

Effect of repeated photo-illumination on the wettability conversion of titanium dioxide

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Received 16 May 2001; received in revised form 19 July 2001; accepted 29 July 2001

Abstract

The effect of the repeated UV illumination on the photo-induced wettability conversion of TiO₂ surface was investigated using rutile single crystal. The hydrophilicizing rate was increased by the repeated UV illumination and this effect was more remarkable on (001) than (110) surface. This crystal plane dependence can be attributed to the differences of the efficiencies of oxygen vacancy creation and the degrees of resultant structural distortion between these two surfaces. These data suggest that the hydrophilicizing process of TiO₂ is a kind of photo-corrosion process occurring at the surface. © 2001 Published by Elsevier Science B.V.

Keywords: Photo-catalyst; Titanium dioxide; Contact angle; Wettability

1. Introduction

The photo-induced reaction of titanium dioxide has been well studied from the discovery of breaking down of water by TiO₂ [1]. Especially, the strong activation powers of photo-generated hydroxyl radicals and super-oxide anions have been well investigated [2] from the standpoint of application for water and air purifications by many researchers [3–6].

Besides these conventional applications of TiO₂ photo-catalyst, we have found another intriguing phenomenon, i.e. the generation of a highly hydrophilic TiO₂ surface by UV illumination [7]. This unique surface exhibits excellent antifogging and self-cleaning properties. Utilizing these properties, the thin film TiO₂ coating has already been applied for various items such as automobile side view mirror, window film, exterior tile, highway road wall panel and so on [8].

The mechanism of the photo-induced hydrophilicity of TiO₂ surface has been intensively studied. According to an atomic force microscope (AFM) study of TiO₂ rutile single crystal [7], it is clarified that the water adsorption does not occur uniformly on TiO₂ surface but produces the surface microstructured composition of hydrophilic and oleophilic

phases, resulting in amphiphilic surface. The hydrophilic domain aligns particularly along the bridging site oxygen configuration. It has been also revealed from the studies by IR and XPS that the amount of OH groups on the TiO₂ surface increases by UV illumination [9,10]. Furthermore, an ultrasonication treatment of hydrophilic surface of TiO₂ in pure water increases the hydrophilic to hydrophobic conversion rates [10]. Based on these results, we proposed the mechanism of the photo-induced hydrophilicity as follows. The TiO₂ surface itself is reacted by the band-gap excitation, forming the oxygen vacancy at definite sites and then water molecules are adsorbed dissociatively at the sites.

If this mechanism is correct, the photo-induced wettability conversion rate should depend on the atomic arrangement in the surface of TiO₂. In fact, the (110) and (100) surfaces of rutile TiO₂, which have bridging site oxygen, exhibit higher hydrophilic conversion rate compared with (001) surface [11]. The proposed mechanism means that the surface structure changes during the reaction. In other words, the rate of photo-induced hydrophilicity may depend on the history of the sample. In the present study, therefore, we have evaluated the effect of repeated photo-illuminations on the wettability conversion rate of TiO₂ rutile single crystals.

2. Experimental

Polished rutile single crystals with (110) plane or (001) plane (Namiki-Hoseki Co., Tokyo, Japan) were employed in this study. These single crystals were washed in pure water

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before contact angle measurements. The AFM observations showed that the variation of surface roughness among the single crystals was ignorable, less than 1 nm, before UV illumination.

Ultraviolet illumination was carried out using a Hg–Xe lamp with an optical fiber coupler, employing a filter to obtain light with a wavelength centered at 365 nm. The intensity of UV illumination was 40 mW/cm^2 . Repeated illumination experiments were carried out as follows. Ultraviolet light was illuminated to rutile single crystals for 24 h. Then the samples were sonicated in pure water for 30 min, and stored within a vessel filled with dry clean air in a dark place for 7 days. These UV illumination, sonication, and dark storage procedures were repeated three times. Both the hydrophilicizing rate during UV illumination and the hydrophobicizing rates during sonication or dark storage were evaluated by contact angle measurements. The sessile drop method was used for contact angle measurements with a commercial contact angle meter (CA-X, Kyowa Interface Science, Saitama, Japan). The droplet size used for the measurements was $0.4 \mu\text{l}$. Microstructural observation by atomic force microscopy (AFM, SPA300, Seiko Instruments Inc., Japan) was conducted on the samples. The observation was carried out in the contact mode with a triangle-type silicon nitride cantilever with the length of $200 \mu\text{m}$.

