

Utilization of TiO₂ photocatalysts in green chemistry*

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Abstract: Environmental pollution and destruction on a global scale have drawn attention to the vital need for totally new environmentally friendly, clean chemical technologies and processes, the most important challenge facing chemical scientists in the field of green chemistry. Strong contenders as environmentally harmonious catalysts are photocatalysts that operate at room temperature and in a clean manner, while applications of such safe photocatalytic systems are urgently desired for the purification of polluted water, the decomposition of offensive atmospheric odors as well as toxins, the fixation of CO₂, and the decomposition of NO_x and chlorofluorocarbons on a huge global scale. To address such enormous tasks, photocatalytic systems that are able to operate effectively and efficiently not only under UV light but also under the most environmentally ideal energy source, sunlight, must be established. To this end, we are moving in a positive direction with various practical applications already at hand, as is described.

The present report involves 1) new approaches in the design and development of second-generation titanium oxide photocatalysts which can operate effectively under visible light and/or solar beam irradiation, 2) practical industrial applications of titanium oxide photocatalysts in Japan, and 3) recent advances in green chemistry in Japan.

NEW APPROACHES IN THE DESIGN AND DEVELOPMENT OF SECOND-GENERATION TITANIUM OXIDE PHOTOCATALYSTS OPERATING UNDER VISIBLE LIGHT IRRADIATION

As shown in Figs. 1a and 1b, when titanium oxides are irradiated with UV light that is greater than the bandgap energy of the catalyst ($\lambda < 380$ nm), electrons and holes are produced in the conduction and valence bands, respectively. The electrons have a highly reactive reduction potential while the holes have a highly reactive oxidation potential, which together induce catalytic reactions on the catalyst surfaces—namely, photocatalytic reactions. Because of its similarity to the mechanism observed with the photosynthesis in plants, photocatalysis may also be referred to as artificial photosynthesis. As will be introduced in the Section “Practical Industrial Applications of Titanium Oxide Photocatalysts in Japan”, there are no limits to the possibilities and applications of titanium oxide photocatalysts and photocatalytic reactions as “environmentally harmonious catalysts”.

However, as can be seen in Fig. 2a and unlike photosynthesis in green plants, the titanium oxide photocatalyst in itself does not allow the use of visible light and can make use of only 3–4% of solar beams that reach the earth. Therefore, to establish clean and safe photocatalytic reaction systems using the solar beam and/or visible light, it is vital to develop titanium oxide photocatalysts that can absorb visible light and operate with high efficiency under solar beam and/or visible light irradiation.

We have applied the metal ion-implantation method to modify the electronic properties of titanium oxide photocatalysts by bombarding them with high-energy metal ions and have found that this advanced physical method is the most suitable and promising for the dramatic modification of the

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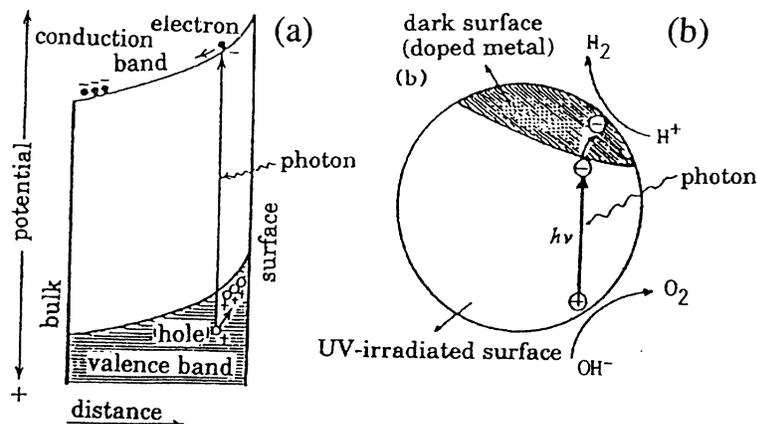


Fig. 1 Schematic representation of the photoexcitation of the titanium oxide photocatalyst (a), photo-formation of electrons (e^-) and holes (h^+) and their charge separation, and the reduction of H^+ to produce H_2 and the oxidation of OH^- to produce O_2 via the formation of OH radicals in an aqueous system (b).

