

Recent advances in heterogeneous TiO₂ photocatalysis

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Abstract. Current progress in the area of photocatalysis is presented, particularly regarding technological applications. Highly efficient TiO₂ films on different substrates such as tile and glass have been developed for indoor environmental clean-up. TiO₂ films coated on SiO₂-precoated soda lime glass showed about 80% transparency and high photocatalytic activity towards the decomposition of thin oil films. A novel phenomenon, superhydrophilicity, has been observed on these transparent TiO₂ coatings. In addition, we have made use of a microelectrode system to monitor oxidation and reduction products separately. The mechanistic and kinetic aspects of TiO₂ photocatalysis are discussed.

Keywords. Titanium dioxide; photo catalysis; hydrophilicity; photo catalytic degradation.

1. Introduction

Titanium dioxide, used for many years in such applications as paint pigments and scratch-resistant optical coatings, can also display high activity for photocatalysis, which chemists and chemical engineers are beginning to exploit. The surface of TiO₂ has a very high oxidation potential (3.0 V vs. SHE), which makes it capable of breaking down many organic substances. The oxidation potential of TiO₂ is considerably higher than that of more conventional oxidizing agents such as chlorine (1.36 V vs. SHE) and ozone (2.07 V vs. SHE). The strong oxidizing power of the photogenerated holes, together with the chemical inertness and non-toxicity of TiO₂, have made it an attractive photocatalyst. The area of photocatalysis has seen explosive growth, particularly during the past five years. The general mechanism of photocatalysis on the TiO₂ surface involves the oxidation of surface hydroxyl groups, which participate in the photocatalytic oxidation process. Although direct oxidation of substrates by photogenerated holes is possible, the involvement of [•]OH in the oxidation process has gained much experimental support. To drive the photocatalytic reaction and maintain charge neutrality, oxygen undergoes reduction in aerated aqueous media, resulting in the formation of O₂^{•-} and H₂O₂, which in turn participate in further oxidation processes. Recently, Heller's group has demonstrated the crucial role of oxygen in the photocatalytic oxidation of certain types of organic substrates and has suggested that, although photogenerated valance band holes initiate the process, the actual oxidizer is a reduced form of molecular oxygen¹. H₂O₂ can also be produced via water oxidation by photogenerated holes. It is not possible to determine the relative extent of these two reactions using conventional analytical methods. Recently we have succeeded in developing novel and simple microsensors systems for the detection of catalytic products in different

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microscopically localized areas of the photocatalyst surface, for example, areas in which oxidation and reduction take place². Using a “wired” horseradish peroxide microsensor, positioned close to the surface of a TiO₂-ITO (indium tin oxide) composite film, H₂O₂ production via photogenerated hole-mediated oxidation of water and photogenerated electron-mediated reduction of oxygen were monitored independently, and it was found that the majority of H₂O₂ was produced via reduction on the ITO portion³.

Much of the scientific knowledge that has been gained in the area of semiconductor/electrolyte interfaces during the past three decades⁴⁻⁷ is now being applied in the area of semiconductor-based photocatalysis⁸⁻¹². In the eighties researchers began investigating the ability of TiO₂ to photocatalyze organic reactions,¹³⁻¹⁶ recover precious metals¹⁷, and treat waste water¹⁸⁻²⁰. While other photocatalysts require intense ultraviolet light to process large volumes of materials, TiO₂ photocatalysts make effective use of weak UV light. One of the particularly noteworthy applications of semiconductor photocatalysis is the development of TiO₂-coated glass microbubbles for use in the photodegradation of oil and chemical slicks on water, as investigated by Heller's group²¹. Researchers are also in the process of developing photocatalytic paints requiring bases resistant to oxidation, which will pave the way for self-cleaning houses, tunnels and roofs. An American company (E. Heller & Co.) in Alameda, California is developing a special binder that does not degrade through photocatalytic oxidation. While most researchers have used strong UV light as the excitation source, we have concentrated on the use of weak UV light, particularly to eliminate malodorous gases, oil stains and bacteria (figure 1), so that the application of photocatalysis in indoor living and working environments becomes more practical.

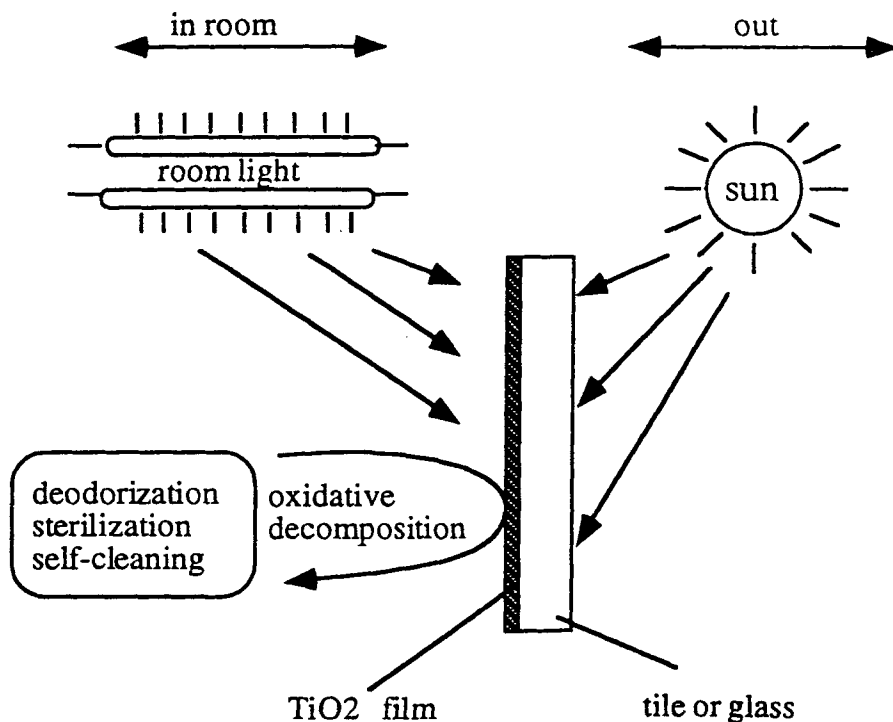


Figure 1. Schematic representation of one of the possible applications of transparent TiO₂ thin film photocatalysts in the indoor environment.

