

# Development and application of photocatalytic technology

## — Industrialization of sustainable eco-technology —

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Photocatalysts are capable of decomposing organic compounds such as toxic and bioresistant pollutants into non toxic gases in the presence of light. Material development and application of a number of photocatalysts have been carried out taking into consideration many factors including application, cost, as well as applicable regulations. As a result of these efforts, a variety of new photocatalytic products are now on the market.

**Keywords :** Environmental purification technology, photocatalytic technology, titanium dioxide (TiO<sub>2</sub>), water purification, air purification, antibacteria and antifungi, antifouling

### 1 Background of photocatalytic technology development

Recently, environmental pollution by hazardous chemical substances including dioxin from incinerators, organotin compounds used in ship bottom paint, PCBs, agrichemicals, solvents, and detergents is occurring at global scale, and it has become serious issue that threatens human survival. These chemicals include substances that are harmful at extremely low concentration of ppb level. They pollute water, air, and soil at global scale, and are very difficult to remove.

Conventionally, treatment of environmental pollutants was done with pyrolytic method that involved collection, concentration, and incineration. However, purification of the environment using this method necessitates treatment of vast quantity of water, air, and soil since the pollution is spread widely. To accomplish such treatment, large amount of energy such as fossil fuel is necessary, and use of such energy produces large amount of carbon dioxide. Also incineration process increases the danger of production harmful substances such as dioxin. Therefore, attempts of removal of environmental pollutants spread widely at low concentration throughout the environment using conventional technology may promote energy crisis, global warming, and further environmental pollution.

The technologies for measurement and analysis of environmental pollution have progressed and the state of environmental pollution is becoming clarified, but development of technology to repair and purify pollution at global scale progressed slowly. Sustainable environmental purification technology, where the environment can be purified without use of fossil fuel or harmful chemicals, was eagerly awaited.

The development of sustainable environmental purification technology is obligation of advanced nations that had been emitting large amount of environmental pollutants. It is an industrial technology that must be developed by Japan that claims to be the leading nation of science and technology. Development of the technology, commercialization, and diffusion of the products will contribute to future development of Japanese industry, and will improve global environment.

Photocatalyst can decompose and detoxify harmful organic chemical substance into carbon dioxide and water upon irradiation of light. Using the photocatalytic technology developed, the environment can be purified without using fossil fuel or harmful chemicals. Wide-ranging application is possible to water treatment, deodorization, VOC treatment, air purification, antifouling, antifogging, antibacteria/fungi, freshness maintenance, and dioxin removal.

While photocatalyst can be applied to various environmental pollutions and is effective method for global environment purification, many problems needed to be solved including technical issues such slow reaction speed, difficulty of handling, and difficulty of application to textiles and plastics, as well as issues of economy and reliability.

### 2 Objectives and goals of photocatalytic technology development

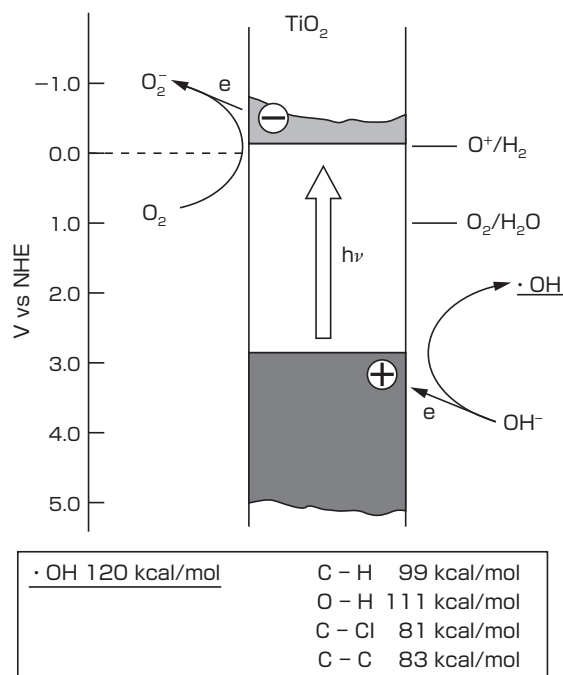
Photocatalyst is a substance that assumes high-energy state by absorbing light and causes chemical reaction by supplying that energy to reactants. Semiconductors and metallic complexes are used as photocatalysts, and most frequently used substance is titanium dioxide (TiO<sub>2</sub>). Titanium dioxide is widely used as pigment. It is safe and nontoxic with

excellent durability, and is used in toothpaste and cosmetics, and is approved as food additive.

