.<sup>39</sup> When the TD spectra were measured for the TiO<sub>2</sub> surface, which had experienced the UV irradiation in UHV and the following water exposure, the increase of the latter desorption peak was observed. It is therefore considered that the latter desorption peak is assigned to that for the hydroxyl groups bound to oxygen vacancy.

It is noted here that the UV irradiation in air increases the total amount of the surface hydroxyl groups as observed by XPS studies, whereas it decreases the amount of the surface hydroxyl groups bound to oxygen vacancy as indicated in TDS experiments. It is therefore considered that UV irradiation should increase the amount of the surface hydroxyl groups, which cannot be observed in TDS experiments. Nakamura et al. have recently reported that UV irradiation on the TiO<sub>2</sub> thin film in air increases the 3270 cm<sup>-1</sup> IR absorption peak, which is assigned to the O–H stretching band.<sup>49</sup> The reason for the invisibility of such hydroxyl groups in the TDS experiments can be considered as follows. The temperature of the sample stage in the XPS chamber was ca. 20 °C, whereas the initial temperature on the sample stage in the TDS experiments was 50–60 °C even before heating. If the desorption temperature for such hydroxyl groups is in the temperature region between these two values, the desorption of such hydroxyl groups should occur before heating in the TDS experiments. Actually, the decrease of the surface hydroxyl groups was observed in the XPS experiment when the measurement was conducted 2–3 h after the introduction of the UV preirradiated sample into the UHV chamber. This suggests that the surface hydroxyl groups formed by the UV irradiation gradually desorb even around the room temperature in UHV. It is also difficult to lower the initial stage temperature because of the ultrahigh vacuum in the chamber. It is, therefore, impossible to observe such hydroxyl groups with the TDS equipment employed.<sup>53</sup>

Based on these results related to the hydroxyl groups of the TiO<sub>2</sub> surface, it is considered that the reconstruction of the surface hydroxyl groups should occur at the oxygen defect site by UV irradiation in air. That is, one OH group doubly coordinated to Ti atoms at the oxygen defect site converts to two OH groups singly coordinated to each Ti atom. The model for the reconstruction of the surface hydroxyl groups is shown in Scheme 1.

**Electrochemical Investigation on the Reconstruction of the Surface Hydroxyl Groups.** Such changes of the surface hydroxyl groups may cause the shift of the flatband potential for the TiO<sub>2</sub> electrodes. The flatband potential of the TiO<sub>2</sub> electrodes is determined by the dissociation of the electric double layer, as shown in eq 1:<sup>54</sup>

$$\Delta U = F^{-1}(\Delta G_0 + RT \ln k) \quad (1)$$

in which  $\Delta U$  is the potential difference of the electric double layer and  $k$  is the dissociation constant of O–H bond of the TiO<sub>2</sub> surface. As the dissociation constant  $k$  becomes large, the flatband potential shifts negative. In general, TiO<sub>2</sub> has two kinds of OH groups on the surface: acid OH groups and basic OH groups.<sup>40–41,55</sup> The former has a large value for the dissociation constant ( $k_1$ ), and the latter has a small value ( $k_2$ ). Then, the eq 1 can be modified to eq 2:

$$\Delta U = F^{-1}(\Delta G_0 + \alpha RT \ln k_1 + \beta RT \ln k_2) \quad (\alpha + \beta = 1) \quad (2)$$

where  $\alpha$  is the ratio of the acid OH groups and  $\beta$  the ratio of the basic OH groups on the TiO<sub>2</sub> surface.