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. TiO₂ photocatalysts thus hold great potential as quiet, unobtrusive self-cleaning materials.

Recently our research group at the University of Tokyo, focused attention on four aspects of semiconductor photocatalysis: (1) development of photoactive TiO₂ films, paints and paper²²⁻²⁴; (2) analysis of the kinetics of photodegradation of various organic compounds on TiO₂ films²⁵; (3) selective monitoring, using microelectrodes of important reactive species that are photocatalytically produced on TiO₂ surfaces^{2,3}; and (4) photoselective destruction of bacteria and cancer cells^{26,27}. We were able to successfully prepare TiO₂ films of about one micrometer thickness on various substrates (including glass, tile, and alumina) using the sol-gel method, titanium acetate-based spray pyrolysis, and dip-coating. We then measured the film's ability to eliminate foul odours, such as those caused by methylmercaptan and aldehydes, kill *E. coli* and other bacteria, and prevent tobacco and oil stains. We were successful in producing a TiO₂ thin film material with a high photocatalytic activity under both black light-type UV lamps, which radiate in the 300 to 400 nm range, and conventional white fluorescent lamps, which radiate mainly in the visible spectral range. The activity of the film was found to be higher than that of the commercial titanium dioxide powder (Degussa P-25).

We have developed transparent coatings that can be used on glass and ceramic tiles. These coatings have been found to be able to photodegrade various noxious, malodorous chemicals, smoke residues and cooking oil residues. Such photocatalytic degradation occurs even under low-intensity indoor light. With our collaboration, the Japanese company TOTO has developed such tiles for use in rest-rooms and hospitals to maintain bacteria-free environments. The Japan Highway Association has recently decided to use lighting systems equipped with photocatalytic glass covers in highway tunnels. Ordinary glass covers quickly become dirty due to oily dust from automobiles. Photocatalytic glass is being investigated by Nippon Soda Co. and Toshiba Litech Co. in collaboration with the Kanagawa Academy of Science and Technology (KAST) in Japan. With a view towards the development of anti-fogging glass and mirrors, we have studied, in collaboration with TOTO, the super-hydrophilicity of TiO₂ photocatalyst thin films upon illumination with UV light. The super-hydrophilic property of the surface allows water to spread completely across the surface rather than remaining as droplets, thus making the surface anti-fogging.

2. Materials and methods

2.1 Development of photocatalytic materials for self cleaning surfaces and indoor air purification

Generally, odours that are objectionable to humans are due to compounds which are present only in 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 TiO₂ photocatalysts are present. In our recent work, we have prepared highly photocatalytically active TiO₂ films with anatase and rutile structures by sintering TiO₂ sols on various substrates. In the case of anatase

films, the TiO_2 sol was prepared by the thermal hydrolysis of titanyl sulfate, as described previously²³. For the preparation of rutile films, titanium tetrachloride was hydrolyzed in aqueous sodium carbonate, and the resulting titanium hydroxide was

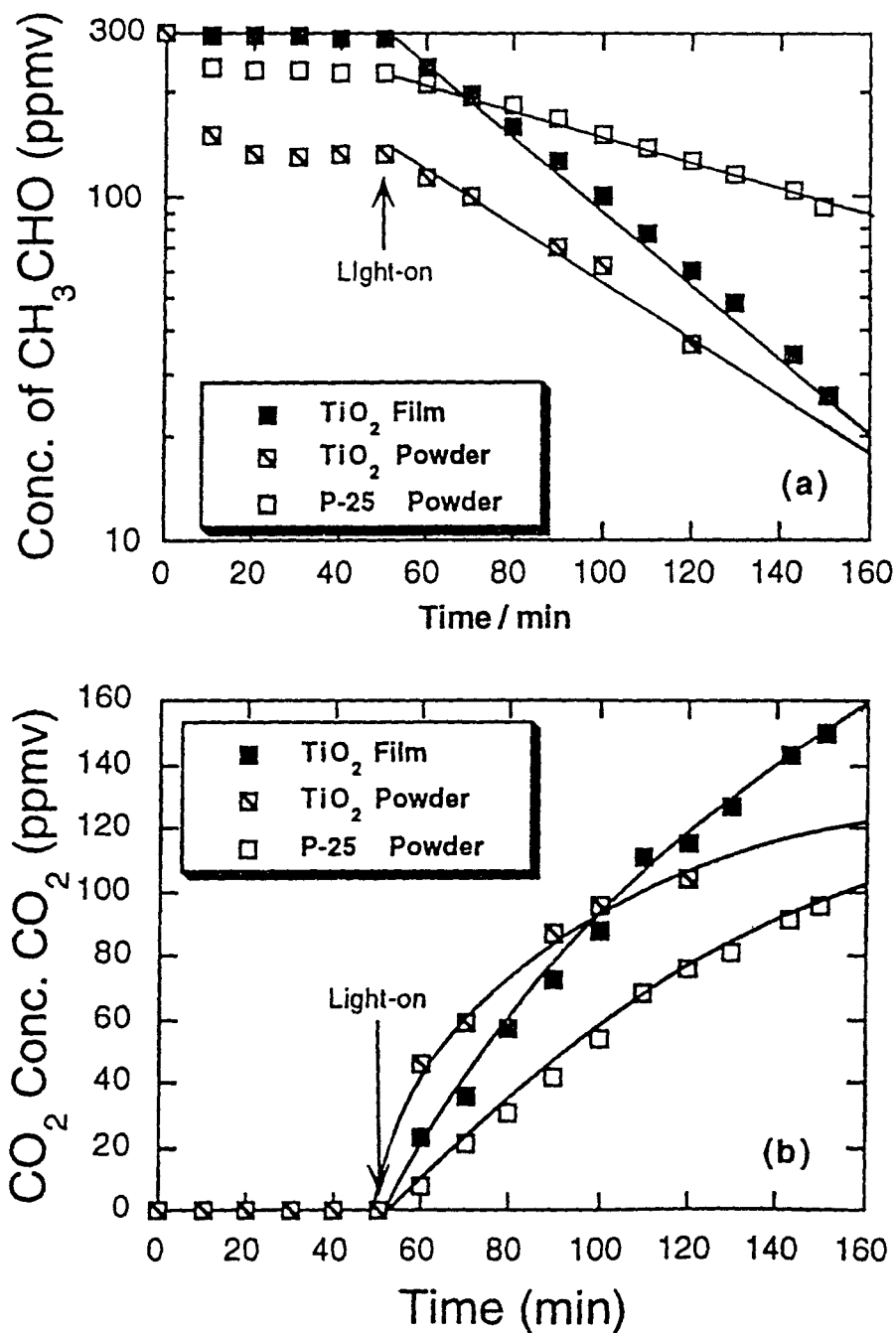


Figure 2. Representative plots showing (a) the decrease in the concentration of acetaldehyde and (b) the increase in the concentration of CO_2 in the presence of an illuminated TiO_2 film as a function of time.

