

Mechanism of Photoinduced Superhydrophilicity on the TiO₂ Photocatalyst Surface

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The physicochemical properties of the H₂O molecules adsorbed on TiO₂ surfaces during UV light irradiation were fully investigated by near-infrared (NIR) absorption spectroscopy. It was found that the H₂O molecules adsorbed on the TiO₂ surfaces desorb during UV light irradiation by the heating effect of the light source. Since the amount of the H₂O adsorbed on the TiO₂ surfaces decreased, the distribution of the hydrogen bonds within the H₂O molecules decreased, resulting in a decrease in the surface tension of the H₂O clusters. The decrease in the surface tension of H₂O under UV light irradiation was found to be one of the most important driving forces in which the H₂O clusters on the TiO₂ surface spread out thermodynamically, forming H₂O thin layers. The partial elimination of the hydrocarbons from the TiO₂ surface by the photocatalytic complete oxidation was seen to be the other important factor, providing free spaces on the surface where the H₂O clusters could spill over and spread out to form the thin H₂O layers. Moreover, the temperature changes of the TiO₂ powder samples during UV light irradiation were found to show a good correspondence with the changes in the contact angle of the H₂O droplets on the TiO₂ thin film surfaces. Especially the time scale for the hydrophilic conversion on the TiO₂ surfaces under UV light irradiation was in good agreement with the decrease in the amount of H₂O molecules adsorbed on the TiO₂ surfaces but not the amount of the hydrocarbons eliminated by the photocatalytic oxidation reactions, showing that the adsorption and desorption of H₂O molecules are generally quite sensitive to the temperature changes of solid surfaces.

Introduction

Since the photoinduced superhydrophilicity of TiO₂ thin films in which H₂O droplets are able to spread out to form H₂O layers under UV light irradiation was discovered in 1997,¹ TiO₂ thin film photocatalysts have attracted much attention as photofunctional materials for self-cleaning, antifogging, antibacterial, and stain-proofing agents.^{2,3} This phenomenon is reported to be achieved by increasing the number of hydroxyl groups of the TiO₂ surfaces during UV light irradiation.^{4–6} Tachiya et al. have studied the kinetics of the photoinduced hydrophilic processes on TiO₂ surfaces by a theoretical method and concluded that the changes of the interfacial energies between solid surfaces and liquid play an important role in the photoinduced phenomenon.⁷ Moreover, the adsorption states of H₂O molecules on TiO₂ single crystals have been investigated by scanning transmission microscopic observations.^{8,9} However, the mechanism of this UV light driven phenomenon has yet to be clarified by experimental results. When a H₂O droplet showing a contact angle of 60° in its initial state spreads out and reaches a contact angle of 1° by the effect of UV light irradiation, the contact area between the solid surface and H₂O droplet can be mathematically calculated to increase up to 17.5 times. Although this phenomenon has been explained by the two-dimensional capillary effect,⁴ the density of the hydroxyl groups on the TiO₂ surfaces must be increased, at least, several times by the effect of UV light irradiation, meaning that the absorbance due to the surface hydroxyl groups of the TiO₂ surfaces, obtained by

Fourier transform infrared (FT-IR) measurements, increases, at least, up to 4 or 5 times. However, direct evidence that the hydroxyl groups on the TiO₂ surfaces (titanol groups) increase under UV light irradiation have yet to be clearly reported since the discovery of this phenomenon. Furthermore, the increase of the physisorbed H₂O on the TiO₂ thin film during UV light irradiation was reported by using surface-enhanced IR absorption spectroscopy (SEIRAS).¹⁰ However, the temperature of the solid surfaces inevitably increases by the effect of irradiation, even with weak light sources, meaning that the entropy of the solid surfaces will always increase during light irradiation. From thermodynamic considerations, the adsorption of H₂O on solid surfaces in which the entropy is increased by light irradiation is never promoted, since the adsorption of H₂O on solid surfaces is quite sensitive to temperature changes. Actually, Munuera et al. have reported that H₂O desorbs from the TiO₂ surface during UV light irradiation as a photodesorption of H₂O.¹¹

In this work, a detailed investigation of the adsorption states of the H₂O molecules on the TiO₂ surfaces during UV light illumination in ambient conditions was carried out by near-infrared (NIR) absorption measurements. The mechanism and its driving force for the photoinduced hydrophilic conversion have been discussed with regard to the surface tension of the H₂O molecules adsorbed on TiO₂ which depended on the distribution of the hydrogen bonds.

Experimental Section

The diffuse reflectance near-infrared (DR-NIR) absorption spectra of H₂O adsorbed on TiO₂ powder (Degussa, P-25) were measured by a UV–vis–NIR spectrophotometer equipped with

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an integrating sphere (Varian, Cary-5). The baseline was calibrated with BaSO₄ powder in diffuse reflectance mode. UV light irradiation on the TiO₂ powder samples was carried out in air by a medium-pressure Hg lamp (Polymer401, Helios Italquartz SRL). The irradiation distance between the light source and powder samples was adjusted to ca. 50 cm. The temperatures of the TiO₂ powder during UV light irradiation were measured by a thermocouple.

