Robust Science & Technology for Safe and Secure Life Space



National Institute of Advanced Industrial Science and Technology **AIST**

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Robust Science & Technology for Safe and Secure Life Space *-Photocatalyst-*

Dr. Tetsuya KAMEYAMA, Director of Ceramics Research Institute

In the 21st century, science and technology is expected to allow us to lead a safe, secure and high quality life in harmony with the global environment. The global environment issues imposed upon mankind are in need of urgent resolution. The photocatalyst reaction utilizing semiconductor materials such as titania is one of the most effective technologies in the field of environmental purification.

Photocatalytic technology has grown in Japan with the AIST as a key institute, that has been developing this world-class technology over a 20-year period, yielding a number of successful cases of commercialization. The followings are the profiles of a variety of products that were developed as a result of technological transfer.

Photocatalyst Activated with Light

Photocatalyst is a light-activated catalyst. When a photocatalyst material is exposed to light, it absorbs photon energy and causes various chemical reactions. Metal complexes and semiconductor catalysts are recognized as photocatalyst materials. Titanium dioxide (TiO_2) is the most commonly utilized semiconductor photocatalyst with highly distinctive properties; water insolublity, cost effectiveness, durability, and resistance to abrasion. Furthermore, it is an abundant resource ensuring good accessibility. TiO₂ in its anatase crystal structure is most popular as photocatalyst.

A TiO₂ generates electrons and holes by irradiation with light. Most of the organic pollutants including dioxins are decomposed into carbon dioxide and water, etc by the effect of the holes with highly oxidative potential.

Such photocatalytic reactions can be applied to the field of environmental clean-up including deodorization, antibacterial/antimold protection, emission gas treatment, self-cleaning, anti-fouling protection, water treatment, and so on.

AIST-born Photocatalyst Materials

TiO₂ Photocatalyst Coatings

Titanium oxide is usually a powdery substance which requires special care in handling. In order to promote the practical application of air cleanup materials, it is necessary to immobilize TiO₂ photocatalyst through coating on the substrate. Photocatalytic coating agent was developed for this purpose. Furthermore, another coating solution was developed, that creates a porous TiO₂ film improving the adsorption effect of pollutants.

Apatite/TiO₂ Photocatalyst

Apatite/TiO₂ photocatalyst is a multifunctional composite material of apatite, an essential component found in bones and teeth, and TiO₂ photocatalyst. Polluting materials including bacteria, toxic chemical compounds etc. are adsorbed by apatite and decomposed by titanium oxide photocatalyst upon the exposure to light (Fig.1). Titanium oxide has a property to decompose contiguous materials such as fiber, resin etc. by the photocatalytic effect. However, using apatite as a spacer, it becomes possible to blend the TiO₂ photocatalyst with these materials and also to coat it on them(Fig.2). This



Fig.1 Environmental purification by apatite coated photocatalyst



Fig.2 Apatite/TiO₂ coated materials and concrete paving blocks

apatite/TiO₂ photocatalyst can be applied to purification of air and water, antifouling protection, bleaching, and cleaning. It can be used with organic substrates including fiber, resin, plastic, wood, paper, and so on.

Visible-Light Photocatalyst

One of the few shortcomings of titanium oxide is that it can be activated only by the irradiation of UV light, that accounts only for several percent of sunlight. To respond to this weakness, AIST has developed TiO₂ photocatalyst responsive to both UV rays ranging from 300 to 600 nm and visible light, by means of plasma processing (Figs. 3, 4 and 5). This photocatalyst is highly effective in both indoor and outdoor environments

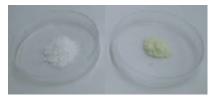


Fig.3 (left) Raw TiO₂, (right) RF-plasma treated TiO₂



Fig.4 Visible-light-responsive TiO₂ photocatalysts. (left) powder, (right) Liquid for coating



Fig.5 Thin-film photocatalyst coated on sheet glass. (left) TiO₂, (right) Nitrogendoped TiO₂ for visible-light activity

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in Indoor Environments

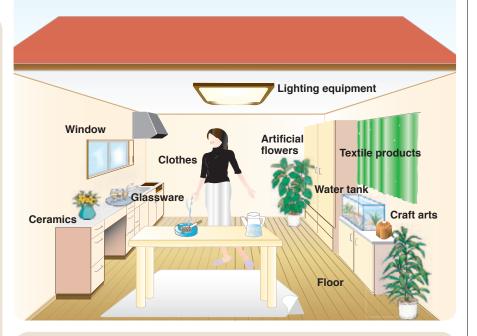


Water purification

The inner surface of the glass vessel is coated with titanium oxide film photocatalyst. Under the irradiation of light, the film oxidizes and decomposes organic compounds into carbon dioxide and water as well as eliminates odor from chlorine. As it also prevents bacteria and mold growth, the water in the glass vessel can be kept fresh and flowers last longer.