From the point of the coordination number to Ti atoms, the OH groups before UV irradiation can be regarded as acid-like OH groups, whereas the OH groups produced by UV irradiation can be regarded as basic-like OH groups. Now, the number ( $\epsilon$ ) of site, in which a hydroxyl group is bound to oxygen vacancy of the TiO<sub>2</sub> surface, is changed by UV irradiation. Then, the eq 2 can be modified to eq 3, because one acid-like OH group converts to two basic-like OH groups at each site, as shown in Scheme 1:

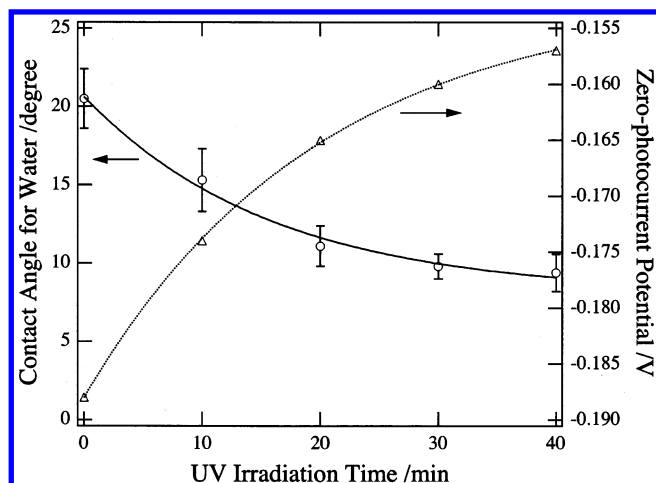
$$\Delta U' = F^{-1} \left( \Delta G_0 + \frac{N\alpha - \epsilon}{N + \epsilon} RT \ln k_1 + \frac{N\beta + 2\epsilon}{N + \epsilon} RT \ln k_2 \right) \quad (3)$$

where  $N$  is the total number of surface hydroxyl group. Therefore, the shift of the flatband potential by UV irradiation can be obtained as follows:

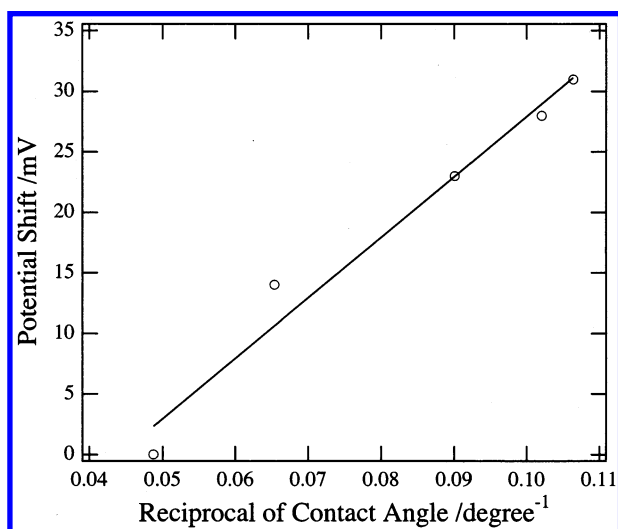
$$\Delta U' - \Delta U = F^{-1} \left\{ \frac{\epsilon(1 + \alpha)}{N + \epsilon} RT \ln \frac{k_2}{k_1} \right\} \quad (4)$$

Because  $k_1$  is much larger than  $k_2$ , the right side of the eq 4 should be negative. It is therefore predicted that the potential shift is in the positive direction, and the value of the shift is proportional to the number of site ( $\epsilon$ ) where the structural change occurs by UV irradiation if  $\epsilon$  is much smaller than  $N$ .

In Figure 6 are plotted both the contact angle and the zero-photocurrent potential versus the UV irradiation time. The UV irradiation and the contact angle measurements on the TiO<sub>2</sub> electrode surface were conducted in air. The measurements of the zero-photocurrent potential were conducted in aqueous solution with electrochemical cell. The electrode potential was set at 0 V for a second and was swept in the negative direction with scan rate of 50 mV s<sup>-1</sup> under UV irradiation. The across potential with the potential axis is the zero-photocurrent potential, and the shift of the zero-photocurrent potential corresponds to that of the flatband potential of the TiO<sub>2</sub> electrode. With the increase of the UV irradiation time before the electrochemical measurement, the potential shifted in the positive direction. The value of the potential shift is plotted against the reciprocal of the contact angle, as shown in Figure 7. The correlation coefficient of the regression straight line was estimated to be 0.986, which shows the strong positive correla-



**Figure 6.** Both changes of the contact angle and the zero-photocurrent potential after UV irradiation in air. The zero-photocurrent potentials were obtained using the  $\text{TiO}_2$  thin film electrodes in an aqueous electrolyte.

