

Mechanism of Hydrophilicity by Radiation-Induced Surface Activation *

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Abstract

When a metal oxide is irradiated by gamma rays, the irradiated surface becomes hydrophilic. This surface phenomenon is called as radiation-induced surface activation (RISA) hydrophilicity. In order to investigate gamma ray-induced and photoinduced hydrophilicity, the contact angles of water droplets on a titanium dioxide surface were measured in terms of irradiation intensity and time for gamma rays of cobalt-60 and for ultraviolet rays. Reciprocals of the contact angles increased in proportion to the irradiation time before the contact angles reached its super-hydrophilic state. The irradiation time dependency is equal to each other qualitatively. In addition, an effect of ambient gas was investigated. In pure argon gas, the contact angle remains the same against the irradiation time. This clearly indicates that certain humidity is required in ambient gas to take place of RISA hydrophilicity. A single crystal titanium dioxide (100) surface was analyzed by X-ray photoelectron spectrometry (XPS). After irradiation with gamma rays, a peak was found in the O1s spectrum, which indicates the adsorption of dissociative water to a surface 5-fold coordinate titanium site, and the formation of a surface hydroxyl group. We conclude that the RISA hydrophilicity is caused by chemisorption of the hydroxyl group on the surface.

Key words: RISA, Photocatalyst, Hydrophilicity, Contact Angle, Titanium Dioxide, Hydroxyl Group

1. Introduction

Titanium dioxide absorbs ultraviolet-ray with energy higher than 3eV and its surface becomes hydrophilic. This phenomenon is well-known as photo-induced hydrophilicity. Hydrophilicity was quantified using a method that trickles water droplet onto sample surfaces as shown in Figure 1. The angle formed between a sample surface and a water droplet surface is called the contact angle θ . A typical example of utilization of a super-hydrophilic ($\theta < 3$ deg) surface is a defogging product that prevents mirrors and windows from fogging where water droplets spread uniformly to maintain a transparent surface.

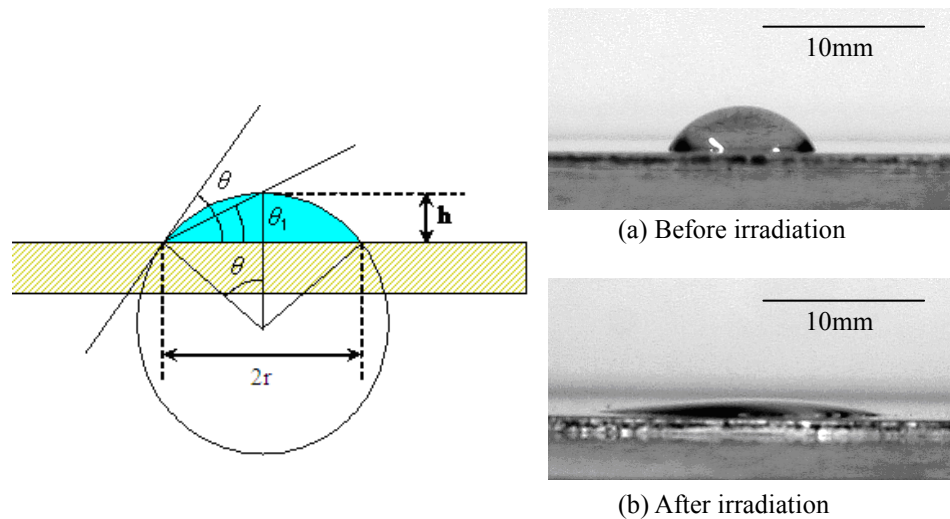


Fig. 1 Measurement of contact angle (left) and water droplet onto TiO_2 surface (right)

In addition, hydrophilic surfaces can enhance⁽¹⁾⁻⁽⁵⁾ boiling and condensation heat transfer. Takata *et al.*⁽⁶⁾ reported the effect of photo-induced hydrophilicity on evaporation heat transfer of a falling film, on minimum heat flux (MHF) in immersed systems, and on pool boiling critical heat flux (CHF).

