

Titanium dioxide photocatalysis

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Abstract

Scientific studies on photocatalysis started about two and a half decades ago. Titanium dioxide (TiO_2), which is one of the most basic materials in our daily life, has emerged as an excellent photocatalyst material for environmental purification. In this review, current progress in the area of TiO_2 photocatalysis, mainly photocatalytic air purification, sterilization and cancer therapy are discussed together with some fundamental aspects. A novel photoinduced superhydrophilic phenomenon involving TiO_2 and its applications are presented. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Starting in the late 1960s, we have been involved in an unfolding story whose main character is the fascinating material titanium dioxide (TiO_2). This story began with photoelectrochemical solar energy conversion and

then shifted into the area of environmental photocatalysis, including self-cleaning surfaces, and most recently into the area of photoinduced hydrophilicity, which involves not only self-cleaning surfaces, but also antifogging ones. One of the most interesting aspects of TiO_2 is that the types of photochemistry responsible for photocatalysis and hydrophilicity are completely different, even though both can occur simultaneously on the same surface. In this review, we will briefly trace the development of these two areas,

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examine the present state of understanding and finally summarize some of the numerous applications, highlighting our own contributions.

2. Background: photoelectrochemical solar energy conversion

Plants capture the energy from sunlight and thus grow. During this process, they produce oxygen by oxidizing water and reducing carbon dioxide. In other words, the oxidation of water and the reduction of CO₂ are achieved with solar energy. By analogy with natural photosynthesis, we began to investigate the photoelectrolysis of water using light energy [1,2]. This approach involves essentially a photochemical battery making use of a photoexcited semiconductor (Fig. 1).

In a solar photovoltaic cell, photogenerated electron-hole pairs are driven efficiently in opposite directions by an electric field existing at the boundary (junction) of n- and p-type semiconductors (or at semiconductor/metal junctions). The maximum conversion efficiency for solid-state devices that employ a single junction has reached ~24% and, for two junctions, ~30%. A potential gradient can also be created at the interface of a semiconducting material and a liquid phase. Hence, if a semiconductor is used as an electrode that is connected to another (counter) electrode, photoexcitation of the semiconductor can generate electrical work through an external load and simultaneously drive chemical (redox) reactions on the surfaces of each electrode. On the other hand, in a system where semiconductor particles are suspended in a liquid solution, excitation of the semiconductor can lead to redox processes in the interfacial region around each par-

ticle. These types of systems have drawn the attention of a large number of investigators over the past 20 years.

Our work originally got started in the late 1960s at The University of Tokyo in research on photoelectrochemical (PEC) solar cells [1,2]. One of the first types of electrode materials we looked at was semiconducting TiO₂, partly because it has a sufficiently positive valence band edge to oxidize water to oxygen. It is also an extremely stable material in the presence of aqueous electrolyte solutions, much more so than other types of semiconductors that have been tried.

The possibility of solar photoelectrolysis was demonstrated for the first time with a system in which an n-type TiO₂ semiconductor electrode, which was connected through an electrical load to a platinum black counter electrode, was exposed to near-UV light (Fig. 2) [3]. When the surface of the TiO₂ electrode was irradiated with light consisting of wavelengths shorter than ~415 nm, photocurrent flowed from the platinum counter electrode to the TiO₂ electrode through the external circuit. The direction of the current reveals that the oxidation reaction (oxygen evolution) occurs at the TiO₂ electrode and the reduction reaction (hydrogen evolution) at the Pt electrode. This fact shows that water can be decomposed, using UV–VIS light, into oxygen and hydrogen, without the application of an external voltage, according to the following scheme:

(excitation of TiO₂ by light)



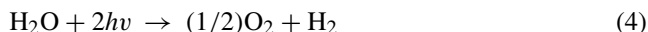
(at the TiO₂ electrode)



(at the Pt electrode)



The overall reaction is



When a semiconductor electrode is in contact with an electrolyte solution, thermodynamic equilibration takes place 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 or downwards, respectively, in the cases of n- and p-type semiconductors. The thickness of the space-charge layer is usually of the order of 1–10³ nm, depending on the carrier density and dielectric constant of the semiconductor. If this electrode receives photons with energies greater than that of the material's 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 takes place at a p-type

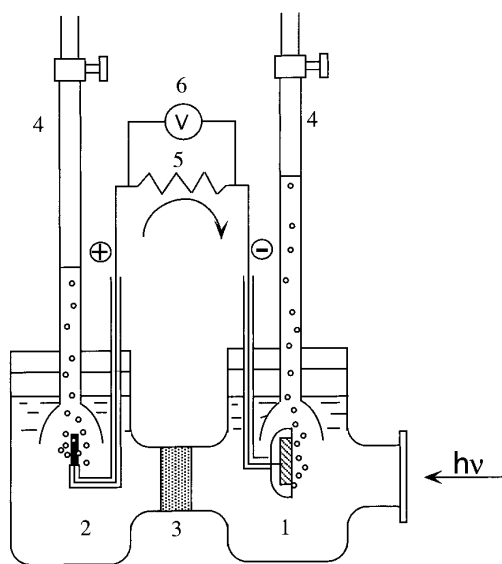


Fig. 1. Schematic diagram of an electrochemical photocell [6]. (1) n-type TiO₂ electrode; (2) platinum black counter electrode; (3) ionically conducting separator; (4) gas buret; (5) load resistance and (6) voltmeter.

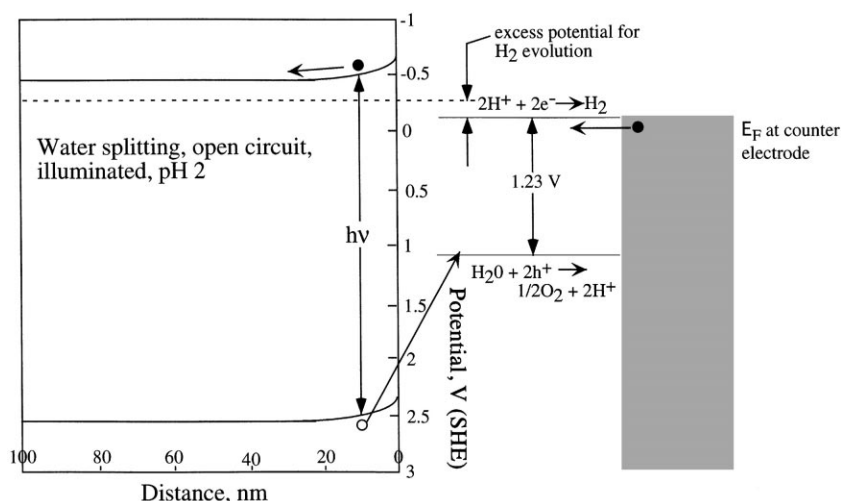


Fig. 2. Schematic representation of photoelectrochemical water electrolysis using an illuminated oxide semiconductor electrode [6]. Open circuit (or small current), pH 2, illuminated conditions are shown for an oxide with an E_{CB} of -0.65 V (SHE) and an E_{VB} of 2.35 V (SHE). With an open circuit, a small excess potential (~ 0.15 V) is available for H_2 evolution, assuming a reversible counter electrode.

semiconductor electrode. These fundamental processes have been discussed in a number of recent reviews [4–8].

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. 1, E_{CB} should be at least as negative as -0.4 V (SHE) in acid solution or -1.2 V (SHE) in alkaline solution. Among the oxide semiconductors, TiO_2 (acid), $SrTiO_3$, $CaTiO_3$, $KTaO_3$, Ta_2O_5 and ZrO_2 satisfy this requirement. On the other hand, the employment of an external bias or of a difference in pH between the anolyte and catholyte is required in the case of the other materials in order to achieve hydrogen evolution. For example, in early $n-TiO_2$ -based photoelectrochemical cells used in our laboratory [3], the problem of E_{CB} being slightly lower (less negative) than that necessary to evolve hydrogen was circumvented by using an anolyte and catholyte with different pH values, higher in the former and lower in the latter. Effectively this decreases the equilibrium cell potential and thus there is excess overpotential with which the cell reactions can be driven to higher current densities. Our group [9] and others [10] also found that $SrTiO_3$, which has a sufficiently negative E_{CB} , was able to photoelectrolyze water without an additional voltage. With its very large band gap, however, the efficiency of solar energy conversion is very low.

It is desirable that the band gap of the semiconductor is near that for optimum utilization of solar energy, which would be ~ 1.35 eV for a solid-state p–n junction or for a PEC cell under ideal conditions [11]. Even when photons are completely absorbed, excess photon energy ($E > E_{BG}$) cannot normally be utilized in a simple, single band-gap device, since vibrational relaxation occurs in the upper excited

states before the charge transfer takes place. Therefore, a fraction of the photon energy is dissipated as heat. When semiconductor electrodes are used as either photoanodes or photocathodes for water electrolysis, the bandgap should be at least 1.23 eV (i.e. the equilibrium cell potential for water electrolysis at 25°C and 1 atm), particularly considering the existence of polarization losses due to, e.g. oxygen evolution.

An alternative approach is to employ an additional solid-state junction, as in the work of Khaselev and Turner [12]. The solid-state tandem cell consists of a GaAs bottom cell connected to a GaInP₂ top cell through a tunnel-diode interconnect. The GaInP₂ band gap is 1.83 eV. The GaAs band gap is 1.42 eV. The theoretical maximum efficiency for a dual band gap is ca. 41%, but the maximum efficiency for this combination of band gaps is 34%. The difference between this type of cell and the fully photovoltaic tandem cell is that the top junction is p/Schottky rather than p/n. H_2 is produced at the semiconductor electrode, which is thus cathodically protected. This system yields 12.4% conversion efficiency for an incident light intensity of 1190 mW cm^{-2} . The H_2 production photocurrent is 120 mA cm^{-2} . The principal shortcoming of this system is the high cost of the multilayer photoelectrode.

Still another approach could involve the photosensitization of TiO_2 . Of course, this approach has been extremely and intensively researched with respect to regenerative photoelectrochemical cells. In these, there is a single redox couple in the solution, and the reduced form is oxidized at the TiO_2 photoanode, and the oxidized form is reduced at the counter electrode. The solar conversion efficiency of such devices has reached 10–11% [13,14]. 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.