The contact angles of the H₂O droplets on the TiO₂ thin films prepared on quartz substrates were measured by a conventional contact angle meter (Kyowa Interface Science Co. Ltd., CA-X). From the X-ray diffraction (XRD) measurements, the crystallinity of the TiO₂ thin films prepared on the quartz and Si wafer substrates were confirmed to be completely in an anatase phase. All of the operations were carried out in a clean room (class 10).

The amount of the hydrocarbons adsorbed on these TiO₂ thin films were estimated by electron spectroscopy for chemical analysis (ESCA) and FT-IR measurements. ESCA analysis of these thin films was carried out by an X-ray photoelectron spectroscopy (XPS) apparatus (Shimadzu, ESCA-3200) under high vacuum conditions (10⁻⁹ kPa range). The FT-IR (middle infrared, MIR) spectra of the TiO₂ thin films were recorded in transmittance mode by an FT-IR spectrometer (Bruker, IFS28). Transparent TiO₂ thin films were prepared on both sides of the Si wafer by a rf-magnetron sputtering deposition method, according to procedures detailed in previous literature.^{12,13} The film thicknesses were about 1 μ m. Since the Si wafers are transparent in the MIR region (4000–2000 cm⁻¹), FT-IR measurements of the TiO₂ thin films could be carried out smoothly. UV light was irradiated using a conventional 24 W fluorescent valve (ca. 25–30 μ W/cm²) and a 100 W high-pressure Hg lamp (Toshiba, SHL-100UVQ-2, UV light intensity; ca. 1.0 mW/cm²).

The photocatalytic reactivities of the TiO₂ thin films were evaluated by the decomposition of acetaldehyde (0.27 kPa) with the coexistence of O₂ or N₂ (1.33 kPa) under UV light irradiation (ca. 1.0 mW/cm²) at 298 K. The reaction products were analyzed by a gas chromatograph equipped with a thermal conductivity detector.

Results and Discussion

Figure 1 shows the changes in the contact angles of the H₂O droplets (a) when the TiO₂ thin film sample was irradiated by UV light (ca. 1.0 mW/cm²) and (b) then stored in dark conditions, and (c) after sample (a) was evacuated at 298 K for just 5 min and then was stored in dark conditions. The contact angles of the H₂O droplets gradually increased in dark conditions after UV light irradiation was ceased. On the other hand, when the TiO₂ sample, which showed superhydrophilic properties upon UV light irradiation, was evacuated at 298 K for 5 min, the superhydrophilicity disappeared immediately. These results could not be explained by the presence of newly formed hydroxyl groups on the TiO₂ surface by UV light irradiation since the hydroxyl groups of oxide surfaces cannot be removed by evacuation at room temperatures. White et al. have also concluded by TPD analyses of TiO₂ single crystals under ultrahigh vacuum conditions that the dissociation of H₂O to form OH groups is not required for wetting phenomena since neither dissociation of H₂O nor oxygen vacancies control hydrophilicity.¹⁴ However, the results in Figure 1 clearly indicate that analyses under high vacuum conditions may not clarify the origin of the photoinduced superhydrophilicity on the TiO₂ surface. The chemical states of the hydroxyl groups on the

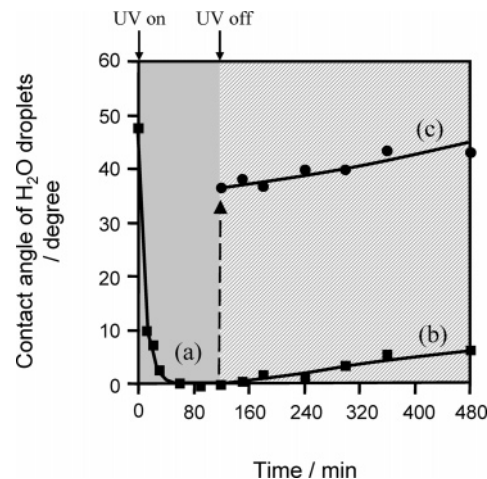


Figure 1. Time profiles of contact angles of H₂O droplets on TiO₂ thin film surfaces: (a) under UV light irradiation (ca. 1.0 mW/cm²), (b) when the samples were stored in the dark, and (c) after the samples in (a) were evacuated at 298 K and then stored in dark conditions.