dispersed by adding nitric acid to produce a rutile sol²⁸. The sol in both the cases was autoclaved for 15 min at 180°C and finally spread onto a glass substrate. Porous films composed of 50 nm sized particles and with a thickness of 10 μm were obtained after sintering at 450°C for 30 min. Saturated gaseous acetaldehyde was injected into a container constructed from Pyrex glass, with a volume of 1 L. On the side exposed to UV light, a transparent silica glass window was used. The UV intensity at the film surface was adjusted to 0.4 mW cm⁻². Similar experiments were also carried out for comparison, using TiO₂ (both anatase and rutile) in powder form, as well as the commercial TiO₂ photocatalyst (Degussa P-25). Figure 2 shows the efficient photocatalytic decomposition of acetaldehyde on anatase-type TiO₂ film as well as anatase powder under low light intensities. It is also interesting to note that the TiO₂ powder prepared in our laboratory showed higher photocatalytic activity than did the P-25 powder. Surprisingly, even the rutile form of TiO₂ powder prepared in this work showed photocatalytic activity comparable with the anatase form (see table 1). The rutile powder made by our method (type A) showed much higher photocatalytic activity than that of a commercial rutile powder (Wako Chem. Ind., Ltd.) and also higher than that of a rutile powder (type B) that was prepared by a procedure described in the literature²⁹, which was considered to have very high activity.

In order to facilitate the use of these photocatalysts in conveniently applied coatings, we have developed fluororesin-bonded TiO₂ films³⁰. The anatase sol prepared as mentioned above was neutralized with sodium hydroxide and was then filtered and washed. To the resulting TiO₂ powder, water was added to make a slurry. After addition of aqueous sodium hydroxide solution to adjust the pH to 10, the sol was aged in an autoclave for 3 h at 150°C. This alkaline slurry was then neutralized with nitric acid, and, after filtration and washing, the resulting TiO₂ powder was dried at 110°C for 3 h. The powder (9.8 g) was added to a mixture of 0.8 g of fluororesin, 0.16 g of isocyanate curing agent, 1.0 g of organotitanium coupling agent, and 23.6 ml of toluene, so that a paint-like sol was obtained. This was then coated onto a glass substrate, followed by drying in air at 120°C for 20 min. The films thus obtained have a high concentration (90 vol%) of TiO₂. The long-term stability of the film was tested by exposure of the film to UV illumination (2.1 mW cm⁻²). Even after 810 hours, the film retained its adherence to the substrate as well as its high photoactivity. It is clear from

Table 1. Quantum yields (Φ) for the photodegradation of 1000 ppmv acetaldehyde gas with various TiO₂ photocatalysts under UV illumination (0.5 mW cm⁻²).

Catalyst	Φ (%)			Φ_{CO_2}
	CO ₂	CH ₃ COOH	Total	$\Phi_{\text{CH}_3\text{COOH}}$
Rutile film	9	22	31	0.4
Rutile powder A ^a	17	28	45	0.6
Anatase film	49	38	87	1.3
P-25 powder	8	26	34	0.3
Rutile powder B ^b	8	12	20	0.7
Wako rutile powder	1	6	7	0.2

^aObtained by drying the autoclaved sol at 110°C.

^bPrepared according to the procedure described in the literature²⁹

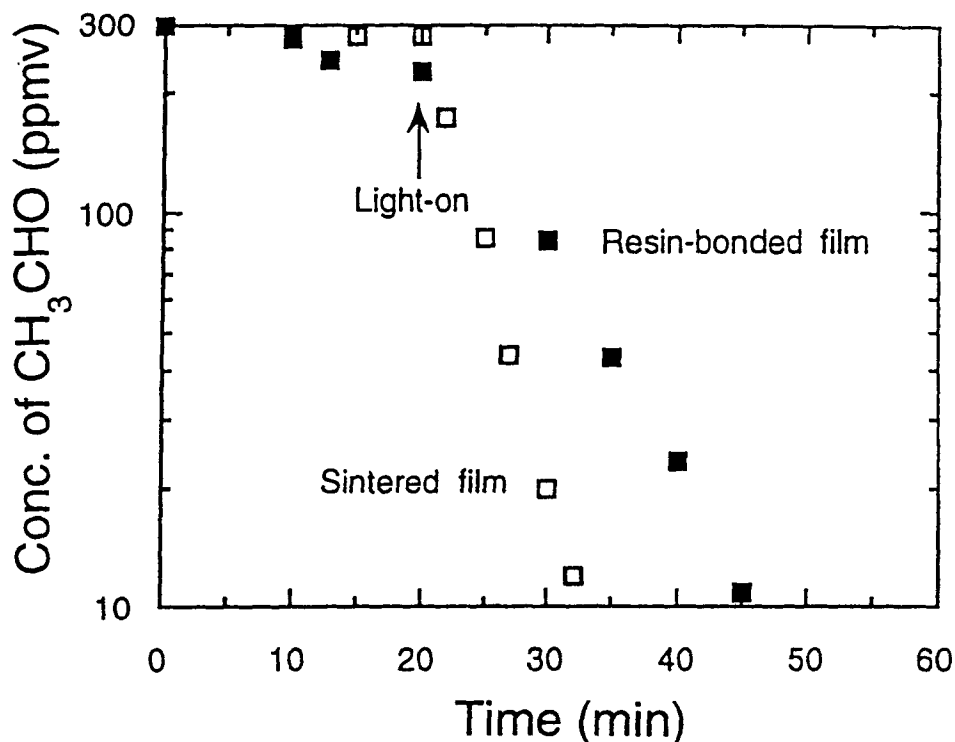


Figure 3. Plot showing the decrease in the concentration of acetaldehyde as catalyzed by a sintered TiO_2 film and a resin-bonded TiO_2 film. The UV intensity applied was 3.6 mW cm^{-2} over an area of 70 cm^2 .

figure 3 that the resin-bonded film showed rather high photocatalytic activity for acetaldehyde decomposition, being only slightly lower than that of the sintered anatase film. Such film type photocatalysts are expected to find extensive practical applications because of their considerable activity, good long-term stability, and coatability onto many types of substrates, including those which cannot tolerate the temperatures needed for the preparation of sintered films.

