

TiO₂ Photocatalysis: A Historical Overview and Future Prospects

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Photocatalysis has recently become a common word and various products using photocatalytic functions have been commercialized. Among many candidates for photocatalysts, TiO₂ is almost the only material suitable for industrial use at present and also probably in the future. This is because TiO₂ has the most efficient photoactivity, the highest stability and the lowest cost. More significantly, it has been used as a white pigment from ancient times, and thus, its safety to humans and the environment is guaranteed by history. There are two types of photochemical reaction proceeding on a TiO₂ surface when irradiated with ultraviolet light. One includes the photo-induced redox reactions of adsorbed substances, and the other is the photo-induced hydrophilic conversion of TiO₂ itself. The former type has been known since the early part of the 20th century, but the latter was found only at the end of the century. The combination of these two functions has opened up various novel applications of TiO₂, particularly in the field of building materials. Here, we review the progress of the scientific research on TiO₂ photocatalysis as well as its industrial applications, and describe future prospects of this field mainly based on the present authors' work.

KEYWORDS: titanium dioxide, Honda-Fujishima effect, photoelectrolysis, redox reaction, hydrophilic conversion, environmental application

1. Historical Background before Honda-Fujishima Effect

TiO₂ powders have been commonly used as white pigments from ancient times. They are inexpensive, chemically stable and harmless, and have no absorption in the visible region. Therefore, they have a white color. However, the chemical stability of TiO₂ holds only in the dark. Instead, it is active under UV light irradiation, inducing some chemical reactions. Such activity under sunlight was known from the flaking of paints and the degradation of fabrics incorporating TiO₂.¹⁾ Scientific studies on such photoactivity of TiO₂ have been reported since the early part of the 20th century. For example, there was a report on the photobleaching of dyes by TiO₂ both *in vacuo* and in oxygen in 1938.²⁾ It was reported that UV absorption produces active oxygen species on the TiO₂ surface, causing the photobleaching of dyes. It was also known that TiO₂ itself does not change through the photoreaction, although the "photocatalyst" terminology was not used for TiO₂ in the report, but called a photosensitizer.

It is equivocal when and who started utilizing first such a photochemical power of TiO₂ to induce chemical reactions actively, but at least in Japan, there were a series of reports by Mashio *et al.*, from 1956, entitled "Autooxidation by TiO₂ as a photocatalyst".³⁾ They dispersed TiO₂ powders into various organic solvents such as alcohols and hydrocarbons followed by the UV irradiation with an Hg lamp. They observed the autooxidation of solvents and the simultaneous formation of H₂O₂ under ambient conditions. It is interesting to note that they had already

compared the photocatalytic activities of various TiO₂ powders using twelve types of commercial anatase and three types of rutile, and concluded that the anatase activity of the autooxidation is much higher than that of rutile, suggesting a fairly high degree of progress of the research.⁴⁾ In those days, however, the photocatalytic power of TiO₂ might have attracted only partially limited scientists' attention in the field of either catalysis or photochemistry, and the study of TiO₂ photocatalysis had not developed widely in either academic or industrial society.

2. Water Photolysis with TiO₂ Electrode in 1970s

In the late 1960s, one of the present authors (AF) began to investigate the photoelectrolysis of water, using a single crystal n-type TiO₂ (rutile) semiconductor electrode, because it has a sufficiently positive valence band edge to oxidize water to oxygen. It is also an extremely stable material even in the presence of aqueous electrolyte solutions, much more so than other types of semiconductor that have been tried. The possibility of solar photoelectrolysis was demonstrated for the first time in 1969 with the system shown in Fig. 1, which was exposed to near-UV light, and was connected to a platinum black counter electrode through an electrical load.⁵⁾ Then, this electrochemical photolysis of water was reported in *Nature* by analogy with a natural photosynthesis in 1972.⁶⁾ In those days, crude oil prices ballooned suddenly, and the future lack of crude oil was a serious concern. Thus, this became known as the time of "oil crisis". Therefore, this report attracted the attention not only of electrochemists but

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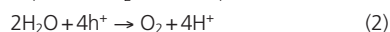
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also of many scientists in a broad area, and numerous related studies were reported in the 1970s.

When the surface of the rutile TiO₂ electrode was irradiated with light consisting of wavelengths shorter than its band gap, about 415nm (3.0eV), photocurrent flowed from the platinum counter electrode to the TiO₂ electrode through the external circuit. The direction of the current revealed that the oxidation reaction (oxygen evolution) occurs at the TiO₂ electrode and the reduction reaction (hydrogen evolution) at the Pt electrode. This observation shows that water can be decomposed, using UV light, into oxygen and hydrogen, without the application of an external voltage, according to the following scheme.



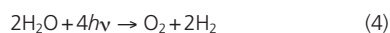
(at the TiO₂ electrode)



(at the Pt electrode)



The overall reaction is



When a semiconductor electrode is in contact with an electrolyte solution, thermodynamic equilibration occurs at the interface. This may result in the formation of a space-charge layer within a thin surface region of the semiconductor, in which the electronic energy bands are generally bent upwards and downwards in the cases of the n- and p-type semiconductors, respectively. The thickness of the space-charge layer is usually of the order of

1–10³nm, depending on the carrier density and dielectric constant of the semiconductor. If this electrode receives photons with energies greater than that of the material band gap, E_G, electron–hole pairs are generated and separated in the space-charge layer. In the case of an n-type semiconductor, the electric field existing across the space-charge layer drives photogenerated holes toward the interfacial region (i.e., solid–liquid) and electrons toward the interior of the electrode and from there to the electrical connection to the external circuit. The reverse process occurs at a p-type semiconductor electrode. These fundamental processes of semiconductor photoelectrochemistry have been discussed in many recent reviews.^{7–11)}

If the conduction band energy E_{CB} is higher (i.e., closer to the vacuum level, or more negative on the electrochemical scale) than the hydrogen evolution potential, photogenerated electrons can flow to the counter electrode and reduce protons, resulting in hydrogen gas evolution without an applied potential, although, as shown in Fig. 2, E_{CB} should be at least as negative as –0.4V versus the standard hydrogen electrode (SHE) in acid solution or –1.2V (SHE) in alkaline solution. Among the oxide semiconductors, TiO₂ (acid), SrTiO₃, CaTiO₃, KTaO₃, Ta₂O₅, and ZrO₂ satisfy this requirement. On the other hand, the employment of an external bias or of a difference in pH between the anolyte and the catholyte is required in the case of other materials in order to achieve hydrogen evolution.

It is desirable that the band gap of the semiconductor is near that for the optimum utilization of solar energy, which would be about 1.35eV. When semiconductor electrodes are used as either photoanodes or photocathodes for water electrolysis, the bandgap should be at least 1.23eV (i.e., the equilibrium cell potential for water electrolysis at 25°C and 1 atm), particularly considering the existence of polarization losses due to, for example, oxygen evolution. Although various semiconductors with smaller band gaps were investigated, none succeeded for the water photoelectrolysis with visible light. This is because they were in most cases corroded in an aqueous electrolyte under irradiation, i.e., the photogenerated holes oxidized the semiconductor itself.

One of the other approaches to utilize longer wavelength light could involve the dye sensitization of TiO₂. This approach, although it is theoretically possible to use it for water photoelectrolysis, has practical problems, principally that most photosensitizer dyes would be far too unstable under these conditions. Therefore, the so-called regenerative photoelectrochemical cells, in which a single redox couple exists, the reduced form is oxidized at the TiO₂ photoanode and the oxidized form is reduced at the counter electrode, were studied intensively. Chlorophyll and various organic dyes, such as xanthene dyes, were used as sensitizers, but neither the solar conversion efficiency nor the stability of the dyes was very high in those days. It is, however, to be emphasized that this approach was intensively researched later by Gratzel *et al.* using porous

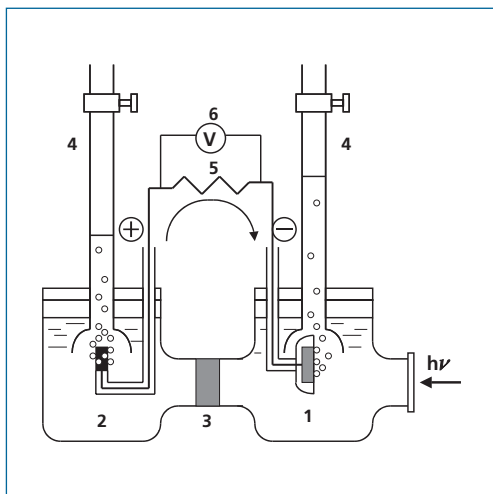


Fig.1. Schematic diagram of electrochemical photocell. (1) n-type TiO₂ electrode; (2) platinum black counter electrode; (3) ionically conducting separator; (4) gas buret; (5) load resistance; and (6) voltmeter.

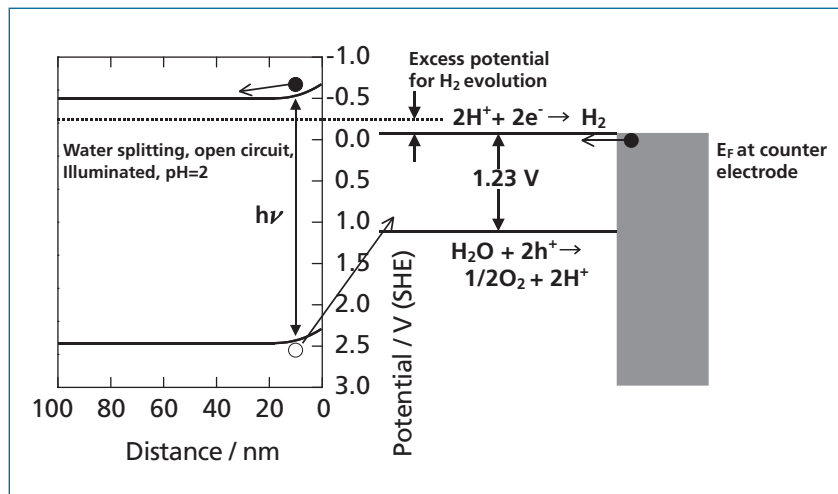


Fig.2. Schematic representation of photoelectrochemical water electrolysis using illuminated oxide semiconductor electrode. An open circuit (or small current), pH 2, and illuminated conditions are shown for oxides with an E_{CB} of –0.65V (SHE) and an E_{VB} of 2.35V (SHE). With the open circuit, a small excess potential (0.15V) is available for H₂ evolution, assuming a reversible counter electrode.