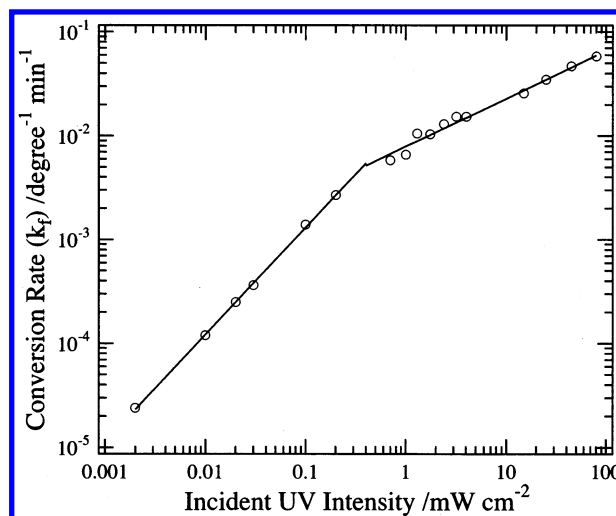


**Figure 7.** Shift of the zero-photocurrent potential plotted against the reciprocal of the contact angle. The solid line is the regression straight line with its correlation coefficient of 0.986.

tion between the shift of the flatband potential and the reciprocal of the contact angle. Because the reciprocal of the contact angle can be regarded as the number of the site for the structural change, the value of the shift was proportional to the number of the site for the photoinduced structural change, as suggested in eq 4. It is therefore confirmed that UV irradiation induces the reconstruction of the surface hydroxyl groups as shown in Scheme 1.

**Application of the Hydrophilic Conversion Rate to Various Situations.** All of the above results have shown that the reconstruction of the surface hydroxyl groups induces the hydrophilic conversion of the  $\text{TiO}_2$  surface, and the reciprocal of the contact angle corresponds to the density of the sites for the surface hydroxyl groups reconstructed by UV irradiation. It is therefore concluded that the hydrophilic conversion rate defined above corresponds to the rate for the reconstruction of surface hydroxyl groups. Next, let us investigate the hydrophilic conversion properties using the conversion rate defined above.

**1. Dependence on the Irradiated UV Light Intensity.** Figure 8 shows a log-log plot of the  $k_f$  versus the incident UV intensity ( $I$ ). Interestingly, this plot gave two kinds of straight lines. The correlation coefficients of the regression straight lines



**Figure 8.** log-log plot of the hydrophilic conversion rate ( $k_f$ ) versus the incident UV intensity ( $I$ ). Each line is the regression straight line for the UV intensity region lower and higher than  $0.4 \text{ mW/cm}^2$ , respectively.

were estimated to be 0.998 and 0.999 for the regions of higher and lower UV intensity, respectively, which also indicate the good linearity. The values of the slope ( $n$ ) were 1.03 and 0.46 in the lower intensity ( $I < 0.4 \text{ mW/cm}^2$ ) and the higher intensity ( $I > 0.4 \text{ mW/cm}^2$ ) regions, respectively, and  $k_f$  was represented as a function of  $I$  as follows:

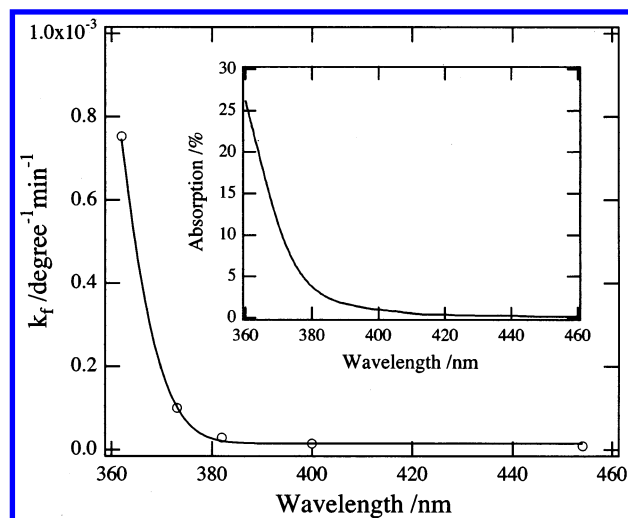
$$k_f = 7.9 \times 10^{-3} I^{0.46} \quad (I > 0.4 \text{ mW/cm}^2) \quad (5a)$$