In collaboration with KAST, we have developed highly transparent, photoactive thin films coated on glass substrates via the sol-gel method³¹. The purpose of this work is to develop TiO_2 -coated glass for use as a window material which utilizes both sunlight and room light (figure 1). We were also successful in coating similar films on glass, quartz soda lime glass (SLG) and SiO_2 -precoated SLG (SiO_2/SLG) substrates via the spray pyrolysis method, using titanium tetraisopropoxide. The films coated by this method showed a transmission of 80% in the visible region. The photocatalytic activity of TiO_2 -coated quartz was found to be much higher than that of TiO_2 -coated SLG. However, the TiO_2 -coated SiO_2/SLG showed much higher catalytic activity than that of films coated on bare SLG, the catalytic activity being similar to that of TiO_2 -coated quartz. This suggests the possibility of Na^+ diffusion from the SLG to the TiO_2 layer during pyrolysis, forming inactive NaTiO_3 . In collaboration with Nippon Soda Co., we have developed similar transparent TiO_2 films with a particle size of 10–20 nm on SLG and SiO_2/SLG substrates for studying the catalytic activity for the

decomposition of oils. The complete decomposition of vegetable oil on a $\text{TiO}_2/\text{SiO}_2/\text{SLG}$ film was observed in 8 h, while a similar layer on bare SiO_2/SLG remained undecomposed (figure 4). Presently, Nippon Soda Co. is developing TiO_2 -containing transparent plastic films utilizing a protective intermediate layer in order to avoid photodecomposition of the plastic substrate. Such lightweight films should prove to be highly versatile in indoor applications.

Our photocatalytic studies on transparent TiO_2 coatings have led us to observe a novel phenomenon, i.e., super-hydrophilicity. The contact angle of water with the transparent film, upon illumination with UV light, decreases drastically to a low value or in some cases nearly to zero (figure 5a). As a result, water can spread completely across the surface, thus making the surface anti-fogging. The water contact angle for a transparent TiO_2 film (thickness, $0.1 \mu\text{m}$) coated on soda lime glass was measured as a function of time in the dark and under weak UV illumination ($0.1 \mu\text{W cm}^{-2}$) (figure 5b). The contact angle decreased upon illumination from 17° to 5° within 5 min. At that point, the light was turned off, and the film, which was in the presence of air saturated with $\text{CH}_3(\text{CH}_2)_6\text{OH}$ vapour, exhibited a gradual increase in the contact angle, indicating that the surface was losing its hydrophilicity. Hydrophilicity was again recovered after 10 min of illumination.

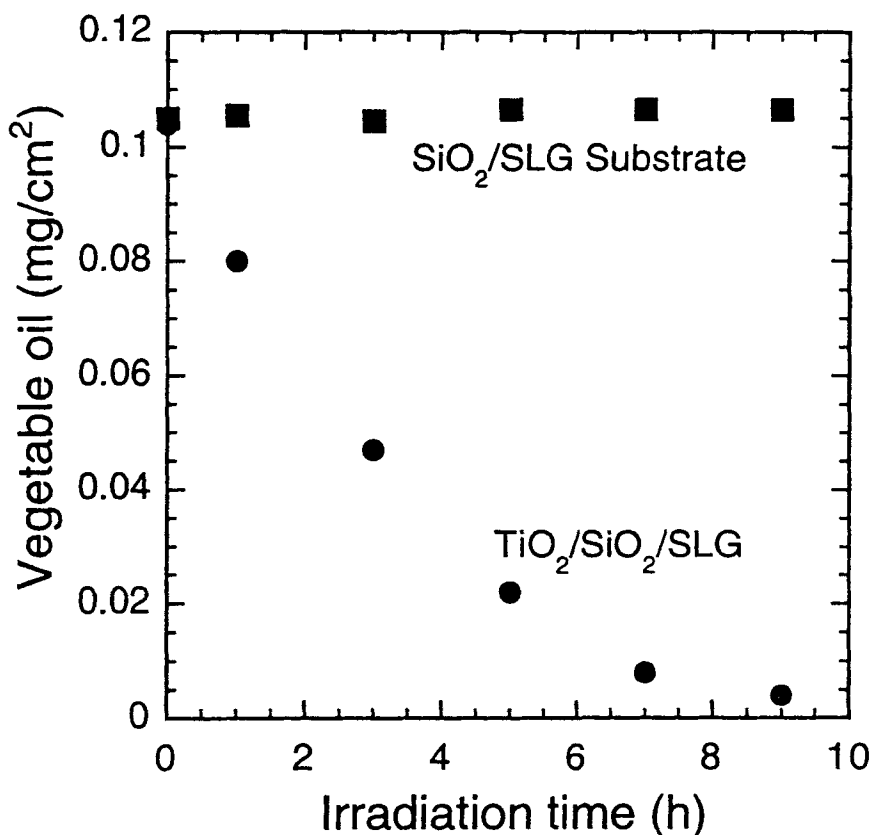


Figure 4. Decomposition of vegetable oil on TiO_2 -coated glass. The oil film on the TiO_2 -coated glass disappeared in 8 hours, while it remained undecomposed on the uncoated glass.