Recently, Takamasa *et al.*⁽⁷⁾ found that radiation-induced hydrophilicity in place of ultraviolet ray. Moreover, when oxide metals were irradiated with gamma rays, the reduction in electrochemical potential of base metal was found to mitigate corrosion. These surface phenomena are called as radiation-induced surface activation (or RISA)⁽¹⁾⁽⁸⁾. In some applications, gamma ray is suitable, since gamma ray can penetrate through the heat exchanger vessel to induce RISA hydrophilicity on the heat transfer surface, where ultraviolet-ray cannot reach.

Available knowledge regarding radiation-induced hydrophilicity is limited, although some papers published⁽⁹⁾⁽¹⁰⁾ which discussed relation between hydrophilicity and microscopic or macroscopic measurement results like as XPS results or atmosphere around specimen. Radiation-induced hydrophilicity has never been compared with photo-induced hydrophilicity.

This study was intended as to investigate the mechanism of gamma ray--induced hydrophilicity by means of surface science analysis and to explore similarities and differences between photoinduced hydrophilicity and RISA hydrophilicity.

2. Experimental Method

2.1 Experimental Setup

Test specimens were prepared by using a spin-coating process to coat 32-mm diameter and 0.4-mm thick titanium substrates with titanium dioxide. Coating was performed with a spin-coater. The coater was operated at 1500 rpm. Titanium dioxide (rutile) powder solution STS-01 from Ishihara Sangyo Kaisha Ltd. (Japan) was diluted with pure water by a factor of 10 and dropped on the substrates. With the spin-coater a dropped solution was spread as very thin layer on which optical interference color was seen after the surface dried. So the spin coated surface was very thin and flat as order of several hundred nm. A base Ti metal's surface roughness was $R_a = 0.18\mu\text{m}$. A spin coated specimen's surface roughness was $R_a = 0.16\mu\text{m}$. This value indicated that TiO_2 thin film softened roughness of the base metal. Wenzel⁽¹¹⁾ reported effect of surface roughness for wettability. Inducing Wenzel theory,

contact angle that smaller than 90 degree become more hydrophilic on rough surface. In this research all contact angle were smaller than 90 degree, so spin coated surface were more hydrophilic than for example mono crystal specimen.

In order to examine hydrophilicity, a small water drop was dropped on the titanium dioxide surface and the contact angle measured. 2 μ l of purified water was taken up with a micropipette, and a water drop slowly pushed out of the pipette's end. The water's surface at the pipette end formed a hemisphere, which was brought into contact with the sample surface.

At this time, the water contact area should be smaller than the diameter of the water drop at time of measurement. The water drop is then pushed entirely out of the pipette, such that the water contact surface gradually enlarges.

During this process, the contact angle formed by the water drop becomes an advancing contact angle. Also, the water drop must not collide with the sample surface. If a water drop were to collide with the sample surface, the contact angle would decrease because of the falling kinetic energy.

The purified water used was ultrapure water with a rate of resistance of at least 18M Ω ·cm. This ultrapure water was made by transmitting a reverse osmosis membrane at first and an ion-exchange resin as the last process. The light source for ultraviolet rays was a UV lamp. The rays were passed through an optical band pass filter to obtain UV-A rays with a center wavelength of 365 nm. Irradiation intensity was measured with a ultraviolet intensity meter for UV-A, that the center wavelength was 365nm. Gamma-ray irradiation was carried out using the Cobalt-60 irradiation facility situated at the Institute of Research and Innovation (now Atox Co.).

2.2 Measurement of Contact Angle

When a water droplet on a flat surface can be approximated as part of a sphere as shown in Fig. 1(left), the contact angle θ can be determined by equation (1) using height h and radius r of the water droplet.

$$\theta = 2\theta_1 = 2 \cdot \frac{180}{\pi} \tan^{-1} \frac{h}{r} \quad (1)$$

A digital camera with a large-magnification macro lens was used to photograph the water droplet. In the case of super-hydrophilic states ($\theta < 3$ deg), the droplet height h is too small to measure accurately. Because we know the volume of the droplets, we used the following formulas to determine the contact angle, using volume instead of droplet height.

$$V = \frac{4\pi}{3} r^3 \left[3 \tan \frac{\theta}{2} + \left(\tan \frac{\theta}{2} \right)^3 \right] = \frac{4\pi}{3} r^3 \left(\frac{3\theta}{2} + \frac{\theta^3}{4} + \dots \right) \quad (2)$$

$$\therefore \theta \cong \frac{V}{2\pi r^3} \quad \left(\theta < \frac{\pi}{12} \text{ rad} \right) \quad (3)$$

2.3 Hydrophilicity measurement

The experiment investigated the relationship between gamma-ray irradiation dosage and enhancement of the contact angle, using samples that could be easily obtained. Spin coating was used to form a thin film of titanium dioxide on a base plate surface of pure titanium.