$$k_f = 1.4 \times 10^{-2} I^{1.03} \quad (I < 0.4 \text{ mW/cm}^2) \quad (5b)$$

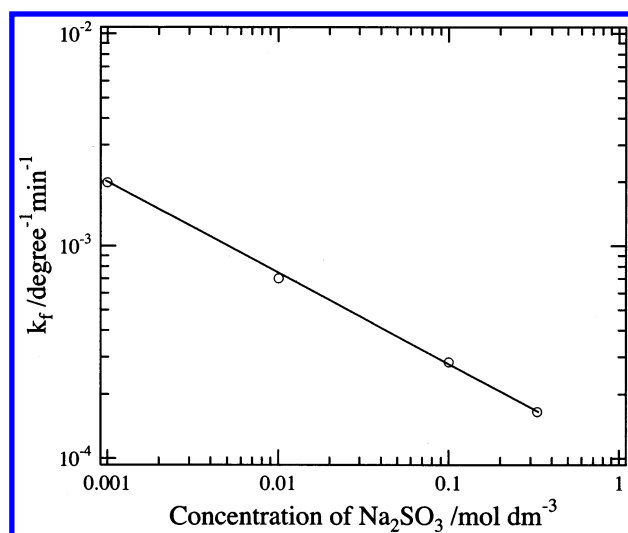
This behavior of the hydrophilic conversion rate against UV intensity resembles that of the heterogeneous photocatalysis.<sup>28–30</sup> It is well-known that the light-limited reaction is represented as  $n = 1$ . Conversely, under light-rich conditions, the reaction rate is often characterized by an  $n$  value of 0.5 because of domination by the second-order-dependent carrier-recombination process. It is therefore considered that the photoinduced hydrophilic conversion also occurs in the light-limited condition under the lower UV intensity, whereas the domination of the recombination of photogenerated electron-hole pairs limited the hydrophilic conversion rate under the higher UV intensity.

**2. Dependence on the Wavelength of Irradiated Light.** The number of incident photon was controlled by monitoring with the spectroradiometer to be ca.  $5.4 \times 10^{13} \text{ quanta cm}^{-2} \text{ s}^{-1}$  for all of the wavelengths. The hydrophilic conversion rate depended strongly on the wavelength of the irradiated light. The contact angle on samples which was irradiated by light whose wavelength was shorter than 382 nm decreased with irradiation time, whereas no changes of the contact angle were observed when irradiated by light whose wavelength was longer than 382 nm. To clarify the threshold of the hydrophilic conversion, the action spectrum for the photoinduced hydrophilic conversion was obtained, as shown in Figure 9. The onset wavelength for the hydrophilic conversion is almost consistent with that for the UV-vis absorbance spectrum, which is shown in the inset of Figure 9. This result clearly shows that the photoinduced hydrophilic conversion requires the band gap excitation of  $\text{TiO}_2$ .

**3. Effect of the Hole Scavenger.** As we have previously reported,<sup>12</sup> the photoproduced holes play the main role in the



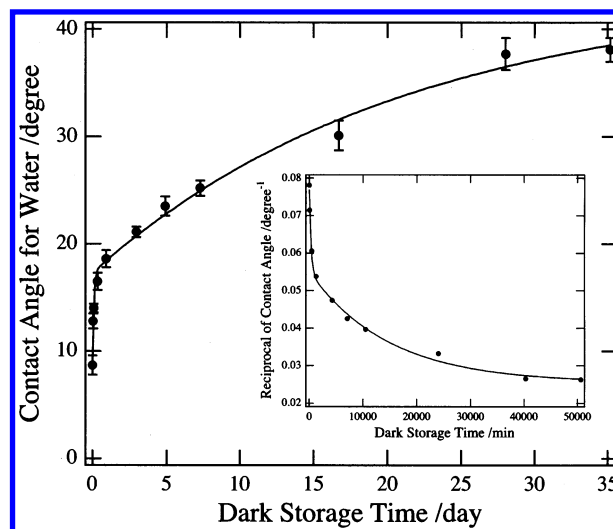
**Figure 9.** Action spectrum of the hydrophilic conversion rate ( $k_f$ ). The number of the incident photons was constant for all wavelengths. The inset shows the UV-vis absorption fraction of TiO<sub>2</sub> thin film, which was calculated by the substitution of transmittance and reflectance from 100%.