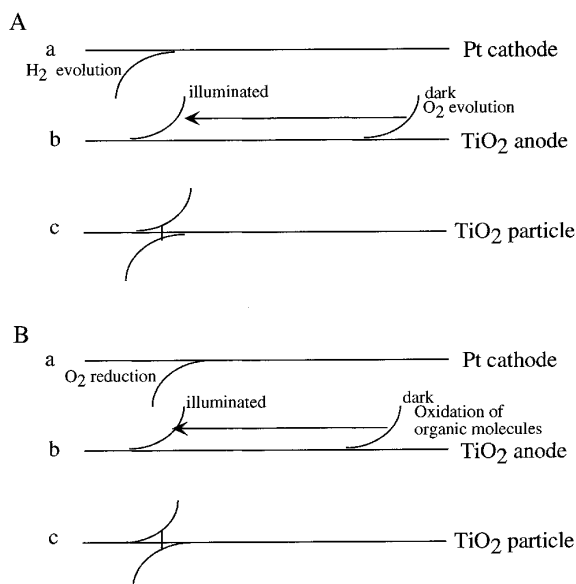


Fig. 3. Schematic diagram of hypothetical electrochemical and photoelectrochemical reactions occurring on a single particle (c) in the absence (A) and in the presence (B) of organic compounds in aqueous environment. For comparison, the corresponding processes occurring on (a) Pt cathode and (b) a TiO_2 photoanode are shown, the latter two being connected to a potentiostat as working electrodes.

The problem of light-assisted water splitting has also been attached using the photocatalytic approach, i.e. essentially using photoelectrochemistry but without an external circuit. Conceptually, this is similar to that of corrosion as being the combination of two short-circuited electrochemical reactions (Fig. 3A). In the case of corrosion, the two reactions might be anodic metal dissolution together with either cathodic H_2 evolution or O_2 reduction. Photocatalytic water splitting has been studied intensively with TiO_2 suspensions, with Pt deposited on the TiO_2 as a cathodic catalyst. This field remains active, with novel layered metal oxides being the favored materials. We have recently reviewed this work [15]. The close relationship between photoelectrochemistry and photocatalysis can also be seen in the next section.

3. Photocatalysis

3.1. General

As has been pointed out by Heller, all of the extensive knowledge that was gained during the development of semiconductor photoelectrochemistry during the 1970 and 1980s has greatly assisted the development of photocatalysis [16]. In particular, it turned out that TiO_2 is excellent for photocatalytically breaking down organic compounds. For example, if one puts catalytically active TiO_2 powder into a shallow pool of polluted water and allows it to be illuminated with sunlight, the water will gradually become

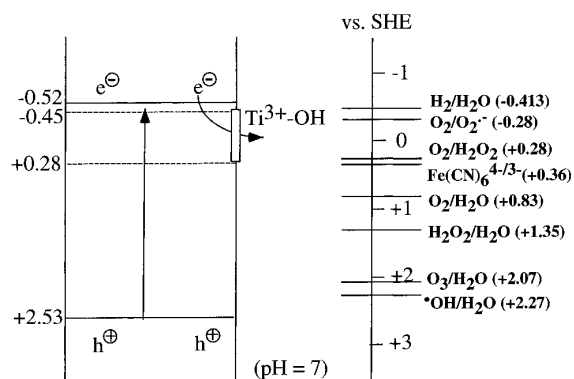


Fig. 4. Schematic diagram showing the potentials for various redox processes occurring on the TiO_2 surface at pH 7.

purified. Ever since 1977, when Frank and Bard first examined the possibilities of using TiO_2 to decompose cyanide in water [17,18], there has been increasing interest in environmental applications. These authors quite correctly pointed out the implications of their result for the field of environmental purification. Their prediction has indeed been borne out, as evidenced by the extensive global efforts in this area [4–11,15,16,19–42].

One of the most important aspects of environmental photocatalysis is the availability of a material such as titanium dioxide, which is close to being an ideal photocatalyst in several respects. For example, it is relatively inexpensive, highly stable chemically, and the photogenerated holes are highly oxidizing. In addition, photogenerated electrons are reducing enough to produce superoxide from dioxygen.

The energy band diagram for TiO_2 in pH 7 solution is shown in Fig. 4. As shown, the redox potential for photogenerated holes is +2.53 V versus the standard hydrogen electrode (SHE). After reaction with water, these holes can produce hydroxyl radicals ($\bullet\text{OH}$), whose redox potential is only slightly decreased. Both are more positive than that for ozone. The redox potential for conduction band electrons is -0.52 V, which is in principle negative enough to evolve hydrogen from water, but the electrons can become trapped and lose some of their reducing power, as shown. However, even after trapping, a significant number are still able to reduce dioxygen to superoxide O_2^- , or to hydrogen peroxide H_2O_2 . Depending upon the exact conditions, the holes, $\bullet\text{OH}$ radicals, O_2^- , H_2O_2 and O_2 itself can all play important roles in the photocatalytic reaction mechanisms, as we will discuss later.

Returning to the idea of short-circuited photoelectrochemical reactions, we can conceptually show O_2 being reduced to either O_2^- or H_2O_2 at a surface catalytic site (Fig. 3B). As an example, a deposited Pt microcrystallite is shown in order to simplify the argument. Of course, the bare TiO_2 surface can also support these reactions, even in the dark, because it is an n-type material. The anodic reaction shown here is the direct oxidation of an organic compound via holes. Since these are minority carriers, they would be in very low con-

centration in the dark but would be in high concentration under illumination. On an electrically isolated TiO_2 particle, the anodic and cathodic currents must balance each other precisely, as shown in the figure.

In order to avoid the use of TiO_2 powder, which entails later separation from the water, various researchers began to work on ways of immobilizing TiO_2 particles, for example in thin film form. One of the first reports on the preparation of TiO_2 films was that of Matthews [43]. This idea has also been worked on by Anderson [44], by Heller [22] and by our group, [45–51]. Our group has been developing ways to put photocatalytic TiO_2 coatings on various types of support materials, for example, ceramic tiles. The various types of TiO_2 -based materials will be discussed again in connection with applications.

3.2. Photocatalytic decomposition of organic compounds

3.2.1. Low intensity illumination

One of the most important aspects of TiO_2 photocatalysis is that, like the photoelectric effect, it depends upon the energy of the incident photons, but, to a first approximation, not on their intensity. Thus, even if these are just a few photons of the required energy, they can induce photocatalysis. This means that even ordinary room light may be sufficient to help to purify the air or to keep the walls clean in the indoor environment, because the amounts of pollutants are typically small. Thus, in a reasonably well-lit room, with a total light intensity of $\sim 10 \mu\text{W cm}^{-2}$, the intensity of UV light with energy exceeding that of the TiO_2 band gap would be approximately $1 \mu\text{W cm}^{-2}$. As shown later, assuming a quantum efficiency of 25%, this would be sufficient intensity to decompose a hydrocarbon layer of approximately $1 \mu\text{m}$ thickness every hour.

Most soilage to the interior of buildings comes from organic substances. Photocatalysts are not especially useful for breaking down large volumes of soilage, but they are capable of destroying it as it accumulates. For example, ordinary room light should be sufficient to prevent cigarette smoke residue stains if the catalyst-coated surface in question is clean to begin with. TiO_2 photocatalysts thus hold great potential as quiet, unobtrusive self-cleaning materials.

In addition, odors that are objectionable to humans are due to compounds which are present only on the order of 10 parts per million by volume (ppmv), and, at these concentrations, the UV light available from ordinary fluorescent lighting should be sufficient to decompose such compounds when TiO_2 photocatalysts are present. Naturally, if higher light intensities are available, larger quantities of material can be decomposed, e.g. using the bright lamps that are used in highway tunnels [23].

Our work with low-intensity light has yielded a number of interesting and important conclusions. The first is that the quantum yield for a simple photocatalytic reaction, e.g. 2-propanol oxidation, on a TiO_2 film in ambient air, reaches a maximum value when the light intensity is low, i.e. minimal

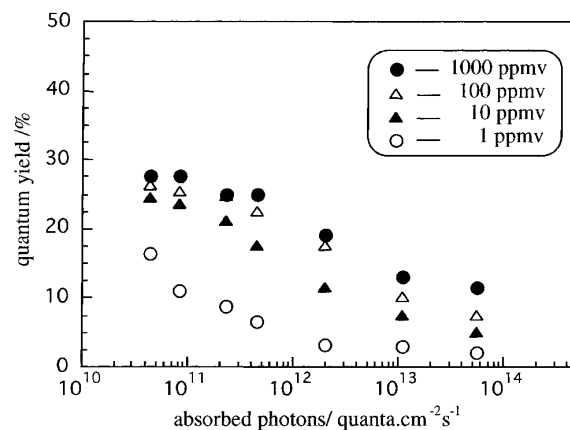


Fig. 5. Quantum yield dependence on absorbed photons at various initial 2-propanol concentrations [52].

recombination losses, and high coverage of the adsorbed organic compound [52].

The photocatalytic decomposition of 2-propanol is a simple model substrate for kinetic studies, because, it is efficiently photodecomposed to acetone, which can be detected by gas chromatography with high sensitivity. The mechanism of photodecomposition of 2-propanol does not involve chain reactions. Only one photon participates in the generation of one molecule of acetone. Hence the quantum yield (QY) is equal to the ratio of the number of generated acetone molecules to the number of absorbed photons.

Fig. 5 shows semilog plots of absorbed photons (I) versus QY values for acetone generation. These plots were obtained for various initial concentrations. The QY values in each plot increased gradually with decreasing I and finally saturated, except for the lowest initial concentration (1 ppmv). Thus, a light-limited condition was reached at lower light intensities. The maximum QY observed was $\sim 28\%$ for the highest 2-propanol concentration (1000 ppmv). Another observation in this figure is that when the 2-propanol concentration was decreased, the curve shifted in the lower light-intensity direction.

Fig. 6 shows the variation of QY as a function of normalized light intensity (I_{norm}), which is defined as the ratio of the number of photons absorbed (per second) to the number of adsorbed 2-propanol molecules, both normalized to the geometric area. The light is absorbed within the thin film, within which the 2-propanol molecules are adsorbed three-dimensionally; the roughness factor is approximately 300, as determined by the adsorption of dye. The plots obtained for different initial concentrations of 2-propanol fall on the same curve, which is a very interesting result, because it indicates that the ratio of photons to molecules is sufficient to determine the QY. This point will be discussed in more detail below. QY increases as I_{norm} decreases and finally becomes constant at $\sim 28\%$ for I_{norm} values below 10^{-4} s^{-1} .