When titanium dioxide is irradiated with light, electrons with negative charge and holes with positive charge are formed, just like in silicon used in solar cells, as shown in Fig. 1. These electrons and holes have extremely powerful reduction and oxidation actions, and active oxygen such as OH radical and super oxide anion ( $O_2^-$ ) are formed by reaction of water and dissolved oxygen. The holes and OH radicals have particularly strong oxidative power. While the bonding energies of carbon-carbon, carbon-hydrogen, carbon-nitrogen, carbon-oxygen, oxygen-hydrogen, and nitrogen-hydrogen bonds in the molecules composing the organic substance are 83 kcal/mol, 99 kcal/mol, 73 kcal/mol, 84 kcal/mol, 111 kcal/mol, and 93 kcal/mol, respectively, the energies of holes and OH radicals are significantly higher at 120 kcal/mol or above, so it can easily break these bonds.

Due to this action, various harmful organic substances including toxic chemicals dissolved in water and chemicals in air such as malodorous substances can be easily decomposed and detoxified by irradiating with light. Moreover, there are several advantages such as ability to treat dispersed environmental pollutants safely, efficiently, and semi-permanently without using harmful chemicals or fossil fuels, instead using clean and inexhaustible sunlight.

In this research, low-cost, high-performance photocatalyst was developed for actual use and specific purpose such



**Fig. 1 Energy level and photocatalysis of titanium dioxide.** V = electrical potential, NHE = normal hydrogen electrode. V vs. NHE is potential against normal hydrogen electrode, or potential when normal hydrogen electrode is used as standard.  $h\nu$  = energy of light.

as water treatment, air purification, antibacteria/fungi, and antifouling. The developed photocatalyst was used in practical application to various environmental fields, and the goal is to purify the earth environment through diffusion of photocatalytic products.

### 3 Research scenario toward accomplishment of goal

It is said that there is “valley of death” that must be overcome to achieve commercialization of new technology. Until now, only the technological aspects or technological breakthroughs were mentioned in the valley of death, but there are also economic and social aspects.

To accomplish realization, there exist not only technological valley of death such as improvement of performance, but economic valley of death such as cost performance against existing technology for same purpose, and social valley of death such as maintaining reliability and safety that are necessary for use and acceptance by consumers. Therefore, to actually apply and realize photocatalytic technology toward commercialization, it was necessary to overcome the three valleys of death including technological, economic, and social valleys.

#### 3.1 Technological valley of death

Photocatalysis was known before the World War II as phenomenon of paint degradation where white pigment containing  $TiO_2$  flaked off when it was exposed to sunlight, and this was considered a problem for long time. Therefore, pigment manufacturers that manufactured titanium dioxide spent effort to prevent degradation by coating the surface of  $TiO_2$  pigment with ceramics that do not undergo photocatalysis.

In the 1950s, Fujio Mashio, Shinichi Kato, *et al* of the Kyoto Institute of Technology engaged in research to utilize photocatalysis reaction in purification of environment and synthesis of useful substances<sup>[1]-[3]</sup>. This was followed by researches around the world on decomposition and detoxification of harmful organic chemical substances using photocatalyst. Experiments were done with various environmental pollutants such as hydrocarbon, organic chloride compounds, agrichemicals, and synthetics detergents, and there were many reports on successful decomposition and detoxification.

However, fine particles were used in these experiments, and practical application did not progress due to disadvantages such as difficulty of separating treated water and photocatalyst, and only batch treatment could be done since the photocatalyst dispersed in water in water treatment. To advance practical use of photocatalyst, it was mandatory to fix the catalyst onto a substrate.

Photocatalyst also had limitation that it could not decompose the target substance unless it came close to the surface, and there were problems of slow reaction speed that posed difficulties in removal of pollutants in high concentration and short treatment time. In addition, when the catalyst was attached to textiles or plastics, the materials were broken down by photocatalysis, and therefore use in textiles and plastics was impossible. Although photocatalyst could be used widely in environmental field, different forms needed to be devised according to use (for example, surface should be smooth for antifouling, while surface should be uneven to increase surface area for deodorization), and it was necessary to develop photocatalysts that matched specific use for practical application and product realization.

Development of effective photocatalyst and photocatalytic products adapted to actual use was the technological valley of death.

### **3.2 Economic valley of death**

Although photocatalytic technology can be widely applicable as mentioned above, cost performance becomes an issue when compared with existing technology.

Titanium ranks 9th in abundance in the earth crust. Titanium dioxide is used as pigment, and it is abundant and low cost as resource. However, titanium dioxide used in photocatalyst is generally nano-sized, ultra-fine particle and is ten times expensive compared to rougher TiO<sub>2</sub> particles used in pigments. Also, it is necessary to use artificial light source for nighttime use or device fabrication. To put photocatalytic technology, which is a novel technology, to practical use, it is necessary to lower the cost to less than or close to the cost of existing technology, or to provide advantage over existing technology. To promote wide use of photocatalytic technology, it must be usable in large scale at civil engineering sites.

