Chapter 16
Development of Highly Active Titanium Oxide Photocatalysts Anchored on Silica Sheets and their Applications for Air Purification Systems

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Abstract The purpose of this study is to develop highly active titanium oxide photocatalysts that can be anchored onto a substrate. We have, thus, prepared a titanium oxide photocatalyst using a wet or dry process and the results of this study have led to the successful development of highly active rectangular column-structured titanium oxide photocatalysts, which can be anchored onto silica sheets. These highly active photocatalysts were then applied to develop an effective air purification system.

1 Introduction

Economic advances in manufacturing and living standards have, unfortunately, led to serious environmental pollution and health hazards caused by chemical substances, bacteria, viruses, and toxic compounds from carbon fuel energy and waste materials. Even in the indoor environment, the volatile organic compounds used in building materials that cause the so-called "sick-house syndrome" have caused serious health problems. Also, contagious diseases such as SARS and bird influenza viruses as well as toxic molds can be easily spread through air. To address these concerns, various air cleaners have been developed and even commercialized. However, most air cleaners use activated carbon and adsorption materials in which the initial adsorptive performance is superior but slowly decreases and finally disappears. Also, unpleasant odors are inevitably caused by the desorption of these adsorptive materials. The used adsorption materials then become industrial waste, leading to greater environmental problems. For this reason, it is necessary to develop air purification systems that do not use such waste-producing adsorption

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methods as well as find new energy resources that are clean and safe. Photocatalytic reactions using ultraviolet light irradiation that can render toxic or odorous organic compounds harmless are considered a promising field of research in the development of new purification methods to replace conventional adsorption systems.

The development of TiO_2 photocatalysts for environmental purification systems is presently being carried out at Andes Electric Co., Ltd., on a commercial scale. Powdered TiO_2 photocatalysts such as the commercially available P-25 was first considered for use in these systems. However, powdered TiO_2 was not easy to use and various binder materials have to be combined to fix or immobilize a powdered photocatalyst onto substrate materials. The binder materials, however, decrease the photocatalytic reactivity of the TiO_2 itself since they act as a physical covering while the mechanical strength of the photocatalyst is also weakened.

We have investigated the development of highly active titanium oxide photocatalysts that can be anchored onto a substrate by using a wet or dry preparation process. These studies have led to the successful development of highly active rectangular column-structured TiO_2 photocatalysts anchored onto silica sheets for applications in effective air purification systems. In this work, the preparation method is described along with a characterization of these rectangular column-structured TiO_2 photocatalysts. Also, their photocatalytic reactivity and actual performance in air purification systems are introduced.

2 Experimental

2.1 Preparation of Rectangular Column-Structured TiO_2 Photocatalysts

Rectangular column-structured TiO_2 photocatalysts were prepared by a wet or dry process, as shown in Fig. 1. The photocatalysts were anchored onto silica sheets in the following ways: First, TiO_2 crystal nuclei were formed on the silica sheet by a sputtering or spray method. Second, synthetic materials consisting of titanium tetraisopropoxide, alcohol, and nitric acid were applied on the TiO_2 crystal nuclei formed on the silica sheets and crystallized with heat treatment by drying at 150°C for about 2 h and annealing at 550°C for about 2 h.

2.2 Characterizations

The surface morphology of the samples was observed by scanning electron microscopy (SEM, Model S-4100, S-5000, Hitachi, Ltd) and transmission electron microscopy (TEM, Model H-800). The X-ray diffraction (XRD) patterns