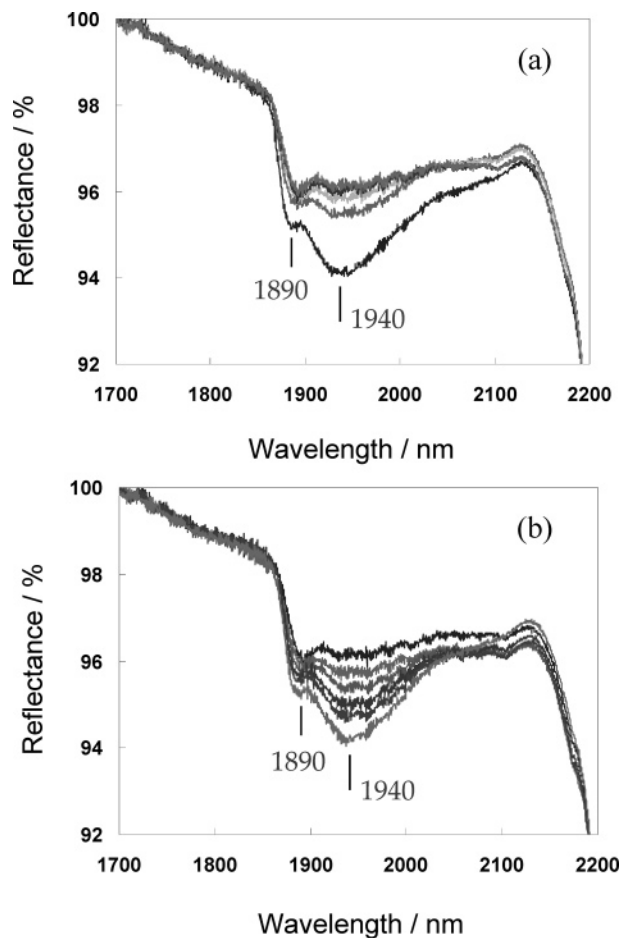


Figure 2. Near-infrared absorption spectra of H₂O adsorbed on TiO₂ surfaces: (a) under UV light irradiation of 0, 10, 60, 120, and 180 min (from bottom to top), (b) after the samples in (a) were stored in the dark for 0, 8, 40, 120, 300, and 1320 min (from top to bottom).

surface and detailed analyses of the adsorption states of the H₂O molecules were, thus, investigated in ambient conditions.

Figure 2 shows the DR-NIR absorption spectra of the H₂O adsorbed on TiO₂ during UV light irradiation without any cutoff filters to control the wavelength of the irradiated light and H₂O filters to prevent the irradiation of infrared light from the UV light source. A broad absorption band around 1850–2100 nm

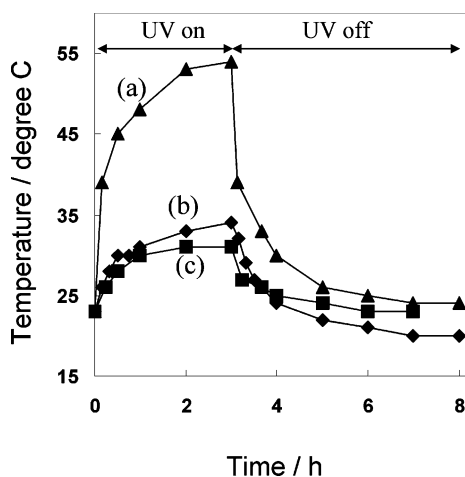


Figure 3. Temperature changes during UV light irradiation for 3 h under various irradiation conditions and storage for 5 h in the dark: (a) without any filters, (b) with ca. 10 mm thick H₂O filter in a Pyrex glass tray, and (c) with both ca. 10 mm thick H₂O filter and H₂O cooling bath.

can be assigned to a combination ($\delta + \nu_3$) mode of the fundamental vibrations (δ , bending; ν_3 , asymmetric stretching) of the physisorbed H₂O molecules.^{15–20} As shown in previous literature,²⁰ a broad absorption peak around 1940 nm and a sharp peak at 1890 nm can be attributed to the hydrogen-bonded H₂O molecules and hydrogen-bond-free H₂O molecules, respectively. The H₂O molecules adsorbed on TiO₂, in particular the hydrogen-bonded H₂O around 1940 nm, were found to decrease when the TiO₂ powder sample was irradiated by UV light. The adsorption of H₂O was then found to recover gradually when the powder sample was placed in dark conditions. After UV light irradiation, when the powder sample was placed somewhere cold, for example on a stone table in a dark room, the adsorption of H₂O on the TiO₂ surface was confirmed to recover very quickly.

Figure 3 shows the temperature changes of the TiO₂ powder during UV light irradiation under different conditions. When a H₂O filter to block infrared beams from an Hg light source was not used, the temperature of the TiO₂ powder was found to increase up to ca. 328 K by the heating effect of the light source. The initial temperature before UV light irradiation was ca. 298 K. When a H₂O filter (thickness ca. 10 mm) in a Pyrex glass tray was used to block infrared beams from the light source, the temperature of the TiO₂ powder increased up to ca. 308 K. Even when a H₂O bath was also used with the H₂O filter in order to cool the powder sample, the temperature of the powder sample increased up to ca. 303 K. Just after the Hg lamp was turned off, the powder sample quickly cooled and then gradually recovered its initial temperature. These results clearly indicate that the H₂O molecules on the TiO₂ surface desorb during UV light irradiation and adsorb again on the TiO₂ surface after UV light irradiation is ceased, depending on the temperature changes of the TiO₂ powder samples. Moreover, the variations in the temperature during UV light irradiation are quite similar to variations in the contact angles of H₂O droplets on TiO₂ surfaces.