Therefore, development of photocatalyst and photocatalytic products with cost performance that allows replacement of existing technology, and development of photocatalyst and photocatalytic products that can be mass-supplied at low cost were economic valley of death.

### **3.3 Social valley of death**

No matter how excellent the technology, it is useless unless it is used in the society. Products that use photocatalysts have characteristic that the effect cannot be perceived immediately. For example, self-cleaning effect takes several months after installation before the effect becomes visible. Therefore, many fake products were marketed and proper products failed to win confidence of the consumers. Also, due to lack of uniform and reliable testing method to evaluate the performance of photocatalysts, comparisons could not be made, and this was a barrier to development

of high-performance photocatalyst. Therefore, education activities for photocatalytic technology and standardization of performance evaluation tests were necessary. Since photocatalysts differ in performance depending on use, it was necessary to develop performance tests for different use. The evaluation test was mandatory as “scale” in developing high-performance catalyst.

Photocatalysts must gain confidence of the consumers before they could be accepted in the society. It was also necessary to follow safety and environmental regulations such as RoHS (Restriction of Hazardous Substances) Directive and the WEEE (Waste Electrical and Electronic Equipment) Directive of the European Council for hazardous substance in electric and electronic appliances, as well as Pharmaceutical Affairs Law, pollution laws, and PRTR (Pollutant Release and Transfer Register). This was the social valley of death.

### **3.4 Scenario to achieve the goal**

The aforementioned three valleys of death had to be overcome before photocatalytic technology could be accepted in the society. The following scenario was considered to overcome them.

First, for technological valley of death, technological development is generally considered to take a linear course from *Type 1* to *Type 2 Basic Research*, and then to development and practical application. However, in photocatalytic technology, there was almost no result of *Type 1 Basic Research* 25 years ago when we started research.

Although Honda-Fujishima effect is extremely famous as principle of photocatalysis, this was actually hydrolysis by photoelectrode reaction of titanium dioxide and did not involve the use of photocatalyst. Also, not much was known about the photocatalysis mechanism except that electrons and holes were produced by irradiation to cause photocatalysis reaction. The only method known to increase performance and reaction speed of photocatalyst was to prevent disappearance of electrons and holes by rebonding, and nothing much was known on how this could be done.

Therefore, high-performance catalysts for particular usages were developed by trial and error by imagining the actual use scene. The substances that must be added to create high-performance catalysis from TiO<sub>2</sub> base were sought by trial and error. Then we developed specific-purpose high-performance photocatalyst by finding the additive, conducted use application, developed higher performance photocatalyst by feeding back the result, and progressed to new application using the higher performance photocatalyst.

In this case, R&D of photocatalyst was interdisciplinary, and it was necessary to collaborate with technologists and companies that possessed advanced technology as

well as specialists of several fields. We encouraged their participation, and conducted R&D strategically and collaboratively.

To overcome the economic valley of death, we developed low-cost photocatalyst and photocatalytic product based on TiO<sub>2</sub> that were inexpensive, safe, and mass-suppliable, using industrial waste as matrix. We worked on application and development with advantage unseen in existing technology. This enabled production of environment purification material from industrial waste, and contributed to recycling industrial waste. It also enabled unique applications untried before.

For social valley of death, we organized research groups and industrial organizations for photocatalyst to standardize evaluation test that was necessary for development of high-performance photocatalysts. We also worked on promoting photocatalytic technology to society through organization of and participation to exhibitions and seminars. We developed photocatalytic technology considering regulations for safety, environment such as RoHS and WEEE, Pharmaceutical Affairs Law, pollution laws, and PRTR laws.

Through these strategies, we attempted to overcome the three valleys of death including technological, economic, and social valleys.

## 4 Execution of R&D toward practical application of photocatalyst

### 4.1 Development and application of high-performance photocatalyst

I shall describe the actual R&D and application in chronological order.

#### 4.1.1 Development of TiO<sub>2</sub> transparent film photocatalyst<sup>[4]</sup>

Photocatalyst has limitation that decomposition does not occur unless the target substance comes in contact upon irradiation, and efficiency increases with larger surface area



Photo 1. Functional glasswares with photocatalyst coated with TiO<sub>2</sub> transparent thin film.

since photocatalysis occurs on the surface. Therefore, high activity titanium photocatalyst in form of ultra fine powder with small particle diameter yet with high surface area had been developed. However, photocatalyst in particle form has disadvantage of being difficult to handle and to collect as they are blown away by wind. It was mandatory to fix the TiO<sub>2</sub> photocatalyst onto substrate for practical use, and various methods were attempted.

