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New Field in Photoelectrochemistry: Photocatalytic, Super-hydrophilic and Super-hydrophobic Functions of TiO_2 Coatings

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Abstract

This article deals with various photochemical processes occurring at TiO_2 surface and its applications in practical living conditions. In the first part, we present an overview of TiO_2 photocatalysis under weak UV illumination with a special emphasis on bactericidal and detoxification properties of TiO_2 films. The second part deals with the photoinduced super hydrophilic TiO_2 surface which has a wide commercial applications. In the last part, we present our recent work on boehmite-based super hydrophobic surfaces containing small amount of TiO_2 to obtain self-cleaning effect.

1. Introduction

Titanium dioxide, an ingredient in paint pigments and scratch-resistant optical coatings, displays high activity for photocatalysis, which chemists and chemical engineers are beginning to exploit. The surface of irradiated TiO_2 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 TiO_2 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 TiO_2, has made it an attractive photocatalyst. The area of photocatalysis has seen explosive growth, particularly during the past five years.

There have been several reports on the use of TiO_2 as a photocatalyst for various applications such as the recovery of precious metals (Li *et al.*, 1986) and waste water treatment (Matthews, 1988). Rosenberg *et al.* (1992) have demonstrated the use of TiO_2-coated glass microbubbles in the photodegradation of oil and chemical slicks on water. TiO_2, due to its wide band gap (3.2 V) cannot make use of solar light effectively, as it requires UV light for excitation. Hence, we have paid attention to make use of the weak UV light available in the solar radiation and in ordinary fluorescent lamps, so that the application of photocatalysis in indoor living and working environments becomes more practical.As a result, we succeded in developing transparent TiO_2 coatings on various substrates such as glass (Sopyan *et al.*, 1994; 1996) and ceramic tiles (Watanabe *et al.*, 1993), which could photodegrade various noxious, malodorous chemicals, smoke residues and cooking oil residues (Sopyan *et al.*, 1996; 1996). The photodegradation was observed even under low intensity indoor light. Based on these developments, the Japanese company TOTO has produced such tiles for use in rest rooms and hospitals to maintain bacteria-free environments. We are also collaborating with other companies to produce photocatalytic cover glasses for lighting systems used in tunnels. In addition to photocatalytic properties, TiO_2 films have exhibited amphiphilic surface wettability induced by UV illumination (Wang *et al.*, 1997; 1998), leading to applications in self-cleaning and anti-fogging glass. The fundamentals and applications of TiO_2 photocatalysis were reviewed recently (Fujishima *et al.*, 1999).

2. TiO_2 photocatalysis

One of the interesting applications of TiO_2 photocatalysis is the bactericidal activity. In general, antibacterial reagents inactivate cell viability, but pyrogenic and toxic ingredients such as endotoxins remain even after the bacteria have been killed. Endotoxin is the cell wall constituent of bacteria which consists of a sugar chain expressed as O-antigen and a complex lipid called lipid A. This endotoxin is toxic and causes critical problems in medical facilities and in factories manufacturing pharmaceuticals and medical devices. We have successfully demonstrated the inactivation of endotoxin and the bactericidal effect using TiO_2 photocatalyst (Sunada *et al.*, 1998).

Photocatalytic TiO_2 thin films were prepared on soda-lime glass plates, previously coated with silica thin films by dip coating method (Sunada *et al.*, 1998). The TiO_2 coated plates were sterilized in an oven at 250°C for 2 h to prevent endotoxin contamination. Precultured *Escherichia coli* (*E. coli*) cells (IFO 3301 strain) were suspended in sterilized water to

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obtain a concentration of 2×10^5 colony forming units (CFU)/mL. 1 mL of this suspension was pipetted into a cylindrical frame placed on a TiO_2-coated glass. The TiO_2 plate was illuminated with UV light from the bottom side. The survival ratio of *E.coli* was determined by counting the number of viable cells in terms of CFU.

Fig. 1 shows the concentration change of endotoxin and survival ratio of *E. coli* as a function of illumination time on uncoated and TiO_2 coated glass plates. Under the black-light illumination without TiO_2 film, the survival ratio of *E. coli* gradually decreased by photodynamic action, and simultaneously, the concentration of endotoxin is increased (Fig. 1A). This is because the endotoxin produced from the cells when they are killed (Sunada *et al.*, 1998). However, on the illuminated TiO_2 film, the concentration of endotoxin in *E. coli* suspension decreased simultaneously with the E-coli survival ratio (Fig. 1B). These results clearly indicate that the antibacterial effects of TiO_2-coated materials involve not only the nullification of the viability of the bacteria, but also the destruction of the bacterial cell.

