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Current Status and Foresight of Photocatalysts

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7.1 Introduction

Photocatalysts work by making use of photo energy. When they absorb light, they are excited to a higher energy state, and accelerate chemical reactions by giving this energy to reactants. This action is called "photocatalysis." The term "photocatalysis" was first used back in the 1930s [1], and the effect of photocatalysis was recognized as the cause of deterioration of pigments contained in coating materials (choking phenomenon) in the 1950s. In those days, therefore, various studies were made for the elimination of photocatalytic reaction that caused detrimental effects such as the deterioration of pigments contained in coating materials. That is, photocatalysis has been regarded with a negative image for a long time[2]. In the 1960s, several groups conducted research on the reactions of organic compounds using the photocatalytic action of zinc oxide powder[3]. However, the research works did not attract much attention because the reaction had a defect that zinc oxide itself dissolves by the effect of light. In the 1970s, Honda, Fujishima, and coworkers discovered that the generation of hydrogen was promoted by irradiating electrodes of titanium oxide with light, which is now called the Honda-Fujishima Effect[4]. With this discovery as a start, technologies in this field have been rapidly developed resulting in a boom in the research on photocatalysts. It was also found in the 1980s that photocatalysis could be applied to the decomposition of harmful materials[5, 6]. Photocatalysts including titanium oxide possess strong oxidative decomposition power, and can completely decompose any compounds. Even organic chlorides are completely decomposed into carbon dioxide and chlorine. There is no possibility of secondary pollution. Thus, photocatalysts are now receiving a great deal of attention as an environmentally friendly material for environmental cleanup that easily detoxificates various difficult-to-decompose chemical substances by just utilizing light.

When photocatalysts such as titanium oxide are irradiated with light, two kinds of reactions take place as shown in Figure 1. One of them is the reaction that completely decomposes substances with strong oxidizing power as has been described above (photocatalytic decomposition reaction), and the other is the reaction in which

Figure 1: Two phenomena occurring on the surface of titanium oxide photocatalyst

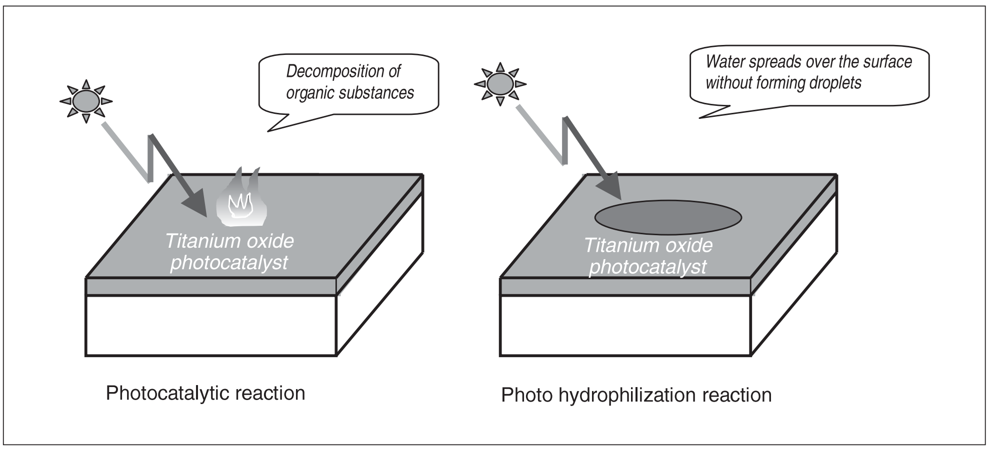
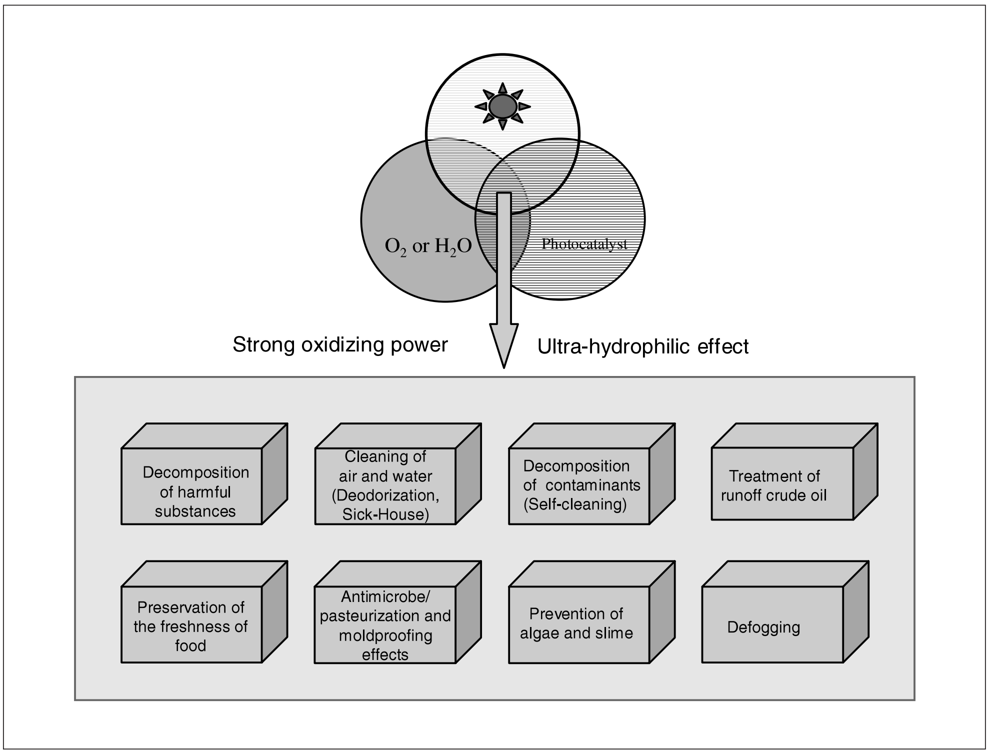


Figure 2: Photocatalyst systems and possible application fields



the surface of catalyst becomes hydrophilic with wettability being increased (photo hydrophilization reaction[7]. Research on the hydrophilicity of photocatalysts has rapidly become very popular recently[8], and practical technologies have been remarkably developed.