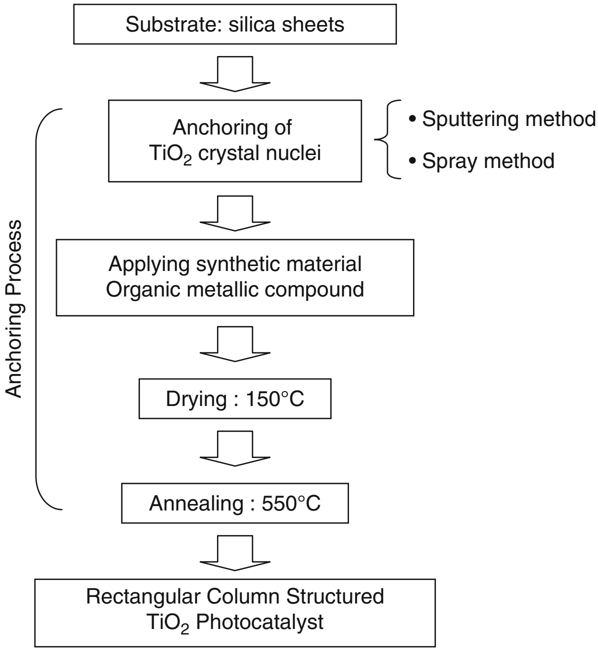

Fig. 1 Synthesis method of the rectangular column titanium oxide photocatalysts anchored onto a silica sheet

of the synthesized samples were recorded with a JEOL JDX-3530 XRD system using CuKα radiation (40 kV and 30 mA) at a scan speed of 1°min^{-1} in 2θ.

2.3 Evaluation of the Photocatalytic Reactivity

To evaluate the photocatalytic reactivity of the synthesized rectangular column-structured TiO_2 photocatalysts, the complete oxidation of organic compounds into CO_2 in a gas phase reaction system was investigated. The complete oxidation of gaseous acetaldehyde (CH_3CHO) was examined by monitoring the gas concentrations of CH_3CHO as well as CO_2 as a function of the irradiation time under a UV black light (λ: 365 nm; irradiation intensity: 4.0 mW/cm^2; irradiation area: 60 $\times$ 60 mm).

The reaction was carried out at 25$\pm$3°C under humidity of 60 $\pm$ 5% in a Pyrex glass reactor with a capacity of 20 L. First, gaseous acetaldehyde (Wako Pure Chemical Industries, Ltd.) was introduced into the reactor at a specified concentration and after reaching an adsorption equilibrium, UV light irradiation was carried out. The decrease in acetaldehyde concentration and its complete oxidation into CO_2 were monitored by a photo-acoustic multi-gas monitor (Model 1312-5, INNOVA).

3 Results and Discussions

3.1 Microstructure

Highly efficient photocatalysts that can be anchored onto a substrate, i.e., "Rectangular column-structured TiO_2 photocatalysts" were successfully developed. Figure 2a, b shows the SEM images of the synthesized TiO_2 photocatalysts. These rectangular column-structured crystals, with a width of 100–500 nm, and length of 1,000–5,000 nm,

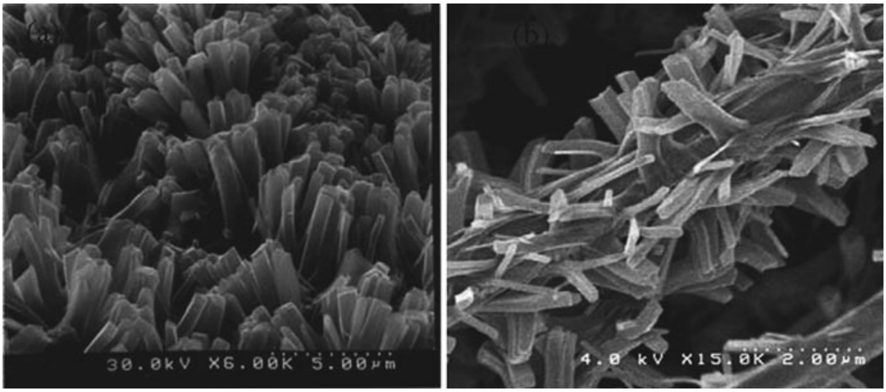

Fig. 2 The SEM images of the rectangular column-structured titanium oxide photocatalysts anchored onto a silica sheet. (**a**) ×6,000, (**b**) ×15,000

