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Sci-Tech Feature

The Light Clean Revolution

Aoki Shin'ichi *explains how recent developments in photocatalytic technology will make life in the twenty-first century safer and more convenient*

A new technology developed by University of Tokyo professor Fujishima Akira is attracting a lot of attention. Fujishima uses photocatalysts and irradiation to break down chemicals. In addition to helping make anti-bacterial tile and air-purification devices, other promising applications of this photocatalyst technology continue to come to light. Japanese scientists are leading the world in every area of this field from basic research to applications.

Take the UST-TSU building standing in front of the central train station in Tsu City, the capital of Mie-ken (prefecture). The building's outside walls are covered with photocatalytic tiles which, according to Tsu's city planning department, have two functions. First, dirt and soot have a hard time adhering to the tiles, which lowers costs for cleaning the building and repairing the tiles. Second, the tiles cleanse the air of pollutants such as NOx gases, which contribute to asthma. The tiles covering the UST-TSU building, some 7,700 square meters of them, reportedly have the same purifying effect on the air as a forest of 200 poplar trees.

The titanium oxide used in the photo-catalysts exhibits two properties when exposed to ultraviolet light: an extremely high affinity for water and a high oxidation potential. Titanium oxide readily sheds water, but when exposed to ultraviolet light it develops a strong affinity for water, known as hydrophilicity. When water comes in contact with the highly hydrophilic coating of the UST-TSU building, the water immediately spreads over the entire surface in a thin, uniform film. Thus, when dirt or soot settles on the building, it actually floats on top of the thin film of water coating the tiles. When rain comes, it washes the dirt away.

Titanium oxide also oxidizes substances on its surface when irradiated with ultra-violet light. Ultraviolet light energizes and rapidly vibrates the electrons within the titanium oxide tiles, and makes them steal electrons from any substances adhering to the surface. The oxidation effect photocatalyzed by titanium oxide at room temperature is equivalent to the oxidation that occurs in a combustion chamber at 30,000 degrees Celsius. The titanium oxide tiles oxidize air pollutants that adhere to them and convert them to harmless substances such as carbon dioxide.

Bathrooms That Clean Themselves

Fujishima has coined the phrase "Light Clean Revolution" to describe the use of photocatalysts in everyday life in ways that mimic plant photosynthesis.Photocatalytic products in Japan now command a 40-billion-yen market, but that is expected to burgeon to ¥1 trillion ($7.86 billion) by 2005.

Fujishima still remembers the wonder he felt as a graduate student 30 years ago upon discovering the photocatalytic effect of titanium oxide. "I was experimenting with titanium oxide crystals," he recalls, "and when light hit [the crystals], water broke apart into hydrogen and oxygen."

Initially, Fujiwara worked on using this effect to make water a hydrogen source for clean-burning hydrogen fuel, but the research never made it to the applied technology level. Hashimoto Kazuhito and Watanabe Toshiya of the University of Tokyo Research Center for Advanced Science and Technology opened the door to applicable uses of titanium oxide photocatalysts. The impetus was the dirty and smelly bathrooms of the university. The idea was that if the reaction for breaking down organic chemicals could be made to occur in bathrooms, the bathrooms would clean themselves.

Watanabe developed this idea into anti-bacterial tiles, which were eventually produced by the bathroom fixture manufacturer Toto, where he once worked. Later, the same principle was used to make street lights and automobile mirrors that resist soiling.

Cool Buildings

Recently, these same two professors have come up with another exciting use for photocatalysts. The walls of houses are thinly coated with the photocatalyst, the extreme hydrophilicity of which results in a thin, uniform membrane of water covering the walls for long periods of time. Hashimoto hopes to use this property of photocatalysts to prevent the "heat island phenomenon" that occurs in large urban areas.

Urban areas filled with concrete buildings have a higher ambient temperature than surrounding areas due not only to the heat absorption of concrete but also to the heat generated by air conditioners and motor vehicles. When buildings are coated with photocatalysts and wetted to create the thin film of water, the evaporation of the water pulls heat off the buildings and effectively cools them down.

Hashimoto began testing his Urban River Project in the summer of 2001. On the roof of a University of Tokyo building, he built a small shed about the size of one tatami mat out of photocatalyst coated glass and wall materials. Water trickled down the sides of the shed and cooled the interior. Even in the middle of the summer, temperatures inside the shed were reduced nearly 10 degrees Celsius.

"I'll definitely commercialize this idea myself," Hashimoto says. He plans on establishing a venture capital company with backing from the university to put the idea into practice.

Cleaner Burning Plastics

Hashimoto and Watanabe, along with scientists at the Kanagawa-ken-funded foundation Kanagawa Academy of Science and Technology, have developed another use for photocatalytic technology that has attracted the attention of composite plastic manufacturers. The technology would reduce environmental dioxin, considered the most dangerous manmade pollutant.

The main source of dioxin in Japan is waste incinerators built in the 1960s and 1970s. When incinerators are operated at temperatures over 1,000 degrees Celsius, almost no dioxin is produced. However, older incinerators cannot be operated at these high temperatures without damaging their own walls. Burdened by falling tax revenues due to the long recession, local governments find it impossible to buy equipment that would rectify the situation.

The research team decided to use technology to change the plastic being burned rather than changing the incinerators. They produced a plastic garbage bag containing around 10 percent titanium oxide and calcium carbonate. The titanium oxide particles have a diameter of about seven nanometers (nano=1 billionth). The plastic bags were then burned with other plastic in the old-style, low-temperature incinerators.

At high temperatures, titanium oxide breaks down organic substances, aiding in the incineration of the waste. In experiments, the addition of the titanium oxide-containing plastic reduced the temperature at which combustion began from 380 degrees to 350 degrees Celsius. When vinyl chloride was incinerated at 400–450 degrees Celsius, the production of dioxin was reduced by a factor of three.