Figure 4 shows the four peaks that were obtained by the deconvolution spectra of the H₂O molecules adsorbed on the TiO₂ surface before and after UV light irradiation for 3 h. The wavenumbers, wavelengths, and relative peak areas of the four components obtained are summarized in Table 1. Since the combination ($\delta + \nu_3$) band attributed to the gas-phase H₂O is observed around 1880 nm,^{15,16,20} a component S₀ can be

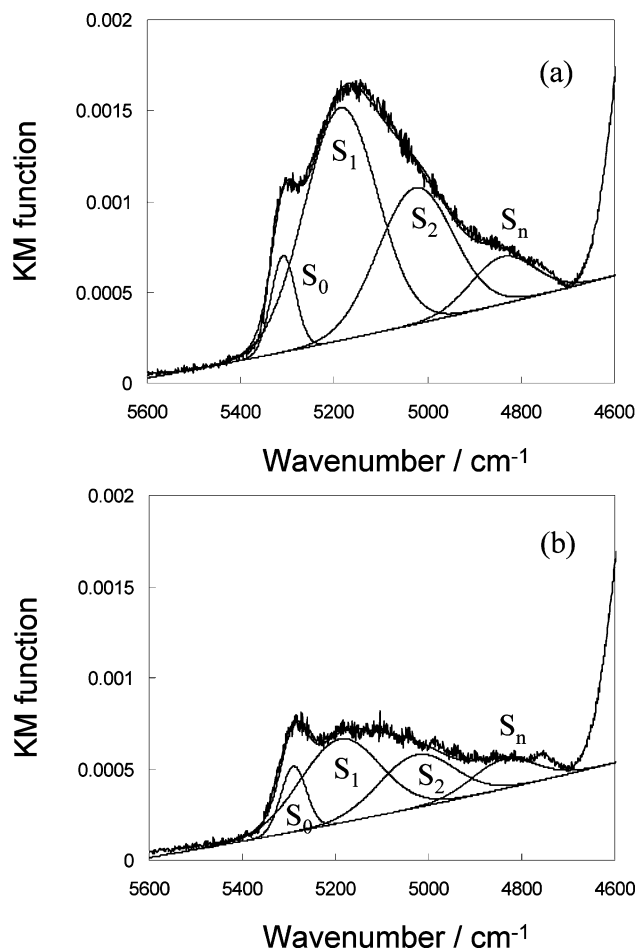


Figure 4. Deconvoluted spectra of combination ($\delta + \nu_3$) bands of H₂O molecules adsorbed on TiO₂ surfaces: (a) before UV light irradiation and (b) after UV light irradiation for 3 h.

TABLE 1: Different Chemical States of H₂O Molecules^a Depending on Number of Hydrogen Bonds on TiO₂ Surfaces Before and After UV Light Irradiation

	wavenumber/cm ⁻¹ (wavelength/nm) (ratio/%)	
	before UV irradiation	after UV irradiation for 3 h
S ₀	5309 (1884) (6.3)	5290 (1890) (11.3)
S ₁	5186 (1928) (50.3)	5190 (1927) (45.4)
S ₂	5028 (1989) (32.4)	5026 (1990) (28.8)
S _n	4840 (2076) (11.0)	4839 (2067) (14.5)

^a S₀, H₂O molecules without any active hydrogen bonds; S₁ and S₂, H₂O molecules with one or two active hydrogen bonds; S_n, polymeric chained H₂O clusters.

associated with the hydrogen-bond-free H₂O molecules. On the other hand, the liquid-phase H₂O is known to show broad absorption bands around 1950 nm which can be deconvoluted to three components (S₁, S₂, and S_n) depending on the number of hydrogen bonds.^{15,16,20} The ratio S₀/(S₁ + S₂ + S_n) of the hydrogen-bond-free H₂O to the hydrogen-bonded H₂O is an important factor in determining the surface tension of the H₂O clusters adsorbed on the solid surfaces. Figure 5 shows the NIR absorption spectra of H₂O adsorbed on TiO₂ surfaces (a) after heating at 338 K by a heater and (b) after cooling at 283 K by ice water. When the TiO₂ powder was heated around 338 K, the desorption of H₂O from the surface (vaporization) could be observed, resulting in an increase in the ratio S₀/(S₁ + S₂ + S_n) and a decrease in the surface tension of H₂O. On the other hand, when the TiO₂ powder was cooled around 283 K, the adsorption of H₂O on its surface (condensation) was promoted,

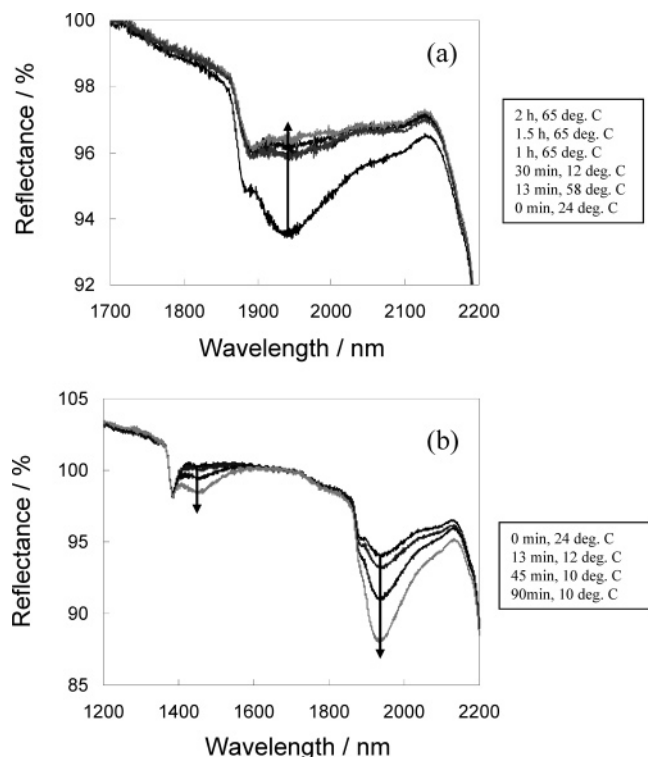


Figure 5. Near-infrared absorption spectra of H₂O adsorbed on TiO₂ surfaces: (a) TiO₂ samples heated using a heater for 0, 13, 30, 60, 90, and 120 min (from bottom to top) and (b) TiO₂ samples cooled by ice water for 0, 13, 45, and 90 min (from top to bottom).