The rotation speed of the spin coater was 1500 rpm, so that excess titanium dioxide suspension would fly off. Film thickness was controlled via rotation speed and a thin film was formed by air drying. Using this thin film, we investigated the influence of gas atmospheres around the sample circumference on the enhancement rate of hydrophilicity.

In the ultraviolet-ray irradiation experiment, in order to control an atmosphere around the above-mentioned sample, the atmospheric gas was ambient air or argon gas replacing the air inside a glove box (acrylic; volume about 100 ℓ).

In order to investigate the influence of sample ambient atmospheres, test pieces were placed in a 20 ml glass bottle with a lid. In the first of the cases, the bottle was filled with argon gas. In the second case, silica gel was enclosed with air as a dehumidification agent. In the third case, the bottle was filled with ambient air.

Ultraviolet-ray irradiation at intensity of $100\mu\text{W}/\text{cm}^2$ was selected for investigation of contact angle changes according to irradiation duration. In atmospheric air, ultraviolet-ray irradiation intensity was changed to 36, 50, and $80\mu\text{W}/\text{cm}^2$, and speed of hydrophilicity enhancement was measured.

The gamma-ray irradiation rates of samples ranged between 0.5 to $6.8\text{kGy}/\text{h}$, with irradiation duration from 5 to 302 hours.

2.4 XPS analysis of Titanium dioxide single crystal

In order to investigate bonding states on the surface of titanium dioxide, the single-crystal plates with a simple nature or configuration were prepared.

The samples were 0.5 mm thick, $10\text{ mm} \times 10\text{ mm}$ square, rutile-type titanium dioxide single crystals. They were made using the Verneuil method. The square surface was chosen as the crystal direction (100). This plane was polished as a mirror surface. It is marketed for optical component applications (purity 99.98%). The perpendicularity of the polishing crystal plane is 15 seconds (1second=1/3600 degree) or less, and the surface roughness is 5\AA or less. (All values are published product specifications.)

The surfaces of some single crystal samples were pretreated with heavy water. The nitrogen gas bubbled through heavy water was introduced into a tube furnace (electric furnace) at 300°C for five minutes. Single titanium dioxide crystals placed in a ceramic combustion boat. The tube furnace's temperature program was actually furnace cooling.

Ultraviolet-ray irradiation intensity was $2.0\text{mW}/\text{cm}^2$. Irradiation time was 60 hours. Gamma-ray irradiation was 85 hours at $1.5\text{kGy}/\text{h}$.

Three kinds of samples, including non-irradiated samples, were examined for differences in atomic bonding using an X-ray photoelectron spectroscopy (XPS) system.

XPS analyzes photoelectron data only from atoms near the surface. In order to analyze samples, the photoelectrons must have been emitted into a vacuum from the sample surface. In other words, it can analyze only near the surface, within a range shallower than that of photoelectrons.

In XPS analysis, the state of interatomic bonds on the surface of samples was analyzed using the photoelectron energy spectrum of the one-second orbital of an oxygen atom's innermost shell (hereinafter, "O1s").

3. Result and discussion

3.1 Effects of irradiation parameters and ambient conditions

Fig. 2 shows the reciprocals of contact angles plotted against ultraviolet-ray irradiation duration. The time differential of the reciprocals of contact angles may indicate the pace of hydrophilicity increase. Hydrophilicity rises at a constant rate during irradiation with

ultraviolet-ray irradiation in ambient air. Photocatalyst research⁽⁹⁾ by Sakai, Fujishima, and the Hashimoto *et al.* reported similarly that hydrophilicity increases during early stages at a constant rate. Irradiation for three hours in argon, on the other hand, showed no significant changes in contact angle.