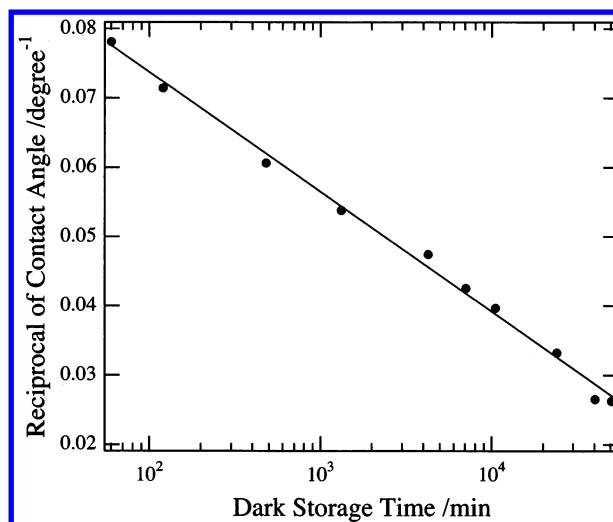
**Figure 10.** Dependence of the hydrophilic conversion rate ( $k_f$ ) of the TiO<sub>2</sub> electrode surface on the concentration of sodium sulfite. The solid line is the regression straight line with its correlation coefficient of 0.999.

hydrophilic conversion, and the existence of a hole scavenger inhibits the hydrophilic conversion, and the increase of the concentration of scavenger drastically decreases the hydrophilic conversion rate. Figure 10 shows the log-log plots of the hydrophilic conversion rate against the concentration of the hole scavenger, Na<sub>2</sub>SO<sub>3</sub>. A linear relation between these two parameters was observed, indicating that the hydrophilic conversion and the oxidation of Na<sub>2</sub>SO<sub>3</sub> competitively occur on the photoirradiated TiO<sub>2</sub> surfaces. This result strongly suggests that the photoinduced hydrophilic conversion and the photocatalytic oxidation competitively occur on the TiO<sub>2</sub> surface under UV irradiation even in air.

**Reverse Process in the Dark and the Critical Contact Angle Under UV Irradiation.** We have also discussed the rate ( $k_b$ ) for the reverse process, that is, the reconversion from the highly hydrophilic state to the less hydrophilic state in the dark. The change of the contact angle in the dark is as shown in Figure 11. The highly hydrophilic surface produced by UV irradiation gradually converted to the less hydrophilic state in several



**Figure 11.** Change of the water contact angle of the TiO<sub>2</sub> thin film surface in the dark after highly hydrophilic state produced by the UV irradiation. The inset shows the reciprocal of the contact angle plotted against the dark storage time.



**Figure 12.** Reciprocal of the contact angle plotted against the logarithm of the dark storage time. The solid line is the regression straight line with its correlation coefficient of 0.998.

weeks. It seems that the rate for the reverse process is much slower than that for the hydrophilic conversion. Because it is considered that the reverse process corresponds to the relaxation process of the reconstructed surface hydroxyl groups, the rate for the reverse process should be represented as the slope of the plot between the reciprocal of the contact angle and the dark storage time. The reciprocal of the contact angle was plotted against the dark storage time, as shown in the inset of Figure 11. The slope of the plot decreased with the time, which increased the contact angle. In other words, the  $k_b$  increases as the hydrophilic conversion proceeds.