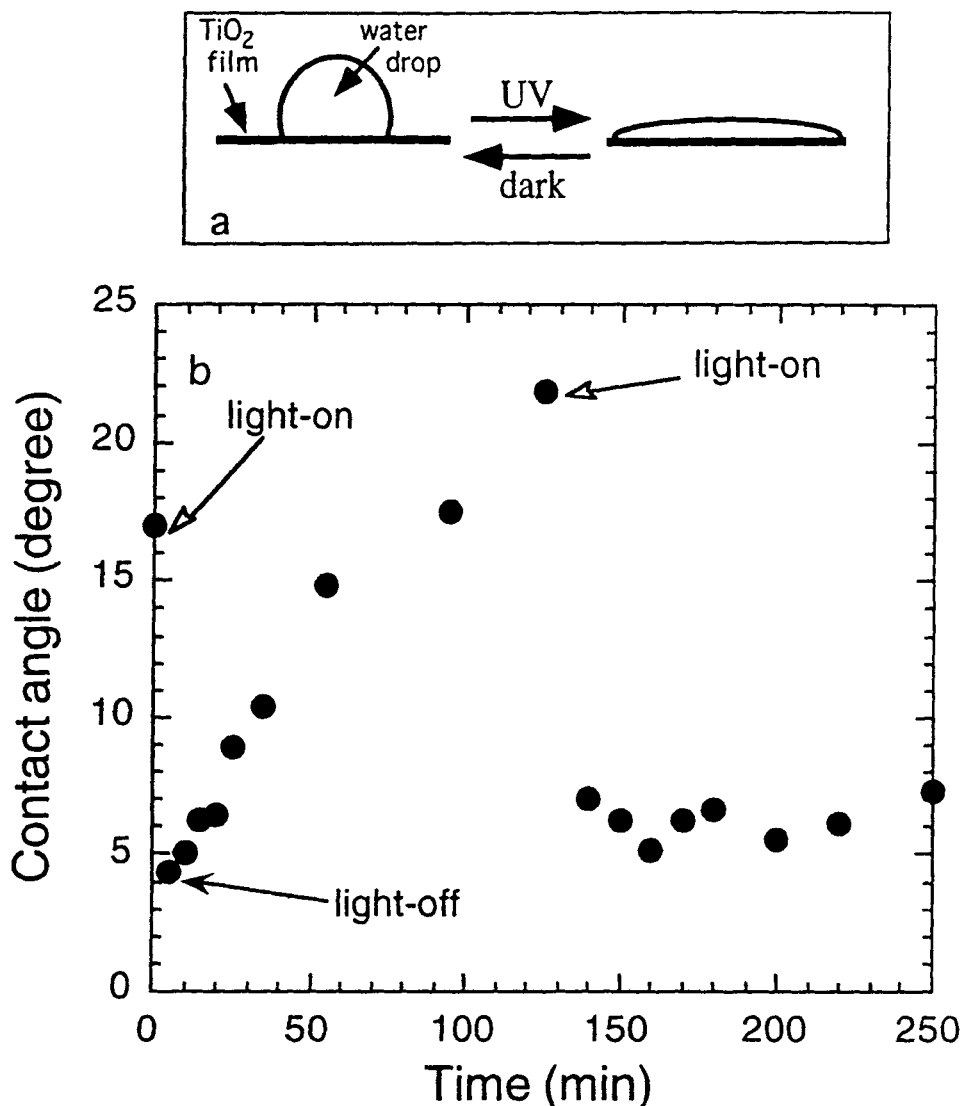


Figure 5. (a) Schematic representation of the super-hydrophilicity phenomenon. (b) Dependence of the water contact angle on TiO₂-coated glass on time.

Although the clean TiO₂ surface is hydrophilic by nature, surface contamination by organic impurities reduces its hydrophilicity. Upon illumination with UV light, the photocatalytic decomposition of these organic contaminants cleans the surface and increases the hydrophilicity to a high degree. A detailed study aimed at understanding the mechanism of this phenomenon will be reported elsewhere.

Other interesting applications of TiO₂ photocatalysis might involve the use of TiO₂-containing paper, for example, in indoor air cleaners. In collaboration with the Gifu Prefectural Paper Research Institute, we have developed TiO₂-containing paper possessing high catalytic activity towards the decomposition of acetaldehyde and cigarette tar. The TiO₂-containing paper was prepared from a mixture of soft-wood kraft-type pulp and

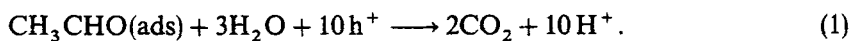
TiO₂ aqueous sol. Details of the preparation were reported earlier²⁴. The amount of added TiO₂ varied from 2 to 10% based on the weight of the pulp. Acetaldehyde degradation was observed with the TiO₂-containing papers even under weak UV illumination (0.08 mW cm⁻²). The decomposition rate was found to increase with increasing amounts of TiO₂ contained in the paper. These papers were also tested for the decomposition of cigarette tar. Sheets of TiO₂-containing paper (5 cm × 5 cm) were first placed in a chamber filled with cigarette smoke. TiO₂-free paper was also used for control experiments. The tar on the TiO₂ paper disappeared after 2 h under black-light illumination (1 mW cm⁻²) and one week under illumination from an ordinary fluorescent lamp (10 μW cm⁻²).

Similarly, TiO₂ films prepared in our laboratory showed excellent photocatalytic activity in decomposing CH₃SH and H₂S and destroying bacteria such as *E. coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*. We also demonstrated the effective use of TiO₂ in selectively killing T24 cancer cells²⁷.