In the method of fixing by mixing TiO<sub>2</sub> powder with organic binders, there was problem with durability since organic material that was used as adhesive was decomposed by photocatalysis and TiO<sub>2</sub> powder gradually dropped out. In method where TiO<sub>2</sub> powder was mixed with inorganic binders such as cement or glaze, the TiO<sub>2</sub> became embedded and light could not reach. The target chemical substance could not come in contact with TiO<sub>2</sub> and the photocatalytic performance decreased. Other methods included CVD, PVD, and sputtering, but they had problems where large surface area was difficult to manufacture since vacuum container was necessary, and the process required large amount of energy.

Therefore, we developed photocatalyst in film form consisting only of TiO<sub>2</sub> fixed onto substrate using sol-gel method that can be conducted simply at low cost (Photo 1). Titania sol was made from alkoxide of titanium. After coating this on glass substrate by dip coating method, it was dried and sintered. By repeating this process, we were able to manufacture TiO<sub>2</sub> thin film photocatalyst that was transparent and had excellent durability and high performance.

This TiO<sub>2</sub> fixed photocatalyst has surface composed entirely of TiO<sub>2</sub> so it can efficiently break down chemical substances that come in contact. After fixing the TiO<sub>2</sub> thin film photocatalyst onto transparent glass substrate, light that passes through the substrate can be used, and water treatment can be done continuously and without maintenance. Moreover, it has antibacterial and superhydrophilic properties.

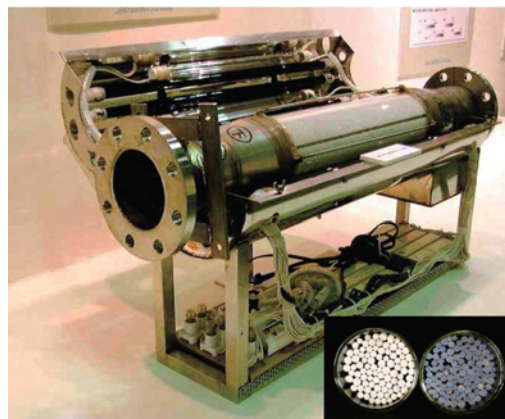


Photo 2. Photocatalytic silica gel (right, left is ordinary silica gel) and dioxin decomposing apparatus.

It is necessary to apply even and thin coat of titania sol on the substrate to manufacture high-performance TiO<sub>2</sub> thin film photocatalyst with excellent transparency and durability. Application with brush produced brush lines, or thin and thick areas that resulted in clouded film. Therefore we employed dip coating. However, in dip coating, when the speed of withdraw was too fast, the film became thick resulting in cloud and brittleness. The film thickness became uneven unless the withdrawal was smooth, and distortion occurred when sintering, and the layer dissociated. Therefore it was necessary to withdraw slowly and smoothly. Since there was no suitable dip coating device on the market, we jointly developed the device with a company in Aichi Prefecture and succeeded in manufacturing TiO<sub>2</sub> transparent thin film photocatalyst.

We conducted further investigation for the application of this TiO<sub>2</sub> transparent thin film photocatalyst, and developed photocatalyst glassware and photocatalyst pellets to purify water, and photocatalyst fluorescent lamp with antifouling, deodorant, and antibacterial functions.

#### 4.1.2 Development of TiO<sub>2</sub> transparent porous photocatalyst

Since photocatalysis is surface reaction, if photocatalyst could be fixed in porous material with large surface area such as adsorbent, the target substance can be attracted by adsorption and then decomposed efficiently by photocatalysis. However, since ordinary porous material is not transparent to light, and reaction does not take place when the photocatalyst is located behind the porous material. Therefore, to increase the function of photocatalyst, we considered using inexpensive, transparent, and porous silica gel as matrix, and developed photocatalyst coated with TiO<sub>2</sub> transparent thin film.

In photocatalytic silica gel, the fine pores within silica gel are coated with TiO<sub>2</sub> film. It can effectively decompose odor and treat water since it has specific surface area of 450 m<sup>2</sup>/g and light can penetrate into the fine pores. Moreover, absorbed harmful chemical substances are broken down safely into carbon dioxide. This porous photocatalyst can be called self-regenerating adsorbent.



Photo 3. Antifouling effect on surface of photocatalytic permeable block (right).

This photocatalytic silica gel had been patented and commercialized by companies. Using this, we developed water treatment and exhaust gas treatment apparatus that can efficiently degrade and remove over 99 % of dioxins in exhaust gas and wastewater from industrial waste incinerators (Photo 2)<sup>[5][6]</sup>. We also developed decolorization system for colored wastewater and photocatalytic human waste treatment system<sup>[7]</sup>.