To discuss the  $k_b$  quantitatively, it is necessary to obtain the equation of the relation between the reciprocal of the contact angle and the time in the dark. When the reciprocal of the contact angle was plotted against the logarithmic scale of the dark storage time, a straight line was obtained, as shown in Figure 12. The correlation coefficient of the regression line was 0.998, which indicates the good linearity. From this plot, the relation between the reciprocal of the contact angle and the dark

storage time is described as

$$1/\theta = 0.1079 - 7.439 \times 10^{-3} \ln(t) \quad (6)$$

where  $\theta$  is the contact angle and  $t$  is the dark storage time in the unit of min. Then we can obtain the slope of the plots in the inset of Figure 11 by differentiating the  $1/\theta$  by the time:

$$d(1/\theta)/dt = -7.439 \times 10^{-3}(1/t) \quad (7)$$

Combining eqs 6 and 7,  $k_b$  can be described as a function of the reciprocal of the contact angle:

$$k_b = -d(1/\theta)/dt = 7.439 \times 10^{-3} \exp\{(1/\theta - 0.1079)/7.439 \times 10^{-3}\} \quad (8)$$

Then we obtained the  $k_b$  quantitatively as a function of the density of the reconstructed surface hydroxyl groups.

Because the reverse process is considered as the relaxation process of the surface hydroxyl groups reconstructed by UV irradiation, the rate for the reverse process depends on the concentration of the hydroxyl groups reconstructed. When the contact angle is large, the rate for the reverse process is slow because the concentration of the surface hydroxyl groups reconstructed is small. However, as the contact angle decreases, the concentration of the hydroxyl group increases and the rate for the reverse process becomes large.

Even in the process under UV irradiation, the relaxation process of the reconstructed surface hydroxyl groups should occur together with the reconstruction by UV irradiation. In Figure 2, because  $k_f$  is much larger than  $k_b$  ( $k_f \gg k_b$ ) in the linear region before the contact angle reaches the saturated value, the hydrophilic conversion rate is described by the  $k_f - k_b \approx k_f$ . As the hydrophilic conversion proceeds, however, the density of the reconstructed surface hydroxyl groups increases, and the  $k_b$  also increases and becomes equal to the  $k_f$  in the region where the contact angle is saturated under UV irradiation. It is therefore expected that the equilibrium between the reconstruction of the surface hydroxyl groups and its relaxation, which is described as eq 9, should give the critical contact angle ( $\theta_c$ ):

$$k_f - k_b = 0 \quad (9)$$

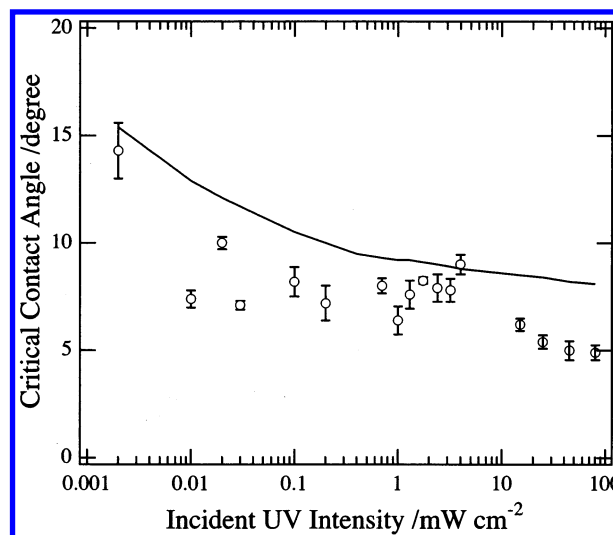
Combining eqs 5a, 5b, and 8 with eq 9,  $\theta_c$  can be obtained as a function of the UV intensity ( $I$ ):

$$1/\theta_c = 3.442 \times 10^{-3} \ln(I) + 0.1084 \quad (I > 0.4 \text{ mW/cm}^2) \quad (10a)$$

$$1/\theta_c = 7.685 \times 10^{-3} \ln(I) + 0.1127 \quad (I < 0.4 \text{ mW/cm}^2) \quad (10b)$$

$\theta_c$  thus obtained as well as the experimental data are indicated in Figure 13. Although the experimental results were ca. 2° lower than the calculated results in all regions of UV intensity, the trends of the dependence of the  $\theta_c$  on the incident UV intensity are almost consistent between the calculated and the experimental results. It is therefore concluded that the critical contact angle can be obtained when the reconstruction of the surface hydroxyl groups and its relaxation are equilibrated under UV irradiation.