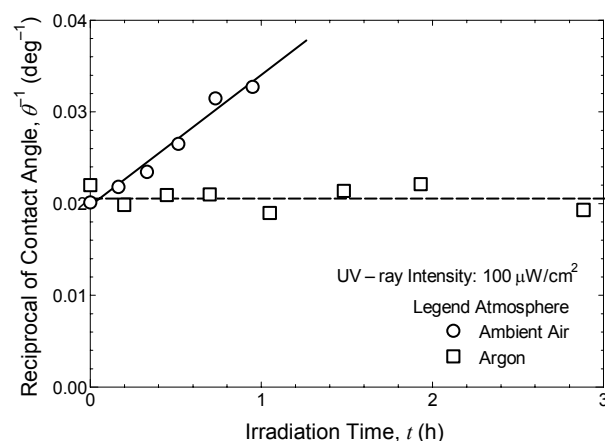


Fig. 2 Photoinduced hydrophilicity rate

Fig. 3 (three lines are for reference) shows the reciprocals of contact angles plotted against gamma-ray irradiation duration in argon gas, dry (low humidity) air, and ambient air. In ambient air, hydrophilicity monotonously increased as the irradiation became longer, as it had similar tendency to monotonously increase with ultraviolet-ray irradiation. On the other hand, when an ambient air and air with a dehumidification agent enclosed, the contact angle at irradiation duration of 42 hours had a low hydrophilicity enhancement rate compared with hydrophilicity in ambient air. Moreover, when argon gas was used, significant changes in contact angle were not found. This was the same result found for ultraviolet-ray irradiation.

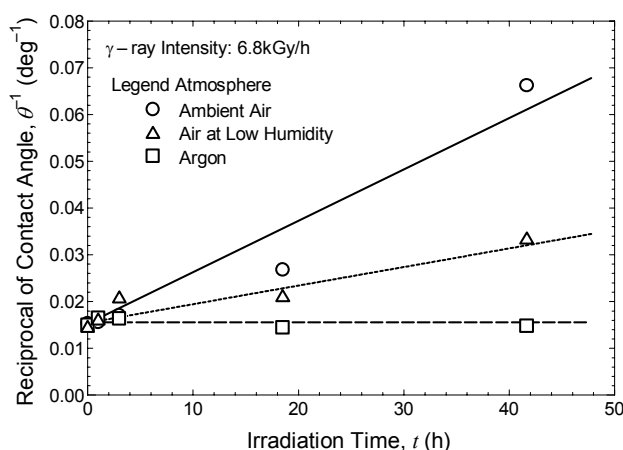


Fig. 3 gamma ray induced hydrophilicity rate

3.2 Surface characteristics found by XPS

In order to investigate microscopic aspects of hydrophilicity, titanium dioxide single crystals with (100) direction planes were used as samples (see Fig. 7 left).

Table 1 depicts the results for light water (H_2O), as stated later, with ultraviolet-ray irradiation induced hydrophilicity and gamma-ray irradiation induced hydrophilicity. Experiments using heavy water were also carried out in this research. It became clear that these two kinds of hydrophilicity phenomena occur not only with light water, but also with heavy water (D_2O), as shown in Table 1.

Table 1 Contact angle θ (deg) for light water and heavy water

	Dark room	UV rays	γ rays
H_2O	67	1.6	1.6
D_2O	56	13	3.2

The contact angle of the sample in a dark room was 56 degrees. Fig. 4 depicts the XPS spectra for O1s. The horizontal axis indicates the binding energy of O1s, and the vertical axis is the number (arbitrary unit) of detected photoelectrons. For the sake of convenience, that is the value of the energy of the excitation X-rays minus the kinetic energy of the photoelectrons. The absolute value of bond energy is subtracted so that it may become larger as it moves to the left of the Figure.

In O1s spectra of TiO_2 rutile mono-crystal many research reported three peaks, and our fitting well supported those results. Non-linear least square method was used. Each spectrum was fitted by linear combination of three Gaussians. And it was sufficient to use linear line as background. Error of each peak height was smaller than 2%.

As indicated in Fig. 4, (a), the largest peak near 530.7 eV, is internal (bulk) 4-fold coordination oxygen (it has bonded with four titanium atoms)⁽¹²⁾.