3. Experimental

3.1 Mechanistic aspects of photocatalysis

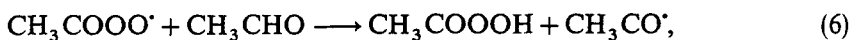
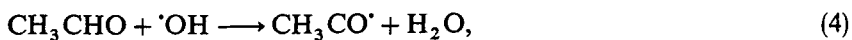
In our investigation of the photocatalytic decomposition of gaseous molecules, we have chosen acetaldehyde for studying the mechanism of degradation process. We have proposed a mechanism based on the fact that quantum yields greater than 100% were observed. Such high quantum yield values have also been reported by Raupp and Junio³². Quantum yields were calculated using the absorbed photon flux rather than the incident flux. If the number of photons impinging on the surface during one second is much higher than the total number of adsorbed molecules, direct oxidation of acetaldehyde is expected to be dominant:



However, when the photon number is less than that of the adsorbed molecules, oxidation of acetaldehyde into acetic acid (2) competes with reaction 1:



Under our experimental conditions, in which the photon flux is low, we observed low rates of CO₂ formation in comparison to the rate of disappearance of acetaldehyde, indicating the formation of acetic acid as an intermediate. Furthermore, quantum yields greater than 100% indicate that the photodecomposition is not exclusively mediated by hole-generated hydroxyl radicals. One of the possible pathways which could explain the high quantum yield value is the direct oxidation of intermediate species by oxygen, as suggested by Heller *et al*³³:

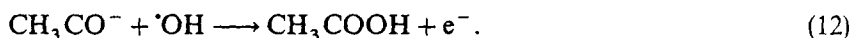
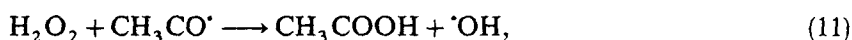
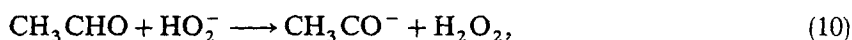


The total reaction is

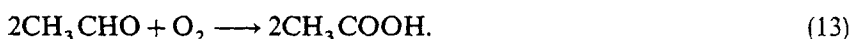


Therefore, one hole oxidizes three acetaldehyde molecules, producing two acetic acid molecules and a reactive radical $\text{CH}_3\text{CO}^\cdot$. Then the carbonyl radical is considered to play a main role in the propagation of chain reactions.

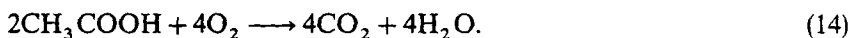
Besides $\text{CH}_3\text{CO}^\cdot$, the superoxide ion resulting from the reduction of oxygen by photogenerated electrons can also possibly participate in the oxidation of acetaldehyde through the following scheme



The total reaction is



When the illumination is intense, the acetic acid intermediate can undergo further oxidation in a similar way:



The oxidation of acetic acid represented in the above reaction was also reported by Carraway *et al.*³⁴. All of the above reactions are believed to be responsible for the observed high quantum yield.

Another of our interests 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 the 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. In our work, we employed a TiO_2 -ITO composite film as a simple model for the metal-deposited photocatalyst². A carbon microelectrode was fabricated to detect the reaction products. By positioning this electrode close to the TiO_2 and ITO surfaces (50–500 μm), the oxidation and reduction reactions were monitored on the TiO_2 and ITO regions respectively. The experimental set-up for the investigation is shown in figure 6. 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. Later, this method was extended to detect hydrogen peroxide at the two types of regions separately³. In this case, a "wired" horseradish peroxidase microsensor was used in place of the carbon microelectrode. By using this microsensor, the formation of H_2O_2 was found to be more efficient on the ITO surface than on the TiO_2 surface. This observation indicates that H_2O_2 was produced mostly at ITO, i.e., by reduction of dissolved oxygen (16), rather than by oxidation of water (15), even in the absence of an electron donor. The possible paths for the formation of H_2O_2 by reduction of molecular oxygen were reported earlier³:



Our recent studies³⁵ on the separate observation of dissolved oxygen in the aqueous solutions at reducing regions (in this case, Pd) and oxidizing regions (TiO_2), using

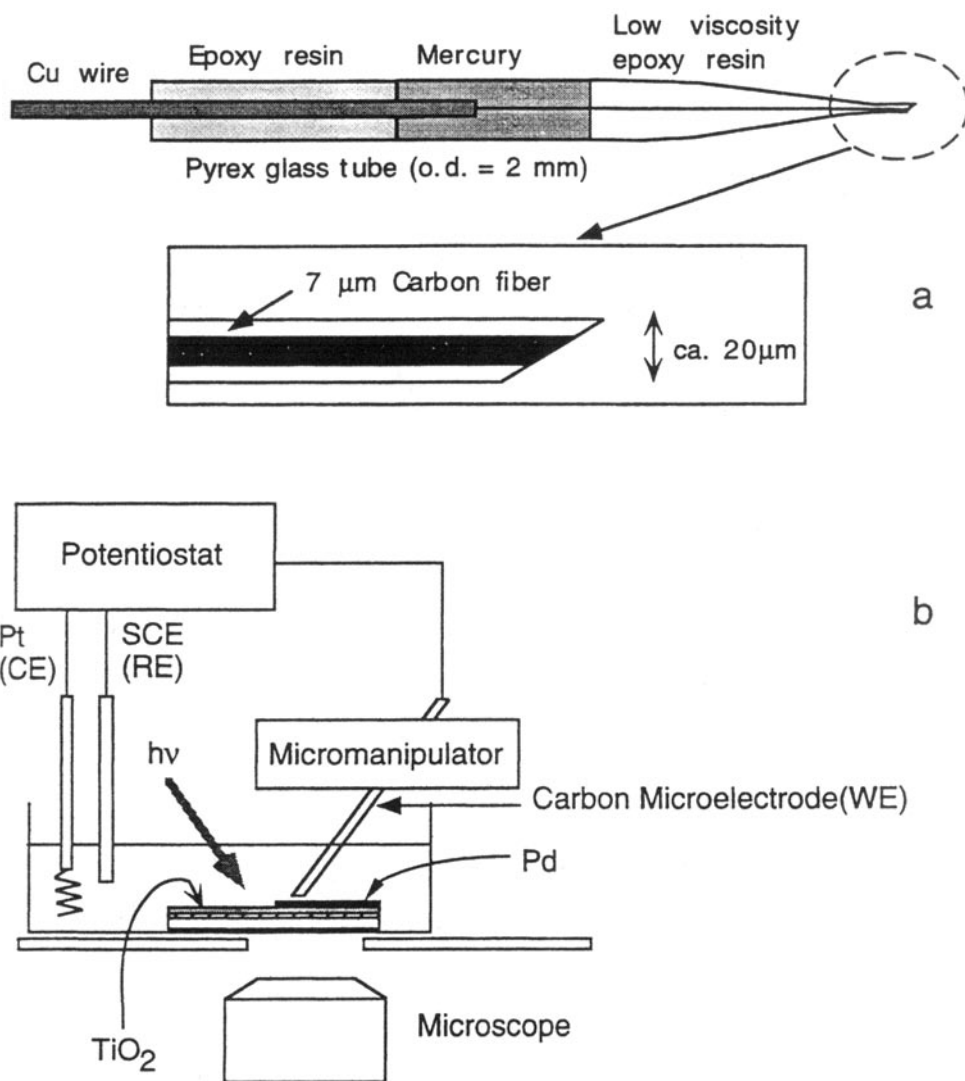


Figure 6. (a) Schematic illustration of the carbon microelectrode structure. (b) Experimental setup for the separate monitoring of oxidation and reduction reactions occurring on the TiO₂-ITO film.