We developed photocatalytic permeation block with photocatalyst applied to the surface of porous concrete block<sup>[8]</sup> (Photo 3). This not only has antibacterial, antifungal, and antifouling effects, but also adsorbs, decomposes, and removes NO<sub>x</sub> and SO<sub>x</sub> in the air. It also can be used for heat island measures since it captures rainwater and surface temperature decreases by evaporation. Waste materials such as coal ash are used as matrix to lower cost. It is used as sound absorbing block of sound barriers, and is also installed in parking lots to purify exhaust gas and as heat island measures.

#### 4.1.3 Development of photocatalyst that can be used in textiles and plastics<sup>[9]</sup>

Since textiles and plastics were degraded by photocatalysis when they were mixed with photocatalyst, it was impossible to apply them to textiles and plastics. We devised ways of coating the surface of TiO<sub>2</sub> with ceramics that had no photocatalytic activity and developed TiO<sub>2</sub> photocatalyst particle in form of muskmelon or kompeito (sea mine shaped sugar candy) (Fig. 2).

Muskmelon-form particle is made by coating the surface of TiO<sub>2</sub> with silica without photocatalytic activity like the net of a muskmelon. When it is mixed into textile or plastics, the silica without photocatalytic activity on the surface prevents contact of TiO<sub>2</sub> with textiles or plastic and decomposition is controlled. This particle can be adjusted by coating the surface of TiO<sub>2</sub> with thick coat of silica with even fine pores.

The *kompeito*-form particles is made by coating the surface of TiO<sub>2</sub> with apatite without photocatalytic activity, like the horn of *kompeito*. Apatite composes bones and teeth, and has excellent biocompatibility. This *kompeito*-form particle can be adjusted as apatite grows naturally, thereby saving

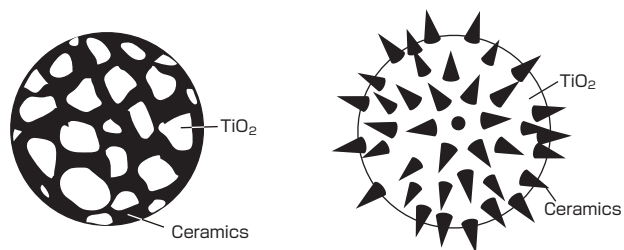


Fig. 2 Muskmelon-form and *kompeito*-form TiO<sub>2</sub> photocatalytic particles.

energy, on the surface of TiO<sub>2</sub> like growth of bone and teeth, by soaking the TiO<sub>2</sub> particle in solution of calcium and phosphate ions. Like muskmelon-form particles, when it is mixed in textiles and plastics, apatite without photocatalytic action on the surface prevents the decomposition of textiles and plastic by TiO<sub>2</sub>. Since apatite can absorb bacteria and fungi, antibacterial and antifungal effects are obtained efficiently using this TiO<sub>2</sub> photocatalyst. The produced apatite is shaped like rose with large surface area, which enables great deodorant effect.

Both TiO<sub>2</sub> photocatalyst particles are patented by companies and are available commercially. Also, many textile and plastic products including curtain, men's suits, student's uniform, socks, mattress, towel, sheets, shoes, stuffed animals, artificial flowers (Photo 4), artificial plants, and wall papers are manufactured and sold in Japan and overseas, and practical application of photocatalysts is spreading dramatically.

By adding the *kompeito*-form TiO<sub>2</sub> photocatalyst particle to activated carbon, we developed functional adsorbent that can be used repeatedly. Active carbon can purify the environment by adsorbing harmful chemicals, odor, and VOC, but loses function when adsorption reaches saturation. When photocatalyst is added to active carbon, it adsorbs harmful chemicals, odor, and VOC without light, and photocatalyst breaks them down in presence of light, so environment can be purified efficiently. However, active carbon is also oxidized into carbon monoxide or carbon dioxide by photocatalysis. Therefore, we developed functional adsorbent that can be used repeatedly by controlling decomposition using *kompeito*-form TiO<sub>2</sub> photocatalytic particles. Active carbon has beautiful blue appearance and can be used as attractive interior piece with purification function (Photo 5).



Photo 4. Environment purifying artificial flower with *kompeito*-form TiO<sub>2</sub> photocatalytic particle.

We worked on various applications using this functional adsorbent, and had succeeded in agrichem-free cultivation of tomato by installing them in the ridge of the greenhouse<sup>[10][11]</sup>. By using functional adsorbent, the airborne bacteria and fungi pores in the greenhouse were reduced and disease and mold were prevented.