TiO₂ electrodes and ruthenium complexes as sensitizers, and that the conversion efficiency reached 10–11% in the 1990s.^{12,13)}

3. Powdered TiO₂ Photocatalysis in 1980s

The problem of light-assisted water splitting has also been focused in the late 1970s with the photocatalytic approach, i.e., essentially with photoelectrochemistry but without an external circuit. Conceptually, this is similar to the process of corrosion, as being the combination of two short-circuited electrochemical reactions. In the case of corrosion, the two reactions might be anodic metal dissolution together with either cathodic H₂ evolution or O₂ reduction. Photocatalytic water splitting has been studied intensively with powdered anatase TiO₂ suspensions, with Pt deposited on TiO₂ as a cathodic catalyst. Although there were several experiments for the simultaneous production of H₂ and O₂ in the powder systems, either such experiments could not be reproduced or the reaction efficiency was very low.¹⁴⁾

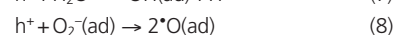
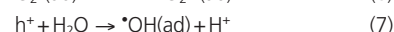
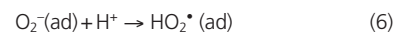
Kawai and Sakata examined, in 1980, the reasons why the water photolysis could not proceed in the powder system, although it could in the electrode one. They concluded that the produced H₂ and O₂ gases might recombine to regenerate water molecules through the back reaction in the powder system, because the production sites of each gas are located close to each other. To solve this problem, they added organic compounds to the aqueous suspension of platinized TiO₂. In this case, water is reduced, producing H₂ at the Pt sites and the organic compounds are oxidized instead of water by photogenerated holes at the TiO₂ sites. The H₂ production proceeds surprisingly efficiently, with a quantum yield of more than 50% in the presence of ethanol.¹⁵⁾ Most organic compounds, including biomass-derived compounds and even waste organisms, can enhance the hydrogen production efficiency. This is because the redox potential for photogenerated holes is +2.53V versus SHE, as shown in the energy band diagram for TiO₂ (Fig. 3), and most organic compounds can be oxidized finally into CO₂. In general, anatase (E_G=3.2eV) gives better results than rutile (E_G=3.0eV) for hydrogen production in powder photocatalysis. One of the main reasons for the higher

efficiency is probably the higher reduction potential of photogenerated electrons in the former than in the latter, i.e., the bottom of the conduction band of anatase is located 0.1V more negative than that of rutile.¹⁶⁾

The first report on the efficient hydrogen production from water and organic compounds was published in Nature at the time of the second oil crisis, and TiO₂ photocatalysis drew the attention of many people as one of the promising methods for hydrogen production. However, even though the reaction efficiency is very high, TiO₂ can absorb only the UV light contained in a solar spectrum, which is only about 3%. Therefore, from the viewpoint of H₂ production technology, TiO₂ photocatalysis is not very attractive. Various other semiconductors with a small band gap, such as CdS and CdSe, were investigated, but their efficiency and stability were much lower than those of TiO₂, and the enthusiasm in the research of the H₂ production was over in the middle of the 1980s.

Instead, the research shifted to the utilization of the strong photoproduced oxidation power of TiO₂ for the destruction of pollutants. The first such reports were those of Frank and Bard in 1977, in which they described the decomposition of cyanide in the presence of aqueous TiO₂ suspensions.¹⁷⁾ In the 1980s, detoxications of various harmful compounds in both water and air were demonstrated using powdered TiO₂ actively as potential purification methods of waste water and polluted air.¹⁸⁾ When the purpose shifted to the oxidation reaction of harmful compounds,

the reduction reaction was not necessarily hydrogen production anymore. The platinization of TiO₂ was not necessary in this case, and TiO₂ powder itself was used under ambient condition. Now both the reduction and oxidation sites are located on the TiO₂ surface, and the reduction of adsorbed oxygen molecules proceeds on the TiO₂ surface. As already mentioned, the holes (h⁺) generated in TiO₂ were highly oxidizing, and most compounds were essentially oxidized completely, i.e., each constitution element of the compounds was oxidized to its final oxidation state. In addition, various forms of active oxygen, such as O₂⁻, [•]OH, HO₂[•] and O[•], produced by the following processes may be responsible for the decomposition reactions.



For the purpose of easy handling of photocatalysts, the immobilization of TiO₂ powders on supports was carried out in the late 1980s.¹⁹⁾ Although many research studies were on the purification of wastewater and polluted air, TiO₂ photocatalysis could not be developed to the stage of a real industrial technology in the 1980s.

4. TiO₂ Film Photocatalysis under Weak UV Light in Early 1990s

In 1990, we carefully determined the reasons, in collaboration with TOTO Ltd., why TiO₂ photocatalysis could not be a practical

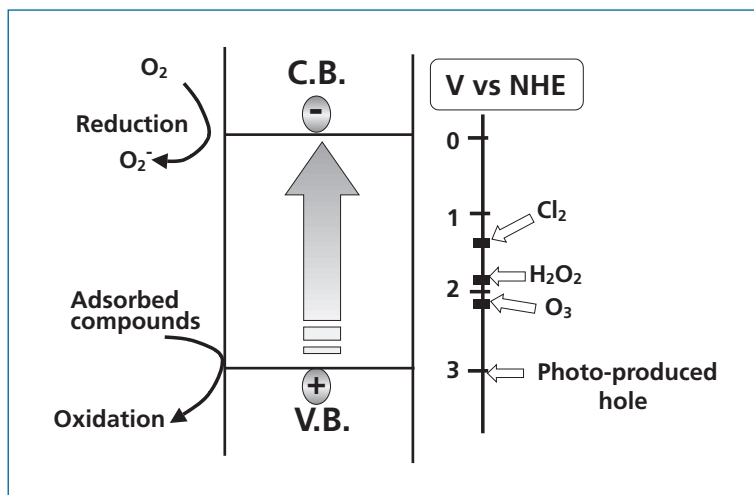


Fig.3. Schematic diagram of energy band for TiO₂.

technology. We came to the conclusion that it is fundamentally inadequate to utilize TiO_2 photocatalysis for either energy acquisition or the treatment of huge amounts of water and/or air, because light energy density is primarily low, and in addition, TiO_2 can utilize only the small amount of UV light contained in solar light. Based on such understanding, we conceived the idea of applying photocatalysis targeting only the substances adsorbed originally on surfaces. In other words, we could take the substances existing on two-dimensional surfaces as the object of decomposition instead of those in three-dimensional spaces

such as water or air. In this case, the absolute amounts of the substances decrease, and thus, the rather weak UV light existing in an ordinary environment could be a sufficient light source for maintaining the TiO_2 surface clean. We thus obtained the novel concept of light-cleaning materials, which would be coated with TiO_2 film photocatalysts.^{20,21)}

4.1 Photocatalytic cleaning effect of TiO_2 -coated materials

There exists typically several hundred $\mu\text{W}/\text{cm}^2$ of UV light even in outdoor shade in

the daytime. This is low from the viewpoint of energy density, but corresponds to about 10^{15} of photons/ cm^2 per second, which is a huge amount compared to the number of molecules adsorbed on the surface. Let us consider, for example, a highly packed organic molecule monolayer. Figure 4 shows the atomic force micrograph (AFM) images of monolayer stearic acid prepared on a TiO_2 rutile (110) single crystal by the Langmuir–Blodgett method.^{22,23)} The thickness of the organic substance was about 2nm, and the number of stearic molecules was roughly estimated to be 10^{16} – $10^{17}/\text{cm}^2$. When this was exposed to UV

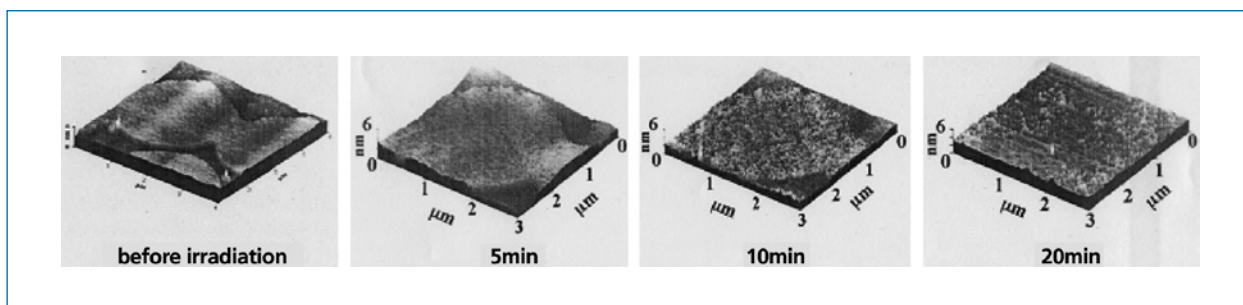


Fig.4. AFM images of monolayer of stearic acid on rutile (100) surface ($1\text{mW}/\text{cm}^2$).

light of about $2.5\text{mW}/\text{cm}^2$, surface morphological changes were clearly observed, i.e., the inhomogeneous pitting of the film was very distinct. Further irradiation merged the pits, producing a mosaic that eventually disappeared with the progress of the reaction. After 20min, the island structure of the LB film was no longer discernible, suggesting the complete decomposition of stearic acid to CO_2 .

This observation suggests a potential utilization of the photocatalysis of TiO_2 -coated materials, i.e., the surface coated with TiO_2 could be kept clean. We first reported this type of photocatalytic cleaning material with a ceramic tile in 1992.²⁴⁾ Heller *et al.* also conceived a similar idea independently.²⁵⁾ One of the first commercialized products using this effect was the self-cleaning cover glass for tunnel light. In most tunnels in Japan, sodium lamps emitting yellow light are used for lighting, and the decrease in light intensity due to filming with exhaust compounds is one of the most serious problems. A high pressure sodium lamp also emits UV light of about $3\text{mW}/\text{cm}^2$ at a position of its cover glass. This UV light had not been considered

in the original purpose of the lighting, but is sufficient to keep the surface clean when the cover glass is coated with the TiO_2 photocatalyst (Fig. 5).²⁶⁾ This light cleaning based on the photocatalytic decomposition effect is used now in other various commercial products such as window blinds. However, it is important to note that this function is effective only when the number of incident photons is much greater than that of filming molecules arriving on the surface per unit time. In other words, the function is not effective when the flux of photons is insufficient compared to that of the organic substances, even though the TiO_2 photocatalyst is a very efficient one.

4.2 Photocatalytic anti-bacterial effect of copper and/or silver-deposited TiO_2 film

A photocatalytic decomposition reaction can be applicable to microorganisms. In fact, *Escherichia coli* (*E. coli*) cells can

completely disappear on TiO_2 after about one week under a UV irradiation of $1\text{mW}/\text{cm}^2$. The cell deactivation can be achieved in a much shorter irradiation time, but still it takes nearly 1 h under outdoor UV light intensity.²⁷⁾

In contrast, the typical indoor UV light intensity is about several hundred nW/cm^2 , which is almost about three orders of magni-



Fig.5. Glass covers on highway tunnel lighting fixtures darkened by automobile exhaust without TiO_2 and maintained clean with TiO_2 .