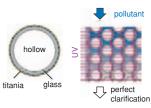
Deodorization

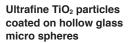
The ultra light-weight porous ceramics with pores sized $10-80\mu$ m is coated with titanium oxide. The porous structure allows light to reach the inside of the material. By illuminating with UV ray, the deodorant photocatalyst module using this material is able to degrade and eliminate odor substances emitted from restaurants, hotels, food processing factories and so on.



Purification of polluted water

Titania coated hollow glass micro sphere has density of 0.92 g/cm³ and floats on water, allowing efficient decomposition of pollutants. In the case example of purification of waste water of laver processing, the quality of purified water exceeded that of sea water. This product can be applied to clean up the crude oil spilled from the wrecked tankers etc.







20 25 30 Flow rate (ml/min)

Antibacteria/antifungal protection of food

1500

<u>)</u> 1000

500

15

C.Dens

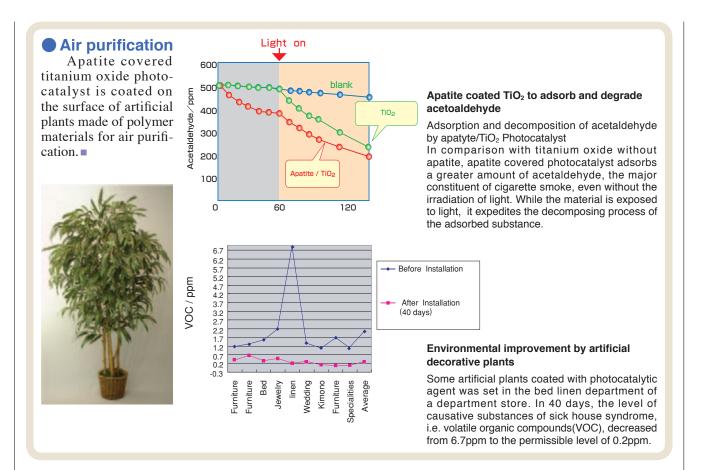
As apatite has high affinity with molds and bacteria, it adsorbs those in the air and also eliminates by photocatalysis. This can be an effective method of antibacterial/antifungal protection of food.



Protection of arts and crafts

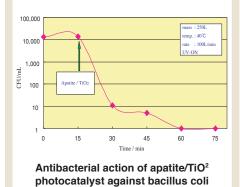
Photocatalytic coating agent can be applied to the surface of Japanese traditional arts and crafts (cultural assets) to avoid dirt and stain as well as discoloration. Furthermore, experiments have been made to apply the coating agent to ceramic ornaments.





Antibacterial function

In general, water purification using the photocatalytic effect may be hindered by high concentration levels of harmful substances that prevents light from reaching the depth. It is possible, however, to prevent slime on the surface of the swimming pool, bath tubs etc. by applying a paint containing apatite covered titanium dioxide. By putting bath powder containing apatite/ TiO₂ of as little as 33 ppm into water and irradiating UV ray, most of the bacillus coli can be eliminated within 1 hour.

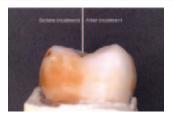


Teeth breaching

This is a novel bleaching agent consisting of titanium dioxide responsive to visible light and of low concentration (3wt%) hydrogen peroxide solution. This agent can be applied directly to the tooth and exposed to visible light to obtain the safe and quick bleaching effect.

Denture washing

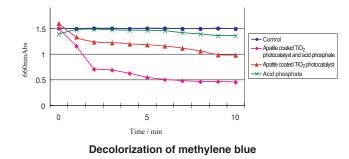
When apatite/TiO₂powder is added by 0.08wt% to a denture cleanser consisting of phosphoric acid and pyrophoric acid, the agent almost totally decolors methylene blue within a few minutes. This agent is effective to clean tobacco stain and dental calculus as well as remove bad odor of artificial teeth in 6 hours.



Bleaching effect of tooth



Cleaning effect of a denture cleanser containing photocatalyst agent



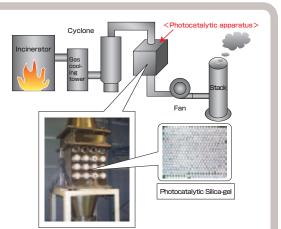
in Outdoor Environments

Decomposition of dioxins in emission gas from waste incinerators

Dioxin is a highly toxic substance contained in incinerator flue gas which is emitted during the process of industrial waste disposal. The gas can be degraded easily by using photocatalyst. A photocatalytic dioxin decomposer is placed behind the dust collector through which waste is processed. The decomposer is filled with silica gel beads (size: approx. 3mm) whose inner surface is coated with titanium oxide. The device can degrade and remove at least 95% of dioxins by the irradiation of UV light. Although conventional technology ex-

perienced difficulties in treating Coplanar PCB, this system is able to resolve this problem. Currently, research efforts are being made aiming at the practical application of this small and economical device.