#### 4.1.4 Compositing of photocatalyst and oxidant<sup>[12]</sup>

When wastewater is treated using photocatalyst, reaction time is high at first, slows down, and finally the reaction ceases. This is because dissolved oxygen is consumed when harmful substances in water undergo oxidative degradation, and it was found that oxygen was necessary to break down harmful substance by photocatalysis. Therefore, to prevent the cessation of photocatalysis, we tried to increase dissolved oxygen by aeration, and also composited photocatalyst and oxidant. When oxidants such as hydrogen peroxide and ozone are used with photocatalyst, the oxidants are converted efficiently to active oxygen by photocatalysis, and oxidative degradation is accelerated.

As application using this reaction, we developed dental bleach to whiten the teeth. This is a combination of TiO<sub>2</sub> and low concentration hydrogen peroxide, and teeth stain is broken down by applying to teeth and irradiating with light. By combining with hydrogen peroxide, the treatment could be done in short time. Teeth whitening used to be done with dangerous drug, but now it can be done safely with this method. When commercializing photocatalytic dental bleach, the Pharmaceutical Affairs Law was a barrier. After preparing safety data, it took three years to obtain approval of the Ministry of Health, Labour and Welfare, and the product was marketed on December 2006.

There is social valley of death for application to drugs, quasi-drugs, and medical equipment, and it is necessary to clear safety standards.

Further developing the photocatalytic dental bleach, we developed photocatalytic detergent for cleaning exterior walls. While antifouling and self-cleaning functions can be



Photo 5. Photocatalytic functional adsorbent that is also attractive as interior piece.

obtained by coating the exterior walls with photocatalyst, the soil is decomposed by photocatalyst and flakes off along with it. Therefore, when applying photocatalyst, cleansing of substrate is extremely important. However, high-pressure water that is used generally requires large amount of water and may harm the exterior wall. Therefore, we developed a water solution of composited photocatalyst and oxidant. This was applied to the wall, left for some time, and then washed with sponge and water to remove the soil (Photo 6).

This photocatalytic detergent is safe and harmless, with only small amounts of  $\text{TiO}_2$  and inorganic ions remaining after use. Moreover, when 300,000 bird flu viri were mixed with photocatalytic detergent, 99 % of them were deactivated 30 minutes later, and excellent effectiveness against bird flu was demonstrated. Also, we obtained deodorant effect along with antibacterial effect, and we developed deodorant and antibacterial apparatus and system using this detergent. It is beginning to be employed as deodorant and antibacterial measures in raw garbage treatment plant and nursing homes, as well as disease prevention in shrimp and fish farms.

We applied this photocatalytic detergent to water treatment by soaking the porous material in this detergent. Cost is an issue since large amount of purifier becomes necessary to purify waters of river and ocean. Aichi Prefecture, a major producer of Sanshu roof tile, disposes 380,000 ton/year of waste tile. Therefore, we developed low-cost photocatalytic water environment purifier using these tiles as matrix. We soaked the safe and harmless pellets made by grinding the roof tiles in photocatalytic detergent, and dried them. When these were dispersed onto the sludge in river or ocean, the sludge was decomposed and purified. This photocatalytic detergent has low cost at less than 100 yen per 1 kg, and use is expected in developing nations.

#### 4.1.5 Development of visible light photocatalyst and new materials

While  $\text{TiO}_2$  photocatalysts have many advantages as mentioned above, it will not function unless irradiated with ultraviolet light that has great energy. There is only 3~4 % ultraviolet light in sunlight, and much lower in fluorescent light. Therefore, to use photocatalyst efficiently indoors, photocatalyst that works under visible light is

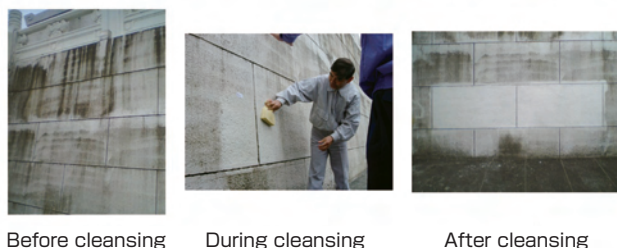


Photo 6. Result of cleansing exterior wall using photocatalytic detergent.

necessary. Currently, photocatalyst that works under visible light includes oxygen-defective and nitrogen-doped  $\text{TiO}_2$  photocatalysts and those that use rare metal, but they cannot be used readily due to high cost.

Therefore, we developed low-cost visible light photocatalyst by combining  $\text{TiO}_2$  and iron, which is low cost, safe, and harmless<sup>[13]</sup>. The cost is one-third of conventional visible light photocatalyst, and it is expected to become used widely mainly for indoor use.