resulting in a decrease in the ratio $S_0/(S_1 + S_2 + S_n)$ and an increase in the surface tension of H₂O. These results indicate that the adsorption and desorption of H₂O molecules on TiO₂ surfaces are sensitive to temperature changes. As summarized in Table 1, the ratio $S_0/(S_1 + S_2 + S_n)$ was found to increase from 6.3 to 11.3% during UV light irradiation. This clearly indicates that the surface tension of the H₂O clusters on the TiO₂ surface decreases under UV light irradiation by a decrease in the amount of H₂O adsorbed on TiO₂ surfaces due to the heating effect from the light source. Nosaka et al. have observed one sharp and two broad signals in the ¹H NMR spectrum and attributed them to the H₂O molecules adsorbed on TiO₂ powder²¹ and TiO₂ thin film.²² They discussed those three different kinds of H₂O signals by a layer model due to their different molecular mobilities but did not mention anything about the different chemical properties of those H₂O molecules in terms of the hydrogen bonds. It is well-known that ¹H NMR spectra due to H₂O molecules in nonpolar solvents, such as deuterium-labeled benzene (C₆D₆) or toluene (C₇D₈), show a sharp peak with a small chemical shift. On the other hand, H₂O molecules in polar solvents, such as deuterium-labeled methanol (CD₃OD) or D₂O, show a broad spectrum with a large chemical shift. These differences in chemical shifts can be explained in terms of the degree of hydrogen bonds that work between the H₂O molecules. The literature²¹ has shown that the broad ¹H NMR peaks decrease remarkably and a sharp peak scarcely changes in its intensity after UV light irradiation. These results can be easily associated to lessening of the hydrogen-bonded H₂O molecules by decreasing the amount of H₂O adsorbed on TiO₂ surfaces under UV light irradiation.

Figure 6 shows the structure models of the H₂O clusters on the TiO₂ surface before and after UV light irradiation. When the TiO₂ surface is irradiated with UV light in ambient conditions, the distribution of the hydrogen bonds in the H₂O

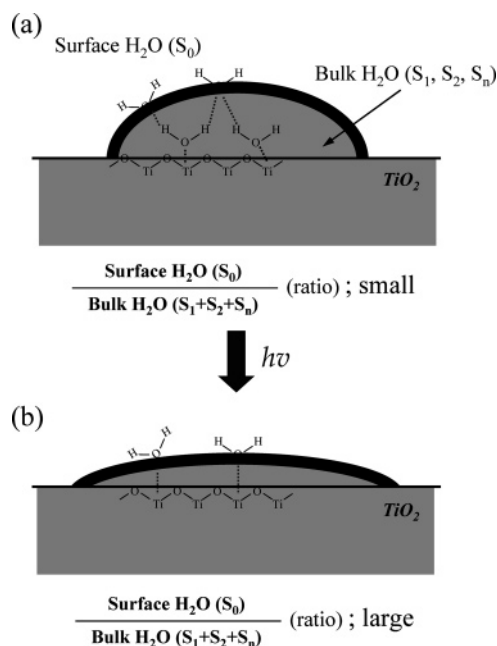


Figure 6. Schematic diagrams of shapes of H₂O clusters on TiO₂ surfaces: (a) before and (b) after UV light irradiation.

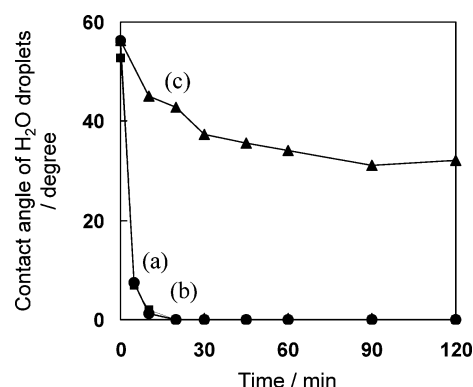


Figure 7. Effect of heating on changes in contact angles of H₂O droplets on TiO₂ thin film surfaces under UV light irradiation (ca. 1.0 mW/cm²): (a) with H₂O filter, (b) without H₂O filter, and (c) during heating around 323 K in the dark.

molecules decreases, resulting in a lessening of the surface tension of H₂O clusters. Moreover, when the amount of H₂O adsorbed on the TiO₂ surface decreases, the outer surface areas of the H₂O clusters also decrease. These findings clearly suggest that the surface relaxation energies of the H₂O clusters are stabilized and the surface areas of the H₂O clusters increase spontaneously. These changes in the surface tension of the H₂O clusters followed by a decrease in the amount of the adsorbed H₂O molecules can be explained as the driving force behind the H₂O clusters spreading out thermodynamically on the TiO₂ surfaces.