As a result of the above-mentioned technological progress, photocatalysts are now behind-the-scene key players for the creation of a comfortable life for human beings by contributing to the detoxification treatment of industrial wastes, air cleaning, cleaning of underground water and lake water, decomposition of contaminants, treatment of runoff crude oil, preservation of the freshness of food, antimicrobial and moldproofing effects, prevention of clouding and slime, and so forth (Figure 2). Furthermore, studies are progressing on the decomposition and elimination of harmful substances contained in the atmosphere in minute amounts including endocrine disrupters (such as environmental hormones) and allergic substances.

Since the research and development of photcatalysts is most actively conducted in Japan, we are responsible for playing the role of leader in the research and development of photcatalysts in the world. For this purpose, it is necessary for us to take the initiative in all of the following aspects: basic studies such as the potentiality and limits of photocatalysts, advantages and disadvantages, detailed surface structure observation of each catalyst, close investigation of the selectivity of catalysts at active sites; application technologies that fully utilize the advantages of photocatalysts; and quality assurance and control procedures that provide reliable products for everybody.

From the above-mentioned viewpoint, the current status and future prospect of the research and development of photocatalyst are described briefly in the following sections.

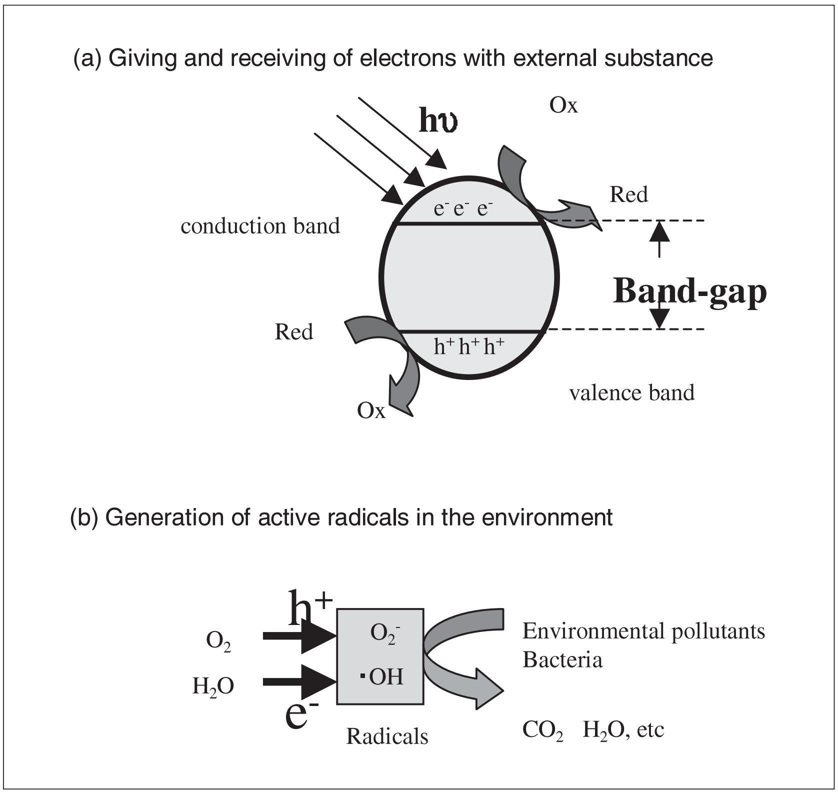
7.2 Mechanism of catalysis

Mechanism of photocatalytic reaction

Semiconductors are used the most as photocatalysts although metal ions and metal-complex compounds are also used. Particularly, oxide semiconductors such as titanium oxide, zinc oxide, tungsten oxide, iron oxide, strontium titanate, and cadmium sulfide are the major materials used for photocatalysts.

Values of the electric conductivity of semiconductors literally lie between those of metals and those of insulators. That is, certain non-conductors that do not pass electricity under normal conditions become able to pass electricity when excited by external stimulus such as light,

Figure 3: Semiconductor photocatalyst under the irradiation with light



heat, or electric fields. In the case where conductivity is obtained by photoexcitation, not all light with any wavelength can excite but only light with a certain wavelength or shorter (i.e., with a photon energy higher than that of a certain wavelength). This energy is called the band gap energy, and is specific to each semiconductor material[9].

Photocatalytic reactions take place when the surfaces of catalysts act on reactants. Figure 3 (a) illustrates, from a chemical point of view, the situation of a semiconductor in touch with the environment when the semiconductor is irradiated with light having an energy equal to or higher than the band gap energy.The electron that is normally in the valence band is raised to the conduction band when excited by the light energy, generating two charge carriers--electron (e-) and positive hole (h+). These carriers diffuse over the surface of the semiconductor and some of them transfer to external substances. When the external substance has received electrons, the substance is said to be reduced. When the external substance reacts with positive holes losing electrons, the substance is said to be oxidized. Therefore, photocatalysts are materials that provoke both oxidation and reduction reactions.

When photocatalysts are used in the natural environment, oxygen and hydrogen existing abundantly in the environment preferentially react with electrons and positive holes and generate superoxide ion ($\bullet O_2^-$) and hydroxyl ($\bullet OH$) radicals. These radicals called reactive oxygen species have oxidizing power stronger than chlorine or ozone, and decompose many substances by oxidation. Most of the diversified functions of photocayalysts derive from the ability to generate the reactive oxygen species.

Characteristics of photocatalytic reactions

Characteristics of photocatalytic reactions from the viewpoint of application are as follows:

(1) Particularly effective for the decomposition of minute amounts of reactants

It has been confirmed that various substances on the surface of photocatalysts from cigarette tar to E. coli decompose. As the name photocatalyst implies, this decomposition reaction takes place using light energy. As a matter of course, this reaction takes place only when the substance to be decomposed is in touch with the surface of catalysts and light exists. This fact is an important point for understanding the photocatalytic reaction and in the consideration of its applications. Due to this characteristic, photocatalysis is not suitable for decomposing a large amount of material within a short time, but is suitable when the substance to be decomposed is in a small amount increasing little by little. Referring to Figure 4, let us compare a case where a tile block coated with photocatalyst is slightly contaminated and a case where the tile block coated with photocatalyst is significantly contaminated. In the former case, the decomposition proceeds effectively, whereas, in the latter case, the surface of the tile block is covered all over by contaminants making it impossible for the light to reach the surfaces of the tile, and decontamination cannot be effected. Since harmful matters in small amounts such as substances with offensive odor and environmental hormones, which are now receiving public attention, present a danger to public health and the environment, they are the most suitable targets for the application of photocatalysis.