Photocatalyst can be applied to antibacterial, antifungal, and freshness maintenance applications, and freshness and quality maintenance can be improved further when deoxidation function is added. Therefore, we developed  $\text{TiO}_2$  deoxidant where oxygen was removed from  $\text{TiO}_2$  by improving oxygen-defective  $\text{TiO}_2$  photocatalyst<sup>[14]</sup>.

As shown in Photo 7, this photocatalyst is blue and returns to white  $\text{TiO}_2$  when it takes in oxygen, so it can be used as oxygen indicator. Unlike conventional iron deoxidant, there are several advantages such as it does not become red when mixed with food, does not combust in microwave oven, and does not sound the metal detector since it is not magnetic. This deoxidant is totally new application of  $\text{TiO}_2$ , and has advantages unseen in conventional deoxidants.

#### 4.2 Collaboration of industry, academia, and government and standardization of testing method for photocatalytic performance

When developing high-performance photocatalyst by trial and error, cooperation of researchers and technologists in various fields such as catalyst science, material engineering, synthetic chemistry, analytical chemistry, applied chemistry, chemical engineering, and reaction engineering are necessary for quick and efficient investigation. Cooperation of companies with excellent production technology is necessary to realize photocatalyst.

In the Chubu region which is Japan's industrial capital, there



Photo 7.  $\text{TiO}_2$  deoxidant before absorbing oxygen (blue) and after absorption (white).

are many companies, universities, and public testing research institutes with excellent capacity for R&D. Therefore, we decided to develop high-performance photocatalyst strategically utilizing and collaborating with their advanced production technology and R&D ability. We transmitted information actively through exhibitions, seminars, newspaper, magazines, and television. To seek collaborative R&D for photocatalysts, we also encouraged participation of researchers and technologists of various companies, universities, and public testing research institutes by holding research seminars for collaboration of industry, academia, and government.

This research seminar was the first photocatalyst industry group in Japan with about 350 members. It developed into the Society of Industrial Technology for Photocatalytic Articles (SITPA), the largest organization for photocatalysis with collaboration of industry, academia, and government, and was succeeded by the Photocatalysis Industry Association of Japan (PIAJ). We worked on setting quality standard for photocatalytic products, standardization of evaluation testing of photocatalytic performance, establishment of SITPA mark, as well as establishment of standard for labeling and terminologies. Our objectives were to prevent proliferation of poor products, to increase confidence for photocatalytic products, and to promote wholesome development of the photocatalysis industry. Moreover we worked on Japanese standardization (Japan Industrial Standard) and international standardization (International Organization for Standardization) for evaluation testing of photocatalytic materials, we organized and participated in international exhibitions of photocatalysts, and worked on education and diffusion of photocatalytic technology. This gathered interest of researchers, technologists, companies, and consumers, which in turn promoted new entries and increased number of cooperating researchers, technologists, and companies. Every year, we conducted 40 to 50 joint researches and technological advising for photocatalysts with various companies.

For evaluation of photocatalytic performance, following standards were adopted as Japan Industrial Standard:

- Fine ceramics (advanced ceramics, advanced technical ceramics) - Test method for air purification performance of photocatalytic materials - Part 1: Removal of nitric oxide (JIS R1701-1)
- Test method for antibacterial activity of photocatalytic products under photoirradiation and efficacy (JIS R1702)
- Test method for self-cleaning performance of photocatalytic materials - Part 1: Measurement of water contact angle (JIS R1703-1) and Part 2: Decomposition of wet methylene blue (JIS R1703-2)
- Test method for water-purification performance of photocatalytic materials by measurement of forming ability of active oxygen (JIS R1704)

- Light source for test of photocatalytic materials used under ultraviolet (JIS R1709)

Of these, testing of nitric oxide purification performance was established as ISO.

## 5 Results and discussions

We conducted development of high-performance photocatalysts that were unavailable before, and worked on various new applications. As result, about 200 patents on photocatalysts were filed in Japan and overseas, and about half of them are registered as patent. About 40 patents and property rights are in effect, and various products are manufactured and sold<sup>[15]</sup>.

Although photocatalysts can be applied in various places, it is necessary to find optimal form and design for each application at product realization level. For example, for self-cleaning and antifouling, contamination is readily removed if the surface of the photocatalyst is smooth, while for water treatment and deodorization, uneven porous surface will absorb more harmful chemical substances. There are many kinds of odors such as acid, neutral, and alkaline, and photocatalysts to match each type are necessary.