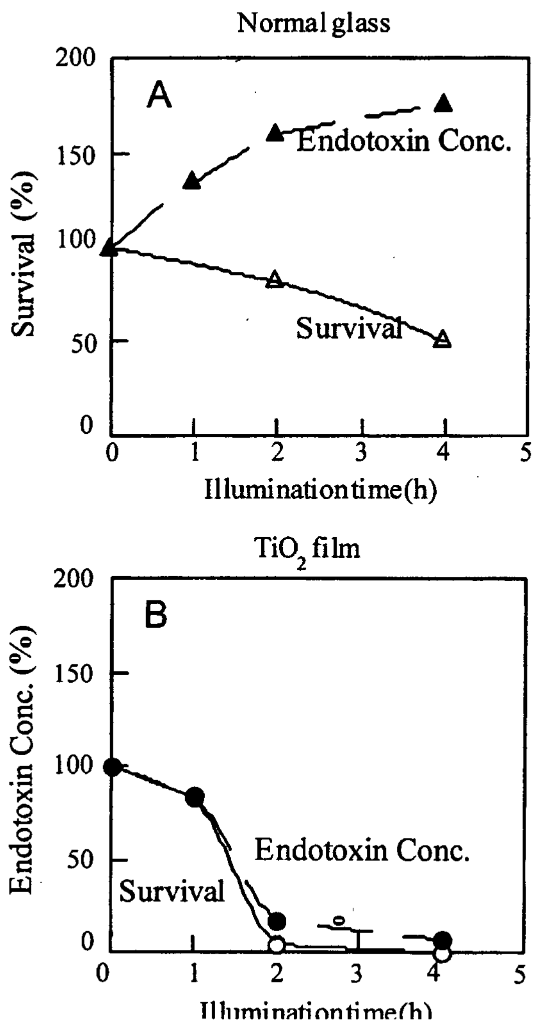

Fig. 1. Concentration change of the endotoxin exhausted from *E. coli* and survival ratio of *E. coli* under UV light illumination (0.4 mW/cm^2) on TiO_2 coated glass and normal glass.

3. Super-hydrophilic TiO_2 surface

In our daily environment, the surface of a material repels water to some degree. On glass or other inorganic materials, water has a contact angle ranging from 20 to 30 degrees. Almost there is no substance which shows water contact angles of less than 10 degrees, with the exception of some water-absorbing substances and surfaces that have been activated with soap or similar agents. These surfaces, however, do not retain long-lasting effects.

A thin film composed of TiO_2 photocatalyst exhibits similar behavior like other surfaces with an initial contact angle of several tens of degrees for water . However, the contact angle decreases gradually by UV irradiation making the water to spread out flat on the surface. Fig. 2 shows the demonstration of this effect on a TiO_2 coated glass. The water droplets on this film have spread out flat after UV irradiation. Such effect was also observed on TiO_2 coated films exposed to water vapor. A fogged surface has changed to a clear surface after UV irradiation making the glass transparent. Such an antifogging effect makes these films very promising for several practical applications. Furthermore, the involvement of TiO_2 provides added advantages due to its photocatalytic self-cleaning property.

Fig. 3 shows the contact angle for water on a freshly prepared TiO_2 film on glass as a function of time under UV irradiation. The film exhibited a water contact angle of 30 degrees before irradiation. After irradiation with weak UV

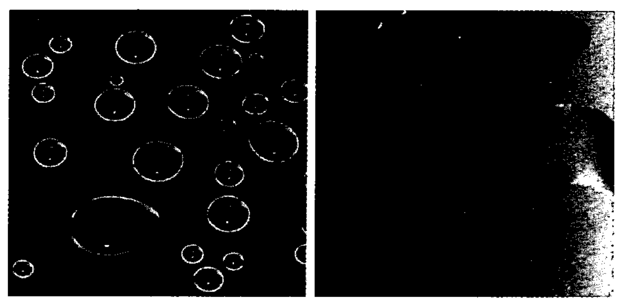

Fig. 2. Change in shape of water droplets after irradiation.

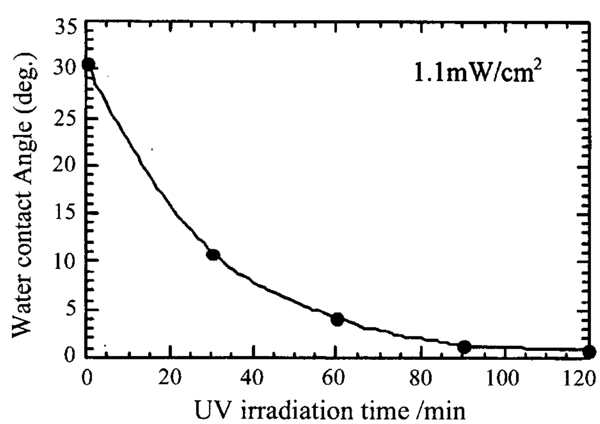

Fig. 3. Effect of UV irradiation on water contact angle.

light, the contact angle gradually decreased to near 0 degree. The decrease was found to be faster at higher light intensities. This effect was also found to be reversible. When the film was left in the dark for some time, the contact angle again increased. It is interesting to note that similar effect was also observed with oils, indicating that the photogenerated surface is amphiphilic in nature (Wang *et al.*, 1997).