(2) Pseudo high temperature effect (producing the effect of burning materials at room temperature)

As has been previously described, when the titanium oxide catalyst absorbs light, two phenomena occur on the surface of catalyst. One is photocatalytic decomposition, in which materials are decomposed and organic materials are decomposed ultimately into carbon dioxide and water. This reaction is the reverse of photocatalytic synthesis and corresponds to a combustion reaction. In order to obtain the same effect by thermal energy as obtained with ultraviolet rays of a wavelength of 380 nm or shorter, a temperature of 30,000 degrees centigrade or higher is required. In the catalytic reaction, however, it is not necessary to raise the temperature and the reaction proceeds at only room temperature. In the combustion reaction, once ignited, the reaction continues until the material burns out. Furthermore, in the photocatalytic reaction, when irradiated with light, the reaction proceeds corresponding to the amount of light absorbed. Thus, it is one of the characteristics of photocatalytic reaction that the reaction can be controlled more easily than combustion reaction.

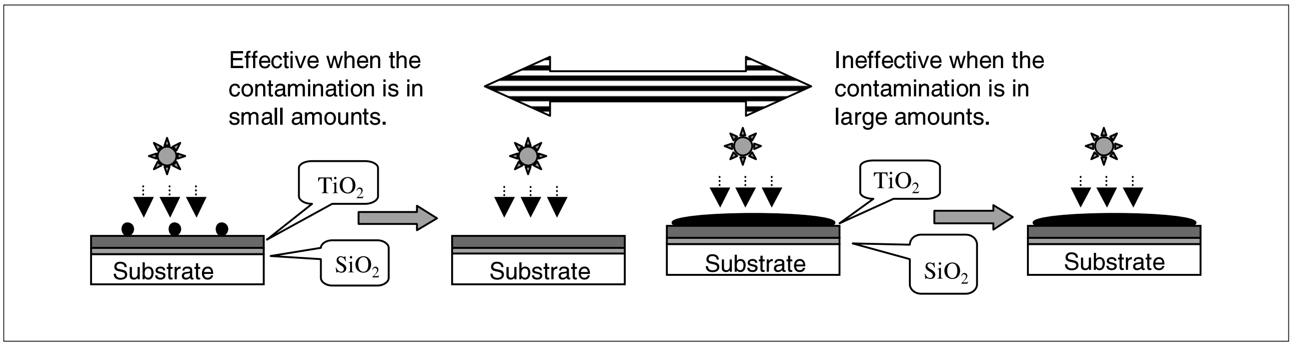
Why is titanium oxide used?

As mentioned above, there are many semiconductor materials that have the photocatalytic function. However, most of the products applying photocatalysis use titanium oxide as the catalyst. Reasons for this are summarized under the following four points:

(1) Extremely stable physically and chemically

Since the main component of sunlight is visible light, it is desirable to use semiconductors with smaller band gaps so that visible light can be used for excitation. However, when materials with smaller band gaps than that of titanium oxide such as cadmium sulfide and cadmium selenide are irradiated with light in water, self-dissolution occurs. This is a phenomenon in which the positive holes generated by the irradiation with light oxidize the semiconductor itself, resulting in the dissolution as metallic ions. Many semiconductors suffer from this phenomenon and are unsuitable as practical materials. Titanium oxide does not exhibit such self-dissolution and is superior to other semiconductors in stability.

Figure 4: Limits of photocatalysis (unsuitable for treating a large amount of material)



(2) High photocatalytic activity

The photocatalytic activity of titanium oxide strongly depends upon its crystal structure. While it is known that titanium oxide has three kinds of crystal structures--anatase, rutile, and brookite--the anatase structure has the highest photocatalytic activity. Therefore, anatase is considered to be most effective for the application of photocatalytic reaction.

(3) Harmless, nontoxic and environmentally friendly

Safety of titanium oxide has been proven as with white pigment and food additives, and there are little adverse effects on the human body and the environment.

(4) Inexpensive raw materials

Titanium itself is a metallic element abundant in natural resources, being the ninth most plentiful element in the earth's crust. Ores used as raw materials to produce titanium oxide are ilmenite which isa compound of oxides of iron and titanium, and rutile. Production processes (chlorination method and sulfuric acid method) are relatively simple and inexpensive.

Judging from the above-mentioned characteristics, titanium oxide has advantages for use in the environment in large amounts. From the viewpoint of stability only, it has been found that strontium titanate and layered potassium niobate have a photocatalytic activity comparable to that of titanium oxide. However, in addition to the problems with complicated production processes and high costs, there is concern that these compounds will have ill effects when released in the environment. Regarding the decomposing ability and costs, zinc oxide has potential as a candidate material but it has the defect of photodissolution, which must be resolved before being put into practical use.

Since the band gap of titanium oxide is 3.2 eV, only ultraviolet radiation is absorbed. In order to improve the effectiveness in utilizing light energy, many research studies are being made to solve this problem.

Light source

As understood from the above-mentioned mechanism of action, "photocatalyst," "water and oxygen," and "light source" are the three major factors required for catalytic reaction. Now let us discuss the third factor,"light source."