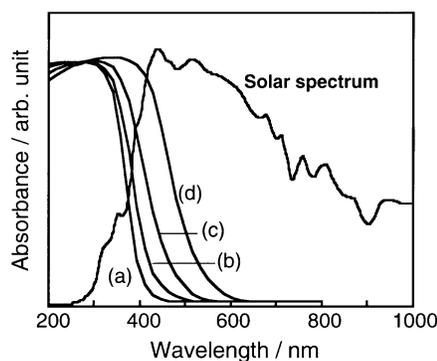


Fig. 2 UV-Vis absorption spectra (diffuse reflectance) of the original un-implanted titanium oxide catalyst (a) and the Cr ion-implanted titanium oxide catalysts (b–d), the action spectrum (open circle points) of the photocatalytic reaction on the Cr ion-implanted photocatalyst corresponding to the spectrum (d), and the solar spectrum which reaches the earth. (amounts of Cr ions-implanted [in 10^{-7} mol/g], b: 2.2, c: 6.6, d: 13, e: 26).

electronic state of the photocatalysts. As can be seen in Figs. 2b–2d, the absorption band of the metal ion-implanted titanium oxide was found to shift smoothly to visible light regions, the extent of the red shift depending on the amount and type of metal ions implanted with the absorbance maximum and minimum values always remaining constant. Such a shift allows the metal ion-implanted titanium oxide to use solar beams more effectively and efficiently, at up to 20–30%.

As mentioned above, with titanium oxide photocatalysts, the photocatalytic reaction does not proceed under visible light irradiation ($\lambda > 450$ nm). However, we have found that visible light irradiation of these metal ion-implanted titanium oxide photocatalysts led to various significant photocatalytic reactions. As shown in Fig. 3, visible light irradiation ($\lambda > 450$ nm) of the metal ion-implanted titanium oxide in the presence of NO at 275 K leads to the direct decomposition of NO into N_2 , O_2 , and N_2O with a good linearity against the irradiation time. Under the same conditions of visible light irradiation, the original non ion-implanted titanium oxide did not exhibit any photocatalytic reactivity. As also seen in Fig. 2, the action spectrum for the reaction on the metal ion-implanted titanium oxide was in good agreement with the absorption spectrum of the catalyst, indicating that only metal ion-implanted cata-

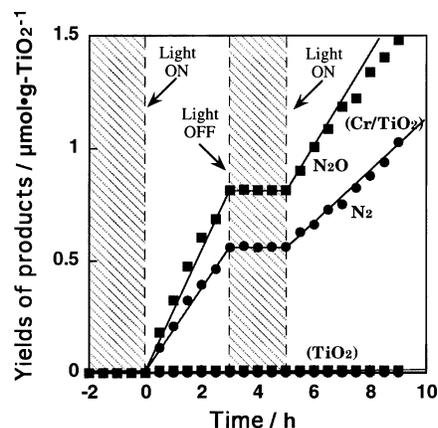


Fig. 3 Photocatalytic decomposition of NO into N_2O as well as N_2 and O_2 on the Cr ion-implanted titanium oxide photocatalyst under visible light irradiation ($\lambda > 450$ nm) at 295 K. Original un-implanted photocatalyst did not show any photocatalytic reactivity under the same conditions.

lysts were effective for the photocatalytic decomposition of NO. Thus, the metal ion-implanted catalysts enabled the absorption of visible light up to a wavelength of 400–600 nm and were able to operate effectively as photocatalysts under visible light irradiation, hence their name, “second-generation titanium oxide photocatalysts”.