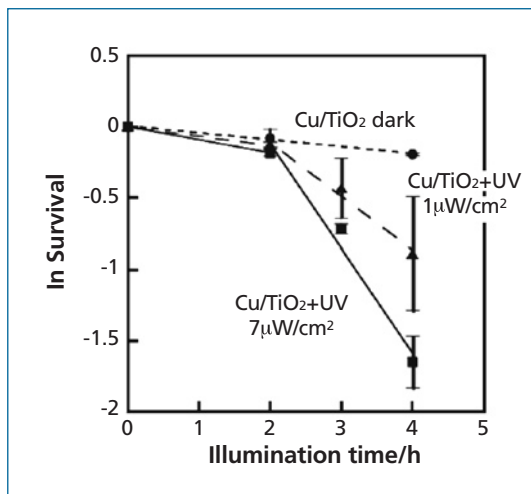


Fig.6. Changes in survival rate of copper-resistant *E. coli* cells on Cu/TiO₂ thin film. Error bars: standard deviations of three replicate experiments.

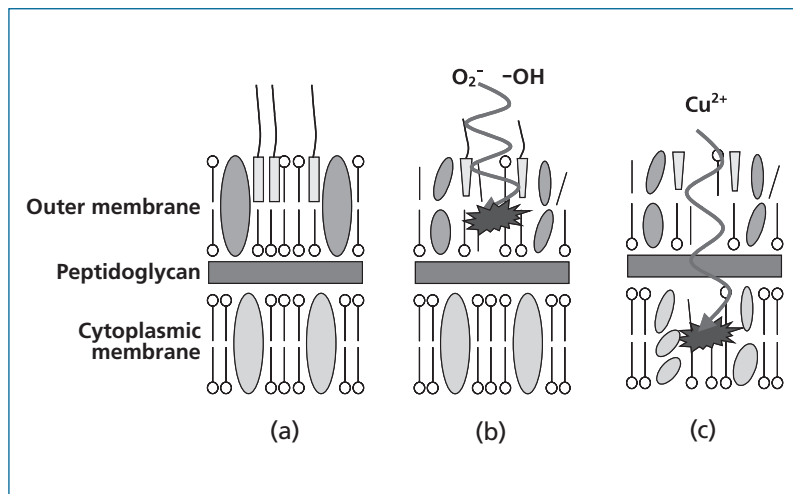


Fig.7. Schematic illustrations of bactericidal process for copper-resistant *E. coli* cells on Cu/TiO₂ thin film under weak UV light irradiation.

tude weaker than the outdoor one. Therefore, the photocatalytic deactivation of microorganism requires a much longer time under indoor conditions than under outdoor ones; thus, it cannot become a real practical technology. However, the anti-bacterial function of a TiO₂ photocatalyst is markedly enhanced even with weak UV light, using a fluorescent lamp and the aid of either silver or copper,²⁸⁾ which is harmless to the human body. Figure 6 shows the changes in the survival of copper-resistant *E. coli* cells on a Cu-photodeposited TiO₂ (Cu/TiO₂) film, indicating that *E. coli* cells survived under dark conditions. However, when the Cu/TiO₂ film is irradiated with very weak UV light, the survival rate begins to decrease. This demonstrates photocatalytic anti-bacterial activity even under weak UV light obtained from indoor lighting from fluorescent light bulbs. The survival decay curves under irradiation in Fig. 6 are not simple exponential curves. Initial illumination had a negligible effect on the survival rate, but after 2h, a marked decrease in survival was observed. We speculate that this cell deactivation proceeds as follows. The first step is that the reactive species generated by the TiO₂ photocatalyst attacks the outer membrane [Fig. 7(b)]. The second step is the effective uptake of the copper ions into the cytoplasmic membrane [Fig. 7(c)]. In this case, the TiO₂ photocatalytic reaction assists the intrusion of the copper ions into the cell, which is probably why the *E. coli* cells are effectively killed on a Cu/TiO₂ film even under very weak UV light.²⁸⁾ It has been reported that the copper

species photodeposited on the TiO₂ film is a mixture of metallic copper (Cu⁰) and copper ions (Cu⁺ and Cu²⁺). When this Cu/TiO₂ film is irradiated, the copper ions can be reduced to metallic copper and metallic copper can be oxidized to copper ions by photogenerated electrons and holes, respectively. Although the oxidation state of copper might change under UV light irradiation, copper ions (Cu²⁺) exist on the Cu/TiO₂ film.²⁸⁾ The enhancement of the antibacterial effect under weak UV light was also observed on the Ag-deposited TiO₂. This antibacterial technique is safe and effective. It was observed that the number of bacteria on the walls decreases to zero after installing the photocatalytic tiles in an operating room. In addition, the bacterial count in air was also significantly decreased. The antibacterial ceramic tile coated with photocatalytic TiO₂ containing Cu and/or Ag started full-scale manufacturing by TOTO Ltd. in 1995, and its technology was exported to Western countries widely.

5. Photo-induced Hydrophilicity

5.1 Water wettability of TiO₂ surface

5.1.1 What is a photo-induced high hydrophilicity?

While investigating the novel concept of light-cleaning materials coated with a TiO₂ film photocatalyst under weak UV light in the 1990s, we have found in 1995 by chance the marked change in the water wettability of the

TiO₂ surface before and after UV light irradiation. With the discovery of this phenomenon, the application range of TiO₂ coating has been largely widened, as will be mentioned in detail later.

The surface wettability is generally evaluated by the water contact angle (CA). The CA (θ) is defined as the angle between the solid surface and the tangent line of the liquid phase at the interface of the solid-liquid-gas phases.

A TiO₂ thin film exhibits an initial CA of several tens of degrees depending on the surface conditions mainly surface roughness. When this surface is exposed to UV light, water starts to exhibit a decreasing CA, that is, it tends to spread out flat instead of beading up.^{29,30)} Finally, the CA reaches almost 0°, as shown in Fig. 8(a). At this stage, the surface becomes completely non-water-repellant and is termed "highly hydrophilic". The surface retains a CA of a few degrees for a day or two under the ambient condition without being exposed to UV light. Then, the CA slowly increases, and the surface becomes the initial less hydrophilic state again, as shown in Fig. 8(b). At this point, the high hydrophilicity can be recovered simply by exposing the surface again to UV light. In short, this type of TiO₂-coated material is the only known practical highly hydrophilic one that shows stable and semi permanent properties.

How can we explain this phenomenon?

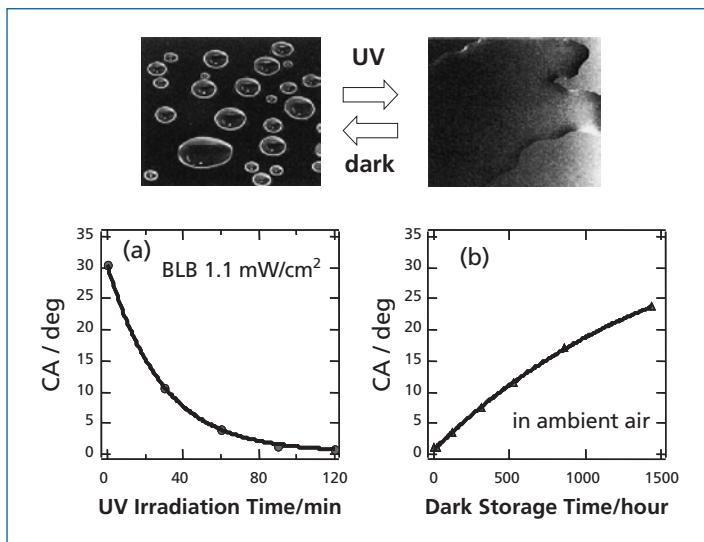


Fig.8. Changes in CA of TiO_2 surface (a) under UV irradiation and (b) in the dark.

We have vigorously attempted to find the answer by analyzing it from various points of view.^{29-31,35-37,39,44,45,48-50,53,54}

5.1.2 Characteristics of photo-induced highly hydrophilic state

First, we considered that this highly hydrophilic conversion originates from the clean surface produced by the decomposition of staining compounds adsorbed on the surface through the conventional photocatalytic oxidation. This is because metal oxides have large surface energies in general, and thus, we considered that a clean TiO_2 surface could be essentially hydrophilic. In fact, several reports have recently been published, in which the photo-produced highly hydrophilic state of

TiO_2 is explained using a simple photocatalytic decomposition mechanism.³²⁻³⁴ However, it is important to note that a completely clean surface cannot be obtained by the photocatalytic reaction because the surface is easily contaminated by airborne stains under the ambient condition. We have obtained many experimental results showing that this highly hydrophilic state is not a simple clean surface but is a structurally changed metastable one. Some of these results will be described below.

(i) Comparison of hydrophilic properties of TiO_2 and SrTiO_3 surfaces

Figure 9 shows the changes in CA under UV light irradiation after applying oleic acid to the surfaces of TiO_2 and SrTiO_3 .³⁵

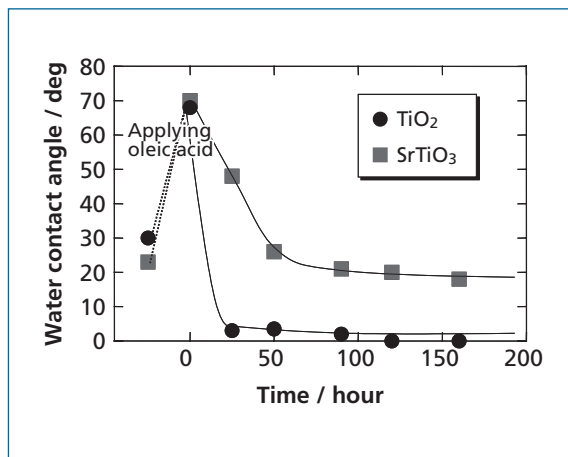


Fig.9. Changes in water contact angle after applying oleic acid to surfaces of TiO_2 and SrTiO_3 .

Just after applying oleic acid, both TiO_2 and SrTiO_3 surfaces were converted to the hydrophobic state with CAs of around 70° due to the hydrophobic property of the oleic acid adsorbed on the surfaces. When UV light was irradiated on the SrTiO_3 surface, the CA decreased to 20° , which was almost the same as that observed before applying oleic acid. As a result of conventional photocatalytic oxidation processes, surface-adsorbed oleic acid was decomposed and almost removed, reproducing the initial surface. For the TiO_2 surface, however, the CA decreased to 0° , which was lower than the initial value, showing that the highly hydrophilic surface of TiO_2 is not simply attributed to the effect of the photocatalytic oxidation power.

(ii) Relationship between amount of stains and contact angle

Figure 10 shows the representative the C 1s spectra of the TiO_2 surface detected by X-ray photoemission spectroscopy (XPS) before and after UV light irradiations (60 min and 12 h). Before UV light irradiation, the carbon peak derived from the stains was detected and the CA on such surface was found to be 56° . After 60 min UV light irradiation, the CA was confirmed to be 0° when the distinct carbon peak was detected, although the amount of stains decreased compared to that before UV light irradiation. After further irradiation for 12 h, the carbon peak still remained and the CA was 0° . These experiments clearly indicate that the highly hydrophilic conversion can be completed even if stains remain on the surface.