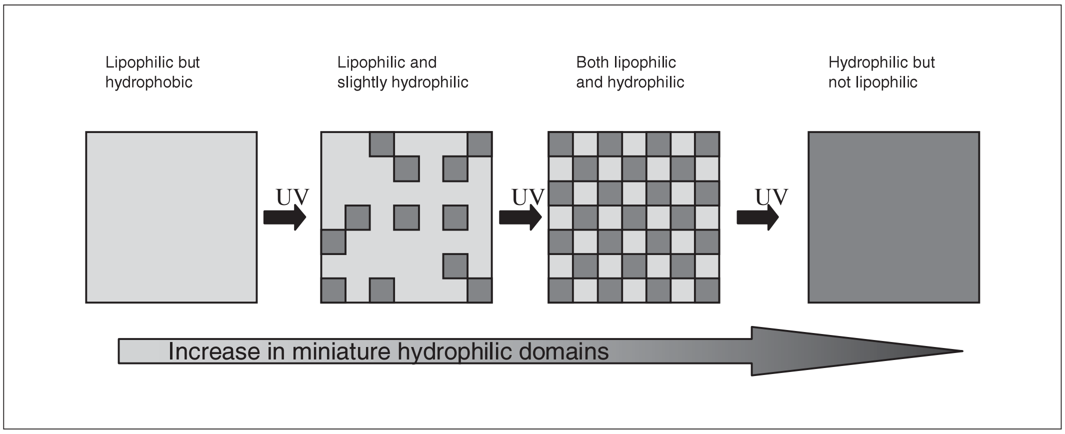
The most readily available light source in nature is sunlight. The light coming from the sun to the earth consists of wavelengths from 290 nm to 4,000 nm. The light with wavelengths up to 400 nm is ultraviolet light; the light with wavelengths from 400 nm to 800 nm is visible light in the order of purple, blue, green, yellow, and red; and the light with wavelengths of 800 nm or longer is infrared light. The spectrum of sunlight exhibits the highest strength around 450 nm in the visible light range. The total amount of light energy that the earth receives every year is 3.0×10^{24} J/year. This energy equals more than 10,000 times the annual consumption by humans using petroleum and coal, and about 4 to 5% is ultraviolet light, about 45% is visible light, and about 50% is infrared light.

Since the photocatalysts in practical use at present are of titanium oxide, the light utilized for the photocatalytic reaction is ultraviolet light. As has been mentioned above, the strength of ultraviolet light in the sunlight is not high, and it is a realistic choice at present to use artificial ultraviolet light sources. Mercury lamps, xenon lamps, black-light lamps, and chemical lamps are commonly used. However, the life of these light sources is several thousand hours and it is

Table 1: List of the selected materials for the research on photocatalysis since 2000 based on a literature search

Materials	Number	%
TiO_2	617	78
ZnO	35	4
WO_3	22	3
Fe_2O_3	14	2
ZrO_2	12	2
$SrTiO_3$	4	1
Nb_2O_5	4	1
V_2O_5	3	0
CeO_2	3	0
Others(including organometallic complex)	76	10
Total	790	100

Figure 5: Structure-change model of the surface of photocatalyst caused by irradiation with light



necessary to replace the lamps about every half a year, restricting the area of application. Furthermore, with normal ultraviolet lamps, the efficiency of conversion from electricity to light is 20% at most and the rest of the energy is wasted as heat. Therefore, it is a serious problem that light sources being used at present cost much more than expected.

As a candidate for alternative light sources that may solve this problem, the light-emitting diode (LED) is being studied. Because the life of a light-emitting diode is as long as about 100,000 hours and power consumption is very low having a high electricity-to-light conversion efficiency of 80% or more, LED is a hopeful light resource that may replace the fluorescent lamp in the future. Recently, short-wavelength LED based on gallium nitride has been developed and air cleaners for vehicles that utilize this LED have been put to practical use in Japan for the first time in the world[10]. It is thought that the development of low-cost, short-wavelength LED is the key to widening the application areas of photocatalysis.

Using visible light for activating photocatalysts

Only ultraviolet light has been used for the photocatalysts that are applied to the production of oxygen and hydrogen with the electrolysis of water or detoxification of environmental pollutants. Since ultraviolet light is harmful to humans in the first place, it causes anxiety to use strong light within a normal environment. Furthermore, in order to improve the efficiency, it is necessary to utilize natural sunlight or room illumination. Therefore, development of photocatalysts that are activated by visible light is now one of the most important targets in this field. Several methods including the following five have been proposed for this purpose: (1) doping of transition metals[11], (2) hydrogen plasma treatment[12], (3) dye sensitization[13], (4) compounded semiconductor that absorbs visible light[14], and (5) replacing oxygen with nitrogen[15, 16]. Method (1) requires expensive equipment for the implantation of metallic ions. In method (2), the ability to absorb visible light is rendered by the oxygen defects generated by the plasma treatment, and the consistency and reproducibility must be fully studied. Method (3), dye sensitization, does not seem to be suitable for photocatalyst application. Because the oxidation ability is rendered to the dye, high oxidizing power cannot be expected. Methods (4), compounded semiconductor, and (5), nitrogen doping, are the most hoped-for methods. Research on the utilization of visible light for photocatalysts is being intensively conducted with focus on these two methods.

Hydrophilicity of photocatalysts

When the photocatalyst of titanium oxide absorbs ultraviolet light, two phenomena occur on its surface (Figure 1). As has been already mentioned, one is the photocatalytic decomposition and the other is photo hydrophilization. Why does the surface of photocatalyst render the photocatalytic characteristic and high wettablity by the irradiation with light? We have reviewed the photocatalytic reaction that utilizes the high oxidizing power of photocatalyst. It has been thought that photo hydrophilization also derives from the high oxidizing power that decomposes organic matters adhering to the surface by oxidation resulting in the their removal. However, the results of recent studies on the surface structure have lead to a new concept that hydrophilizaton by irradiation with light derives from the change in the surface structure of titanium oxide. Figure 5 illustrates a structure-change model of the surface of photocatalyst. Before the irradiation, the surface of titanium oxide is uniformly hydrophobic. With the irradiation, minute hydrophilic domains are formed, and, finally, the hydrophilic domains cover the entire surface. The mechanism of the formation of hydrophilic domains is still under study. But judging from the results of various experiments, the most probable process is that the positive holes generated by irradiation with light are oxidized by the oxygen of titanium oxide resulting in oxygen defects in the lattice, and water is absorbed at these defects forming hydrophilic domains[17].

Affinity of photocatalysts for water is greatly increased when exposed to light due to their hydrophobic property in addition to the various catalytic functions. Discovery of new functions such as photo ultra-hydrophilicity (property or phenomenon in which the contact angle with a liquid is 0 degree) seems to promise the possibility of new products such as defogging mirrors and windows for high-rise buildings that do not require cleaning (self-cleaning effect), and prevention of snow accumulation on power transmission lines in snowy districts and on roofs to reduce the burden of snow removal by combining photocatalysts with alumina that has ultra-water-repellency (property or phenomenon in which the contact angle with a liquid is 150 degrees or more).