The sigmoidally decreasing curve for QY with increasing log of light intensity can be simulated by assuming that the

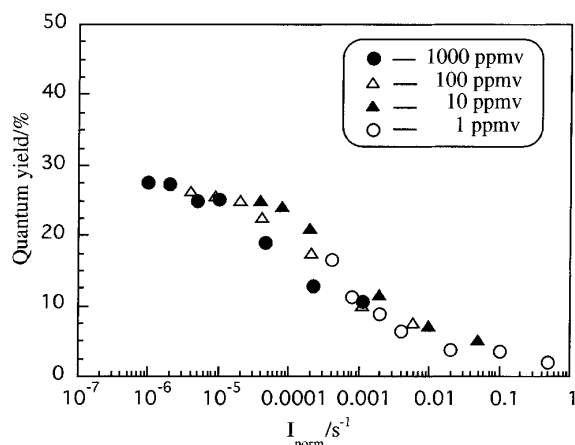


Fig. 6. Quantum yield dependence on normalized absorbed photon number (I_{norm}) at various initial 2-propanol concentrations [52].

recombination rate is second-order in the light intensity, as is generally found with photocatalytic reactions. However, the fact that this behavior scales over such a wide range of coverage of adsorbed 2-propanol is a novel result and is not quite so easily explained. We are still working on the details, but a qualitative explanation is that the adsorbed organic molecules help to inhibit recombination, as also shown by Semenikhin et al. [53]. The organics may adsorb at surface sites that are involved with recombination or they may compete with water molecules for such sites. The exact contributions of the various recombination reactions remain to be worked out, however.

There is also the question of whether holes react directly with the organic compounds or whether they react first with water molecules to produce hydroxyl radicals, which then react. This question is a continuing source of controversy within the photocatalysis field, but previous work has shown that holes are important precisely when the coverage is very high. Our recent work also indicates that holes are more important than hydroxyl radicals [54]. It was found that the measured QY values that could be attributed to a reaction involving hydroxyl radicals were several orders of magnitude smaller than those that could be attributed to reactions involving holes.

Another interesting aspect of our results with very low light intensities is the existence of a maximum quantum yield, which is constant over a range of low intensities. We also found that the maximum QY varies from film to film, which indicates that there are recombination losses that are intrinsic to each film, due probably to recombination at bulk defects [55]. Thus, these processes control the numbers of electrons and holes that can reach the surfaces of the particles. This idea has practical consequences in that the intrinsic quality of the TiO_2 particles, in terms of purity and crystalline quality, together with the film quality, must be important in determining the maximum attainable QY.

Serpone and coworkers have discussed the QY as a way of comparing different types of TiO_2 , e.g. from different

manufacturers [56]. Because it is somewhat difficult to quantify the actual light intensity that is absorbed, these workers have proposed that the photodegradation of phenol in water be used as a model reaction and that the QY for a particular reaction of interest should be normalized to that for phenol. This idea certainly has merit: a similar proposal could be made for the case of gas-phase photocatalysis. Here, the photodecomposition of 2-propanol could be a good candidate.

3.2.2. Mechanistic studies

Usually it is simply assumed that oxidative and reductive photocatalytic reactions take place simultaneously on TiO_2 particles, because it is very difficult to confirm this assumption by direct experimental measurements. As already discussed, it is a reasonable assumption, because otherwise, charge would build up on the particle. However, it is possible to set up a simple macroscopic model system that can be used to simulate model individual particles and is compatible with microelectrode detection of reaction products [57–62]. Such a system, shown in Fig. 7, involves a film that is half-covered with TiO_2 and half-covered with metallic regions, e.g. Pd or ITO. A scanning microelectrode can be positioned close to the surface, as close as $50 \mu\text{m}$. Its potential can be set at values at which either O_2 or H_2O_2 , for example, can be monitored as a function of time.

Our interest is to monitor the oxidation and reduction reactions separately in order to obtain information with which to determine the mechanism of the photocatalytic reaction. In photocatalytic reactions with metal-deposited TiO_2 particles and films, the deposited metal acts as a reduction site, thereby increasing the efficiency of photogenerated charge separation. Thus, a TiO_2 –ITO composite film can act as a simple model for the metal-deposited photocatalyst. A carbon microelectrode is employed to detect the reaction products. By positioning this electrode close to either the TiO_2 or the ITO surface (50 – $500 \mu\text{m}$), the oxidation and reduction reactions, respectively, can be monitored on these regions. Initially, the feasibility of the microelectrode method was confirmed by observing the cathodic current at the microelectrode in the vicinity of the TiO_2 surface and the anodic current next to the ITO surface in aqueous KCl solution under illumination [57]. Later this method was extended to detect hydrogen peroxide at the two types of regions separately by use of a ‘wired’ horseradish peroxidase microsensor fabricated on the carbon microelectrode surface [58]. Still later, it was found that peroxide could also be detected adequately by setting the microelectrode potential at a very positive potential ($+1.0 \text{ V}$ versus SCE) [60]. In addition, the carbon microelectrode is able to detect O_2 by setting the potential at a negative potential (-1.0 V versus SCE).

Some examples of the results obtained with this system are summarized below. In one of the early studies, it was found that H_2O_2 is produced to a much greater extent at the ITO portion of the illuminated TiO_2 –ITO composite surface, due to O_2 reduction [58]. In a subsequent study on the

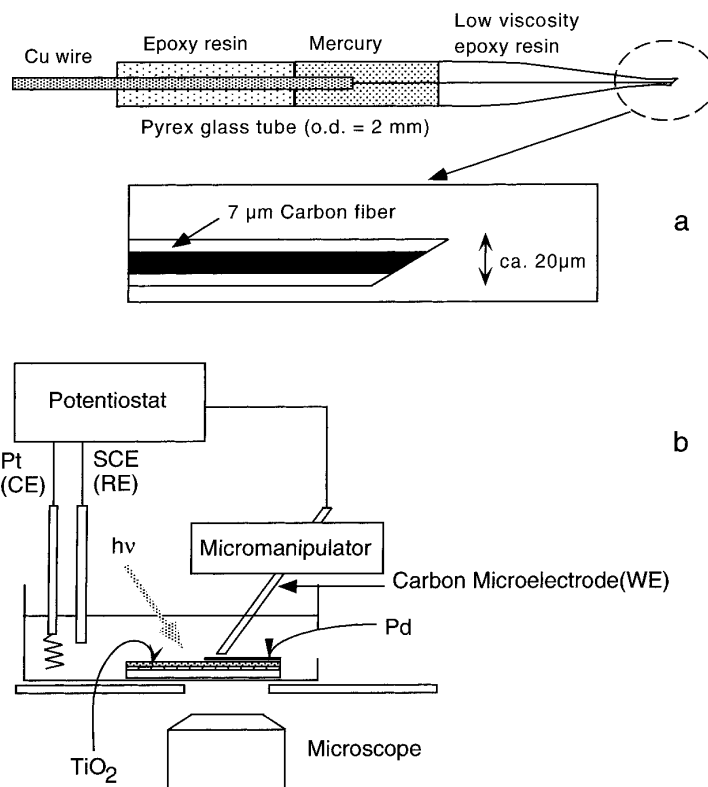


Fig. 7. (a) Schematic illustration of the carbon microelectrode structure; (b) experimental setup for the separate monitoring of oxidation and reduction reactions occurring on the TiO₂-ITO film.

separate detection of dissolved oxygen in aqueous solution at reducing regions (in this case, Pd) and oxidizing regions (TiO₂), using a carbon microelectrode, we found an increase in O₂ concentration near the TiO₂ surface and a decrease in the O₂ concentration near the TiO₂ surface under illumination (Fig. 8) [60]. Oxygen is produced via water oxidation on TiO₂:



Oxygen is consumed at the metallic electrode (ITO or Pd) via reduction, principally to peroxide.



although reduction to superoxide



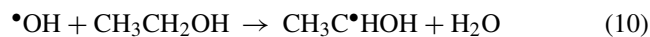
or to water may also contribute:



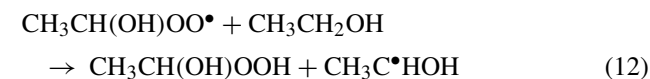
On an actual TiO₂ microparticle, depending upon whether there is a deposited catalyst, there can also be varying contributions of these latter three reactions. As discussed later, some photocatalytic reaction pathways can involve •O₂⁻ and, therefore, it appears to be a desirable product; as such, metallic catalysts may in fact be counter-productive in this

respect, if they promote the two- or four- electron reduction reactions.

In the presence of ethanol, however, dissolved oxygen was consumed at both TiO₂ and Pd sites, the consumption of oxygen being larger at the TiO₂ surface (Fig. 9) [60]. A possible scheme that is consistent with O₂ consumption at TiO₂ is:



producing an organoperoxy radical, which can either participate in a chain-type process



or can react further with O₂ to produce a tetroxide intermediate, as discussed later. The importance of radical intermediates was found to be great, as evidenced by the strong decrease in O₂ consumption in the presence of phenol, a radical scavenger.