We have carried out several experiments to find the mechanism of this effect. At present, the phenomenon is tentatively attributed to the production of "oxygen defects" on the surface of TiO_2. Friction force microscopic (FFM) measurements on rutile TiO_2 (110) single crystals have indicated the formation of micrscopic domains corresponding to hydrophilic and hydrophobic areas due to UV irradiation. Oxygen vacancies are likely to be created at two co-ordinated bridging sites, resulting in the conversion of Ti^{4+} sites to Ti^{3+} sites, which are favourable for water adsorption. Adsorbed water on the hydrophilic domains was confirmed by XPS. For further evidence, the water contact angle on a TiO_2 film was observed in the dark under exposure of O_2 gas. A rapid increase in the contact angle was observed, which can be attributed to the healing of Ti^{3+} defect sites (Wang *et al.*, 1998).

4. Super hydrophobic surface containing TiO_2

Although super-hydrophilic surface is very useful, in some cases, super-hydrophobic surface is more preferable. For example, it is more useful to windshields of automobiles because the blowing wind causes view distortion on a hydrophilic film on a rainy day. For such applications super-hydrophobic surfaces exhibiting water contact angles higher than 150 degrees are required. Such films could be prepared through a combination of surface roughening and lowering surface energy. Apart from the high contact angle of water, the surface should also possess low sliding angle. This is an important requirement from the view point of the practical clearance water droplets from the surface.

In the design of the super-hydrophobic films, methods such as hydrophobic coating and surface roughing are commonly adopted. One of the problems associated with surface roughing is that the transparency usually decreases due to light scattering. When transparent super-hydrophobic films are to be designed, it is necessary to control the surface roughness within 100 nm which is much below the visible light wave length. We have developed such transparent super-hydrophobic films from an ethanolic suspension containing boehmite (AlOOH) and aluminium acetylacetonate ($Al(C_5H_7O_2)_3$) by spin coating. Calcination of these films at 500 degrees resulted in a transparent super-hydrophobic film. The most hydrophobic film obtained by this method showed a water contact angle of 160 degree and a sliding angle of 0.7 degree, indicating its super-hydrophobic nature (Fig. 4).

Although, it has become possible to prepare super-hydrophobic transparent film, the achievement of a long lasting super-hydrophobic property is a challenge. Usually, the deterioration of super-hydrophobic property after long term outdoor exposure is expected due to the accumulation of oily

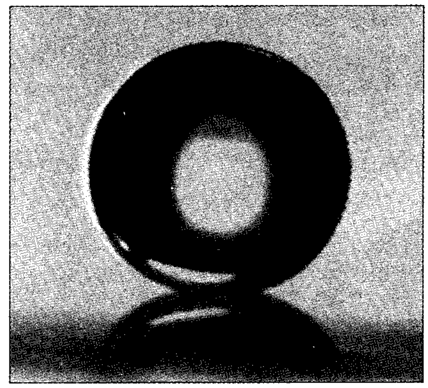

Fig. 4. The shape of water droplet on the super-hydrophobic film.

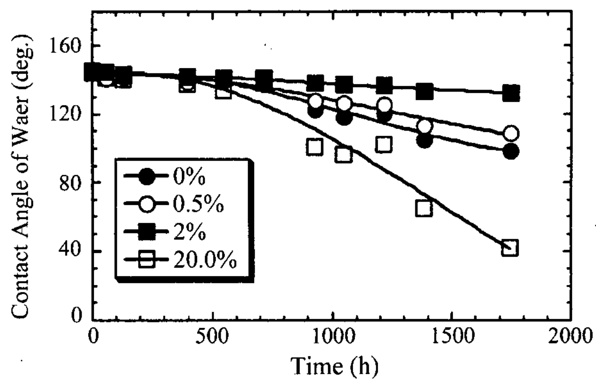

Fig. 5. The effect of TiO_2 addition on the water contact angle during outdoor exposure.

stains on the surface. This is where TiO_2 plays a major role. Due to its high photocatalytic activity, TiO_2 incorporation into the super-hydrophobic film makes it self cleaning and improves the life time of the effect. Fig. 5 shows the effect of TiO_2 incorporation in the boehmite-based super-hydrophobic film. A TiO_2 loading of 0.2 % was found to maintain the high transparency and high contact angle even after 1000h out door exposure. The degradation of water repellent agent should also be considered in the development of these films.

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