Decomposition of water by photocatalysis

As is well known, hydrogen is attracting attention as an energy resource that is environmentally friendly. However, a problem still to be solved is how hydrogen should be produced. One possible method is the decomposition of water using photocatalyst. Initially, this triggered the attention to photocatalyst, and basic research works including the search for adequate materials are being made. However, no material superior to titanium oxide has been found. Titanium oxide photocatalysts have a problem that the quantum efficiency is quite low when used for the decomposition of water. It is said that the efficiency is 1% or less, which is significantly lower than that of solar cells used for converting light energy to electric energy. The immediate target is 10%, and the issue of hydrogen resource will be solved once and for all if the efficiency reaches 30% in the visible light range with the wavelengths of 600 nm or shorter. For the application to the decomposition of water, the problem of the response to visible light still remains as in the case with other photocatalysts.

Evaluation of photocatalytic performance

Many evaluation methods have been proposed by researchers according to the applications including pigmentolysis, fluorescence method, and analysis of reaction products. In the method by the analysis of reaction products, reactants and reaction products are usually analyzed by gas chromatography or high-performance liquid chromatography after the actual photocatalytic reaction. The reaction apparatus is classified as follows according to whether the catalysts are in the form of membrane or plate (fixed type) or powder, and also whether the reaction media are liquid or gas:

(1) Fixed type photocatalyst: gas phase: reactants are introduced into the reaction cell (closed type or flow type) together with a medium gas (usually air) and made to react by irradiation with light. (2) Fixed type photocatalyst: liquid phase: basically the same as the gas phase method. This method is advantageous for the cleaning of water because it is not necessary to remove the photocatalysts. (3) Powder photocatalyst: gas phase and (4) Powder photocatalyst: liquid phase are also used.

The Society of Industrial Technology for Photocatalytic Articles has published methods for the evaluation of photocatalytic performance and performance standards (http://www.photo cataoysis.com). In the published evaluation methods, “ Method for the Evaluation of Photocatalytic PerformanceáT(liquid film close contact method)” relates to the evaluation of plate type photocatalysts, "Method for the Evaluation of Photocatalytic Performance IIa (gas bag A method)" relates to photocatalysts of powders and granules, and "Method for the Evaluation of Photocatalytic Performance IIb (gas bag B method)" relates to the evaluation of the performance of photocatalysts with strong adsorption. However, these methods cannot meet the requirements for the various applications described in this report, and are still insufficient as standard procedures.

7.3 Actual applications of photocatalysis

As previously described, full-scale research on photocatalysis started in the 1970s and various new materials related to photocatalysis have been developed. One of the characteristics of the research on photocatalysis compared to other research areas is that the process from basic research to application is very short and the development of materials are immediately reflected in the development of practical products. Furthermore, when a new material has been developed, new applications are soon developed thereby accelerating the commercialization of products. Products related to photocatalysts are expected to be used in our daily life in simple and safe manners, familiar to everybody from the aged to children and usable anywhere as long as light is available. Particularly, these products are suited for developing countries where energy is insufficient. In order to realize such targets, diversified products utilizing photocatalysis have been created as a result of ingenious efforts of many private companies and research organizations. The following are some examples of these products.

•Example•1
Antimicrobial stain-proofing photocatalytic tile

The photocatalytic tile, which was originally developed for medical application, was the first product using photocatalysis and put into practical use as early as 1994. Since it was found that photocatalytic tiles are effective for MRSA (methicillin-resistant staphylococcus aureus), which causes hospital infection and is resistant to antibiotics, they have become widely used in operation rooms and other places in hospitals. Furthermore, these tiles that exhibit high performance in medical applications are now being used in houses. These tiles are most suitable for damp places such as the bathroom and kitchen where microorganisms and trash accumulate. Figure 6 shows the production process for photocatalytic tiles. It should be noted that copper metal, which has an intrinsic antimicrobial property, is fixed on the surface of titanium oxide aiming for a complex effect in order to promote antimicrobial functions in dark places.

•Example•2
Air cleaning photocatalyticacoustical board

The color of the sound-insulating walls installed on both sides of express highways is now changing from dark gray to white. The reason is because air cleaning photocatalytic acoustical

Figure 6: Production process for photocatalytic tiles

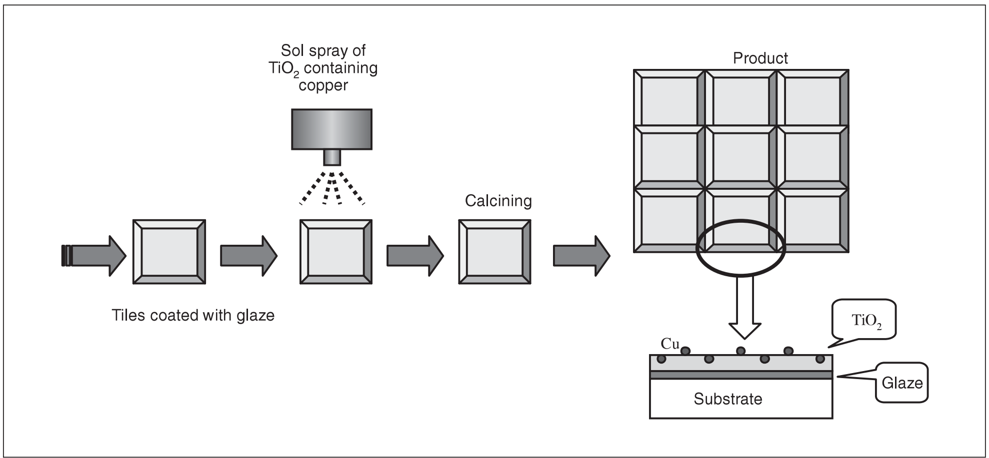
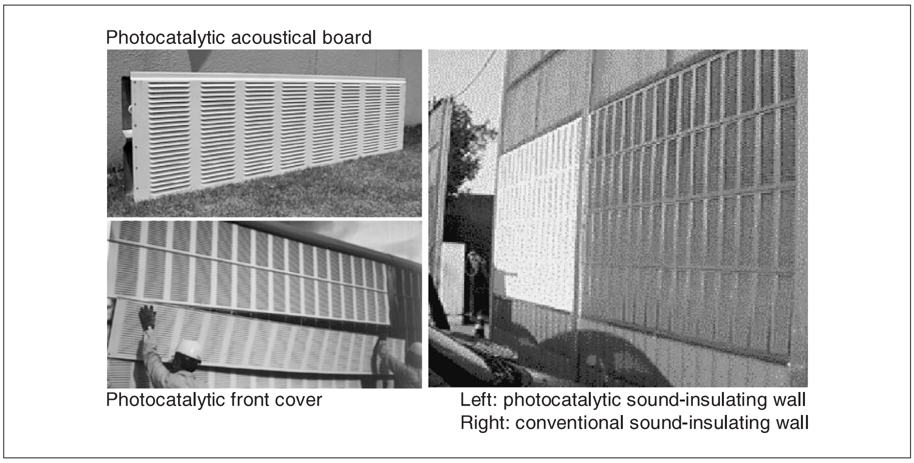