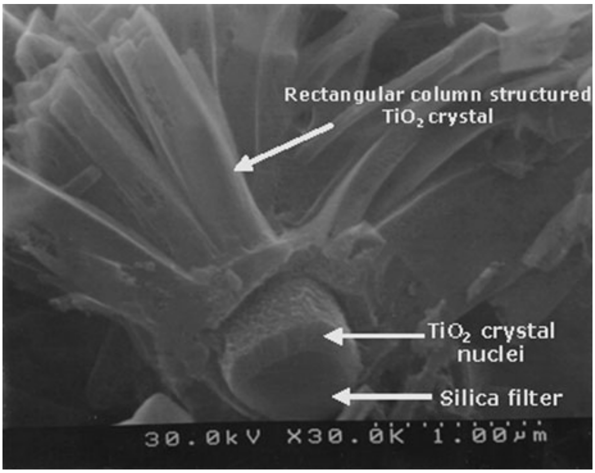

Fig. 3 A cross-sectional SEM image of the rectangular column-structured titanium oxide photocatalysts anchored onto a silica fiber

were observed to be anchored perpendicularly to the substrate in a very dense state and stable mechanical strength.

A cross-sectional SEM image of these rectangular column-structured TiO_2 photocatalysts shows that crystal nuclei of around 20–60 nm are formed on silica fibers of about 0.5–0.8 μm in diameter, as can be seen in Fig. 3. These TiO_2 crystal nuclei were prepared by a sputtering method; however, it was also possible to prepare them in a similar way with the spray method. On the contrary, rectangular column-structured TiO_2 crystals could only be formed on seeds of titanium oxide, which allowed the crystallization of the TiO_2 on the seeds.

However, without the titanium oxide seeds, even by applying the sputtering or spray methods, such rectangular column-structured TiO_2 crystals could not be formed. The preparation method for the TiO_2 crystal nuclei was, thus, seen to be the most important factor for the silica fibers, TiO_2 crystal nuclei, and rectangular column-structured TiO_2 crystals to be chemically combined in order to synthesize a stable photofunctional material.

TEM micrographs revealed that the TiO_2 crystal has a hollow structure which consists of an outer TiO_2 shell with high density and an inner region with low density, as shown in Fig. 4. The thickness of the shell was observed to be around 50 nm. Figure 5 shows the cross-sectional SEM image of the TiO_2 crystal. The inner region of the agglomerated 20–30-nm TiO_2 particles is covered by a dense TiO_2 wall, indicating that rectangular column-structured TiO_2 crystals have a high

Fig. 4 TEM image of the rectangular column-structured titanium oxide crystals

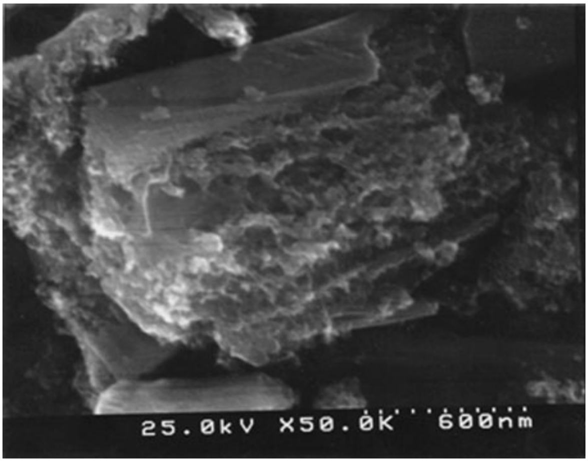

Fig. 5 Internal structure of the rectangular column-structured titanium oxide crystals

surface area of about 70 m^2/g. Moreover, XRD analysis revealed that the TiO_2 crystals have an anatase polycrystalline structure.