In fact, as can be seen in Fig. 4, under outdoor solar light irradiation at ordinary temperatures, the metal ion-implanted catalyst exhibited photocatalytic reactivity several times higher than the original non ion-implanted catalyst, showing the great possibility of the use of solar energy in an effective and efficient manner by the application of second-generation titanium dioxide photocatalysts.

Photocatalysts implanted with Cr or V ions were found to exhibit the largest shift to visible light regions up to a wavelength of 550–600 nm. However, the implantation of Mg^+ , Ti^+ or Ar^+ ions scarcely

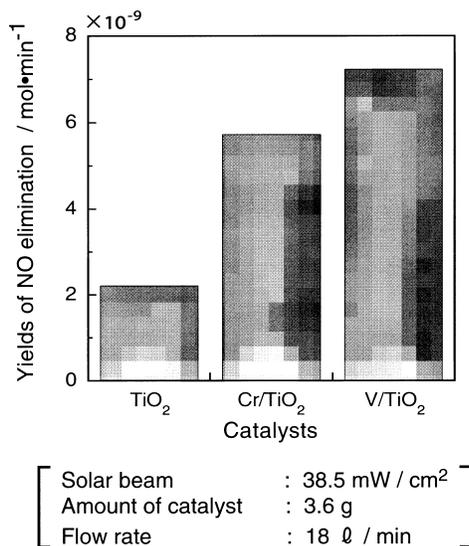


Fig. 4 Effect of the metal ion-implantation on the photocatalytic reactivity of titanium oxide photocatalysts under solar beam irradiation at 295 K.

changed the absorption band of the photocatalyst. We have found that metal ions implanted within the bulk of the catalyst modified the electronic properties of the titanium oxide photocatalyst in which the d-electrons of the implanted metal ions may be associated with this phenomenon, showing that photocatalytic reactions can take place under visible light.

On the other hand, the photocatalytic decomposition of NO into N_2O as well as N_2 and O_2 proceeded both on the original non ion-implanted titanium oxide and on the metal ion-implanted titanium oxide photocatalysts under UV light irradiation ($\lambda > 380$ nm). Under UV light irradiation, the photocatalytic reactivity for the decomposition of NO on the metal ion-implanted photocatalyst was almost the same as for the non ion-implanted photocatalyst, suggesting that the implanted metal ions that are highly dispersed inside the deep bulk of the photocatalyst do not work as the electron-hole recombination center but only work to modify the electronic property of the catalyst, enabling the absorption of visible light.

The principles of titanium oxide photocatalysts and photocatalytic reactions have been briefly introduced as compared to the photosynthesis in green plants. Photocatalysis can be considered the most important and new, environmentally friendly, clean chemical technology for green chemistry. In fact, various applications of titanium oxide photocatalysts have already been developed to better our environment. Especially, these include successful developments in the purification of the polluted atmosphere as well as toxic water using ultraviolet light having a wavelength shorter than 380 nm (i.e., a larger energy than the bandgap of the titanium oxide photocatalysts). Furthermore, this advanced metal ion-implantation method has been successfully applied to modify the electronic properties of the photocatalysts enabling the absorption of visible light even longer than 550 nm so that they are able to operate more efficiently under visible or solar light irradiation. The design and development of such unique titanium oxide photocatalysts can be considered a breakthrough in the efficient and large-scale utilization of solar energy.

In the next section, several practical industrial uses of photocatalysts to green chemistry which have already been adapted for industrial applications in Japan have been described.

PRACTICAL INDUSTRIAL APPLICATIONS OF TITANIUM OXIDE PHOTOCATALYSTS IN JAPAN

The photocatalytic reactivity of titanium oxides under UV irradiation using a special black lamp or UV light from solar beams (3–4% of solar beams are made up of UV light) can be applied for the reduction



Fig. 5 View of soundproof highway walls coated with titanium oxide photocatalysts for the elimination of NO_x. These new walls were constructed in Osaka, April 1999.

or elimination of polluted compounds in air such as NO_x (Fig. 5), cigarette smoke, as well as volatile compounds arising from various construction materials. Also, such high photocatalytic reactivity can be applied to protect lamp-houses and walls in tunneling, as well as to prevent white tents from becoming sooty and dark. The reactivity is high enough to decompose or kill bacteria so that new cement and tiles mixed with titanium oxides can be commercialized and may even be used in operating rooms in hospitals to keep them sterile and bacteria-free.