A later study found that the consumption of O₂, over the illuminated TiO₂ portion is faster for the photodecomposi-

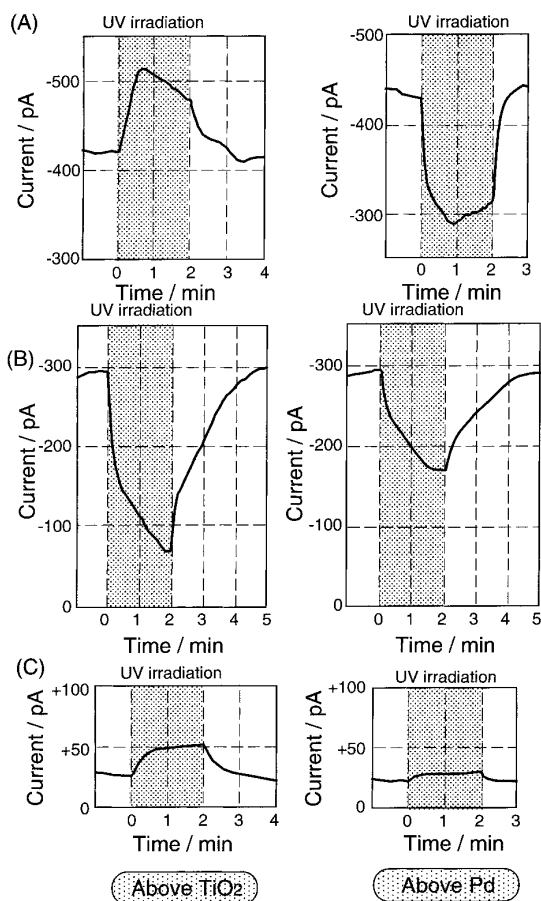


Fig. 8. Concentration changes of dissolved oxygen (directly proportional to cathodic current, -1 V vs. SCE) or H_2O_2 (proportional to anodic current, $+1\text{ V vs. SCE}$), measured separately above TiO_2 and Pd, caused by the photocatalytic reaction in the absence and presence of ethanol in aqueous solutions [60]. Hatched areas represent the time duration of the photoirradiation. (A) Concentration changes of dissolved oxygen due to photocatalytic reactions in aqueous solution without EtOH (light intensity, 9.5 mW cm^{-2}). (B) Concentration changes of dissolved oxygen due to photocatalytic reactions in 5 vol.% ethanol aqueous solution (light intensity, 2.5 mW cm^{-2}). (C) Concentration changes of H_2O_2 due to photocatalytic reactions in 5 vol.% ethanol aqueous solution (light intensity, 2.5 mW cm^{-2}).

tion of acetaldehyde compared to ethanol, due to the strong contribution of radical chain reactions for the latter [61]. In the presence of superoxide dismutase, the O_2 consumption decreased significantly in the case of ethanol but negligibly in the case of acetaldehyde (Fig. 10). Thus, it appears that the tetroxide pathway may be important for ethanol. It is well known, however, that aldehydes can decompose via radical-initiated chain reactions, consuming O_2 but not $\cdot\text{O}_2^-$, as shown in Fig. 11 [63]. Interestingly, we were also able to observe clear evidence for the chain-type mechanism in experiments involving acetaldehyde decomposition in the gas-phase [64], similar to those already discussed for 2-propanol [52]. With acetaldehyde, the QY exceeded the maximum value obtained for a certain film for 2-propanol oxidation (28%), (Fig. 12). As already discussed, the latter value may be considered to be an intrinsic maximum QY

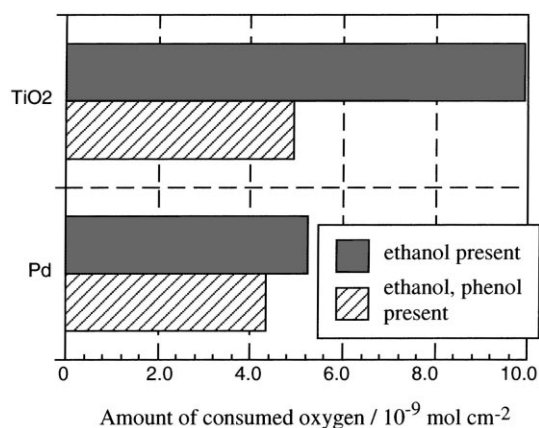


Fig. 9. Amounts of O_2 consumed as a result of photocatalytic reactions in ethanol-containing aqueous solution, with and without 0.1 M phenol present, under UV irradiation for 1 min [60]. The amount of O_2 consumed was estimated using a finite difference method from the oxygen concentration vs. time curves (light intensity, 2.5 mW cm^{-2} ; microelectrode potential, -1 V vs. SCE).

value for this particular film, suggesting that approximately 72% of the photogenerated electron-hole pairs recombine within the TiO_2 particles, before reaching the surface. Therefore, if the QY exceeds the intrinsic maximum value, it indicates that radical chain reactions are important, i.e. a single photon can cause more than one photodecomposition reaction.

Returning to the reaction pathways that involve superoxide, these have been treated in detail by Schwitzgebel et al. [65], as shown in Fig. 13. These reactions can operate on alkanes and their oxidation products, so that, with the exception of aldehydes, as noted above, any of the main types of C–H–O compounds, i.e. alcohols, ketones and carboxylic acids, can be decomposed in this fashion completely to CO_2 and TiO_2 . These pathways are probably also important in the decomposition of long-chain hydrocarbons, carboxylic acids, fats, oils and even long-chain polymers [66,67]. In these cases, it seems obvious, and indeed there is direct infrared evidence, that the hydrocarbon chains can be attacked at any point along their length, with C–C bond scission and subsequent degradation via the resulting aldehydes (Fig. 14). The latter may be unstable enough to account for the fact that they are not detected by IR on the TiO_2 film. Also, it is important to note that no gas phase products other than CO_2 are detected in the decomposition of octadecane, stearic acid and glycerol trioleate, demonstrating the safety of the photocatalytic approach to self-cleaning technology.

Additional fundamental understanding has been gained for the photocatalytic decomposition of stearic acid Langmuir–Blodgett films on both polycrystalline anatase films [68] and single crystal rutile [69] with the AFM technique. These studies have shown that, for less than full coverage, the photocatalytic decomposition process takes place at random locations on the film. In the case of full monolayers, the film structure very quickly is disturbed, with molecules aggregating into relatively tall ridges. It

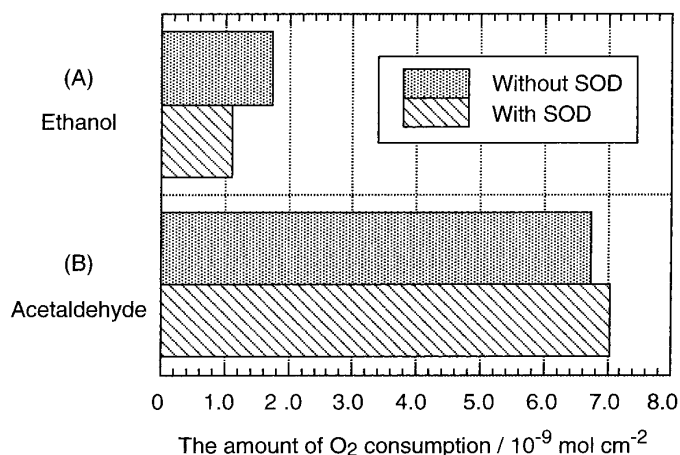


Fig. 10. Amounts of O_2 consumed during the initial 10 s by the photo-oxidation under UV irradiation in the absence and presence of SOD (5 mg l^{-1}) (microelectrode potential, -0.8 V vs. SCE; light intensity, 3 mW cm^{-2}): (A) amount of O_2 consumed in the 5% ethanol-containing PBS solution and (B) amount of O_2 consumed in the 5% acetaldehyde-containing PBS solution [61].

appears that there are randomly located active sites, which can become passivated by reaction products, and new sites can also form. In contrast to results obtained with thicker layers (100 nm), for which zero order kinetics were obtained, the LB film results obeyed first-order kinetics, which is reasonable because of the extremely limited amount of material.

One of the most interesting results that we have obtained is that photocatalytic degradation can take place at a distance of as much as $500 \mu\text{m}$ away from the TiO_2 surface [70]. Of course, the reaction rate decreases with distance, however, as shown by measurements in which films of methylene blue on glass were separated from a TiO_2 film by a gap, which was varied from 12.5 to $500 \mu\text{m}$. Surprisingly, the effect observed in both dry and humidified oxygen atmosphere was similar, indicating the possibility of a species such as singlet oxygen being an active agent. However, small amounts of moisture in the film may have been involved, so that a species like H_2O_2 could also be an active agent. More detailed results are needed before the active agents can be conclusively identified. As discussed later, it was also found that bacteria can be killed at distances of $50 \mu\text{m}$ from a TiO_2 surface [71]. In that case, the active agent was proposed to be H_2O_2 , although other active oxygen species were thought to be involved in a cooperative effect.

It should be pointed out that, aside from very low intensity illumination, over a wide range of experimental conditions, photocatalytic decomposition follows reasonably well-known behavior, i.e. first-order kinetics in the adsorbed concentration of the organic compound and one-half order in light intensity, due to recombination.

$$r = k\Gamma I^{1/2} \quad (14)$$

Here r is the reaction rate, k the first-order rate constant, Γ the concentration per unit real surface area, and I the light intensity. Many organic compounds, as well as noxious gases such as H_2S , follow Langmuir adsorption behavior, so

that this simple equation can be converted into the familiar Langmuir–Hinshelwood form by substituting the expression for Γ

$$\Gamma^{-1} = \Gamma_0^{-1} + (K_{\text{eq}}c)^{-1} \quad (15)$$

where Γ_0 is the surface concentration at full coverage, K_{eq} the adsorption equilibrium constant and c the gas-phase or liquid-phase concentration.

An example of this type of behavior is provided by our recent work with the gas-phase decomposition of formaldehyde and acetaldehyde, which have been implicated in the ‘sick-building’ syndrome [72]. These two compounds were found to obey Langmuir adsorption, and Langmuir–Hinshelwood kinetics were followed (Fig. 15). It was also found that formaldehyde adsorbs relatively strongly on the TiO_2 surface, which means that TiO_2 can be effective even at low formaldehyde concentrations. The adsorption characteristics of TiO_2 in this case are similar if not better than those of activated carbon.

Under conditions of high light intensity and low reactant concentration, it is possible to reach a point at which the mass transport of the organic compound is no longer sufficient to maintain the adsorption equilibrium. Such conditions have been explored in further work with 2-propanol as a model reactant [73]. These results show that it is possible to clearly distinguish the experimental conditions under which various types of kinetics are operative, e.g. light-limited, ordinary Langmuir–Hinshelwood type, and mass-transport-limited. These types of conditions can be seen in a plot of light intensity versus reactant concentration (Fig. 16). Such plots must also take into account the Langmuir isotherm characteristics of the particular reactant of interest on the type of TiO_2 being considered.