The small discrepancy between the experimental and the calculated results of the critical contact angle may be due to the existence of another kinetics for the reverse process in the dark. Although the linear relationships were observed between the  $1/\theta$  and the logarithm of the dark storage time in all of the



**Figure 13.** Dependence of the critical contact angles on the incident UV intensity. The plots are the experimental results, and the solid line is the calculated result from eq 10.

time range, as shown in Figure 12, a breakpoint can be seen at about 1–2 days of dark storage (Figure 11 and the inset of Figure 11), suggesting that different kinetics exist before and after this point. Because the calculation of the critical contact angle was based on the assumption that the equilibrium between the hydrophilic conversion rate and the rate for the reverse process gives the critical contact angle, such small discrepancy was considered to be observed. The kinetics and the mechanism for the reverse process in the dark should need further investigation.

**Proposed Mechanism for the Photoinduced Hydrophilic Conversion of the TiO<sub>2</sub> Surface.** On the basis of all of the above results, it is concluded that the UV irradiation in air causes the reconstruction of the surface hydroxyl groups, whose density is strongly correlated with the reciprocal of the contact angle. The dependence of the hydrophilic conversion rate on various parameters shown above has clarified that the photoproduct holes play a main role in the reconstruction of the surface hydroxyl groups. Although the photoexcited electrons are captured by the molecular oxygen, the holes diffuse to the TiO<sub>2</sub> surface, being trapped at a lattice oxygen. Then, it weakens the binding energy between the Ti and the lattice oxygen, and one molecule of water interrupts this bond, forming new hydroxyl groups. In the dark, the hydroxyl groups gradually desorb from the surface in the form of H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O + O<sub>2</sub>, as indicated in Scheme 1.

It is considered that the OH groups produced by UV irradiation are thermodynamically less stable compared to the OH groups bound to oxygen vacancies because the desorption temperature for the former is lower than that for the latter. This is also supported by the results that either the ultrasonic treatment<sup>4</sup> or the wet rubbing treatment<sup>56</sup> can cause the removal of such OH groups, making the highly hydrophilic surface to the less hydrophilic state immediately. It is therefore considered that the reconstruction from the stable OH groups to the thermodynamically metastable OH groups increases the surface energy of the TiO<sub>2</sub>, causing the hydrophilic conversion.

## Conclusion

We have shown that the reciprocal of the contact angle plotted against UV irradiation time gives the straight line, whose slope can be defined as the hydrophilic conversion rate, which is



independent of the initial value of the contact angle. The spectroscopic and the electrochemical investigation have indicated that there exists strong correlation between the reciprocal of the contact angle and the amount of the surface hydroxyl groups reconstructed by UV irradiation, suggesting that the hydrophilic conversion rate corresponds to the rate for the reconstruction of surface hydroxyl groups.

The quantitative investigation on the relations of the hydrophilic conversion with various parameters such as the UV intensity, the wavelength of irradiated light, and the effect of hole scavenger has shown that the photoinduced hydrophilic conversion and the photocatalytic oxidation process competitively proceed on the TiO<sub>2</sub> surface under UV irradiation. A change of the ratio of both processes may cause a drastic increase of the quantum efficiency (QE) for the former process, whereas the decrease of the QE for the latter process is negligible. For example, a 3-fold increase of the QE for the former process can be obtained by only a 0.1% decrease of the QE for the latter process because the QE for the former process is considered much smaller than that for the latter process.<sup>57</sup> This is the important strategy for the sensitization of the photoinduced hydrophilic conversion.

The comparison of the hydrophilic conversion rate with the rate for the reverse process has clarified that the equilibrium between the reconstruction of the surface hydroxyl groups and their relaxation process gives the critical contact angle under UV irradiation. The suppression of the relaxation process by some methods such as the geometrical modification of the TiO<sub>2</sub> surfaces is also one of the strategies for the sensitization of the photoinduced hydrophilic conversion.

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