The heating effect on the surface wettability of the TiO₂ thin films was investigated. Figure 7 shows the changes in the contact angles of the H₂O droplets on the TiO₂ thin films when the samples were heated on a hot plate at ca. 323 K in a dark room or were irradiated with UV light (ca. 1.0 mW/cm²) with or without a H₂O filter to block the heating effect from the Hg lamp. The superhydrophilic state could be obtained by strong UV light within 30 min of irradiation despite the use of a H₂O filter. Moreover, when the TiO₂ thin film was heated at 323 K in dark conditions, the contact angles of the H₂O droplets were found to decrease until ca. 30° and then level off. The surface

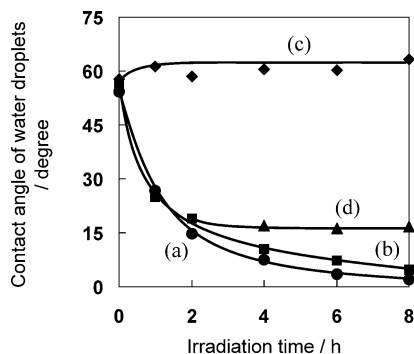


Figure 8. Effects of coexistence gases under UV light irradiation (ca. 25–30 $\mu\text{W}/\text{cm}^2$) on changes in contact angles of H₂O droplets on TiO₂ thin film surfaces: (a) in synthetic air (N₂/O₂ = 4/1), (b) in O₂ (purity >99.9%), (c) in N₂ (purity >99.9%), and (d) when O₂ flow was switched to N₂.

of the TiO₂ thin film did not show a superhydrophilic state; the surface wettability was improved only by heating at 323 K. The surface wettability against H₂O could be improved by heating, and the adsorption of hydrocarbons was inhibited by the heating effect.²³ However, since the hydrocarbons adsorbed on the TiO₂ surfaces could hardly decompose by heating around 323 K, hydrophilic conversion by the effects of heating could be associated with the desorption of the H₂O molecules from the TiO₂ surface. From these results, the important role of UV light irradiation for the photoinduced superhydrophilicity of TiO₂ surfaces is considered to be the mild heating of the thin film surfaces.

To elucidate other important factors, the surface wettability changes in the TiO₂ thin films under UV light irradiation under different atmospheres were investigated. As shown in Figure 8, when the TiO₂ thin films were irradiated with UV light (ca. 25–30 $\mu\text{W}/\text{cm}^2$) under O₂ (purity >99.9%) or synthesized air (O₂/N₂ = 1/4) flow, the thin films were found to reach a superhydrophilic state. However, when these TiO₂ thin films were irradiated under a flow of N₂ (purity >99.9%), the contact angles of the H₂O droplets did not change at all. Moreover, when the O₂ flow was switched to N₂, the hydrophilic conversion of the TiO₂ surface was found to stop and level off. These results clearly indicate that the coexistence of O₂ is necessary for the photoinduced hydrophilic conversion of the TiO₂ surfaces to occur.

To clarify the role of O₂, the photocatalytic decompositions of acetaldehyde with sufficient amounts of O₂ or N₂ on the TiO₂ thin films under UV light irradiation (ca. 1.0 mW/cm²) were investigated. When the TiO₂ thin film was irradiated with UV light in O₂ atmosphere, the acetaldehyde was mainly decomposed into CO₂ and H₂O in an efficient photocatalytic reaction, as shown in Figure 9. On the other hand, when the TiO₂ thin film was irradiated in N₂ atmosphere, the acetaldehyde could hardly be decomposed and small amounts of CO were formed as a partial oxidative product. Moreover, when these TiO₂ thin films were irradiated in O₂ or N₂ atmospheres under the same irradiation conditions, as shown in Figure 8 (ca. 25–30 $\mu\text{W}/\text{cm}^2$), the amount of hydrocarbons adsorbed on the TiO₂ surfaces could be estimated by the intensities of the C 1s XPS spectra. As can be seen in Figure 10, the intensity of the C 1s peak decreased only when the TiO₂ thin films were irradiated with UV light in O₂ atmospheres. These results obtained by ESCA analyses were found to completely correspond to the results of the photocatalytic decomposition of acetaldehyde in O₂ or N₂ atmospheres. The relative amounts of hydrocarbons before and after UV light irradiation were also estimated by FT-IR

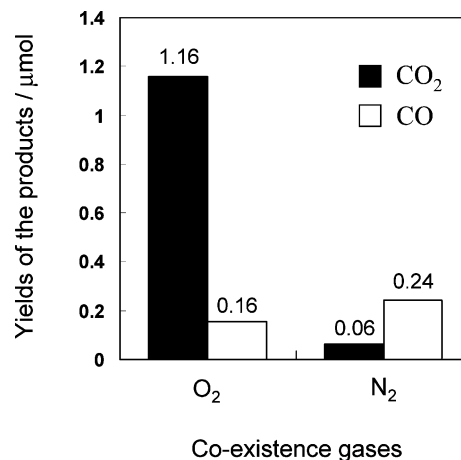


Figure 9. Photocatalytic degradation of acetaldehyde in the presence of O₂ or N₂ on TiO₂ thin films prepared on quartz substrates under UV light irradiation (ca. 1.0 mW/cm²) for 3 h.