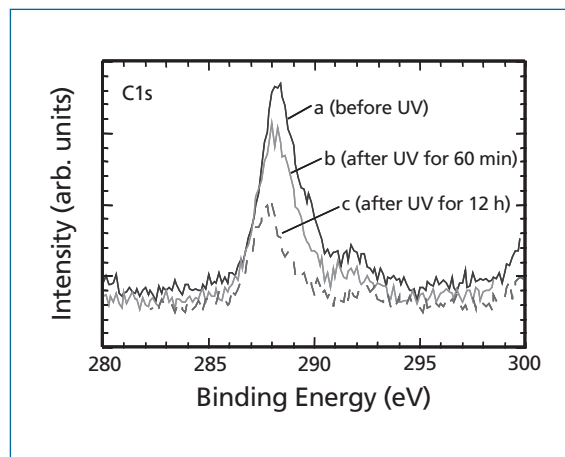


Fig.10. Change in XPS spectrum of TiO_2 in C 1s peak region before and after UV illumination with an intensity of $2.0\text{mW}/\text{cm}^2$.

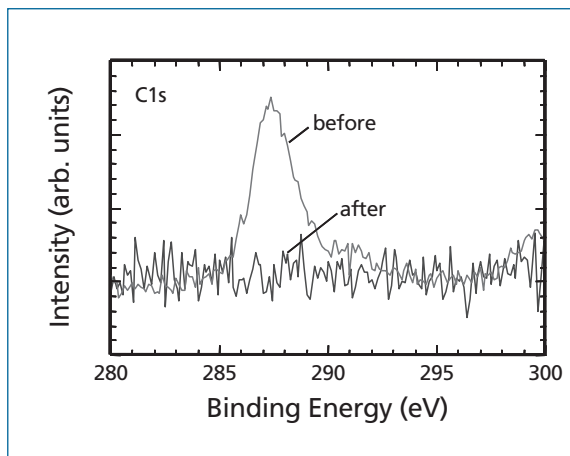


Fig.11. Change in XPS spectrum of TiO_2 in C 1s peak region before and after rinsing in warm 4M NaOH solution (50°C).

Figure 11 shows the changes in the C 1s XPS spectra before and after the treatment of the TiO_2 surface in a warm concentrated NaOH solution. No distinct carbon peak was detected within the experimental error. Although the surface stains were nearly completely removed by this treatment, we found that such a "nearly clean" surface does the CA of 20° , which is much higher than that of 0° induced by UV light.³⁶⁾ By considering these findings, only the removal of stains cannot lead to the highly hydrophilic state under the ambient condition.

(iii) Stability of photo-produced highly hydrophilic TiO_2 surface

When the highly hydrophilic TiO_2 film prepared by UV light irradiation was sonicated in pure water, the CA was found to increase to around 10° , as shown in Fig. 12.³⁷⁾

Subjected to cycles of alternating ultrasonic treatment and UV light irradiation, the water contact angles switched between 0 and 10° reversibly. It is hardly believed that the ultrasonic treatment makes the surface fouler.

Similarly, the highly hydrophilic state is turned to a less hydrophilic one by a "wet rubbing" method, which is a type of mechanochemical surface treatment with clean lint-free paper. Kamei and Mitsuhashi reported that the CA increases drastically from 3 to 80° by the wet rubbing method.³⁸⁾ These results indicate that the photo-produced highly hydrophilic state is broken by external stimuli.

(iv) Temperature dependence of back reaction in the dark³⁹⁾

As was described previously, the CA of the photo-produced highly hydrophilic TiO_2

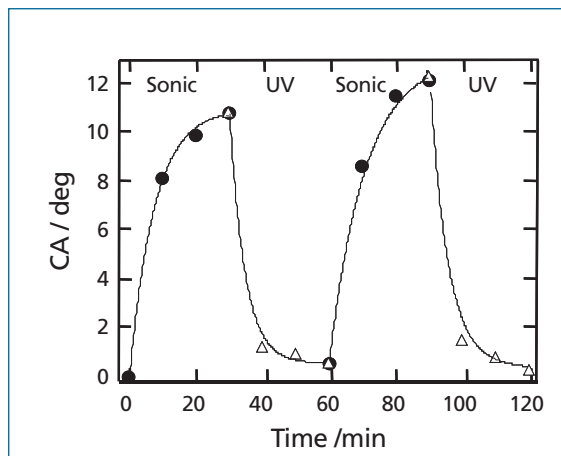


Fig.12. Changes in water contact angle for TiO_2 film subjected to alternate ultrasonic treatment in pure water (\bullet) and UV light irradiation (Δ).

surface increases gradually toward the initial value in the dark even without any external stimuli. However, the rate of this back reaction strongly depends on the ambient temperature. Figure 13 shows the result. Because this measurement was carried out in a vessel filled with synthetic air under the same conditions other than temperature, even if the surfaces were adsorbed with stains, their influence could be ignored. It is obvious that the apparent rate was enhanced by increasing the temperature. To estimate the activation energy for this transformation, we used the rate (k_b) obtained by the reciprocal plot of CA against the logarithm of the dark storage time.^{31,40)}

Figure 14 shows the natural logarithm of k_b obtained at CA of 20° versus the reciprocal of the absolute temperature. According to Fig. 14, the activation energy was calculated to be 62.4kJmol^{-1} .

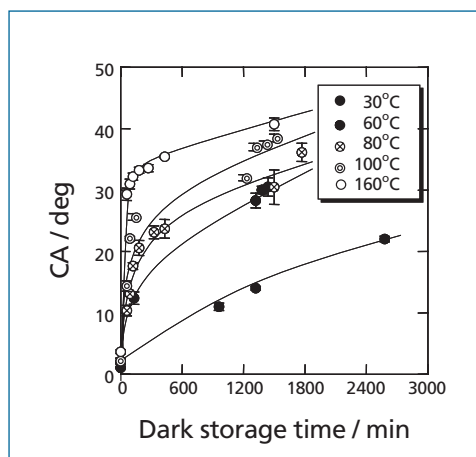


Fig.13. Ambient temperature dependence on less hydrophilic conversion for TiO_2 film maintained in the dark.

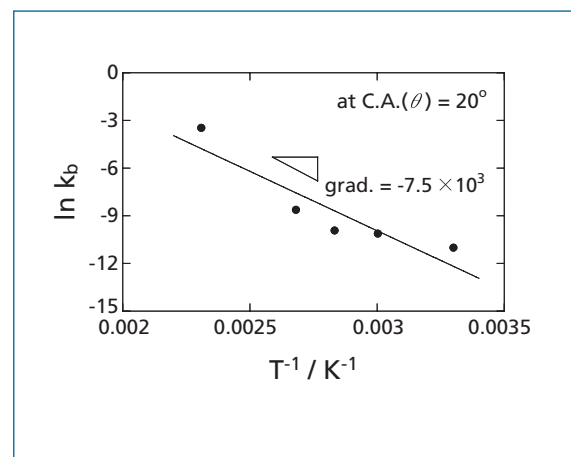


Fig.14. Activation energy of less hydrophilic conversion for TiO_2 film kept in the dark.

Taking all the above experimental results into consideration, we are certain that the photo-produced TiO_2 surface is not completely clean but contains some stains, although it is highly hydrophilic with a CA of almost 0° . In other words, the removal of stains by oxidative decomposition can make the surface only moderately hydrophilic, with a CA of $10\text{--}20^\circ$ under the ambient condition. In addition, it seems that the highly hydrophilic state is not the most stable state but forms some metastable one. In fact, evidence has been obtained, showing that the surface structure of TiO_2 is changed by UV light irradiation, which will be shown below.

5.1.3 Wettability of solid surface

Before examining some evidence for surface structural changes accompanying the highly hydrophilic conversion, let us briefly review a classical theoretical treatment for the wettability of the flat solid surface. It is commonly evaluated in terms of the CA, which is given by Young's equation:⁴¹⁾

$$\gamma_S = \gamma_{SL} + \gamma_L \cdot \cos\theta, \quad (9)$$

where γ_S and γ_L are the surface free energies per unit area of the solid and liquid, respectively, and where γ_{SL} is the interfacial free energy per unit area of the solid-liquid interface. In addition, γ_{SL} can be approximated using the Girifalco-Good equation,^{42,43)} with γ_S and γ_L , as

$$\gamma_{SL} = \gamma_S + \gamma_L - \Phi(\gamma_S/\gamma_L)^{1/2}. \quad (10)$$

Here, Φ is a constant parameter ranging from 0.6 to 1.1, depending on the solid. In addition, γ_L is the water surface free energy, which

has a constant value of 74mJ/m^2 . Therefore, by combining eqs. (9) and (10), the CA can be simply expressed as

$$\cos\theta = c\gamma_S^{1/2} - 1 \quad (c: \text{constant}). \quad (11)$$

This final equation shows that the CA decreases simply with increasing γ_S . Therefore, it can be considered that the highly hydrophilic state with a CA of 0° is achieved by the generation of some states with large surface energies when irradiated with UV light. As previously mentioned, the highly hydrophilic state generated by UV light gradually returns to the initial less hydrophilic state in the dark. Moreover, we showed that some external stimuli and a higher ambient temperature increase the rate of the back reaction. All these suggest that the photo-produced state with a large surface energy is metastable.

5.1.4 Structural changes on TiO_2 surfaces irradiated with UV light

(i) Domain formation after UV light irradiation

To gain information about surface changes at the microscopic level, friction force microscopy (FFM) was utilized. A rutile $\text{TiO}_2(110)$ single crystal was used. Before UV light irradiation, no difference in contrast was observed, indicating microscopically homogeneous wettability. After irradiation, the hydrophilic (bright) and hydrophobic (dark) areas of $30\text{--}80\text{nm}$ were clearly observed (Fig. 15).²⁹⁾ A gradual reversion to a smaller contrast was observed during the storage of the crystal in the dark. In this study, we concluded that the nanoscale separation between the hydrophilic and hydro-

phobic phases accounts for the highly hydrophilic characteristic on the TiO_2 surface.

(ii) Surface hardness change after UV light irradiation

Hardness changes before and after irradiation with UV light on the surface of the rutile $\text{TiO}_2(110)$ single crystal were also observed. Figure 16 shows the repetition of UV light on and off dependence of surface hardness (within 50nm from the surface), inner hardness (300nm from the surface), and CAs.⁴⁴⁾ When irradiated with UV light, CAs decreased to 0° , accompanied by an increase in surface hardness. In contrast, the inner hardness remained constant. These findings suggested that the highly hydrophilic surface is subjected to compressive stress caused by the expansion of the surface volume.