a carbon microelectrode on partially Pd-loaded TiO₂ film, indicated an increase in O₂ concentration near the TiO₂ surface via an oxidation reaction (17) and a decrease in the O₂ concentration near the TiO₂ surface via a reduction reaction (18). When the microelectrode, which was biased at -1.0 V vs. SCE in order to detect the reduction current of O₂ to H₂O, was placed close to the Pd-TiO₂ film, the cathodic current at the microelectrode decreased above the Pd-covered surface and increased above the TiO₂ surface under illumination (figure 7).



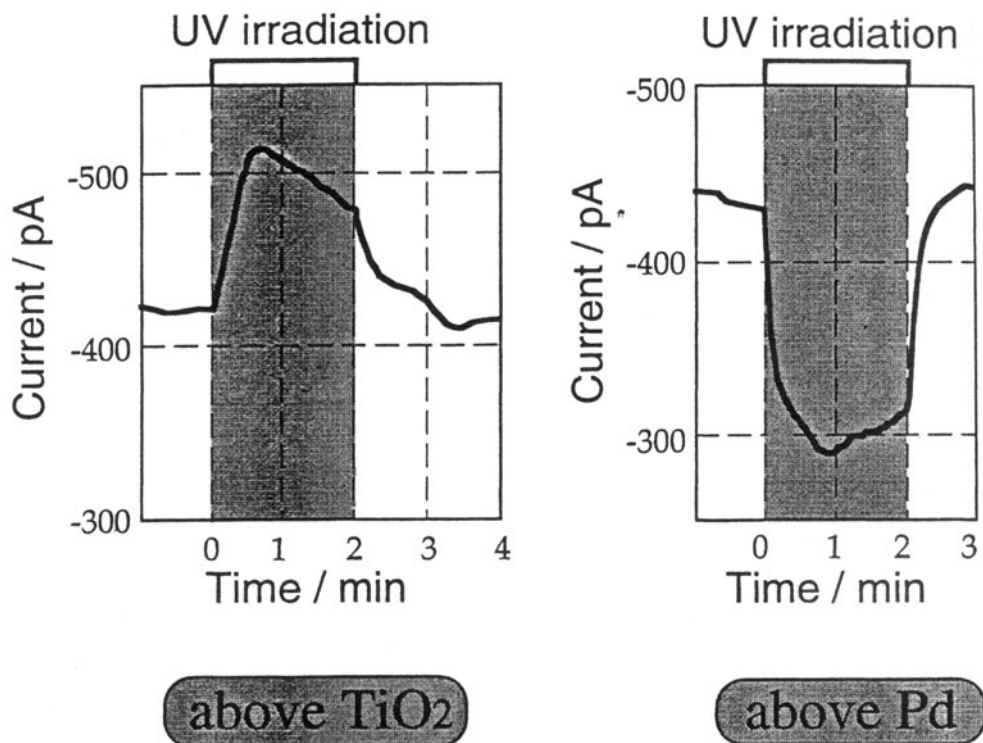
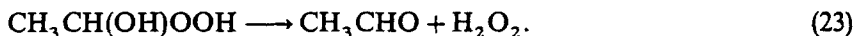
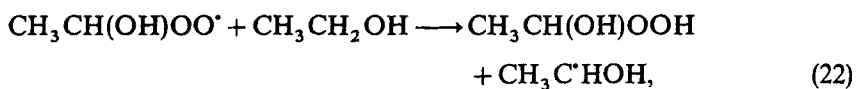
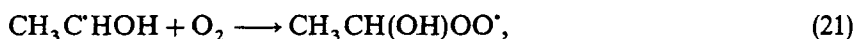


Figure 7. Cathodic currents observed at the carbon microelectrode above Pd and TiO₂ regions on the composite film. The microelectrode was kept at -1.0 V vs. SCE. The UV intensity was $95 \times 10^{-6}\text{ W cm}^{-2}$.

In the presence of ethanol, however, the dissolved oxygen was consumed at both TiO₂ and Pd sites, the consumption of oxygen being larger at the TiO₂ surface.



These results suggest the involvement of a radical chain reaction in the oxidation of ethanol.

3.2 Kinetic studies of photocatalysis

There are several reports available in the literature reporting that rates of photodegradation of chemical compounds on semiconductor surfaces follow the classical Langmuir-Hinshelwood (LH) kinetic expression³⁶⁻³⁸. The LH model includes the assumption that the Landmuir adsorption isotherm is valid for the photocatalytic

surface reaction. In other words, the rate of the reactant disappearance is simply the product of an apparent rate constant and the Langmuir adsorption term, and hence mass transport does not control the overall photodegradation reaction rate. Thus the rate of a unimolecular surface reaction obeys the following expression:

$$R = k\theta = \frac{kKC}{1 + KC} \quad (24)$$

where R and k represent the degradation rate and the apparent first order reaction rate constant, respectively. K is the adsorption equilibrium constant. The linearity of a plot of $1/R$ versus $1/C$ tests the validity of the LH model:

$$\frac{1}{R} = \frac{1}{kKC} + \frac{1}{k} \quad (25)$$

Based on the basic assumption of the LH kinetic model, i.e., surface preadsorption, a broad range of reaction rates might reasonably be expected from differences in adsorptive affinity of different substrates on a given semiconductor surface.