3. Results and discussion

Fig. 1 shows the changes of water contact angle of rutile (001) and (110) surfaces by the repeated UV illumination. Photo-induced hydrophilicizing rate of TiO_2 is commonly evaluated from the contact angle change and corresponding UV illumination time in relatively early stage of hydrophilicizing process, and depends on photo-catalytic activity, surface microstructure, and UV intensity [12–14]. At the first cycle, a fully hydrophilicized (001) surface was obtained

after $\sim 300 \text{ min}$ UV illumination, which was almost three times longer than the case for (110) surface. This slow rate is rationalized on the basis of the lack of bridging site oxygen atoms on (001) surface [11]. The photo-induced hydrophilicizing rate of (001) surface was, however, clearly increased after repeating the illumination, sonication and dark storage cycle described in Section 2. At the third cycle, the fully hydrophilicized surface was obtained only by 50 min illumination. This conversion rate is even faster than that of (110) surface. Such a change by repeating the illumination cycle was much less remarkable on (110) surface.

It should be noted that saturated contact angle for (110) surface by UV illumination does not follow the order of illumination cycle. It is known that the saturated contact angle in hydrophilicizing process is not always determined by the total number of photon illuminated, and the concern of some non-linear process is suggested [13]. Dominant factors that determine the saturated contact angle in hydrophilicizing process by UV illumination are still unclear, and further investigation is required.

Fig. 2 shows the change of water contact angle in the dark of these two surfaces after UV illumination. The repeated UV illumination cycles also affected on the hydrophobicizing process in the dark. The saturated contact angle value decreased with more illumination cycles. This effect is clearer on (001), than on (110) surface. It should be noted here that such changes of hydrophilicizing rate under UV illumination and saturated contact angle values in the dark were observed even without sonication process.

TiO_2 has been believed to be very stable under UV illumination. However, the present experimental data suggest that the surface was changed by UV light illumination. As was reported previously, the photo-induced surface structural changes are considered to be due to the formation of oxygen defect where water molecule coordinates. On (001) surface, there does not exist bridging site oxygen, therefore the formation of defect causes a large distortion (Fig. 3).

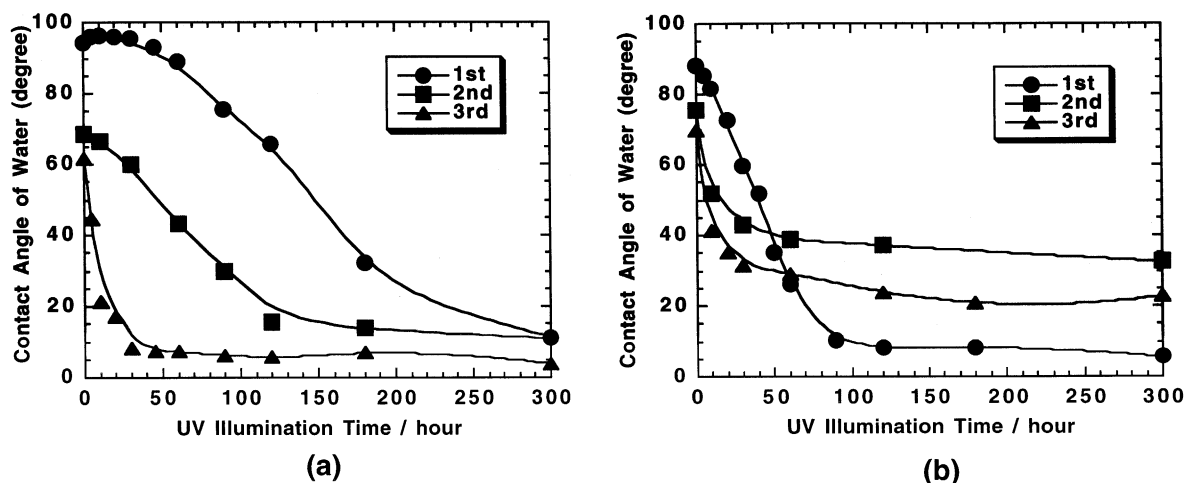


Fig. 1. Effect of the repeated UV illumination (40 mW/cm^2) on the photo-induced hydrophilicizing rate of rutile (001) surface: (a) (001) surface; (b) (110) surface. (●) First, (■) second, (▲): third (see Section 2).