5.1.5 What is the metastable state?

We have shown that the surface structure of TiO_2 changes after UV irradiation, forming a metastable state. Then, what is this state? Thus far, we have not yet obtained a definite answer. However, several experimental data indicate that the metastable state could be caused by an increase in the number of hydroxyl (OH) groups on the TiO_2 surface.³¹⁾

This increase could be detected by X-ray photoemission spectroscopy (XPS).³⁶⁾ The O 1s spectrum for the highly hydrophilic TiO_2 surface exhibited a broad shoulder to the higher binding energy side of the main O 1s peak. The shoulder was fitted with two bands, which are associated with the dissociatively

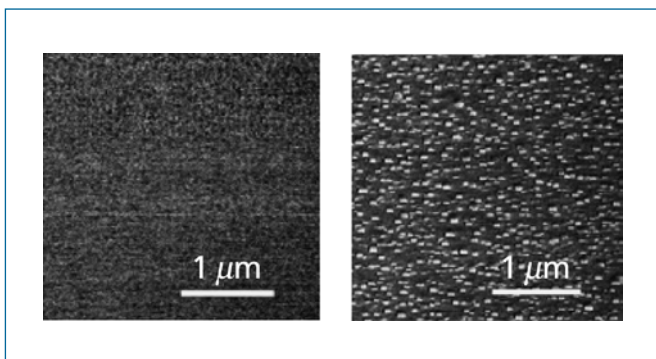


Fig.15. FFM images of rutile $\text{TiO}_2(110)$ single crystal surface before (left) and after (right) UV light irradiation.

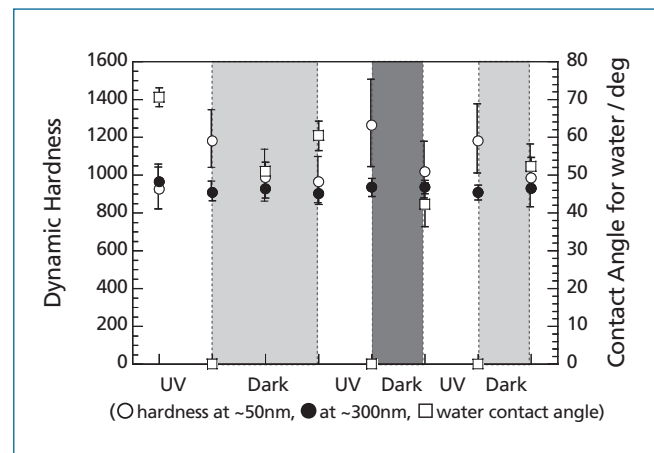


Fig.16. Relationship between changes in water contact angle and hardness at surface of TiO_2 film (within 50nm) and inside (300nm).

adsorbed water on the TiO₂ surface as well as the physically adsorbed molecular water on the dissociatively adsorbed OH groups. The shoulder gradually decreased in size during storage in the dark. Therefore, these photo-generated surface OH groups were considered to be thermodynamically metastable.

Fourier transformation infrared (FTIR) spectroscopy provides another method of investigating the relationship between hydrophilicity and the amount of OH groups.⁴⁵⁾ TiO₂ shows IR bands positioned at 3695cm⁻¹, assigned to the stretching of OH groups chemisorbed on the surface, 3300cm⁻¹, assigned to hydroxyls for both dissociated water and molecularly adsorbed water, and 1623cm⁻¹, pertaining to H–O–H bending for molecular water. This observation denotes the coexistence of dissociated water and molecular water on the TiO₂ surface. Storage in the dark for one week resulted in the decrease of all the bands, correlated with both dissociated and molecular water desorptions. The significant increase in CA after the dark storage is consistent with this surface conversion. The surface conversion is ascribed to the removal of the chemisorbed hydroxyl groups. With UV light irradiation, however, the intensity of the 1623cm⁻¹ band decreased, whereas the 3695cm⁻¹ band increased, demonstrating the increase in the amount of adsorbed dissociated water and the decrease in that of adsorbed molecular water. Nakamura *et al.* also reported that the increase in the amount of chemisorbed H₂O on the TiO₂ surface after UV light irradiation was observed (a band at 3270cm⁻¹), by

surface-enhanced IR absorption spectroscopy (SEIRAS).⁴⁶⁾

Recently, Uosaki *et al.* reported the differences in interfacial water structures at TiO₂ surfaces between before and after UV light irradiation by sum frequency generation (SFG) spectroscopy.⁴⁷⁾ It was shown that UV light irradiation led to an increase in the amount of the ordered adsorbed water on the TiO₂ surface (a broad band with a peak at 3400cm⁻¹ and a shoulder at 3200cm⁻¹), confirming the increase in the hydrophilicity of the surface.

5.1.6 Mechanism for highly hydrophilic conversion

On the basis of the previous studies mentioned above and some electrochemical experiments,⁴⁸⁾ which show that the photo-generated holes, not the electrons, are responsible for the highly hydrophilic conversion, we proposed a mechanism for the highly hydrophilic conversion under UV light irradiation, as shown in Fig. 17.³¹⁾ That is, the photogenerated holes produced in the bulk of TiO₂ diffuse to the surface and are trapped at lattice oxygen sites. Most trapped holes are consumed to react with the adsorbed organics directly, or adsorbed water, producing OH radicals. However, a small portion of the trapped hole may react with TiO₂ itself, breaking the bond between the lattice titanium and oxygen ions by the coordination of water molecules at the titanium site. The coordinated water molecules release a proton for charge compensa-

tion, and then a new OH group forms, leading to the increase in the number of OH groups at the surface. It is considered that the singly coordinated new OH groups produced by UV light irradiation are thermodynamically less stable compared to the initial doubly coordinated OH groups. Therefore, the surface energy of the TiO₂ surface covered with the thermodynamically less stable OH groups is higher than that of the TiO₂ surface covered with the initial OH groups. Because a water droplet is substantially larger than the hydrophilic (or hydrophobic) domains, as shown in Fig. 15, it instantaneously spreads completely on such a surface, thereby resembling a two-dimensional capillary phenomenon.

5.2 Application

5.2.1 Self-cleaning function

The finding of the photo-induced hydrophilicity has markedly widened the application range of TiO₂-coated materials.⁴⁹⁾ That is, the stains adsorbed on the TiO₂ surface can easily be washed by water, because water soaks between stain and the highly hydrophilic TiO₂ surface. In other words, this has removed the limitation of the cleaning function of the TiO₂ photocatalysis, that is, the function is limited by the number of photons. Even though the number of photons is not sufficient to decompose the adsorbed stains, the surface is maintained clean when water is supplied there.

Thus, the TiO₂-coated materials used outdoors where they are exposed to rainfall

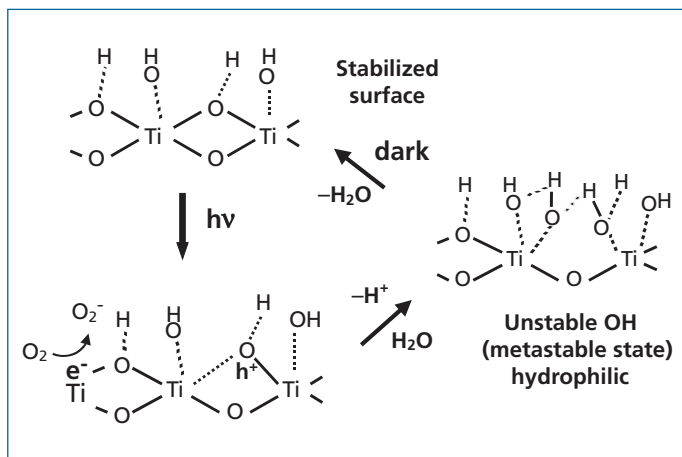


Fig. 17. Schematic illustrations of reversible changes in amount of hydroxyl groups on TiO₂ film under UV light irradiation and in the dark.

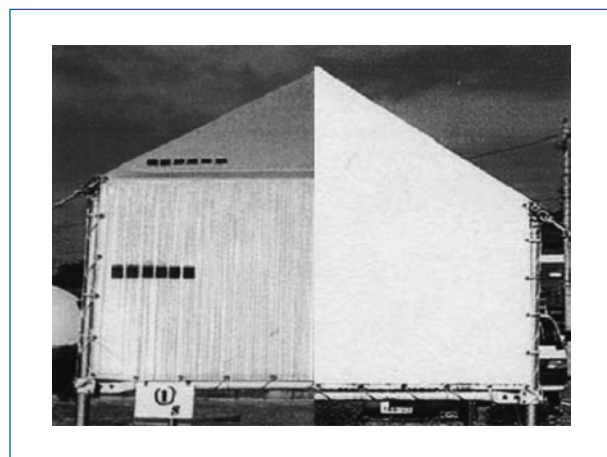


Fig. 18. Conventional tent material (left) and TiO₂-coated tent material (right).



Fig.19. Anti-fogging effect of automobile side-view mirror: conventional mirror (left) and TiO₂-coated mirror (right).

show a very effective self-cleaning function, i.e., stains are decomposed partially by the conventional photocatalytic reaction as well as washed by rainwater. Such materials, which we call "photocatalytic building materials", e.g., exterior tiles, glass, aluminum walls, and PVC fabric (Fig. 18), have already begun to be commercialized. For example, the photocatalytic exterior glass with an area of 20,000m² was installed in the terminal building of Chubu International Airport opened in 2005.

5.2.2 Anti-fogging function

Another function blessed with the photo-induced hydrophilicity is the anti-fogging function. The fogging of the surfaces of mirrors and glasses occurs when steam cools down on these surfaces to form many water droplets. On a highly hydrophilic surface, no water drops are formed. Instead, a uniform thin film of water is formed on the surface. This uniform water film prevents the fogging. Once the surface turns into the highly hydrophilic state, it remains unchanged for several days or one week. Thus, we expect that various glass products, mirrors and eyeglasses, for example, can be imparted with antifogging functions using this technology, with simple processing and at a low cost. In fact, Japanese-made cars are being equipped with antifogging highly hydrophilic side-view mirrors, as shown in Fig. 19.

6. Photocatalysis in 21st Century

As was described above, TiO₂ photocatalysis has become a real practical technology after the middle of the 1990s, particularly in the field of building materials. It is, however, surprising that a research study on TiO₂ photo-

catalysis is still carried out for developing both its science and technology after the 21st century. In the following, some of the recent development will be introduced.

6.1 Design of nanostructure of TiO₂ surface for highly sensitive hydrophilicity

When utilizing the photooxidative decomposition properties, TiO₂ has already been applied to indoor use with the aid of either copper or silver for anti-bacterial purpose, as mentioned in §4.2. However, as for neither the decomposition of VOC nor the utilization of hydrophilic properties, TiO₂ has yet to be applied to indoor use. For example, the TiO₂ surface does not undergo the highly hydrophilic conversion when the UV light has an intensity of 1μW/cm², available in an ordinary living environment. Thus, a highly sensitive

TiO₂ that undergoes highly hydrophilic conversion has been required. We have intensively investigated this on the basis of the mechanism for the highly hydrophilic conversion, as described in §5.1.6.