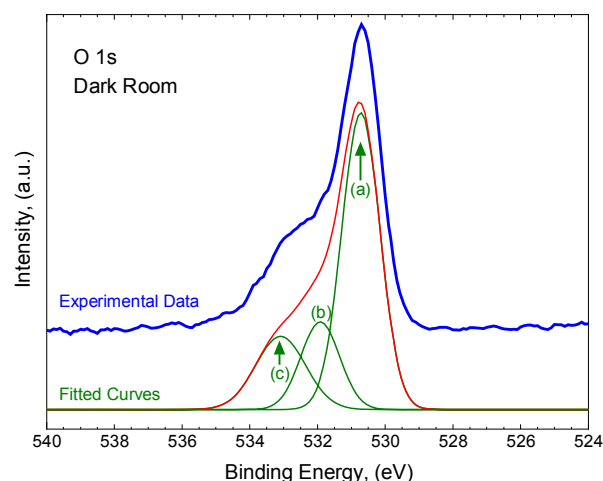


Fig. 4 O 1s XPS spectra for TiO_2 surface dark room

The energy peak (b) at 531.9 eV is the photoelectron peak from Ti-O-Ti that is bridging oxygen existing on the surface⁽¹³⁾. In the plane (100), bridging oxygen exists more densely than on other direction surfaces⁽¹⁴⁾.

A previous study⁽¹⁵⁾ on the emitting angle of photoelectrons did not find a peak (b) on the O1s spectrum of a clarified (001) surface, but it found such a peak when the (001) surface was roughened and the (100) surface appeared as a surface. It is therefore clear that the peak (b) on the (100) surface is bridging oxygen that does not exist on the (001) surface.

The peak at 533.1 eV (c) is a hydroxyl group dissociative adsorption process⁽¹³⁾. The spectrum peak originating in carbon-oxygen bond contamination in this spectral range can be disregarded, because there is so little of it on the C1s spectrum. The O1s spectrum therefore consists of three components at 530.7, 531.9, and 533.1 eV. Peak fitting combined with intensity distribution are shown on Fig. 4. As the Figure indicates, the three components of O1s are accurately identified.

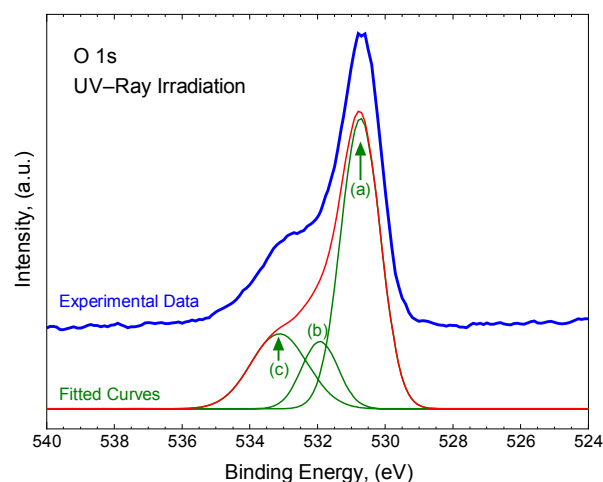


Fig. 5 O1s XPS spectra for TiO₂ surface irradiated by UV rays at 2mW/cm² for 60 h

Fig. 5 shows the result of XPS analysis of hydrophilicity induced in single crystals by ultraviolet-ray irradiation. Hydrophilicity experimentation with another sample prepared under the same conditions as the sample in this analysis found the heavy water contact angle to be 13 deg, as shown in Table 1. Fig. 5 depicts the XPS spectrum of O1s orbital energy spectra before inducement of hydrophilicity (see Fig. 4).

As with the sample stored in a dark room, it is clear from the fitting of a graph that the spectra consists of three peaks, (a) 530.7, (b) 531.9, and (c) 533.1 eV. They can be identified as (a) 4 coordination oxygen in bulk, (b) surface bridging oxygen, and (c) adsorbed hydroxyl group. While the peak of bridging oxygen is small compared with the result of the sample stored in a dark room, the peak resulting from a hydroxyl group was higher.