One additional topic related to the mechanisms of photocatalytic reactions has to do with the fact that, under ordinary conditions, TiO_2 can be used without an additional

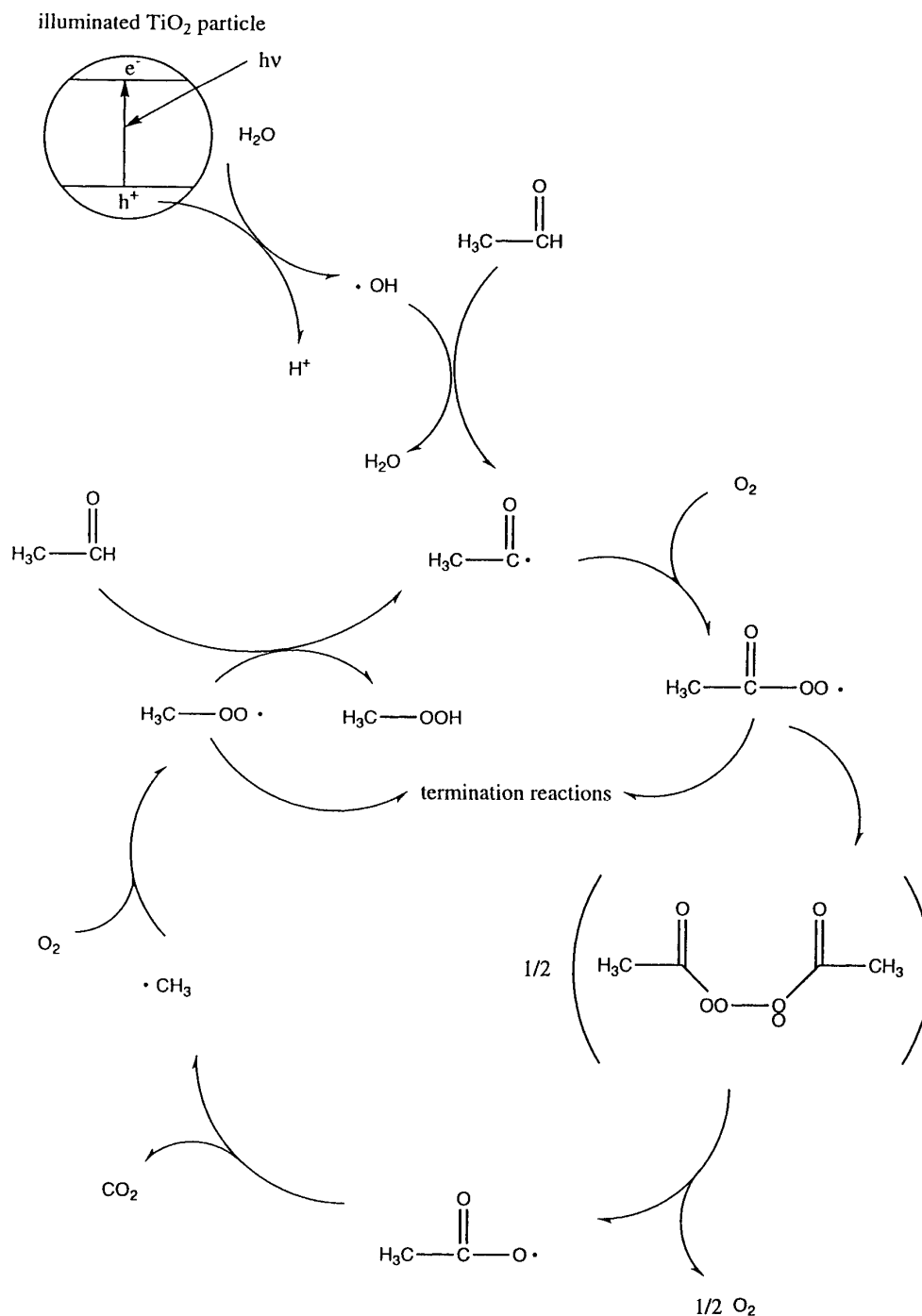


Fig. 11. Schematic diagram of processes occurring during photocatalytic oxidation of acetaldehyde on an illuminated TiO_2 particle [6].

catalyst. With the use of the scanning microelectrode technique, we were able to show clearly that both oxidation and reduction reactions can take place on the illuminated TiO_2 surface (Fig. 17) [62]. This is a crucial point, which needs to be further explored in detail on the microscopic scale. We must answer the question of where each type of reaction takes place within a TiO_2 film or even on an individual particle.

3.2.3. Applications

Over the past several years, a large number of applications of photocatalytic technology have been examined in Japan. One measure of the level of interest is the large number of participants (close to 800) that attended a recent symposium on photocatalysis in Tokyo. Some selected applications of photocatalytic technology are listed in Table 1.

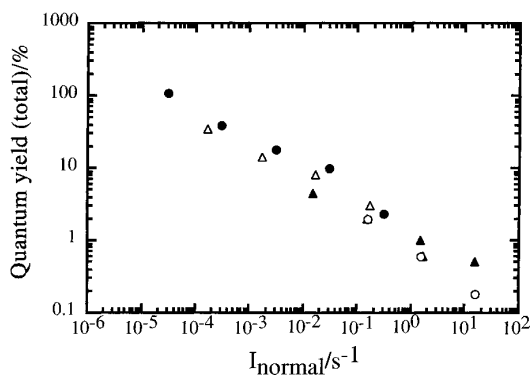


Fig. 12. Plots of QY_{total} values vs. I_{norm} , defined as the ratio of the number of absorbed photons to the number of adsorbed acetaldehyde molecules (initial acetaldehyde concentration: (●) 1000 ppmv; (Δ) 100 ppmv; (▲) 10 ppmv and (○) 1 ppmv) [64].

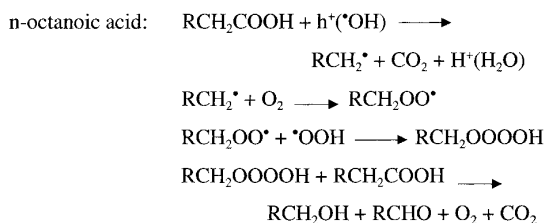
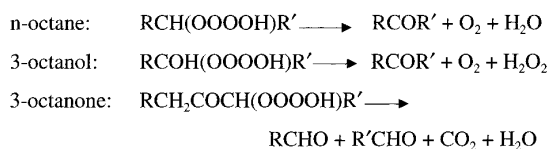


Fig. 13. Decomposition reactions of tetraoxide intermediates formed in the photocatalytic reactions of various substrates involving superoxide [65].

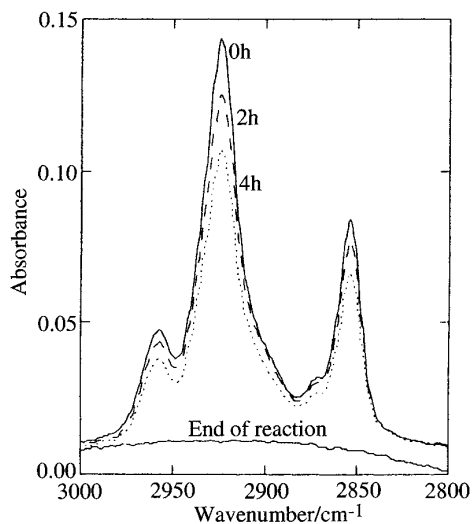


Fig. 14. A typical IR composition profile for octadecane at 25°C. Incident light intensity = 1.1 mW cm^{-2} [66].

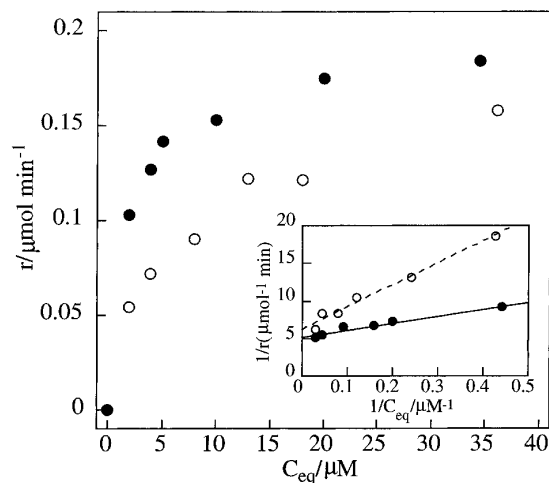


Fig. 15. Dependence of reaction rates on the initial reactant concentrations [72]. Open circles (○) represent acetaldehyde whereas the filled circles (●) represent formaldehyde. The reaction rates were calculated within 10 min of reaction. The initial concentration of formaldehyde was varied from 30 to 2000 ppmv, respectively, under otherwise standard reaction conditions, i.e. $I=1.0 \text{ mW cm}^{-2}$; temperature, $\approx 22^\circ\text{C}$; and relative humidity, 40%.

Some of the applications and supporting technology have also been reported in the literature. These have included the development of TiO_2 films [45,46,48,74], TiO_2 -containing paper [75], microporous textured TiO_2 films [50], self-cleaning TiO_2 -coated glass covers for highway tunnel lamps, [23] and a flow-type photoreactor for water purification [76].

There have also been significant developments in photocatalytic technology in the US. For example, TiO_2 -coated glass microbubbles have been developed for the specific

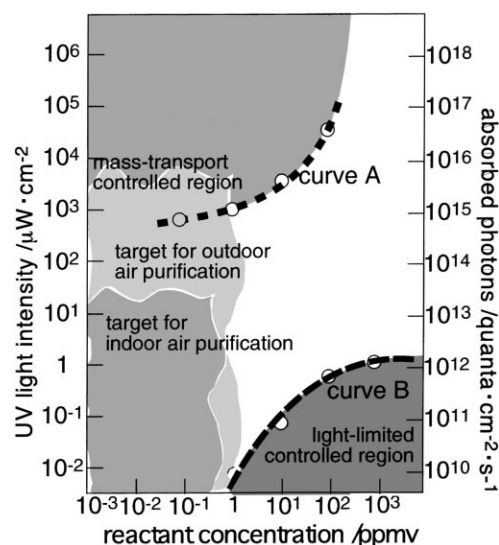


Fig. 16. Plots of light intensity vs. initial reactant concentration showing pure mass transport-limited and pure light intensity-limited conditions for photodegradation of gas-phase organics [73].