In our study, the LH model was tested for the photocatalytic degradation of acetaldehyde on different forms of TiO_2 prepared in our laboratory and on commercial P-25 TiO_2 powder. Figure 8 shows a plot of the reciprocal of the initial degradation rate R^{-1} versus the reciprocal of the equilibrium concentration C_{eq}^{-1} . The rate,

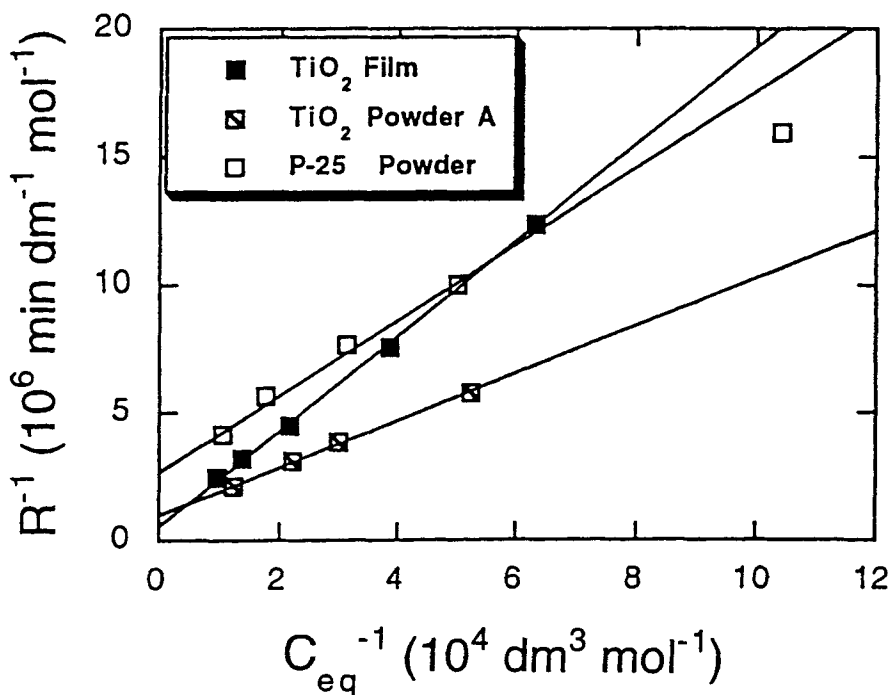


Figure 8. Plots of the reciprocal of the initial degradation rate, R^{-1} , versus the reciprocal of the equilibrium concentration, C_{eq}^{-1} , for the degradation of acetaldehyde gas on TiO_2 film and powders. The UV intensity was 0.4 mW cm^{-2} .

Table 2. The apparent first-order degradation rate constant (k) and photoadsorption constant (K) for the photodegradation of gaseous acetaldehyde over anatase film, anatase powder and Degussa P-25 powder, as analysed in terms of the Langmuir-Hinshelwood kinetic model.

Catalyst	$k, \mu\text{mol min}^{-1} \text{dm}^{-3}$	$K, \text{m}^2 \mu\text{mol}^{-1}$
Anatase film	1.50	—
Anatase powder	1.00	0.61
P25 powder	0.30	0.35

R ($\text{mol dm}^{-3} \text{min}^{-1}$), was calculated based on the concentration change during the initial 20 min. The plots shown in figure 8 are linear, indicating that the photocatalytic acetaldehyde oxidation in contact with the three photocatalysts in the study obey LH kinetics. The LH parameters obtained from the plots (figure 8) are shown in table 2. The first order rate constant for the TiO_2 film is much higher than that for the powder form, which may involve a higher degree of crystallinity due to the sintering of the particles during film preparation. Furthermore, the rates for the film and corresponding powder were ≈ 3 –5 times larger than that for P-25 powder. This implies that the intrinsic photocatalytic properties were superior for our photocatalysts than for P-25 powder. The adsorption equilibrium constant for TiO_2 powder ($0.61 \text{ m}^2 \mu\text{mol}^{-1}$) and P-25 powder ($0.35 \text{ m}^2 \mu\text{mol}^{-1}$) obtained from the kinetic analysis are in good agreement with those obtained from the adsorption analysis ($0.83 \text{ m}^2 \mu\text{mol}^{-1}$ for our TiO_2 powder and $0.38 \text{ m}^2 \mu\text{mol}^{-1}$ for P-25 TiO_2 powder), thus confirming that, in the initial stages of the photocatalytic reaction, the adsorption-desorption equilibrium was maintained, and the kinetics of the photocatalytic reaction were independent of mass transport.

Similar analysis was carried out on the decomposition reactions of ammonia and hydrogen sulfide on anatase and rutile TiO_2 films. All of these reactions were found to follow LH kinetics. The rate constant observed for the reactions is much lower than that obtained for acetaldehyde. Furthermore, the degradation rates for all of these gases were much higher on the anatase films than on the rutile films. Detailed analysis of these studies will be reported elsewhere.

It should also be pointed out that, under certain conditions, for example, very low-intensity illumination, LH kinetics are no longer obeyed³⁹. This is because the reaction rate becomes almost completely limited by the photon flux.

4. Conclusions

Titanium dioxide is a promising photocatalyst for the cleaning of both the indoor and outside environments. The titanium dioxide films prepared in this laboratory showed excellent photocatalytic activity in decomposing foul-smelling gases such as acetaldehyde, H_2S , and ammonia and in killing bacteria such as *E. coli*. These catalyst films are much superior to the benchmark titanium dioxide photocatalyst powder P-25. Highly transparent TiO_2 films have also been developed with a view to their application as window glass for buildings and cars. Films with transmissivities as high as 80% were obtained and their photocatalytic activity for decomposing thin oil films was

found to be very high. Such films have also shown super-hydrophilicity under illumination with UV light. A novel microelectrode system was developed to monitor the oxidation and reduction products separately in order to understand the reaction mechanism. A microelectrode was also used to demonstrate the killing of T24 cancer cells. The reaction kinetics of the decomposition of acetaldehyde, H₂S and ammonia gases were found to follow L-H kinetics, and the kinetic parameters which were obtained supported the conclusions drawn from the catalytic studies, thus confirming the efficient photocatalytic behavior of the TiO₂ films. Commercial products based on these studies have started entering the market and more are on the way. Many more rapid advances are expected in photocatalysis which may benefit mankind.

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