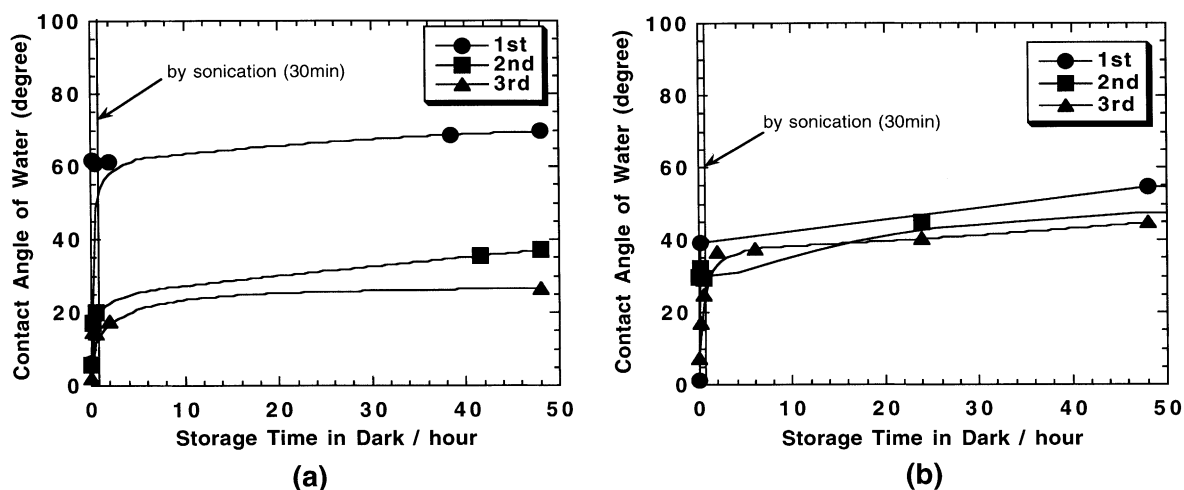


Fig. 2. Effect of repeated UV illumination (40 mW/cm^2) on the hydrophobicizing rate of rutile (001) surface in the dark: (a) (001) surface; (b) (110) surface. (●) First, (■) second, (▲) third (see Section 2).

The replacement of in-plane oxygen with water resulting in breaking down the microstructure. This structural change may be not so easy to recover the original one by replacing water with oxygen after stopping UV illumination. Thus, the effect of UV illumination history remains on the surface and the improvement of the sensitivity of photo-induced hydrophilicity is remarkable for (001) surface.

On the contrary, bridging site oxygens, which are higher in position and energetically more reactive than their surrounding atoms, exist on (110) surface. The photo-induced hydrophilicity of (110) surface will be caused by the creation of vacancies at the sites of bridging site oxygen and curing them by the dissociated water (Fig. 3). Thus, the surface structural change on (110) surface by UV illumination