As the reconstruction of surface OH groups is responsible for the hydrophilic conversion, different types of hydrophilic conversion behavior among the various single crystal faces are expected to be observed by comparing their surface atom alignments. In fact, the (100) and (110) faces of a rutile single crystal exhibited a higher hydrophilicity than the (001) face, as the former faces have two-fold oxygens, which are higher in position and energetically more reactive than their surrounding atoms and are so-called the "bridging site oxygens", whereas the latter has three-fold oxygens, which are lower in position and energetically more inactive.⁵⁰ Therefore, the (100) and (110) faces are favorable for increasing the number of OH groups. This finding could serve as a guideline for selecting the appropriate faces of the TiO₂ crystal for surface exposure.

To obtain the appropriate faces, the photoetching technique was applied to the (001) face of a rutile single crystal. As shown in the inset of Fig. 20, a large number of rectangular porous holes shaped like wells, with a size of 50–100nm, emerged with a fairly regular arrangement. According to Sugiura *et al.*⁵¹ and Nakato *et al.*,⁵² rectangular holes

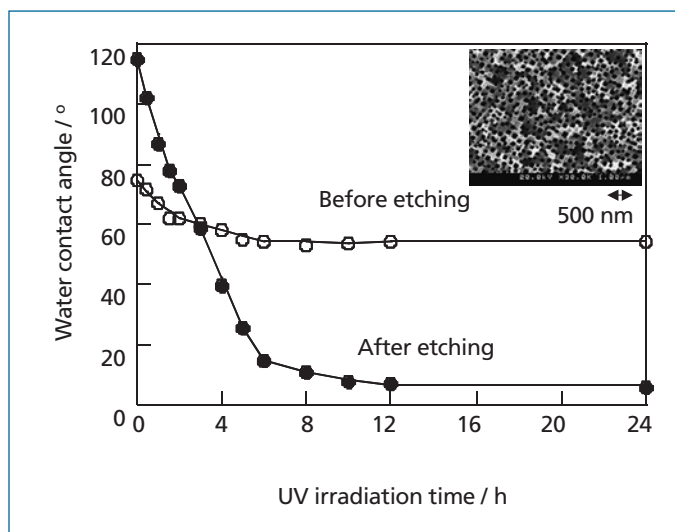


Fig.20. Changes in water contact angles on rutile (001) surface with and without photoetching treatments. The inset shows a SEM image of rectangular holes emerged by photoetching treatment on a (001) surface.

proceed toward the $\langle 001 \rangle$ direction (*c*-axis direction), and the (100) face or equivalents are exposed selectively on the walls. This rectangular porous surface increased the sensitivity of the photoinduced hydrophilic reaction and achieved a high hydrophilicity under UV light irradiation of $1\mu\text{W}/\text{cm}^2$, whereas the surface without a photoetching treatment did not, as shown in Fig. 20.⁵³⁾ Because the surface roughness enhances the hydrophilicity, the high sensitization for hydrophilic conversion by the photoetching treatment was caused by the exposure of faces with bridging site oxygens and the increase in surface roughness. This high sensitization was also observed on the rutile polycrystal by the photoetching treatment, which suggested that this technique is applicable to anatase thin films.

The introduction of residual tensile stress to anatase thin films is also a candidate method to increase the sensitivity. As the hydrophilic conversion is caused by the increase in the number of surface OH groups, the Ti–O bond length should be larger in the highly hydrophilic surface than in the less hydrophilic surface. In fact, as previously mentioned, the surface volume increased after UV light irradiation. Therefore, it can be expected that the TiO₂ surface in the presence of tensile stress is favorable for hydrophilic conversion. The residual tensile stress in the anatase thin film fabricated by the sputtering technique greatly enhanced the hydrophilic behavior, compared to a thin film without residual stress, as shown in Fig. 21.⁵⁴⁾ In contrast, the compressive stress degraded the hydrophilic behavior. The photocatalytic oxidation activities were identical

regardless of the residual stresses. The surface morphologies of the four films were controlled to be the same, and therefore, the residual stress is an important factor influencing the highly sensitive photoinduced hydrophilicity of a film.

The other highly sensitive system we produced is the heterogeneous TiO₂/WO₃ one.⁵⁵⁾ As photogenerated holes are effectively accumulated on TiO₂ without recombining with electrons, and as WO₃ could absorb visible light contained in the fluorescent light up to a wavelength of around 440nm due to its bandgap of 2.8eV, the reaction responsible for the increased hydrophilicity was greatly enhanced, and the high hydrophilicity was achieved on this system irradiated with extremely weak UV light with an intensity of $1\mu\text{W}/\text{cm}^2$ from a fluorescent lamp. As such, the high sensitization of TiO₂ under weak UV light is expected to increase the application areas to indoor conditions.

6.2 Visible-light-sensitive TiO₂

The current area of interest in this field has been the modification of TiO₂ sensitive to visible light. One approach was to substitute Cr, Fe or Ni for a Ti site.^{56,57)} Another approach was to form Ti³⁺ sites by introducing an oxygen vacancy in TiO₂.⁵⁸⁾ However, these approaches were not widely accepted due to the lack of reproducibility and chemical stability.

In 2001, several groups reported visible-light-sensitive TiO₂-based powders and thin

films.^{59–61)} Subsequently, nitrogen-doped TiO₂ has attracted considerable attention.^{62–64)} In fact, similar photocatalysts sensitive to visible light have already been reported in 1986.^{65,66)}

Yellow and transparent nitrogen-doped TiO₂ thin films can be fabricated by sputtering a Ti or TiO₂ target in a gas flow that contains N₂O or N₂.⁶¹⁾ The N 1s XPS peak at 396eV indicates that the dopant nitrogen is located at an oxygen site.^{60,61)}

Figure 22(a) shows the hydrophilic conversion behaviors of the nitrogen-doped TiO₂ thin film irradiated with visible light (400–530nm). The nitrogen-doped TiO₂ thin film underwent hydrophilic conversion; however, irradiating only with visible light did not achieve the high hydrophilicity. Irradiating with UV light (300–400nm), the nitrogen-doped TiO₂ thin film underwent highly hydrophilic conversion, as shown in Fig. 22(b). The photocatalytic activities (both oxidative decomposition and hydrophilic conversion activities) generated by visible light-induced holes are inferior to those generated by UV light-induced ones.⁶⁷⁾

Before discussing the reason for this, let us discuss the origin of visible light sensitivity. When the N atoms are substituted as N³⁻ ions at O²⁻ sites, the impurity (acceptor) level, composed of 2p orbitals of N (N 2p), is formed above the valence band. Electron vacancies exist at the acceptor level. Therefore, nitrogen-doped TiO₂ should be a p-type semiconductor as electrons are thermally excited from the valence band. However, we have photoelectrochemically and electrochemically determined that the nitrogen-doped TiO₂ was an n-type semiconductor and the carrier concentration increased as the dopant concentration increased. Actual TiO₂ is known to be nonstoichiometric and have oxygen defects. Oxygen defects generate electrons, which leads to the n-type semiconductor. The amount of electrons, originated from oxygen vacancies, is considered to be larger than that of electron vacancies, originated from the nitrogen substitution at O sites. Therefore, the nitrogen-doped TiO₂ should be an n-type semiconductor. Thus, with increasing dopant nitrogen, the carrier concentrations should decrease. However, the experimental results are the opposite. When nitrogen is incorporated, because an increase in the amount of intersti-

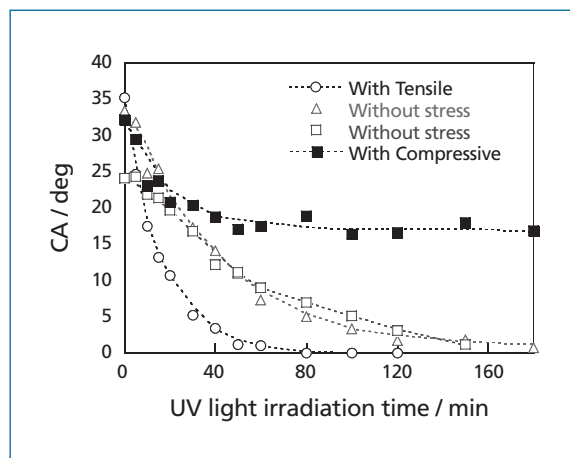


Fig.21. Changes in water contact angles on TiO₂ films when irradiated with UV light, without residual stress and with residual tensile/compressive stresses.

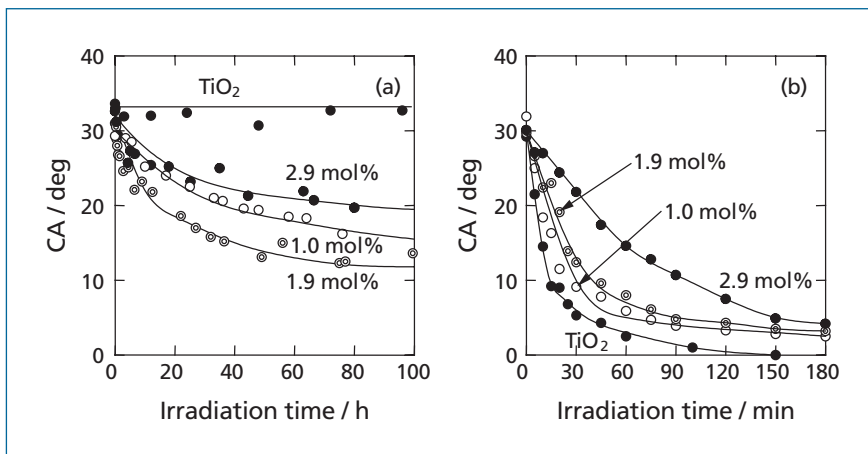


Fig.22. Changes in water contact angles on TiO₂ and nitrogen-doped TiO₂ thin films irradiated with (a) vis and (b) UV lights.

tial titanium is clearly not possible, an oxygen vacancy is simultaneously produced. Therefore, the schematic illustration in Fig. 23 is the essential procedure when oxygen is replaced by nitrogen.

The Ti 3d impurity (donor) level, derived from oxygen vacancies, is known to be non-visible light sensitive. In fact, hydrogen-reduced TiO₂ (TiO_{2-x}) powders, which have a gray color, do not show visible light sensitivity. The N 2p level exists much deeper than the Ti 3d donor level, from which we can consider that the N 2p level has a much more oxidation power than the Ti 3d level. Therefore, the origin of visible light sensitivity of nitrogen-doped TiO₂ is considered to be the N 2p narrow band.

Thus, the reason that irradiating the nitrogen-doped TiO₂ with UV light resulted in higher photocatalytic activities than irradiating with visible light is as follows. Irradiating with UV light excites electrons in both the valence band composed of O 2p and the narrow band composed of N 2p, but irradiating with visible light only excites electrons in the narrow band of N 2p. In addition, the hole mobility in the isolated narrow band should be low. Therefore, the hydrophilic properties when irradiating with UV light were higher than when irradiating with visible light. Although the nitrogen concentration increases, it is not suggested by the density of states (DOS) calculations that the bandgap narrowing by mixing N 2p with O 2p occurs.