Figure 7: Air cleaning photocatalytic acoustical boards and sound-insulating walls for express highways



Source: two photos on the left,[18] photo on the right [19]

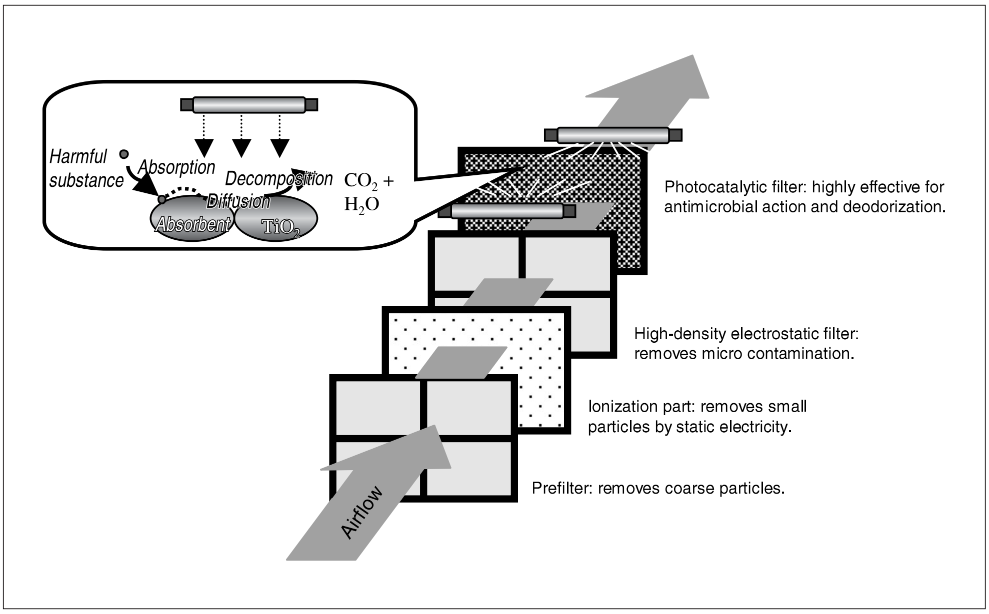
boards are being attached to the surface of conventional acoustical boards.

These air cleaning photocatalytic acoustical boards can completely oxidize the NO_X gas emitted from vehicles into harmless nitrate ion without emitting harmful intermediate compounds. These acoustical boards also have a stain-proofing function and maintain their appearance for a long time due to the self-cleaning function. This is a typical example of air cleaning systems that work only with natural energy. Figure 7 shows pictures of highways provided with air cleaning photocatalytic acoustical boards[18, 19]. About 4,000 m^2 of such air cleaning photocatalytic acoustical boards have been installed across the whole country. The success of air cleaning photocatalytic acoustical boards has led to the demonstration test of photocatalytic paving concrete blocks with an air cleaning function. The application of photocatalysis technology in the field of road construction materials has just started, and it is expected that many practical products will be developed in the future.

•Example•3
Filters for deodorizing and air cleaning equipment

Recently, airtight and insulated houses are increasing to improve the efficiency of air conditioning and energy saving. This has caused a problem in that the living environment is contaminated with harmful substances and

Figure 8: Structure of an air cleaner equipped with photocatalytic filters



bacteria. Newspapers and TVs are reporting on the sick house syndrome and new house sickness. Volatile organic compounds (such as formaldehyde and toluene) are believed to be causing such sickness. Offensive odors from cooking, garbage, cigarette, and bathrooms not only make people feel sick but also have harmful effects on the human body, staying for a long time in the house. Air cleaners equipped with a photocatalytic function now play important roles in decomposition and removal of these harmful substances in minute amounts. Figure 8 illustrates the structure of filters used for air cleaners using titanium oxide. These filters have the feature that they are combined with absorbents such as activated carbon to improve cleaning efficiency. The combination with absorbents is essential because titanium oxide cannot efficiently absorb molecules of harmful substances by itself. These harmful substances are first captured by the absorbents and then diffuse onto the surface of the titanium oxide for decomposition. Furthermore, antimicrobial and antiviral effects are expected because airborne bacteria and virus cannot live on the surface of photocatalytic filters.

Deodorization is the easiest part of the application of photocatalysts and many practical products have been introduce into the market including deodorizing air cleaners, air conditioners and refrigerators, all of which are equipped with the antimicrobial function.

•Example•4

De-fogging glass

On rainy days, water droplets attached to the windshield and sideview mirrors distract the driver. Particularly at night, droplets on the sideview mirrors reflect the beams of headlights, making the driver's vision blurry. The surface of titanium oxide becomes highly hydrophilic when exposed to only a small amount of ultraviolet light during the day, and the formation of droplets is prevented by this effect. When used for the prevention of water droplets on sideview mirrors, however, the effect is workable in daylight but is difficult to maintain for a long time after sunset or in dark places, thereby making hybridized technology indispensable.