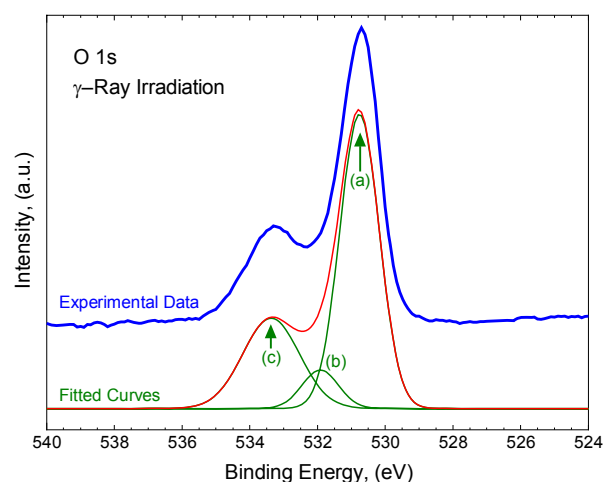


Fig. 6 O1s XPS spectra for TiO₂ surface irradiated by γ rays at 1.5kGy/h for 85 h

Additionally, Fig. 6 illustrates the O1s XPS results for single crystals with gamma-ray irradiation. The contact angle was 3.2 degrees. In this case as well, the fitting result for the O1s spectra included three peaks, identified as (a) 4 coordination oxygen in bulk, (b) surface bridging oxygen, and (c) adsorbed hydroxyl radicals. In the hydrophilic state induced by gamma-ray irradiation, the peak of bridging oxygen (b) is low, as with ultraviolet-ray irradiation, and the peak from the hydroxyl group (c) is high.

3.3 Role of water molecules in hydrophilicity

Fig. 2 shows the relationship between the reciprocal of contact angle and irradiation time with ultraviolet-rays. The intensity of ultraviolet rays was $100\mu\text{W}/\text{cm}^2$. In the case of irradiation in ambient air, hydrophilicity increased at a constant rate. This result is consistent with the earlier results reported in many papers, where the enhancement rate of hydrophilicity during the early stage of irradiation is constant. On the other hand, in the case of irradiation in argon gas, no significant change in hydrophilicity was observed for irradiation up to three hours. The difference in hydrophilic response between air and argon gas is attributed to the humidity of the irradiation atmosphere.

Fig. 3 depicts the relationship between the reciprocal of contact angle to γ -ray irradiation duration. The dose rate of γ -ray irradiation was $6.8\text{kGy}/\text{h}$. In the case of irradiation in ambient air, the reciprocal of contact angle increased at a constant rate, as in the case of ultraviolet rays. When air and a dehumidification agent were enclosed in a bottle, however, the reciprocal of contact angle was lower than in the case of ambient air. The authors therefore conclude that when the humidity in the air is low, water molecules to be photo-catalytic oxidized by the holes on the surface are few, resulting in a low enhancement rate of hydrophilicity. In the case of argon gas, the contact angle remained at the initial value, as in the case of irradiation by ultraviolet ray.

3.4 Surface adsorbed substances

We showed that a surface hydrophilic group arose under gamma-ray irradiation under the same manner as in ultraviolet-ray irradiation. As found in the experimental results, XPS results could be analyzed and the quantitative alteration of bridging oxygen and a hydroxyl group could exist in the O1s spectrum on the surface of single crystal before and after irradiation.

Before and after irradiation, about change of the state of Ti bonding, detailed experimental results showed that the change in XPS spectrum is extremely small⁽¹⁵⁾. Changes in Ti bonding are presumed to be similarly small, so the spectrum of Ti was not analyzed.

The peak for bridging oxygen with ultraviolet-ray irradiation is low compared with the results in a dark room, while the peak for the hydroxyl group is high (Fig. 5). High hydrophilicity was shown, with a heavy-water contact angle of about 13 degrees. It therefore appears that ultraviolet-ray induced hydrophilicity is enhanced by generation of a surface hydroxyl group with dissociative adsorption of water molecules on the surface. As discussed in Section 3.1 above, this interpretation is consistent with gamma-ray induced hydrophilicity phenomena in experiments performed in ambient air. This conclusion also conforms to the case with gamma-ray irradiation, as will be described and discussed in detail below.

In the spectra in case of gamma-ray irradiation as well, the peak of bridging oxygen is low and the peak of hydroxyl group is high compared with non-irradiated samples. These amounts of change are larger than the case of ultraviolet-ray irradiation, probably because more hydroxyl groups had formed.