Furthermore, titanium oxide thin films have been found to exhibit a unique and useful function (i.e., a super-hydrophilic property). Usually, metal oxide surfaces such as titanium oxides become cloudy when water is dropped on them because the contact angle of the water droplet and the surface is 50–80 degrees. However, under UV light irradiation this contact angle becomes smaller, its extent depending on the irradiation time. Thus, under UV light irradiation, titanium oxide surfaces never become cloudy, even in the rain. This remarkable function can also be applied for the production of new mirrors that can be used in bath areas and the side mirrors of cars.

Some practical applications are as follows:

1. Air cleaner containing TiO_2 photocatalysts: Sharp Co., Ltd.; Daikin Ind., Ltd.; and Toyota Home, Ltd.
2. White paper containing TiO_2 photocatalysts: Mitsubishi Paper Mills, Inc.
3. Antibacterial textile fibers containing TiO_2 photocatalysts: Kurare, Inc.
4. Systems for the purification of polluted air, e.g., the elimination of NO_x (Fig. 5): Furukawa Kikai-Kinzoku Ind., Inc.
5. Super-hydrophilic, self-cleaning systems, and coating materials for cars: Toto, Inc.
6. Soundproof walls using TiO_2 photocatalysts: Furukawa Kikai-Kinzoku Ind., Inc.
7. Photocatalyst coated lamps (or lamp covers): Toshiba Light. & Tech., Inc.
8. Cement containing TiO_2 photocatalysts: Taiheiyou Cement, Inc.
9. Architectural materials coating aluminum: YKK, Inc.
10. Coating materials for architectural walls: National, Inc.
11. Self-cleaning tent: Taiyo Ind., Inc.
12. Glass tableware: Kato Machinery, Ltd.
13. Outdoor antenna: NTT Adv. Tech., Inc.

RECENT ADVANCES IN GREEN CHEMISTRY IN JAPAN

In Japan, several organizations such as the Chemical Society of Japan and the Chemical Engineering Society of Japan are involved in the development and promotion of green chemistry. Recently, the Ministry of Science and Technology has also created a special committee to discuss and investigate the many possibilities for the sustainable chemistry and/or the green chemistry movement, and to educate the general public on its need and significance. This committee is made up of many of the most active specialists and academics in the area of environmental science.

The last annual spring meeting of the Chemical Society of Japan held in Yokohama, March, 1999 was, in fact, centered around a special symposium on green chemistry with a special invited lecture by one of the leading figures of this movement in the United States, Dr. P. Anastas of the U.S. Environmental Protection Agency, who presented the recent progress in Green Chemistry in the United States today. Other invited lectures were as follows:

- “The green chemistry movement in Japan” by Dr. H. Ida, Ministry of International Trade and Industry
“Recycling processes for industrial by-products using supercritical water” by Dr. S. Suzuki, Takeda Chemical Industry, Ltd.
“Production of plastics using bioprocesses” by Dr. Y. Doi, Riken Research Institute
“Prospects for catalysis in green chemistry” by Prof. M. Misono, Tokyo University; Chairman of Green Chemistry Committee

“Environmentally harmonious plastics used in electronics” by Dr. M. Ichi, Hitachi Research Center

The various investigations carried out on the reduction of industrial byproducts in manufacturing, as well as efforts in realizing low-energy industrial production processes will contribute greatly to the green chemistry movement in Japan. These invited lectures from government, academia, research institutes, and industry were representative of the most recent advances in green chemistry today.

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