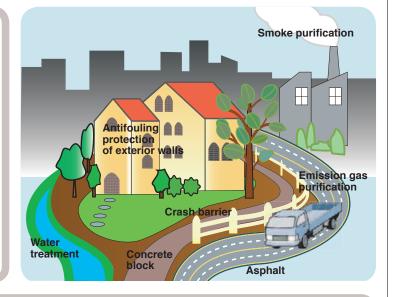


Decomposition system of dioxins(in emission gas from waste incinerators)

Antifouling protection of exterior walls

Apatite/TiO₂ paint applied to exterior walls decomposes organic products that cause fouling. As exterior walls of a building normally require cleaning every 5 years, a considerable reduction of facility maintenance cost is expected by coating this photocatalytic paint.





Purification of car exhaust emission

Air pollution is attributed mainly to nitrogen oxide (NOx) and sulfur oxide (SOx) contained in automobile exhaust. Purification of polluted air is attempted by utilizing acoustic panels coated with photocatalyst for the sidewalls of a road. A porous material which is made from ceramic waste is used for the panel. The thin-film titanium oxide coated on the surface of the panel almost totally oxidize the pollutants, decomposing them into nitric or sulfric

Sample	NOx concentration (ppm)			NOx removal (%)
	NO	NO2	NOx	
Blank (without light)	4.6	0.3	4.9	-
without photocatalyst	4.6	0.3	4.9	0
1 coating sample	0.2	0.1	0.3	94
3 coating sample	0.1	0.0	0.1	98

Performance of photocatalyst that eliminates NOx

acid by reaction with water. These chemicals are washed away by rainfall.

Furthermore, in being coated with apatite covered titanium oxide, the substrate adsorbs harmful chemical substances with or without the irradiation of light. This can be applied to a permeable block with a function to degrade such toxic substances when exposed to light. The block can be utilized for paving.



Paving blocks for NOx removal (right top ■) and Permeable blocks coated with apatite-covered titanium dioxide (right bottom ■)

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Utilization of Photocatalysts in Everyday Life

AIST's Future Plan as a Pioneer in Research on Photocatalyst

Brief History of R&D on Photocatalytic Technology

In 1970s, it was discovered that titanium oxide activated by light illumination decomposes water by electrolysis (Nature 1972). This phenomenon was known as the "Honda-Fujishima effect". Based on this discovery, such products as titanium oxide coating films, composite material etc. have been developed and applied to water purification, antifouling protection and so on.

In 1990s, it was reported that titanium oxide photocatalyst has a function to degrade and remove nitrogen oxides at an international conference. Following this, AIST has been playing a major role in promoting the practical application and commercialization of photocatalysts as environmental purifying agents. The institute's research and development efforts yielded results including coating material that produces a porous effect of TiO_2 film and multifunctional composite material using apatite.

Recently, research on photocatalysts responsive to visible light is being conducted.

Eyeing the Global Market - For Further Development of Technology

Aiming to reduce production cost and broaden application of photocatalytic technology, AIST intends to further R&D projects on highly efficient, sophisticated photocatalysts.

Development of Highly Efficient Photocatalytic Materials

In terms of material development, there is a demand for the creation of a multifunctional, highly efficient photocatalytic material ap-

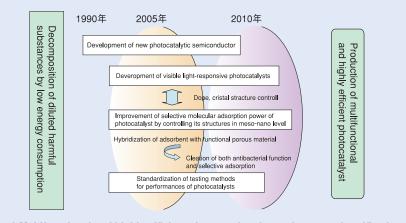


Fig. 6 Multifunctional and highly efficient photocatalyst for environmental purification

plicable to environmental purification (Fig.6). The research on visiblelight photocatalysts attracts much attention among others. It has already been discovered that plasma treated titanium oxide responds to light at approximately 600 nm (Fig.7). If visible light can activate photocatalyst function, the efficiency of photocatalytic action will increase up to tenfold.

Further efforts are being made in the research for the improvement of adsorptivity, antibacterial and decomposing functions by means of meso-nano structure control.

Standardization of Photocatalytic Materials

According to the forecast on the photocatalyst market issued a few years ago, the market size was expected to expand to the order of 10 billion dollar by 2005 (Fig. 8). However, the market was estimated at approximately 0.4 billion dollar in 2002. In order to achieve the aforementioned goal, it is essential to cultivate the market both in Japan and abroad not only by introducing innovative high-efficient photocatlytic materials but also by reducing the production cost. Photocatalysts are the materials developed in Japan and AIST has been the center of the industrialization of the technology. The institute is also required to strive for market expansion. Seeking the establishment of the international standard of photocatalysts, four working groups have been organized under the chairmanship of Dr. Fujishima, Chairman of Kanagawa Academy of Science and Technology. AIST presides two of the working groups on air and water purification.

For those who are working on research and development of photocatalytic technology, there is certainly a positive desire to establish international standards in this field without falling behind Western countries, through the close collaboration among industry, academia, and government.

AIST has the determination to enhance the research cooperation among the related research units, with a view to the development of new photocatalytic materials and the establishment of the standard. The achievements will be publicized both in Japan and in the international market to contribute to the global environmental clean-up.

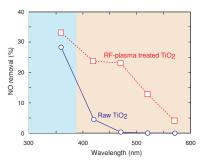


Fig. 7 Properties of photocatalyst responsive to visible light



Fig. 8 Estimated market size of photocatalytic products in Japan(2005)

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