Calcium carbonate strongly absorbs dioxin, thereby trapping the dioxin in the ash rather than allowing it to be released into the atmosphere. When the ashes are removed from the incinerator and exposed to sunlight, titanium oxide in the ash catalyzes the breakdown of most of the dioxin within 72 hours.

"Our generation has consumed fossil fuels at a furious pace, which has polluted the environment," Hashimoto explains. "I would like to use the power of nature to resolve some of the problems we have caused."

Rust Prevention

Research into the use of photocatalyts to combat rusting is making progress. Tatsuma Toru, associate professor at University of Tokyo and a former student of Fujishima, has developed this technology with Koyo Engineering, a maker of electrical transmission lines in Utsunomiya-shi, Tochigi-ken.

Metal rusts when negatively charged hydroxide ions attach to the positively charged surface of the metal. Metal gains a positive charge because it tends to lose electrons. Rust prevention can be accomplished by preventing water and oxygen from coming in contact with the metal surface or supplementing the electrons lost from the metal surface so that hydroxide ions are not attracted to it.

Metals can be coated to prevent oxygen in the air from touching their surface, but any peeling or cracking of the coating makes the process ineffectual. Therefore, Tatsuma and his team instead decided to try to supplement lost electrons using photocatalysts.

When titanium oxide is exposed to ultraviolet light, it releases electrons. Since titanium oxide acts as a catalyst, it is not consumed in the process, meaning that as long as ultraviolet light is present the reaction can continue indefinitely.

To test the rust prevention effect of titanium oxide, the team soaked steel in saltwater. The untreated steel clearly showed signs of rust after one hour whereas the titanium oxide coated steel showed no rust. Even if the titanium oxide layer becomes partially damaged or partially removed, enough electrons are still released from the surrounding areas to prevent rusting. "Implementing this technology would mean a major reduction in maintenance costs covering the repainting of steel towers, says Saito Shuichi of Koyo Engineering.

Glass Surfaces

Other areas in which major demand for photocatalysts is expected to rise include window glass in buildings and automobile windshields. Conventional methods for coating and glazing glass with a liquid containing titanium oxide, however, result in a layer of uneven thickness that interferes with vision, destroys the appearance and also peels off quickly.

Shigesato Yuzo, professor at Aoyama Gakuin University, has developed a technology that avoids these problems. Fujishima calls it "the achievement that has had the greatest impact on industry over the past several years."

Shigesato adapted a method called the spatter technique used for surface treatment of specialty glass and steel plates and also used in the manufacture of semiconductors. Titanium plates that will become the photocatalytic material are placed in a vacuum where they are hit with an electric current from two electrodes that alternate to the tune of 50,000 times per second. This blows titanium nuclei off of the titanium plates, which are then oxidized to form photocatalytic titanium oxide. The titanium oxide is built up on the surface of glass sheets or construction materials. When this coating is hardened at temperatures of 300–600 degrees Celsius, it forms a very hard, thin film.

A film 30–40 nanometers thick can be applied in one minute. Modification of existing production equipment for specialty glass makes it possible to coat glass plates several meters wide with a thin film of the photocatalyst and keeps down costs for mass production.

Visible Light

Much work is also being done to develop photocatalysts that react under visible light, rather than just in the ultra-violet spectrum. Although efficiency is low, visible light photocatalysts are being used for some applications.

In October 2001, the University of Tokyo's Hashimoto held a seminar on visible light photocatalysts in Tokyo for businesspeople. Hashimoto praised the photocatalyst developed by the Toyota Central R&D

Labs, a Toyota Motor Corporation funded research center in Toyota, Aichi-ken. The photocatalyst replaces some of the oxygen atoms in titanium oxide with nitrogen atoms.

The photocatalyst exhibits a strong oxidation potential at a wavelength of 520 nanometers, which is in the visible light spectrum, and can break down organic molecules.

Previous photocatalysts could only react under short-wavelength ultraviolet light, so they only worked when exposed to direct sunlight. Only three percent of sunlight is ultraviolet light. A photocatalyst that reacts in visible light can be used anywhere with a relatively bright light source, including most indoor lighting.

Ecodevice, a venture capital company headquartered in Tokyo's Sumida-ku (Ward), put a visible light photocatalyst on the market before Toyota Central R&D Labs. Ecodevice marketed a type of photocatalyst called "oxygen defect," which was jointly developed by the National Institute of Advanced Industrial Science and Technology (AIST), an independent government foundation under the umbrella of the Ministry of Economy, Trade and Industry, and Kinki University.

Hardening the photocatalyst at a slightly lower temperature (400 degrees Celsius) produces a crystal with less oxygen. This oxygen defect reportedly makes the process possible in visible light.

AIST developed a more efficient visible light photocatalyst in December 2001 and published its report in the British science journal *Nature*, leading to a lot of attention.

A team led by Arakawa Hiroyuki, director of the Photoreaction Control Research Center at AIST, replaced part of an oxide semiconductor called indium tantalumate with nickel. This new photocatalyst was made into a powder and mixed with water in a glass container. When exposed to light, the water broke down into its component parts: hydrogen and oxygen were released from the surface of the photocatalyst particles in a two to one ratio, making it the first photocatalyst that has completely broken water down in the presence of visible light.

However, with the current photo-catalyst, only a small part of the energy from visible light goes into producing hydrogen. Before the technique can be used for hydrogen generation, the energy conversion efficiency will have to be increased by over 100 times.

Despite the challenges, these new technologies and applied research projects go beyond the limits of conventional wisdom and are promoting the spread of photocatalysts in real-world applications. Photocatalytic technology originating in Japan promises to make life in the twenty-first century safer and more convenient.

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