For detailed discussion, the ratio of the surface concentration of bridging oxygen to the hydroxyl group was estimated from the experimental results. The 4-fold coordination oxygen (surface density a) of bulk is suitable for comparing and contrasting, since it exists

Table 2 Surface density of bridging oxygen and hydroxyl group

	Hydrophilicity		Bridging oxygen area density ratio ρ_b		Hydroxyl area density ratio ρ_c	
	Contact angle θ	$1/\theta$	Area density ratio	Difference from dark room	Area density ratio	Difference from dark room
	deg.	1/deg.				
Dark room	56	0.018	0.30	Base (assigned 0%)	0.24	Base (assigned 0%)
UV rays	13	0.075	0.23	-23%	0.26	+5.3%
γ rays	3.2	0.31	0.134	-55%	0.31	+27%

throughout the range of XPS observations of multiple atomic layers. The surface density is less than one for bridging oxygen (surface density b) and surface hydroxyl group (surface density c), but the surface density of 4-fold coordination oxygen existing in bulk is greater than 1 (surface density $a > 1$). Thus, the signal strength of 4-fold coordination oxygen was reset to 1, and the values of the surface-density ratios (surface density ratio $\rho_b = b/a$, $\rho_c = c/a$) of each site are as shown in Table 2. The signal strength used here is the height of the fitting curve for each site. In this table, the difference after subtraction of density ratio data on non-irradiated samples is expressed as a percentage.

Area density ratio of bridging oxygen site :	b_0/a_0
Area density ratio of hydroxyl group site :	c_0/a_0
Differential area density of bridging oxygen site :	$(b_1/a_1) - (b_0/a_0)$
Differential area density of hydroxyl group site :	$(c_1/a_1) - (c_0/a_0)$

The subscript 0 means non-irradiated, while 1 means irradiated. Although hydroxyl groups existed in non-irradiated samples, the quantity after irradiation is larger. Looking at ultraviolet-ray irradiation and gamma-ray irradiation in this experiment as well, the change in hydroxyl group surface density is proportional to the change in the reciprocal of contact angle, but the relationship does not correlate to change in bridging oxygen surface density. Therefore, it was found that hydrophilicity increased along with the adsorbed hydroxyl group that increased by irradiation. This is discussed semi-quantitatively in section 3.5.

In the case of gamma-ray irradiation, bridging oxygen is lost and the hydroxyl group is adsorbed, as with ultraviolet-ray irradiation. From these results, the authors conclude that the area density ratio was increasing. The irradiated energy appears to have accumulated not only as electronic electron hole pairs in bulk but as surface energy. This is because if defects and adsorption arise on the crystal surface, the rutile crystal structure grows unstable and surface energy increases.

Research on rutile (110) surfaces⁽¹³⁾⁽¹⁴⁾⁽¹⁶⁾⁽¹⁷⁾ has considered changes of the surface structures of crystals and proposed that dissociative adsorption of water molecules to 5-fold coordination titanium takes place⁽¹⁶⁾. In addition, research indicates that water molecules attach to 5-fold coordination titanium by hydrogen bond or physical adsorption⁽¹⁷⁾.

In the case of hydrophilic TiO_2 induced by ultraviolet-ray irradiation, it has been proposed that bridging oxygen dissociated to produce two hydroxyl groups⁽⁹⁾.

Regarding these proposals, in addition to the difference using the rutile (100) surface, this research found a difference in the interpretation of the XPS spectra themselves. Because XPS captures data on chemical rather than physical bonds, the peak at 531.7 eV should be interpreted as an indication of bridging oxygen rather than physical adsorption of water⁽¹³⁾.