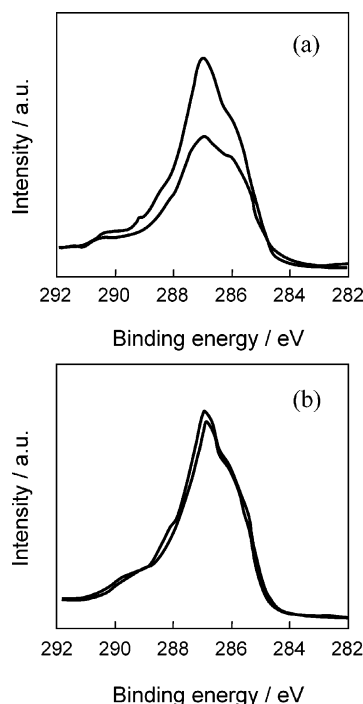


Figure 10. C 1s XPS spectra of TiO₂ thin film surfaces under UV light irradiation (ca. 25–30 $\mu\text{W}/\text{cm}^2$) for 8 h in the presence of (a) O₂ and (b) N₂ gases.

measurements of the TiO₂ thin films prepared on both sides of the Si wafers. From XRD analyses (data not shown here), the crystalline structures of the TiO₂ thin films prepared on the Si wafer substrates were the same as those of the thin films prepared on quartz substrates in an anatase polycrystalline structure. Figure 11 shows the FT-IR spectra of the TiO₂ thin films (a) before UV light irradiation, (b) after UV light irradiation in air on both sides for 1 h, and (c) after storage in dark conditions for 70 h. About half the amount of hydrocarbons adsorbed on both sides of the TiO₂ thin films could be decomposed as a photocatalytic reaction. The TiO₂ thin films prepared on the Si wafers could, thus, be confirmed to show the superhydrophilic properties under the same irradiation conditions. When these TiO₂ thin films were then stored in the dark, reabsorption of hydrocarbons on the thin films could be confirmed, although the adsorption rate was too slow even after storage in the dark for 70 h. These results clearly indicate that

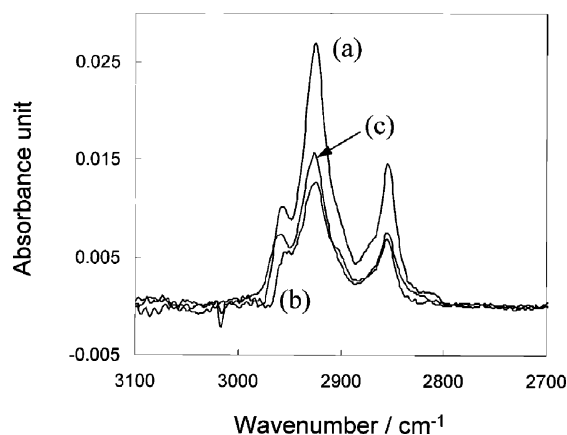


Figure 11. FT-IR spectra of methylene groups of hydrocarbons adsorbed on TiO₂ thin films prepared on Si wafers: (a) before UV light irradiation, (b) after UV light irradiation for 1 h, and (c) after (b), when the samples were placed in the dark for 70 h.

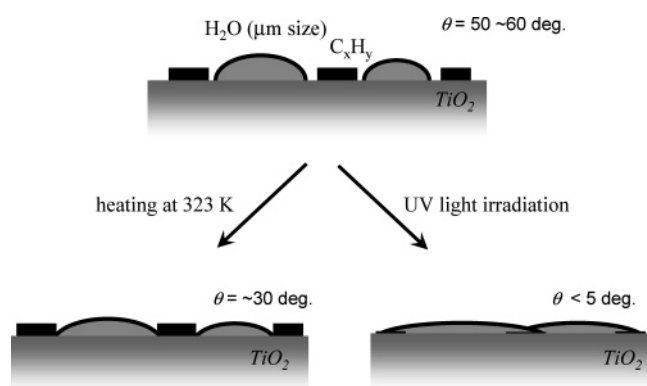


Figure 12. Proposed mechanism for improvement of surface wettability of TiO₂ photocatalyst surfaces under UV light irradiation.

the hydrocarbons adsorbed on the TiO₂ surfaces are efficiently decomposed only when the TiO₂ surfaces are irradiated with UV light under O₂ atmosphere. From these various investigations, the role of O₂ for the photoinduced superhydrophilicity on TiO₂ surfaces could be seen to be significant for the partial elimination of hydrocarbons adsorbed on the TiO₂ surfaces photocatalytically.

From these detailed investigations, the mechanism behind the photoinduced superhydrophilicity of the TiO₂ surfaces could be proposed, as shown in Figure 12. When the TiO₂ thin films were heated at ca. 323 K under dark conditions, the H₂O molecules desorbed from the TiO₂ surfaces; however, the hydrocarbons were not removed, leading to a decrease in the contact angles of H₂O droplets until 30° and then leveling off. On the other hand, when the TiO₂ surfaces were irradiated with UV light, the H₂O molecules desorbed from the surfaces by the effect of heating from the light sources and, at the same time, the hydrocarbons adsorbed on the TiO₂ surfaces were partially decomposed photocatalytically. Since the hydrocarbons are partially removed from the surfaces, the H₂O molecules can spill over onto the free spaces of the TiO₂ surface, resulting in the formation of a widely spread out H₂O multilayer. The TiO₂ surfaces on which the H₂O and hydrocarbons are reduced exhibited high surface wettability against H₂O. Furthermore, the relationship between the contact angles of the H₂O droplets and the relative amounts of the hydrocarbons determined from the C 1s XPS peak intensities was investigated. The TiO₂ thin films after calcination at 723 K in air for 1 h showed 0° contact angle of H₂O while more than half the amount of hydrocarbons