Compared with the conventional TiO₂, the advantage of nitrogen-doped TiO₂ is the increased absorbed photon number, but the disadvantage is the decreased photocatalytic activity. Therefore, whether to use nitrogen-doped TiO₂ or conventional TiO₂ depends on the light source.

In addition to nitrogen, the sulfur-doped and carbon-doped TiO₂ systems are reported to be visible-light-sensitive photocatalysts.⁶⁸⁻⁷¹ However, the visible-light-induced photocatalytic activities of these anion-doped TiO₂ are insufficient and should be further enhanced. This is because the introduced 3p orbitals of S (S 3p) and 2p orbitals of C (C 2p), similar to N 2p, also formed the localized narrow band in the forbidden band, by not mixing with the valence band composed of O 2p. Thus, it can be speculated that mixing the introduced anion 2p (or 3p) with O 2p, leading to the bandgap narrowing, is the key method of enhancing the visible-light-induced photocatalytic activities. We have found using the DOS calculations that the simultaneous doping of nitrogen and sulfur into TiO₂ could narrow the bandgap of TiO₂ by mixing N 2p and S 3p with the valence band composed of O 2p. It can be expected that the broad expansion of the electronic state, compared with the isolated one,

will show the higher photocatalytic activities irradiated with visible light. This investigation is now under way.⁷²

These anion-doped TiO₂ are candidate photocatalysts in terms of reproducibility and chemical stability. Therefore, further research and practical applications are desirable.

6.3 Hydrophobic TiO₂ surface

As the discovery of the photo-induced hydrophilicity has markedly widened the application field of TiO₂-coated materials, a highly hydrophobic TiO₂ surface could open a new application field. In addition, if it is realized, we will be able to control the wettability on a TiO₂ surface using external stimuli, such as UV light, which we believe is both scientifically and practically very important.

Let us try to design the hydrophobic TiO₂ surface. As previously mentioned, the wettability of a flat solid surface is determined simply by the surface free energy of solid as described in eqs. (9) and (11). As for a non-flat surface, however, surface roughness affects the wettability. Wenzel modified Young's equation by considering the surface roughness to obtain⁷³

$$\cos\theta' = r \cos\theta, \quad (12)$$

where θ' is the apparent contact angle and r is the surface roughness ratio between the

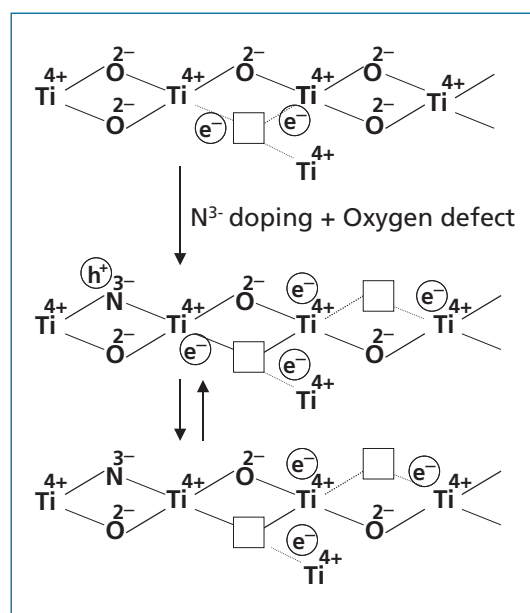


Fig.23. Schematic illustration of nitrogen doping into oxygen site.

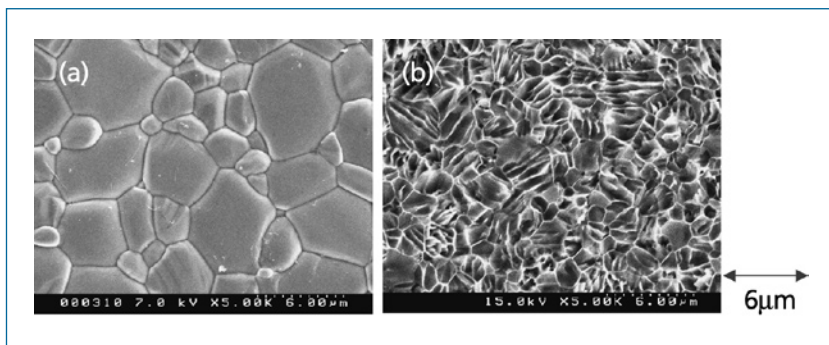


Fig.24. SEM images for polycrystalline TiO₂ surfaces (a) before and (b) after etching treatments.

actual surface area and the apparent surface area. This equation indicates that the surface roughness enhances the hydrophilicity of hydrophilic surfaces ($\theta < 90^\circ$) and also enhances the hydrophobicity of hydrophobic surfaces ($\theta > 90^\circ$) since the r value is always larger than 1. Because the CA of a flat TiO₂ surface is always less than 90° , the hydrophobic TiO₂ surface cannot be obtained by considering only the Wenzel equation. To realize the hydrophobic TiO₂ surface, we must introduce a different concept to describe the CA (θ') on a rough surface. Cassie proposed an equation for a surface composed of solid and gas.⁷⁴⁾ When a unit area of the surface has an area fraction, f , where a water droplet contacts the solid surface with a CA of θ , the θ' on the surface can be expressed as follows, called Cassie's equation, in which the CA for air is assumed to be 180° :

$$\begin{aligned} \cos\theta' &= f\cos\theta + (1-f)\cos 180^\circ \\ &= f\cos\theta + f - 1. \end{aligned} \quad (13)$$

Considering eq. (13), the θ' increases with decreasing f value. Thus, the hydrophobic TiO₂ requires surface roughness where air can intrude between the water droplet and the TiO₂ surface.

To achieve such a rough surface, we applied a photoetching technique to a rutile pellet. Before the etching treatment, grains and grain boundaries were observed, which is typical of a polycrystalline pellet, as shown in Fig. 24(a). After etching, the surface structure changed and was accompanied by an increase in surface roughness. Random directions of digging "ditches" as shown in Fig. 24(b) were plausible, considering the polycrystalline pellet. The pellets with the etched and non-etched surfaces were stored in the dark

at room temperature in a clean vessel filled with synthetic air. Maintaining the samples in the dark for 15 days caused the CA to reach approximately 120° on the etched surface, whereas the CA was around 80° on the nonetched surface, indicating that we could obtain the hydrophobic TiO₂ surface, on which Cassie's mode dominates, by the photoetching process (Fig. 25).

The UV irradiation of this hydrophobic TiO₂ markedly changed the surface wettability, i.e., the CA decreased to 0° . In addition, storing the samples in the dark for a long time caused the CA on the etched surface to further increase to approximately 140° , whereas the CA on the nonetched surface remained constant at around 80° . We can thus control the surface wettability from highly hydrophilic to hydrophobic repeatedly by alter-

nating between UV light and dark storage.⁷⁵⁾ At present, the hydrophobic conversion takes much time, and must be further enhanced.

In addition, the surface with a CA above 150° is called the super-hydrophobic surface, and such a surface is attracting considerable attention at present,⁷⁶⁻⁸⁴⁾ because the limited contact area between the solid surface and the water could change chemical reactions and/or bond formation through water, introducing novel properties on the surface. Therefore, if one succeeds in the preparation of the TiO₂ surface with a CA of more than 150° , it indicates that the surface property of TiO₂ can be markedly controlled.

6.4 New environmental applications

TiO₂-coated materials practically used thus far have been provided with self-cleaning, antibacterial and/or anti-fogging functions based on the photo-induced decomposition reaction and photo-induced hydrophilicity. It is important to note that these functions are obtained without using any chemicals, but with only sunlight and rainwater. Therefore, these TiO₂-coated materials can be classified as being environmentally friendly. In this section, we will show further applications of TiO₂ photocatalysis, which can actively contribute to environmental preservation and/or improvement technologies.

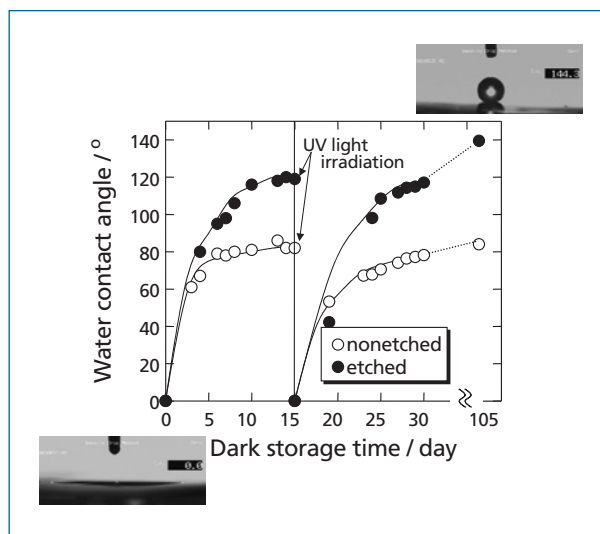


Fig.25. Back reactions on etched and nonetched polycrystalline TiO₂ surfaces as a function of storage time in the dark.

6.4.1 Photocatalytic decomposition of pollutants

Environment pollution, including water, air and soil is becoming an increasingly serious problem today. There have been many reports aiming at applying TiO_2 photocatalysis to pollution clean-up since the 1970s. However, the purification of the three-dimensional spaces by photocatalysis is much more difficult than that of the two-dimensional surface of building materials due to the following two reasons. One is that photocatalytic reactions are surface reactions and thus the reactants must be captured by the photocatalyst surface. The other is that the total amount of reactant is, in general, higher in three-dimensional spaces than on a two-dimensional surface, indicating that much more light energy is necessary for the purification of the three-dimensional space. Therefore, practical technologies have not been obtained in this field. However, we have recently succeeded in the construction of practical purification systems for wastewater from agriculture and soil polluted by volatile organic compounds (VOCs). These systems are based on TiO_2 photocatalysts and use only solar light.

Important keys for these successes are (1) the utilization of nanosized TiO_2 photocatalyst powders dispersed on substrates with extremely large surface areas, and (2) spreading them on the ground widely to collect sunlight. Because the concentrations of environmental pollutants are low in general, the UV light contained in sunlight is sufficiently strong to decompose them by TiO_2 photocatalysis, if we can collect the light from a broad area.

(i) Detoxification of wastewater used for rice hull disinfection

Disinfection solutions for rice hulls (to stop the spread of plant diseases) contain highly concentrated agricultural chemicals. The corresponding wastewater is mostly disposed of by pouring onto the ground, which causes soil pollution. The amount of wastewater from rice hull disinfection amounts to about 500,000 metric tons/year in Japan, for example. Such a problem could also become much more serious in developing countries.