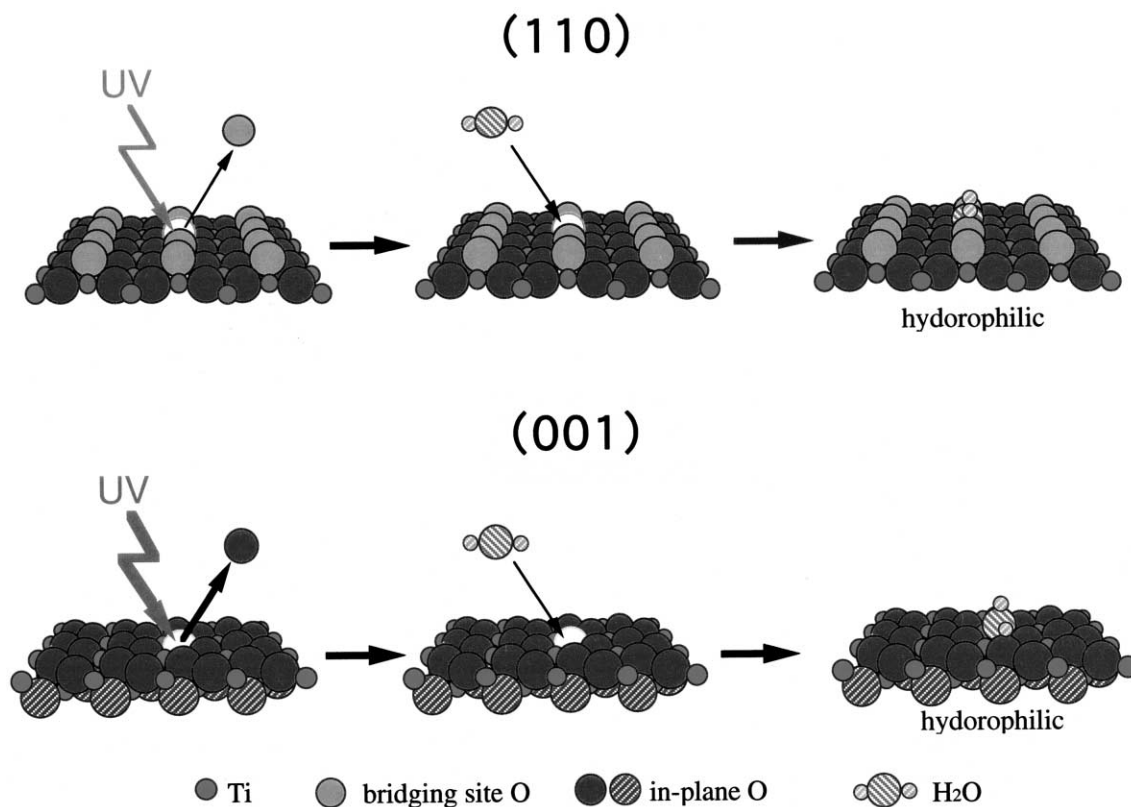


Fig. 3. Schematic illustration of the surface of rutile single crystal and oxygen defect formation.

does not introduce a large distortion and is easy to recover the original structure by the exchange of the water with oxygen from ambient air after stopping UV illumination.

As for photo-induced breaking down, of the topmost surface structure, such a microstructural change is very similar to the well-known mechanism of the photo-corrosion of semiconductor such as ZnO in water [15]. Although TiO₂ is commonly regarded as a non-corrosive material by UV illumination, the results obtained in this study suggest that the photo-induced hydrophilicity is caused by a kind of photo-corrosion at the topmost surface layer of TiO₂. Actually, most recently, we have found the similar increase of the photo-induced hydrophilicizing rate for the reduced rutile (001) single crystal after a photo-etching treatment in a sulfuric acid [16]. On the basis of the mechanism of photo-induced wettability conversion of TiO₂, which is quite different from that of conventional photo-catalytic oxidation process in terms of relation to surface structural change, it is reasonable to assume that at least topmost photo-corrosion is necessary to arise the photo-induced wettability conversion. This assumption is also consistent to the experimental results that photo-corrosive ZnO exhibits clear photo-induced hydrophilicizing effect [17] and little photo-corrosive SrTiO₃ exhibits little wettability conversion by UV excitation [18]. Although the topmost surface photo-corrosion is consistent to the experimental results, the detailed mechanism is still not fully clarified. Especially in order to clarify the reason why the area of such photo-corrosion is restricted in topmost layer in the case of TiO₂, further investigations should be carried out.

4. Conclusions

In the present study, it was revealed that the sensitivity of photo-induced hydrophilicity of TiO₂ rutile single crystal. This effect depends on the crystal plane, and is remarkable on the surface without bridging site oxygen as like rutile (001) surface. The crystal plane dependence is attributable to the difference of oxygen vacancy creation and the degree of resultant structural distortion by the replacement of

oxygen with the dissociated water. Based on these results, it is deduced that the photo-induced hydrophilicity of TiO₂ surface is caused by a kind of photo-corrosion in the surface.

The current work demonstrates the effect of photo-illumination history on the photo-induced wettability conversion of TiO₂ photo-catalyst. Further investigation on the relationship between the repeated UV illumination and wettability conversion may provide the coatings with high sensitivity for photo-induced hydrophilicity by optimizing the condition of pre-illumination history of UV light.

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