This problem has been solved dramatically by the addition of silica. It is known that silica strongly absorbs water molecules on its surface. It is thought that the surface of silica is cleaned by the photoexcitation reaction of the titanium oxide, so that water molecules are strongly absorbed on the clean silica and the hydrophilicity can be maintained in dark places, and, as such, it has become a real possibility to apply this technology to the sideview mirrors. Figure 9 shows the production process for the sideview mirrors of automobiles. The intermediate silica layer has been introduced to prevent the diffusion of sodium ions contained in the glass into the layer of photocatalytic titanium oxide. Regarding

Figure 9: Production process for sideview mirrors for automobiles

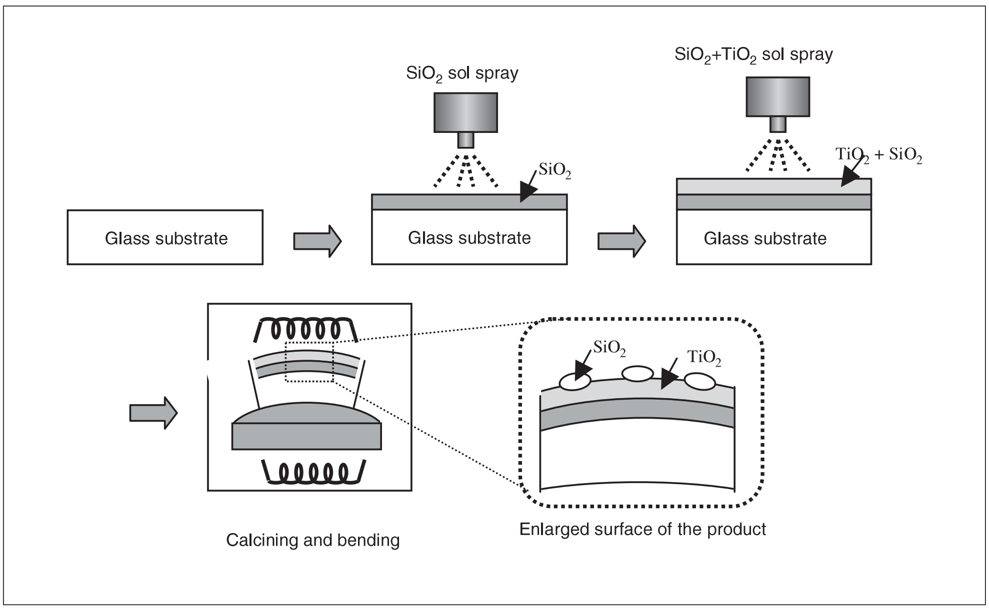
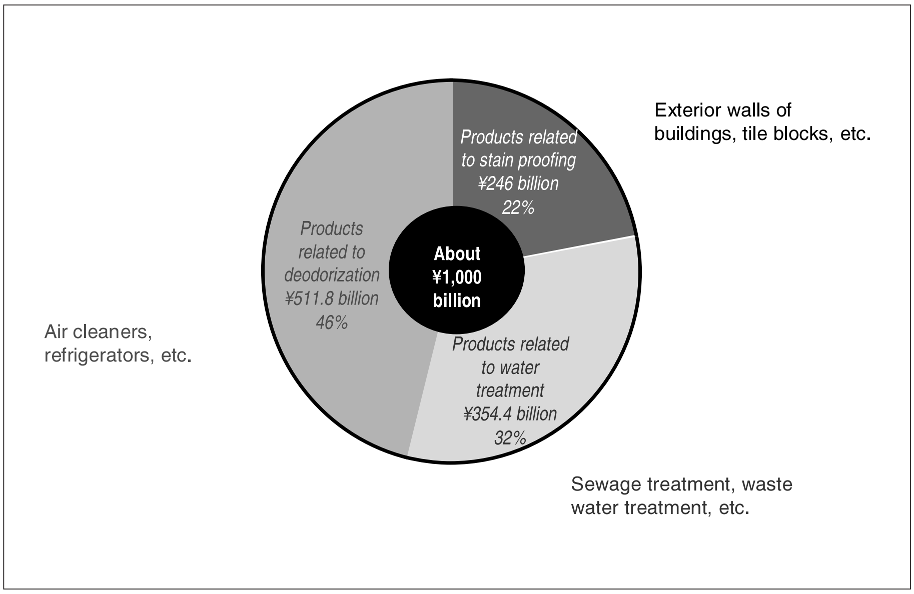


Figure 10: Forecast for photocatalyst market in 2005



Source: Authors' compilation based on a report by Mitsubishi Research Institute

automobile components that apply photocatalysis, not only new sideview mirrors but also photocatalytic films with adhesives for attaching to existing sideview mirrors are available on the market.

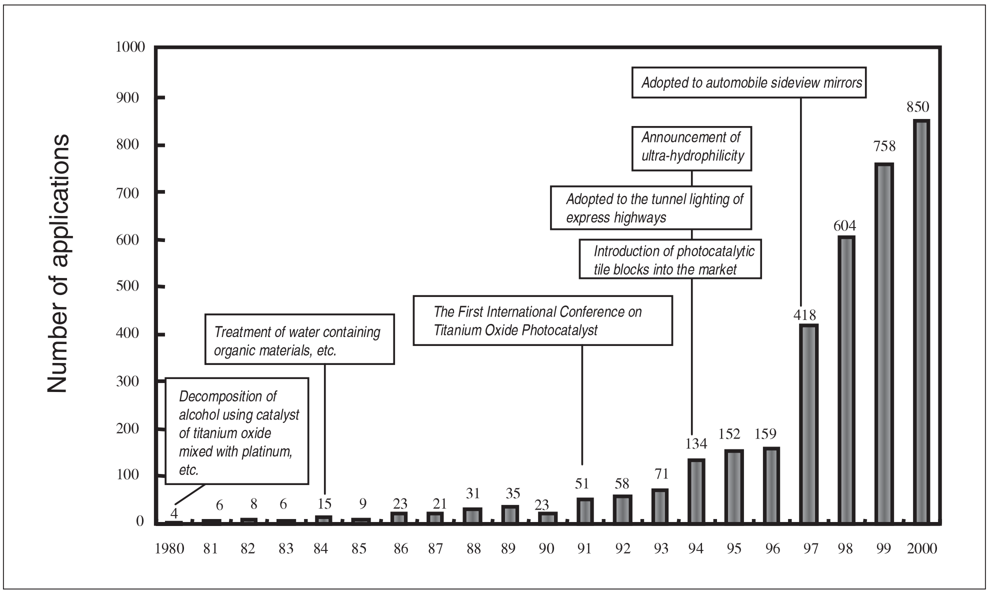
Four application examples and their structures and production processes have been briefly explained. Photocatalysis was at first expected to provide a technology for the production of hydrogen as in the Honda-Fujishima Effect. Then, the technology developed into the field of air cleaning and water treatment, and the applications have been drastically expanded to a wide range of areas including construction materials and automobiles since the thin film coating was devised. In the future, further expansion is expected with the progress of photocatalytic technologies. Now it is not a mere dream that photocatalysts will be incorporated in almost all of our daily commodities, and that we will enjoy the diversified benefits of photocatalysis in the near future.