By keeping specific use of the products in mind, we successfully developed various high-performance photocatalysts and photocatalytic products for specific purposes, and developed environmental purification technology using photocatalysis including water treatment, deodorization, air purification, self-cleaning, antifouling, antifogging, antibacteria/fungi, and dioxin treatment. Since the issue of cost is the greatest concern in commercialization, we worked to lower cost by using waste material and energy conserving manufacture method. As result, we realized practical use and commercialization of photocatalysts and environmental purification to some degree. However, achievement of goal of global purification is still ahead, and further research and diffusion of products are necessary.

## 6 Future issues

Photocatalyst can be used easily and safety, and it can be used anywhere in the world as long as there is light. Therefore, it can be used in developing nations as well as advanced nations, and it is a scientific technology that can contribute greatly to the world.

To realize purification of the earth environment, diffusion of photocatalyst in various countries around the world is necessary. Therefore, it is necessary to collaborate with research institutes and companies of East Asian and Southeast Asian countries where environmental pollution have become extremely serious due to rapid economic growth, to develop photocatalytic technologies corresponding



to the situations of individual countries. For example, in areas where concentration of environmental pollutants is high, performance or surface area of photocatalyst must be increased or combined with other technologies. Also, cost reduction is necessary for diffusion of photocatalyst, and it is necessary to utilize waste materials and unused resource of that country. If we can develop a photocatalyst that matches the country, new application using it progresses and photocatalytic technology develops further.

Currently, associations for photocatalysts are established in China, Taiwan, and Korea and commercialization and diffusion of photocatalytic technology is progressing. However, to spread this technology to the rest of the world, further collaboration with technologists of various countries is necessary. We are working actively on cooperation and advising for research institutes and companies of various countries such as China, Taiwan, Korea, Thailand, Philippines, Vietnam, Europe and others.

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## Discussion with Reviewers

### 1 The progression of R&D

#### Comment (Hisao Ichijo)

I think the selection and integration of elemental technology is difficult to understand. The process by which R&D progresses while moving back and forth between *Type 1* and *Type 2 Basic Researches* is important. To enhance understanding of readers outside the specialty, the part that corresponds to *Type 1 Basic Research* should be explained briefly by citing original papers.

#### Answer (Hiroshi Taoda)

When developing catalysts and new drugs, there are support system to raise probability for how to raise effectiveness and performance by adding what, but basically it is done by trial and error. It is also a research for discovery and is *Type 1 Basic Research*. In general, technological development is thought to progress linearly from *Type 1* to *Type 2 Basic Research* and then to development and realization. However, it doesn't always

happen that the knowledge (elemental technology) of *Type 1 Basic Research* are arranged neatly on the kitchen counter, and you can simply put them together and cook up a dish (*Type 2 Basic Research*). *Type 1 Basic Research* is done by trial and error, and the results are used to conduct *Type 2 Basic Research* and development/realization, and then *Type 1 Basic Research* is conducted again by feeding back the results. It is necessary to circulate *Type 1*, *Type 2*, and realization, and I believe this is *Full Research*. How I conducted research and thinking behind them were explained as much as possible in the individual sub-sections under chapter 4. Also, I added patents in the Reference to clarify the part that corresponds to *Type 1 Basic Research*.

## 2 The three “valleys of death”

### Comment (Yoshiro Ohwadano)

I think it is interesting view that there were three kinds of “valleys of death” of technological, economic, and social valleys before photocatalytic technology could diffuse into the society. I think the whole article will become easier to understand if you provide description along this structure.

Specifically, please explain (1) where was the “technological valley of death” and how it was overcome, (2) where was the “economic valley of death” and how it was overcome, and (3) where was the “social valley of death” and how it was overcome.

This will sublimate the article to general knowledge that can

be applied to other themes, and the article will become valuable.

### Answer (Hiroshi Taoda)

(1) Technological valley of death was the fact that powder of photocatalyst was difficult to handle and photocatalytic performance was low. We overcame these issues by devising method for increasing effective surface area by fixing the photocatalyst onto transparent porous matrix. We also found ways to prevent decomposition of matrix, and improved performance by widening the sensitivity to visible light range. The function of photocatalysts increased significantly, and use and handling became easier.

(2) Economic valley of death was that the competitive power was lower compared to existing technology in terms of cost. We overcame this by cost reduction and seeking original usages. We used inexpensive base material such as waste material, and devised ways of fixing photocatalyst on transparent base and textiles.

(3) Social valley of death was legal regulations and low social acceptance. We overcame this by taking time to obtain approval. We also established performance evaluation method and worked on JIS and ISO standardization by organizing technological association under cooperation of industry, academia, and government. We also worked on education and diffusion of photocatalytic technology by appealing appropriate use of photocatalysts.