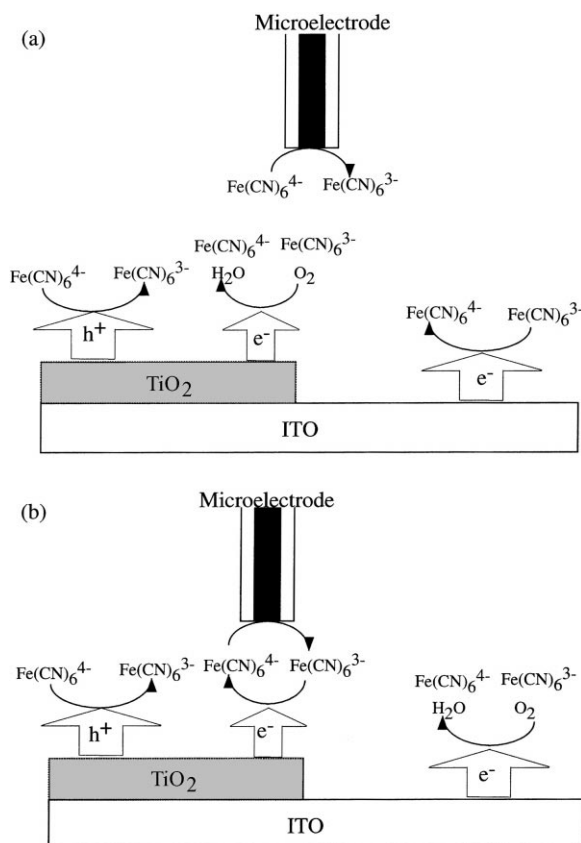


Fig. 17. Mechanisms proposed for the photochemical reactions between the microelectrode and the irradiated TiO₂ surface when the microelectrode is located at a position (a) where the positive feedback effect is negligible and (b) where the positive feedback effect is nonnegligible [62].

application of cleanup of oil films on water, particularly after the major portion of an oil spill has been removed. Self-cleaning window glass has been developed, as well as TiO₂-containing, self-cleaning paint.

3.3. Photocatalytic sterilization

As already mentioned, TiO₂ photocatalysts can be used to kill bacteria and, therefore, self-sterilizing surfaces can be prepared. The first work of this type was carried out with *E. coli* suspensions [71,77]. A typical experiment involves placing 150 μ l of an *E. coli* suspension, containing 3×10^4 cells on an illuminated TiO₂-coated glass plate (1 mW cm^{-2} UV light) [71]. Under these conditions, there were no surviving cells after only 1 h of illumination. By contrast, after 4 h under UV illumination without a TiO₂ film, only 50% of the cells were killed. As mentioned, even when the cells were separated from the TiO₂ film by a 50 μ m PTFE membrane, with 0.4 μ m pores, the cells were still killed: after 4 h, there were none remaining. There was little effect of mannitol, a hydroxyl radical scavenger. Peroxide was identified as one of the active agents.

Food poisoning from *E. coli* is potentially highly dangerous: in the summer of 1996 in Western Japan, there was

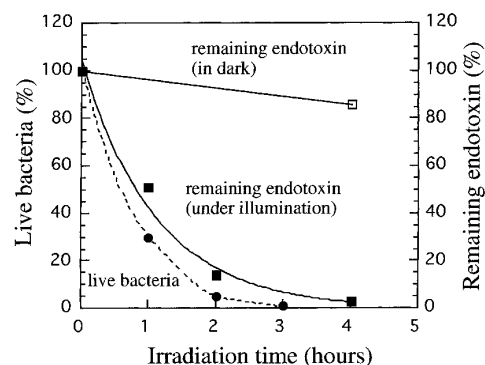


Fig. 18. Sterilization of *E. coli* and endotoxin decomposition (endotoxin amount: 3–8 EU/cc=100%) [77]. Both sterilization and endotoxin decomposition commence immediately.

a serious outbreak, in which nearly 1800 people, including many children, were hospitalized and twelve died.¹ The poisoning was caused by the O-157 endotoxin. Subsequently, our group examined TiO₂ photocatalysis as a means of decomposing this deadly toxin. It was found that 2 h were required to decompose most of the toxin and 4 h were required to completely decompose it under UV illumination (0.4 W cm^{-2}) on a TiO₂ film (Fig. 18) [77]. This can be contrasted with other techniques that have been developed, e.g. thermal treatment at 250°C for 30 min or chemical treatment in ethanol containing NaOH.

3.4. Photocatalytic cancer treatment

Cancer treatment is one of the most important topics that is associated with photocatalysis. While surgical, radiological, immunological, thermotherapeutic, and chemotherapeutic treatments have been developed and are contributing to patient treatment, cancer has remained the top cause of death in Japan since 1980.

As far back as the mid-1980s, we were interested in using the strong oxidizing power of illuminated TiO₂ to kill tumor cells [78]. In the first experiments a polarized, illuminated TiO₂ film electrode, and an illuminated TiO₂ colloidal suspension was also found to be effective in killing HeLe cells. A series of studies followed, in which we examined various experimental conditions [79–81], including the effect of superoxide dismutase, which enhances the effect, due to the production of peroxide. In addition, it was found possible to selectively kill a single cancer cell using a polarized, illuminated TiO₂ microelectrode [82].

While we were pursuing this idea, we were able to start joint research with urologists at the School of Medicine, Yokohama City University. As part of this collaboration, we began to conduct animal experiments. We implanted cancer cells under the skin of mice to cause tumors to form. When

¹ Statistics provided by the Ministry of Health and Welfare of Japan.

Table 1
Selected applications of photocatalysis

Property	Category	Application
Self-cleaning	Materials for residential and office buildings	Exterior tiles, kitchen and bathroom components, interior furnishings, plastic surfaces, aluminium siding, building stone and curtains, paper window blinds
	Indoor and outdoor lamps and related systems	Translucent paper for indoor lamp covers, coatings on fluorescent lamps and highway tunnel lamp cover glass
	Materials for roads	Tunnel wall, soundproofed wall, traffic signs and reflectors
	Others	Tent material, cloth for hospital garments and uniforms and spray coatings for cars
Air cleaning	Indoor air cleaners	Room air cleaner, photocatalyst-equipped air conditioners and interior air cleaner for factories
	Outdoor air purifiers	Concrete for highways, roadways and footpaths, tunnel walls, soundproof walls and building walls
Water purification	Drinking water	River water, ground water, lakes and water-storage tanks
	Others	Fish feeding tanks, drainage water and industrial wastewater
Antitumor activity	Cancer therapy	Endoscopic-like instruments
Self-sterilizing	Hospital	Tiles to cover the floor and walls of operating rooms, silicone rubber for medical catheters and hospital garments and uniforms
	Others	Public rest rooms, bathrooms and rat breeding rooms

the size of the tumors grew to about 0.5 cm, we injected a solution containing fine particles of titanium dioxide. After 2 or 3 days, we cut open the skin to expose the tumor and irradiated it. This treatment clearly inhibited the tumor growth (Fig. 19). After 13 more days, we repeated the treatment with the titanium dioxide photocatalyst and observed a further marked antineoplastic effect. The results were reported subsequently reported in Cancer Research [83].

However, this technique was not effective in stopping a cancer that had grown beyond a certain size. We then developed a device to allow the cancer to be exposed to light while titanium dioxide powder was being added to the tumor (Fig. 20). This device, built by modifying an endoscope, should make it possible for us to access various parts of the human body.

There are still some problems to be solved before such a device can be put into practical use. However, because the photocatalytic reactions only occur under illumination, it is possible to selectively destroy cancer cells, if there is a technique available for illumination of the tumor.

Although this device requires further refinement, it appears likely that it could be used on many types of cancer. Tumors of organs that can be irradiated by the use of an endoscope could be treated in this way, e.g. those of the digestive organs, such as the stomach and colon; respiratory organs, such as the pharynx and bronchus; urinary system organs, such as the bladder and ureter; reproductive organs, such as the uterus and cervix; and, of course, the skin.

Obviously, the excitation light should not cause mutations in normal cells. The results of animal experiments have shown that near-UV rays, with wavelengths of 300–400 nm, which are used in photocatalytic reactions, are safe.

4. Photo-induced superhydrophilicity

4.1. Background

It is one of the unique aspects of TiO_2 that there are actually two distinct photo-induced phenomena: the first is the well-known original photocatalytic phenomenon, which leads to the breakdown of organics, and the second, more recently discovered one involves high wettability. This latter phenomenon we have termed ‘superhydrophilicity’. Even though they are intrinsically different processes, they can, and in fact must, take place simultaneously on the same TiO_2 surface. Depending upon the composition and the processing, the surface can have more photocatalytic character and less superhydrophilic character, or vice versa.

The photocatalytic phenomenon has been studied intensively now for a number of years by many groups, and it is fairly well understood. Because TiO_2 is a semiconductor with a band gap of about 3.0 eV, UV light (with wavelengths shorter than ~ 400 nm) can excite pairs of electrons and holes, as already discussed. The photogenerated electrons then react with molecular oxygen (O_2) to produce superoxide radical anions ($\text{O}_2^{\cdot-}$), and the photogenerated holes react with water to produce hydroxyl (OH^{\cdot}) radicals. These two types of rather reactive radicals then work together to decompose organic compounds. The longer the film is illuminated with UV light, the more organic material can be decomposed, so that, for example, an oily stain on the surface would gradually disappear.

The second phenomenon, superhydrophilicity, has only recently been studied. This effect was actually discovered by accident in work that was being carried out at the laboratories of TOTO Inc., in 1995. It was found that, if a TiO_2 film

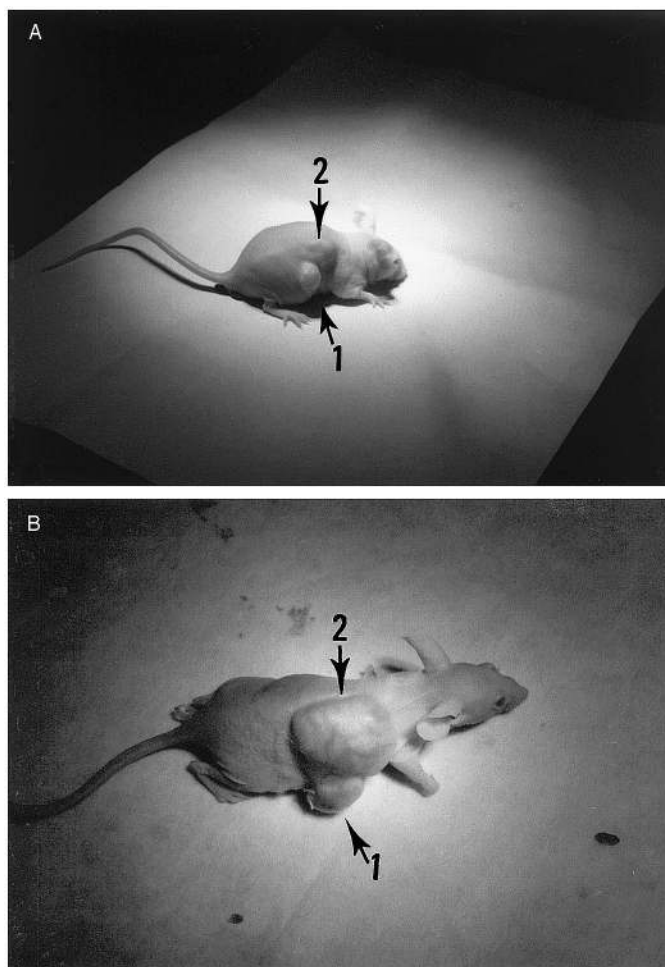


Fig. 19. Animal test of photocatalytic cancer therapy; photograph of nude mouse just after initial treatment (A) and 4 weeks after treatment (B) [21]. TiO_2 powder (0.4 mg) was injected into Tumor 1. Tumor 2, which was not injected with TiO_2 particles, was also opened surgically. Both tumors were irradiated by a Hg lamp for 1 h.

is prepared with a certain percentage of SiO_2 , it acquires superhydrophilic properties after UV illumination. In this case, electrons and holes are still produced, but they react in a different way. The electrons tend to reduce the Ti(IV) cations to the Ti(III) state, and the holes oxidize the O^{2-} anions. In the process, oxygen atoms are ejected, creating oxygen vacancies (Fig. 21). Water molecules can then occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic. The longer the surface is illuminated with UV light, the smaller the contact angle for water becomes; after about 30 min or so under a moderate intensity UV light source, the contact angle approaches zero, meaning that water has a tendency to spread perfectly across the surface.