We developed a glass wool mat with a

large surface area deposited with very photo-active TiO_2 nanoparticles; we were able to show that the wastewater solution is easily purified using the photocatalytic mat under only solar light. The treatment method is very simple, i.e., the wastewater is poured onto mats that are spread over a wide area on the ground. The agricultural chemicals were completely decomposed under sunlight in a few days. It is surprising that the initial total organic carbon (TOC) values of several hundred to one thousand ppm decreased to nearly zero in one week. This could be one of the simplest and easiest environmental technologies.

(ii) Water treatment of hydroponic culture system

Most of the hydroponic culture installations are adopting run-to-waste systems (as opposed to recirculating). The nutrient solution contains highly concentrated nitrogen and phosphorus compounds, and thus, the wastewater causes soil pollution. From the viewpoint of environmental problems, the recycling of nutrient solutions is desirable. However, organic contaminants accumulate in the solution, inhibiting plant growth.

We succeeded in constructing a recycling system in a tomato hydroponic culture system using the TiO_2 photocatalyst and solar light. The system is schematically illustrated

in Fig. 26. The wastewater from the hydroponic tomato culture with a planting area of about 80m^2 was introduced into a shallow vessel with a bottom area of 4m^2 and a depth of 10cm in which porous ceramic plates coated with TiO_2 photocatalyst nanoparticles were placed. The organic contaminants in the wastewater were easily decomposed under solar light, but the nutrient compounds containing nitrogen, phosphorous and potassium were not, because these components existed in their most oxidized forms, NO_3^- , PO_4^{3-} and K^+ , in the nutrient solution. Therefore, this system is also expected to serve as a nutrient-saving technology.

(iii) Treatment of VOC-polluted soil

Volatile chlorinated organic compounds (VOCs), such as trichloroethylene and tetrachloroethylene, have been widely used as solvents for the dry cleaning of clothes and washing of semiconductors. They had been indiscriminately disposed by the middle of the 1980s, causing soil and groundwater pollution. These types of pollution are serious environmental problems, because the carcinogenic and toxic chemicals had been widely disposed. The most common method of treating the polluted soil is either the simple replacement with clean soil or the heating of the soil to volatilize the VOCs into air. It is obvious that these methods do not truly purify the environment.

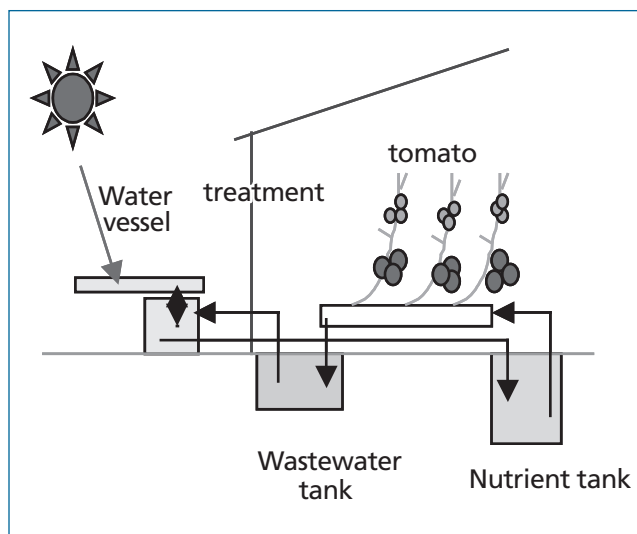


Fig.26. Novel photocatalytic water recycling system of tomato hydroponic culture.

We designed photocatalytic sheets to purify the polluted soil on the ground using sunlight. As shown in Fig. 27, the polluted soil is dug up and covered with the sheet, which is made of corrugated paper containing both TiO_2 powder adsorbed on activated carbon powders. Then the covered soil is heated (for example, by mixing with calcium oxide), volatilizing the pollutant gases captured by adsorption on activated carbon incorporated in the sheet material. The sheet is allowed to remain undisturbed under sunlight, while TiO_2 in the sheet decomposes the pollutants completely by photocatalytic reaction. We have examined the efficacy of this method at an actual polluted field and confirmed that the VOCs became completely harmless after several weeks. This purification method could be one of the real environmental purification technologies.

6.4.2 Efficient water evaporation from hydrophilic surfaces

Rapid increases in the absorption of solar energy and increases in energy consumption in large cities cause a temperature increase, the so-called heat island phenomenon. The former is due to the coverage of the ground surface by artificial structures, such as buildings and paved roads, and the latter is due to the heat emissions from automobile traffic and air conditioners. An effective method of preventing the heat island phenomenon is increasing the area of green tract land or the

surface area of water. Thus, the cultivation of rooftop plants and/or the construction of artificial lakes or marshes are currently under way. However, the areas of green tract land and water surfaces cannot be secured easily due to the high land value in urban areas.

We are proposing a method of securing water surfaces by continuously sprinkling water onto the surfaces of buildings that will be covered with a TiO_2 photocatalyst (Fig. 28). The surface coated with TiO_2 becomes highly hydrophilic and plays an important role in minimizing the amount of sprinkling water required to form a water film. A very thin water layer of approximately 0.1mm thickness can cover all of the highly hydrophilic TiO_2 material; the water can be continuously supplied in small quantities for a vertical building.

It is important to emphasize that the buildings and surroundings are not cooled by water itself, but by the latent heat flux when water evaporates. In fact, it is often observed that the temperature of a wall surface is lower than that of sprinkling water. The thinner the water layer is, the more effectively the building surface temperature and surrounding air temperature decrease as the amount of latent heat flux decreases to cool down the thin water film. Although the margin of the temperature drop depends on the color and/or type of building material, as well as the atmosphere temperature and humidity, it

was confirmed on a clear day in the middle of summer that the temperature drops were 15°C on window glass and $40\text{--}50^\circ\text{C}$ on black roof-tile surfaces. Moist surfaces easily mildew, but since a TiO_2 photocatalyst has oxidation activity in addition to a high hydrophilicity, this problem is not an issue.

The cooling of the building surface also results in the reduction in the amount of electricity consumed for air conditioning. We measure this effect quantitatively with a real house and building and observe that the amount of electricity consumed is reduced by ten to several tens of percentage. Therefore, TiO_2 -coated materials could also contribute to the development of energy-saving technologies.

7. Conclusions

In this paper, an overview of the development of TiO_2 photocatalysis and its future prospects from both scientific and technological viewpoints are given. It is interesting to note that this field has experienced major developments every ten years for the last thirty years, namely, water photoelectrolysis (Honda–Fujishima effect) in the early 1970s, photocatalytic H_2 production in the 1980s, and the photocatalysis and hydrophilicity of TiO_2 films in the 1990s. Based on the basic research results, real industrial applications have been achieved since the end of the 1990s. In addition, this field is still being developed further in the 21st century. We believe that TiO_2 photocatalysis is one of the best examples how, on the time scale of tens of years, basic scientific knowledge can be developed into a technological field and can produce a new industry.

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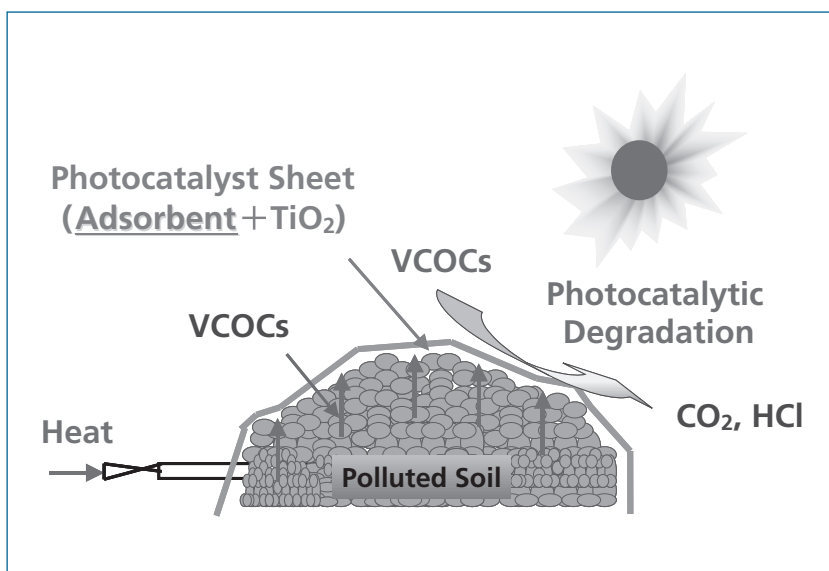


Fig.27. Purification system for polluted soil utilizing solar energy and photocatalyst sheets.

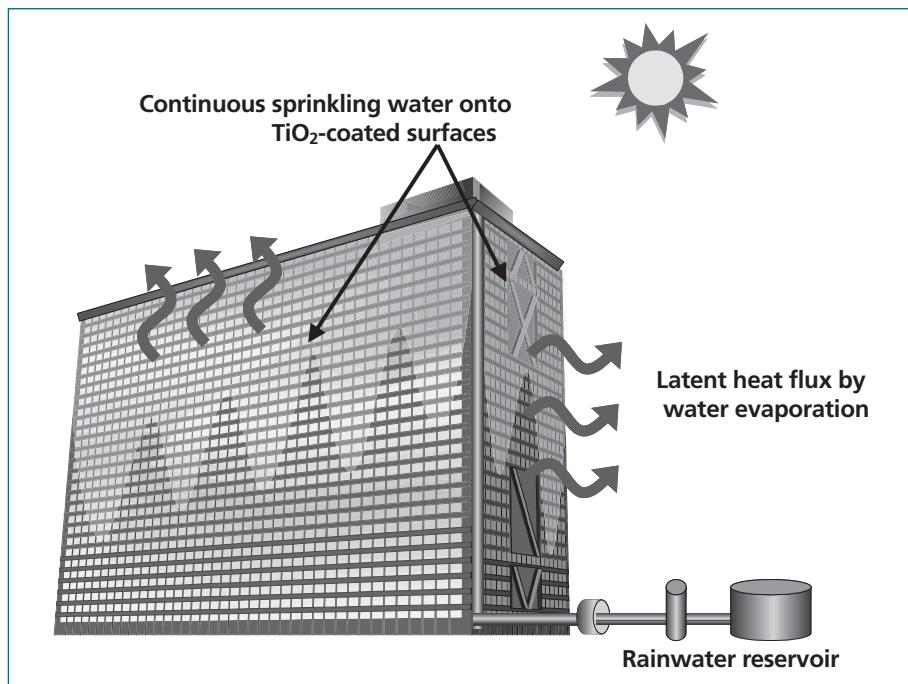


Fig.28. Energy-saving system using solar light and stored rainwater.

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$$1/\theta = a - b \times \ln(t)$$

$$d(1/\theta)/dt = -b \times (1/t)$$
 Combining these equations, k_b can be described as a function of $1/\theta$:

$$k_b(\text{deg}^{-1}\cdot\text{min}^{-1}) = -d(1/\theta)/dt = b \times \exp((1/\theta - a)/b).$$

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