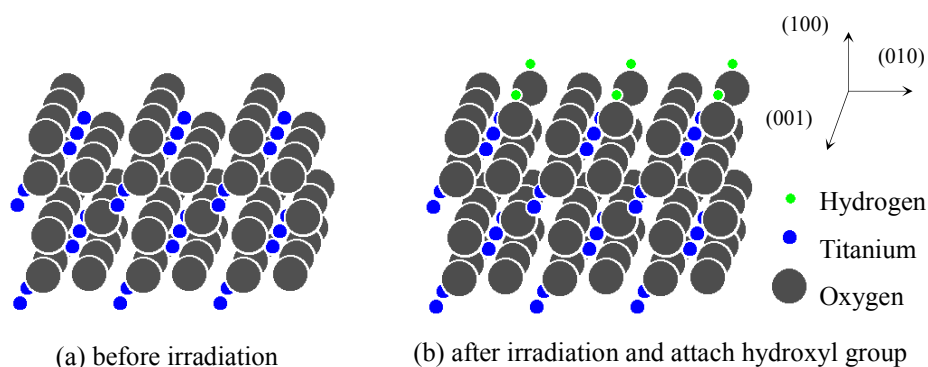


Fig. 7 Rutile-type TiO_2 (100) surface

Fig. 7(a) depicts the surface structure of a rutile (100) surface. The bridging oxygen aligns in a direction [001] such that two titanium atoms are connected to the surface. Although titanium atom is 6-fold coordinated in bulk, on the outermost surface it has dangling bonds and easily loses single oxygen atoms. Fig. 7(b) depicts the adsorption of a surface hydroxyl group. This is further described below.

If all of the hydroxyl groups undergo dissociative adsorption at the site of bridging oxygen, the ratio between the increase of hydroxyl groups to the decreases of bridging oxygen is 1:1. If it responds to the coordination number of titanium that bridging oxygen has bonded together, the ratio is 2:1. Actual measured values, however, varied widely, from 1:2 to 1:4 (Table 2). A single increase in hydroxyl groups therefore corresponds to a decrease of 2 to 4 in bridging oxygen. Although it has been proposed that a bridging oxygen bond breaks and two hydroxyl groups arise on a rutile (110) surface⁽⁹⁾, this proposal cannot explain the phenomenon.

From these research cases, water forms surface hydroxyl groups with (100) surface and undergoes dissociative adsorption. Because the peak (b) that appeared in the O1s spectra of XPS analysis is from bridging oxygen, it is natural to conclude that two bridging oxygens disappear and one hydroxyl group forms, as shown in Table 2.

If the only surface reaction is dissociative adsorption, a water molecule will dissociate to a hydroxyl group and a hydrogen atom. Because ion balance is also maintained and there is no inconsistency with one hydroxyl group and one hydrogen atom adsorbed by the two disappearing bridging oxygen sites, this hypothesis was adopted in this research.

Although the hydrogen atom was described in Fig. 7(b), the geometric spatial relationships are unknown.

3.5 Process of hydrophilicity

Since these experiments are usually carried out in environments where water molecules exist, it is probable that dissociative adsorption reactions bring water molecules to a more stable condition on the TiO_2 surface. Logically, hydrophilicity is not enhanced in

environments where water molecules do not exist, as demonstrated in experiments in an argon atmosphere.

In addition, it has been reported⁽¹⁸⁾ that when TiO_2 is ignited, hydroxyl groups cannot be adsorbed even they disappear and the sample is dipped in water. In our experience as well, ultraviolet-ray irradiation cannot enhance the hydrophilicity of samples after ignition, but there are cases where hydrophilicity was shown after dripping two or three drops of water. Clearly, hydrophilicity does not appear unless water molecules contact or hydroxyl groups form on the sample surface.

In other words, in order to enhance hydrophilicity the exposed irradiation energy must be accepted as surface energy that generates hydroxyl groups on the surface.

In the case of gamma-ray irradiation where hydrophilicity is high, the peaks of bridging oxygen are small, and the peaks of hydroxyl groups are increased by gamma-ray irradiation, as found in the results of XPS analysis. In the case of ultraviolet-ray irradiation, hydrophilicity is relatively low, peaks of bridging oxygen are not small, and peaks of hydroxyl groups are conversely small. These facts in XPS analysis demonstrate that more hydroxyl groups need to form on a surface in order for hydrophilicity to become high.

4. Conclusion

In order to investigate radiation-induced and photo-induced hydrophilicity, experiments were carried out in which the contact angles of water droplets on a titanium dioxide surface were measured. The following results were identical for both radiation-induced and photo-induced hydrophilicity.

- (1) The reciprocals of contact angles proportionally increase with irradiation time during the initial state of hydrophilicity.
- (2) Certain humidity is required in ambient gas to take place of RIS hydrophilicity.
- (3) When the contact angle becomes smaller due to gamma ray irradiation, an XPS analysis indicates that the surface density of bridging oxygen becomes smaller. When the surface is irradiated by gamma ray, metastable hydroxyl groups chemisorbed on the surface, which induce hydrophilicity in the same manner as that in photo-induced hydrophilicity.

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