TABLE 2: Relationship between Contact Angles of H₂O Droplets on TiO₂ Thin Films and Relative Amounts of Hydrocarbons As Determined by Intensity of C 1s XPS Spectra after Various Pretreatments

pretreatment	H ₂ O contact angle (deg)	rel intensity of C 1s peak at 286.4 eV ^a
(1) before pretreatment	49.3	100
(2) washed by distilled H ₂ O for 1 min	20.1	98.5
(3) rinsed in NaOH soln (2 M, 323 K) for 1 min	11.2	71.2
(4) calcination at 723 K for 1 h	0	40.1
(5) UV light (1 mW/cm ²) irradiation for 3 h	0	64.7

^a The influence of hydrocarbons from the XPS apparatus was not subtracted.

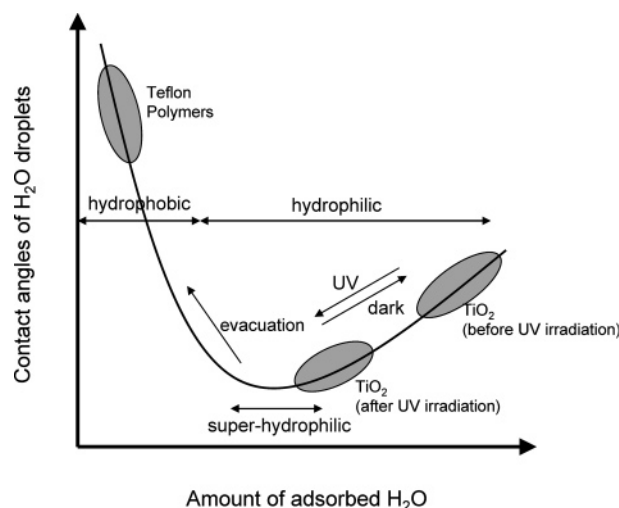


Figure 13. Relationship between surface wettability against H₂O and amount of H₂O adsorbed on solid surfaces.

was found to be removed, as is summarized in Table 2. The TiO₂ thin films after rinsing in 2 M NaOH solution at 323 K for 1 min showed a contact angle of 11° and the removal of about 30% of the hydrocarbons. Moreover, the hydrocarbons could hardly be removed by washing in distilled H₂O, although these TiO₂ thin films showed 20° for the contact angle of the H₂O droplets. These results clearly suggest that the surface wettability of the TiO₂ thin films can also be improved by the removal of the hydrocarbons by the different treatments from UV light irradiation. It has been reported that the surface wettability of nonalkaline silica glasses can be improved by vacuum UV light (172 nm) irradiation in O₃ atmosphere, since the hydrocarbons adsorbed on the glass surfaces were seen to be decomposed.^{24,25} Iso et al. have also reported that the surface wettability can be improved by vacuum UV light irradiation in a synthesized air (N₂/O₂ = 4/1) atmosphere; however, the contact angles of the H₂O droplets on silica glasses did not change by vacuum UV light irradiation in N₂ atmosphere.²⁴ SiO₂ surfaces generally do not show any photocatalytic reactivity for the degradation of hydrocarbons in air; however, the hydrocarbons adsorbed on silica surfaces have been reported to be decomposed by vacuum UV light (172 nm) irradiation in O₃ or O₂ atmospheres, leading to an improvement of the surface wettability.

The wettability of solid surfaces can generally be discussed by surface properties such as the hydrophilicity or hydrophobicity. Highly hydrophilic surfaces are believed to show a high wettability against H₂O. However, as shown in Figure 13, the surface wettability was not considered to be in good proportion to the amount of H₂O adsorbed on solid surfaces. Since the surface tension of H₂O molecules is quite large compared to

that of other liquids, large amounts of H₂O adsorbed on solid surfaces aggregate and form large and bulky H₂O clusters, providing free adsorption sites accessible to the hydrocarbons. These TiO₂ surfaces show a high contact angle of H₂O around 60° before UV light irradiation at the initial state. When the TiO₂ surface is irradiated with UV light, the hydrocarbons on the TiO₂ surfaces are decomposed as a photocatalytic reaction and the H₂O molecules adsorbed on the surfaces are vaporized by the effect of heating, resulting in H₂O clusters with smaller surface tension that can spread out thermodynamically.

Conclusions

The photoinduced superhydrophilicity of TiO₂ photocatalyst surfaces was found to originate by the desorption of H₂O molecules from TiO₂ surfaces by the effect of heating from the light sources and the partial elimination of hydrocarbons by photocatalytic decomposition under UV light irradiation. The reduction of the surface tension of H₂O clusters followed by a lessening of the amount of H₂O adsorbed on TiO₂ surfaces during UV light irradiation was found to play a major role as the driving force behind the photodriven phenomenon. The superhydrophilic properties of the TiO₂ photocatalyst surfaces by lessening in the amount of H₂O adsorbed on the surfaces can be expressed as hydrophobic compared with the initial state before UV light irradiation.

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