Various companies have been trying to develop self-cleaning surfaces, especially windows, for a long time. One approach has indeed been to try to make the surface highly hydrophilic, so that a stream of water would be enough to displace stain-causing organic compounds. Such approaches have often involved the use of surfactants. The objective,

in effect, is to make the glass permanently surface-active. However, the problem is that such coatings lack durability, hardness and weather resistance.

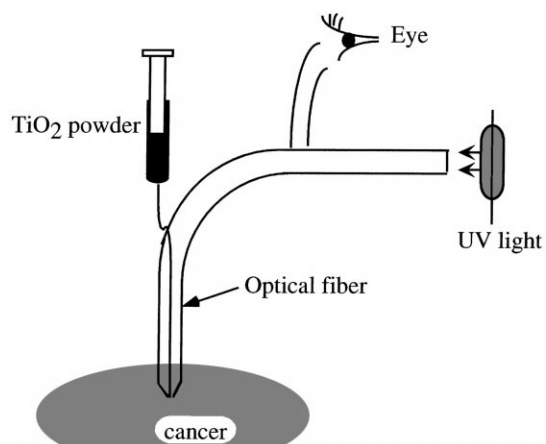


Fig. 20. Future process of photocatalytic cancer therapy [21].

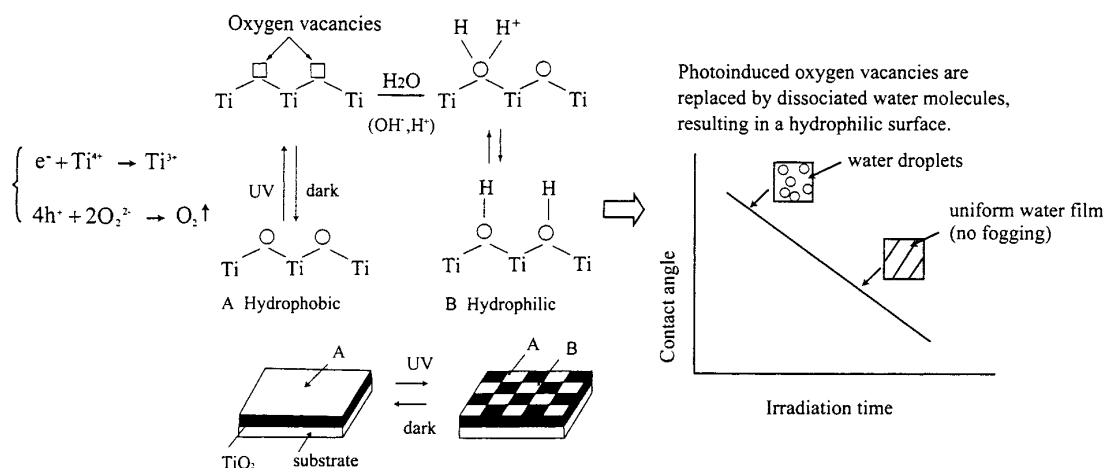


Fig. 21. Mechanism of photo-induced hydrophilicity [21].

In contrast, TiO_2 coatings can maintain their hydrophilic properties indefinitely, as long as they are illuminated. Making use of the idea of cleaning by a stream of water, coated windows can be cleaned by rainfall.

Other related applications for hydrophilic glass include windows that are easily cleaned by water alone, and anti-fogging or anti-beading windows and mirrors. Beading of rainwater on automobile side-view mirrors can be a serious safety problem, and now this problem has been virtually solved. We will discuss applications in further detail later.

4.2. Fundamental studies

In our first published study on the superhydrophilic effect, we reported results of friction force microscopy (FFM) on an illuminated rutile single crystal [84]. Specifically, it was found that the initially featureless surface become covered with rectangular domains oriented parallel to the (001) direction (Fig. 22). The light-shaded domains exhibit greater frictional force, indicating that they are hydrophilic, because the Si_3N_4 cantilever tip itself is hydrophilic. The gray shade of the background indicates that it has remained hydrophobic. The particularly interesting characteristic of the surface is that it is not only hydrophilic but also oleophilic. In fact, this is the only report of which we are aware of a single surface exhibiting both hydrophilic and oleophilic properties. The implication is that oil can displace water as well as water displacing oil. The latter effect can be seen clearly in the series of photographs in Fig. 23.

The examination of amphiphilic surfaces is typically carried out by means of contact angle measurements for water or other liquids on TiO_2 anatase thin films. For example, the water contact angle for a freshly prepared film averages $15 \pm 1^\circ$. At this point, if the surface is illuminated with UV light of $\sim 1 \mu\text{m cm}^{-2}$ for only ~ 30 min, the wetting properties change drastically. After the sample has been stored in the dark for 2 months, the water contact angle increases to

$72 \pm 1^\circ$. When a water droplet touches the UV-illuminated film, it spreads immediately, leaving an irregular shape on the surface with a contact angle of $0 \pm 1^\circ$. The contact angle for glycerol trioleate (GT), a common component of vegetable oils, for the TiO_2 surface has also been measured. Prior to UV illumination, the GT contact angle averages $10 \pm 1^\circ$, indicating that the surface is oleophilic in addition to being hydrophobic, as already discussed. Surprisingly, after UV illumination, a GT droplet also spreads out, resulting in a contact angle of $0 \pm 1^\circ$. Additional experiments were

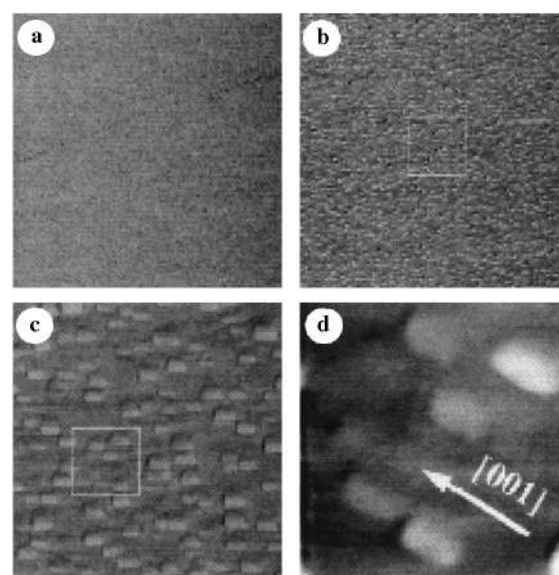


Fig. 22. (a) FFM image ($5 \mu\text{m} \times 5 \mu\text{m}$) of the TiO_2 (110) surface before UV illumination; (b) FFM image ($5 \mu\text{m} \times 5 \mu\text{m}$) of the same surface after UV illumination; (c) a medium scale ($1000 \text{ nm} \times 1000 \text{ nm}$) FFM image showing the enlargement of the framed area in (b) and (d) a further enlarged topographic image ($240 \text{ nm} \times 240 \text{ nm}$), corresponding to the framed area in (c) [85].

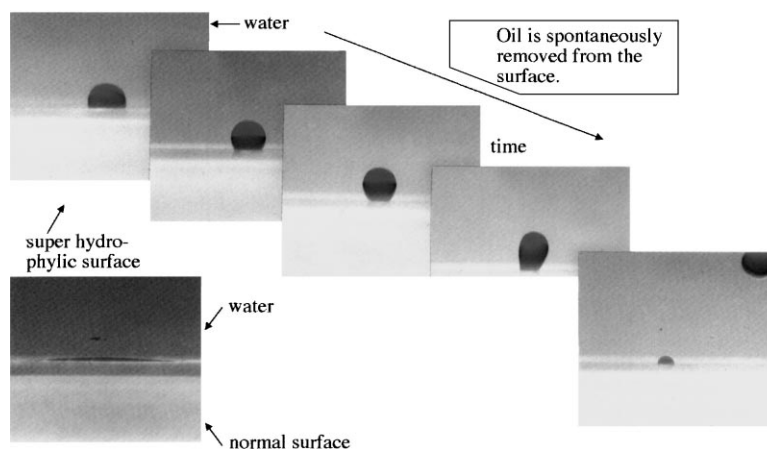


Fig. 23. Easily washable surface due to the superhydrophilic effect [21].

carried out using other liquids, e.g. hexadecane, ethylene glycol, and tetralin. Distinct, non-zero contact angles resulted for the hydrophobic TiO_2 surface. However, all of the liquids spread completely on a UV-illuminated TiO_2 surface, with contact angles of $0 \pm 1^\circ$. From these results we conclude that UV illumination creates a surface that is both highly hydrophilic and highly oleophilic. These wettability changes have been observed on both anatase and rutile TiO_2 surfaces, in the form of either polycrystalline films or single crystals, independent of their photocatalytic activities. Even after TiO_2 films have been stored in the dark for a few days, the high amphiphilicity of the TiO_2 surface is maintained. During longer storage periods in the dark, the water contact angle gradually increases in, showing that the stable condition is hydrophobic. However, the high amphiphilicity can be repeatedly regenerated by means of UV illumination [85].