7.4 Markets created by photocatalysts

In recent years, environmental contamination on a global scale has progressed and the environmental problem has become a very important issue that threatens the existence of human beings. In such a situation, photocatalysis is a hopeful technology for the 21st century that is called "the century of environment," because it is applicable to a relatively wide area of environmental issues including cleaning of air and water, measures for the sick house syndrome, deodorization, stain-proofing, and antimicrobial action. And yet, no harmful substances are emitted after treatment with photocatalysts. Development and practical application of high-performance photocatalysts have rapidly advanced, and it is estimated that about 3,000 companies have already entered this market.

The present market size of photocatalysts is estimated at ¥40 billion, and a research report published by Mitsubishi Research Institute expects that the market will grow to over ¥1,000 billion in 2005 (Figure 10)[20]. In the forecast, products related to deodorization for air cleaner and refrigerator account for ¥511.8 billion, those related to water treatment including sewage water and waste water for ¥354.4 billion, and stain-proofing of outside walls and tile blocks for ¥246 billion, amounting to ¥1,112.2 billion in total. Furthermore, the environmental industry market is expected to grow to ¥37,000 billion in 2010, and the photocatalyst industry is considered to be promising, playing a major role in the market. On the other hand, it is true that the present market size remains below expectations. The reason for this is that the cost of the catalyst is too high and

Figure 11: Number of patent applications related to photocatalyst



Source: Reference [21]

not that there are technical problems (reference[20] :"The World of Photocatalysts," p. 124). While it is not clear how much the cost hinders the growth of the industry, the recent rapid expansion of applications indicates that the cost related problem is being solved.

It is also possible that products not counted in the estimation may enter the market as a result of technical progress. For example, in agriculture, photocatalysts may be used in storage facilities for fruits and vegetables, utilizing their action to decompose and remove ethylene gas that accelerates the putrefaction of such fruits and vegetables. Also in the food manufacturing industry, where the control of bacteria in facilities is always a major issue, application of photocatalysts is expected. Since resistant microbes are generated when a large amount of disinfectants are used, the sterilizing power of photocatalysts that is not affected by the type of bacteria is the focus of attention as a very important function. It is expected that a new field of application will be developed as the research on photocatalysts advances.

Japan, where the world's most extensive research on photocatalysts is being conducted, has taken the leadership in its research and development. According to data from the Japan Patent Office, the number of patent applications in Japan over the past 20 years from 1980 to 2000 totaled 2,860 (Figure 11). This number significantly surpasses the number of registrations in the U.S. (409) and the number of applications in Europe (390) for the same period[21]. This indicates that patent application in Japan is very active compared to other countries and the number of applications accounts for almost 90% of the total of the world. Judging from this number of patent applications, Japanese photocatalyst technology is highly competitive in the world, and may offer a ray of hope to the Japanese long slumping economy.

7.5 Conclusion

Attracting attention as a new environmentally friendly technology, photocatalysts have a rapidly expanding market and are being used in our daily living environment.

In addition to the investigation to maximize the possibilities of individual photocatalyst, it is also expected in the future that completely new systems will be developed based on multi-photocatalyst systems, in which different types of catalyst cover the shortcomings of each other by combining their individual advantages, or transfer engineering, in which the photocatalytic function is combined with technologies of completely different fields.

As an immediate problem, cheap products with insufficient qualities are flowing in from overseas due to the present boom in photocatalyst development. Therefore, it is indispensable to establish standards such as JIS and ISO in the future.

Although the development of industrial applications for photocatalysts using titanium oxide as the major material is intensively advancing, these applications are essentially functioning as complementary roles for other technologies. Since photocatalysis is basically a clean technology, it has limitless possibilities if some kind of technical breakthrough can be achieved. There are two basic subjects in the research and development of photocatalysts.

One is the low quantum efficiency. In order to solve this problem, it is necessary to elucidate the basic mechanism of photocatalysis, and further, to search for materials that have quantum efficiency higher than that of titanium oxide. As has been previously described, one of the problems of titanium oxide is its high cost that prevents the prevalence of photocatalysts. If the problem of photodissolution is solved, for example, zinc oxide that is less expensive than titanium oxide can be used to achieve a breakthrough in the expansion of the market. Such basic research and development cannot be done by the industry, which is trying to develop the technology using titanium oxide as the major material. In a sense, this trend in the industry prevents the prevalence of the photocatalysis technology.

Another basic subject is the development of materials that respond to visible light. In this area, as has been already described, some trial tests have been made by adding nitrogen and transition metal elements. But the search for new materials has just started and satisfactory results have not yet been obtained. The initiative of technology in the post-titania age will be held by those who secure the basic materials. Since such search for materials is accompanied with a great deal of risk, it is difficult for the industry whose top priority is to make profits to undertake this.

Practical application of the photolysis of water is unforeseeable. Since the mechanism has not been elucidated, it is difficult to propose guidelines for the searching of materials. Therefore, it is indispensable to promote basic research as quickly as possible.

As explained above, in order to maintain and further develop the advantage Japan now enjoys in photocatalysis technology, it is insufficient to rely only on the efforts of the industry. It is essential to render political backing for the research and development. Particularly, the clarification of the photocatalysis mechanism provides the basis for the material search, and requires organizing physical and chemical knowledge theoretically. Even though Japanese private companies have intensively achieved their search for materials in the past, it is now economically difficult for them to search for materials even for their main lines of business. Essential materials for the next generation must be searched for from a national point of view. In the application of titanium oxide that is the major material at present, Japan is far ahead of other counties. However, a quarter of a century has past since titanium oxide was first used for photocatalysis. To establish a new phase for the photocatalyst industry, it is essential for Japan to develop materials for the next generation that supersede titanium oxide. It is most efficient if a wide range of public institutions take the charge of elucidating basic catalytic phenomena and searching for new materials, and this should be done urgently.

In order to complete photocatalysis technology that is friendly to all creatures on earth including human beings, we must make all-round efforts including a wide range of research and development from fundamentals to practical applications as well as the establishment of standards for the assurance of product quality.

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