Fourier transform infrared measurements showed that an illuminated anatase TiO_2 thin film reversibly adsorbs water, both dissociatively and without dissociation, as a result of UV illumination [85]. Subsequent X-ray photoelectron spectroscopic measurements (O 1s) also clearly showed evidence for dissociatively and non-dissociatively adsorbed water. However, there was surprisingly little change in the Ti 2p peaks. More Ti^{3+} might be expected to show up as a low binding energy shoulder. Research is currently in progress to establish the mechanisms for the hydrophilic effect in detail. However, for the time being, the scheme shown in Fig. 21 is a reasonable one, with photons of $>3.0\text{ eV}$ inducing the ejection of oxygen anions that are bonded to only two Ti^{4+} cations rather than three. The bridging oxygens are easier to remove due to the smaller number of bonds. Thus, it should be easier to produce hydrophilic surfaces on crystal faces that intrinsically contain larger numbers of bridging oxygens. For example, the (100) faces of rutile should contain the largest coverage of such sites, followed by the (110) and (001) faces (Fig. 24). Indeed it was found that the (001) face was significantly less active in terms of acquiring hydrophilic properties compared to the other two faces. For

example, starting at a water contact angle of ca. 55° , the angle decreased to below 5° in 15 min on the (100) face, whereas, starting from an angle of ca. 75° , it only decreased to ca. 50° after 15 min on the (001) surface [86]. In the latter case, it is possible that the surface can undergo some restructuring under illumination, so that bridging sites are slowly created.

The general model of the TiO_2 surface becoming slightly reduced under illumination is supported by the fact that ultrasonic treatment can rather rapidly reconvert a hydrophilic surface to the hydrophobic state [87]. Ultrasonication of water is known to produce $\bullet\text{OH}$ radicals, which would effectively remove surface $\bullet\text{H}$ species in an oxidative reaction.

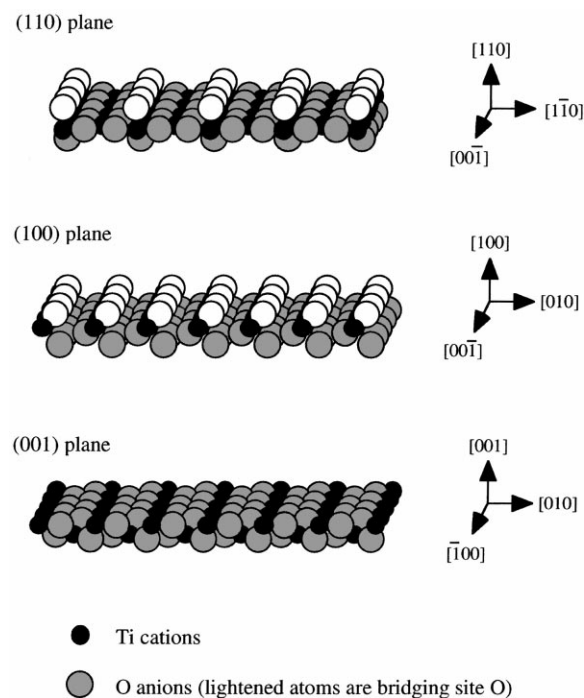


Fig. 24. Schematic illustration of the atomic alignments on ideal TiO_2 (110), (100), and (001) single crystal faces [86].

Table 2
Applications of superhydrophilic technology

Property	Category	Application
Self-cleaning	Roads	Tunnel lighting, tunnel walls, traffic signs and sound proof walls
	Houses	Tiles on kitchen walls and bathrooms, exterior tiles, roofs and windows
	Buildings	Aluminum panels, tiles, building stone, crystalized glass and glass film
	Agriculture	Plastic and glass greenhouses
	Electrical and electronic equipment	Computer displays and cover glass for solar cells
	Vehicles	Paint work, coatings for exterior surfaces of windows and headlights
	Daily necessities and consumer products	Tableware, kitchenware and spray-on anti-fouling coatings
Anti-fogging property	Paint	General-purpose paints and coatings
	Roads	Road mirrors
	Houses	Mirrors for bathrooms and dressers
	Stores	Refrigerated showcases
	Electrical and electronic equipment	Heat exchangers for air conditioners and high-voltage electric transmission equipment
		Inside surfaces of windows, glass films, rear-view mirrors and windshields
		Spray-on antifogging coatings and films
	Daily necessities and consumer products	General-purpose paints and coatings
	Paint	Optical lenses
	Optical instruments	
Bio-compatibility	Medical instruments and supplies	Contact lenses and catheters

As already mentioned, the mechanisms involved in the superhydrophilic effect continue to be a subject of intense research. An interesting aspect is that a number of different metal oxides have now been examined in terms of both hydrophilic properties and photocatalytic properties [88]. Out of a large number examined, there were examples of all four possible combinations of behavior: (1) both photocatalytic and hydrophilic effects are observed; (2) only the photocatalytic effect is observed; (3) only the hydrophilic effect is observed and (4) neither effect is observed. Thus, the fundamental explanations of both types of effects will eventually have to take into account these fascinating results. It may also be possible to fine-tune materials, through the use of mixed oxides, for example, to design precisely controlled properties, including the band-gap energy.

4.3. Applications

There is an extremely wide range of applications for superhydrophilic technology; selected ones are listed in Table 2; and new ones are being contemplated all the time. Here, we will briefly discuss a two typical examples, antifogging surfaces, and self-cleaning building materials.

Fogging of the surface of mirrors and glass occurs when humid air condenses, with the formation of many small water droplets, which scatter light. On a superhydrophilic surface, no water droplets are formed. Instead, a uniform film of water can form on the surface, and this film does not scatter light. It is also possible, depending on the humidity, for the water film to be sufficiently thin that it evaporates quickly.

The opposite approach, i.e. making water droplets easier to remove by imparting water repellency to the surface of

glass, has also been the subject of intense research efforts. This approach also has merit; with it, the water droplets merely roll off the surface, as shown in a recent paper by Nakajima et al. [89] in which a superhydrophobic surface was reported.

Returning to the subject of hydrophilic surfaces, we have compared the behavior of a superhydrophilic mirror and a normal mirror when exposed to steam. The normal mirror quickly fogs, but the superhydrophilic one retains its clarity. Mirrors with superhydrophilic coatings retain their capacity for photoinduced wetting semipermanently, at least for several years. Various glass products, i.e. mirrors and eyeglasses, can now be imparted with antifogging functions using this new technology, with simple processing and at low cost. In fact, many models of Japanese cars are being equipped with antifogging, antibeadng superhydrophilic side-view mirrors.

Stain-proofing, self-cleaning properties can now be bestowed on many different types of surface by means of the superhydrophilic effect. To take an example, a plastic surface smeared with oil can not normally be cleaned unless one uses detergent. A superhydrophilic surface, even though it is amphiphilic, however, has a higher affinity for water than for oil, that is, when water is in excess, the opposite being true when the oil phase is in excess. Thus, an oil smear on a plastic utensil can be spontaneously released from the surface when it is simply soaked in water (Fig. 23). Based on this characteristic, a kitchen exhaust fan which is likely to be covered with oil, could be easily cleaned by water if the fan blades were coated with a superhydrophilic film.

Outdoor applications of this technique are also possible. Next to highways, most of the exterior walls of buildings

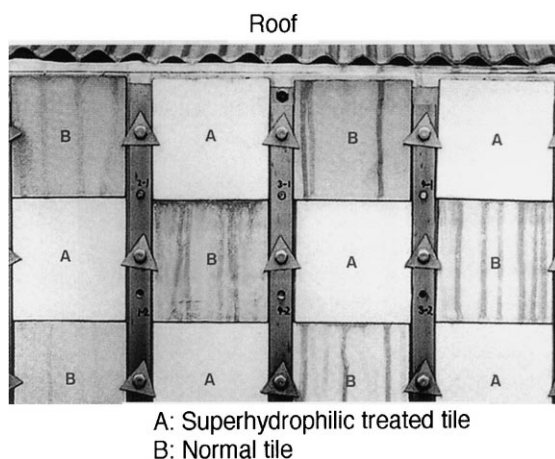


Fig. 25. Field test of stain-resistant exterior tiles in polluted urban air [85].

become soiled from automotive exhaust fumes, which contain oily components. If the building materials are coated with a superhydrophilic photocatalyst, the dirt on the walls can be washed away with rainfall. Alternatively, the walls can be sprayed with water.

The susceptibility of an exterior building material to soiling is closely related to its contact angle with water. A material used on the outside walls of a building is actually more likely to be soiled if it is more water-repellent. Thus, plastic is more likely to be soiled than sheet glass or tiles. A water-repellent material like a fluorocarbon plastic is the most likely to be soiled. A superhydrophilic material that shows a water contact angle of zero degrees is far less likely to be smeared than any other material. Shown in Fig. 25 is the smear-resistant effect of a superhydrophilic coating on an exterior concrete wall. Specially treated panels were mixed with regular concrete panels in a checkerboard pattern; the contrast was strong between the regular ones, on which soiling was very conspicuous, and the hydrophilically coated material, which were not soiled at all. This type of coating is projected to have a life of at least 10 years.

As already mentioned, the superhydrophilic coating has the characteristic that water droplets tend to spread out, meaning that they can dry quickly. The formation of dew on indoor glass panes, which often happens in winter, may be prevented by use of hydrophilic glass. In vinyl greenhouse farming, coating the inside surface of the vinyl with a superhydrophilic film can prevent the formation of dew, which might otherwise drop on the plants and cause rotting. Superhydrophilicity can also prevent underwater bubbles from forming on a surface, suggesting many possible applications based on this characteristic.

The photocatalytic technology described in earlier chapters has been applied to the decomposition of noxious gases, odor-causing gases, dirt, etc. In other words, that particular technology involves materials that have been carried to the surface from the surrounding environment. The superhy-

drophilic effect, on the other hand, is based on a concept of altering the properties of the surface itself by photocatalytic action. While both technologies are applied to the prevention of soiling, their basic mechanisms are quite different from each other. The basic idea is that the same titanium dioxide material can have both types of properties, photocatalytic and superhydrophilic, in varying proportions, depending on the composition and the manufacturing process. For a given application, the desired proportions of these properties must be carefully designed.

Thus, the applications of superhydrophilic technology are certainly not limited to antifogging and self-cleaning. The scope of this technology will no doubt be extended to as yet unknown fields.

Photocatalytic technology inherently requires a certain minimal light intensity, and the superhydrophilic effect is similar. When it is to be used indoors, the quantity of light provided by indoor lighting may not be sufficient. In the future, our research and development efforts will focus on this point. In particular, we will focus on the areas of material properties and lighting techniques, so that the maximum possible use can be made of available light in order to achieve the desired effect.

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