3.2 Photocatalytic Reactivity

The photocatalytic reactivity of the photocatalysts was examined for the decomposition of gaseous acetaldehyde by measuring the changes in the gas concentration as a function of the irradiation time under UV light. The reaction time profiles of the complete oxidation of acetaldehyde (CH_3CHO) compared with those of the most efficient marketed powdered photocatalyst (P-25) are shown in Fig. 6, and it can be seen that the acetaldehyde concentration decreased rapidly under UV light irradiation. The rectangular column-structured TiO_2 sample showed the fastest decrease in acetaldehyde concentration compared with P-25 and commercial slurry-type samples of powdered TiO_2 photocatalysts with binder materials. Thus, the rectangular column-structured TiO_2 showed a higher photocatalytic reactivity for the complete oxidation reaction of acetaldehyde as compared to a commercial powdered photocatalyst (Degussa, P25).

The reaction time profiles of the repeated and continuous oxidation of acetaldehyde in concentrated amounts are shown in Fig. 7. The complete oxidative decomposition of CH_3CHO into CO_2 was carried out six consecutive times in high concentration atmosphere to study the stability and efficiency of the photocatalysts. Figure 8 shows these rectangular column-structured TiO_2 to exhibit a constant and high reactivity for the complete oxidation of concentrated amounts of acetaldehyde into CO_2, indicating that this type of structure is stable during the reaction since the TiO_2 crystals are anchored onto the silica fiber in a very dense state with stable chemical bonds.

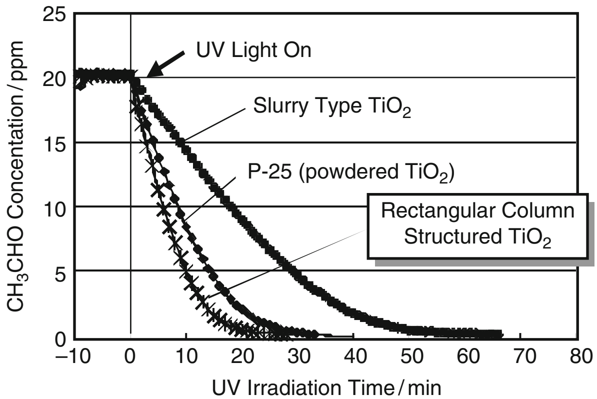

Fig. 6 Comparison of the reaction time profiles of the photocatalytic decomposition of CH_3CHO using various TiO_2 photocatalysts

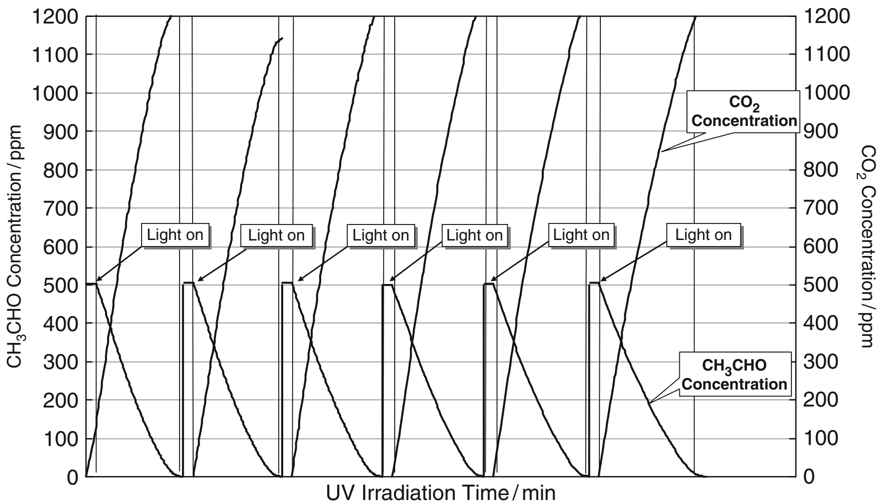

Fig. 7 The reaction time profiles of the photocatalytic decomposition of CH_3CHO into CO_2 and H_2O on the rectangular column structured titanium oxide photocatalysts anchored onto a silica sheet at 295 K

3.3 Applications for Rectangular Column-Structured TiO$_2$ Photocatalysts

The air purifying systems incorporating the rectangular column-structured titanium oxide photocatalysts are shown in Fig. 8. Figure 8a shows the air purifier which addresses the noxious fumes which cause “Sick House Syndrome” (Model

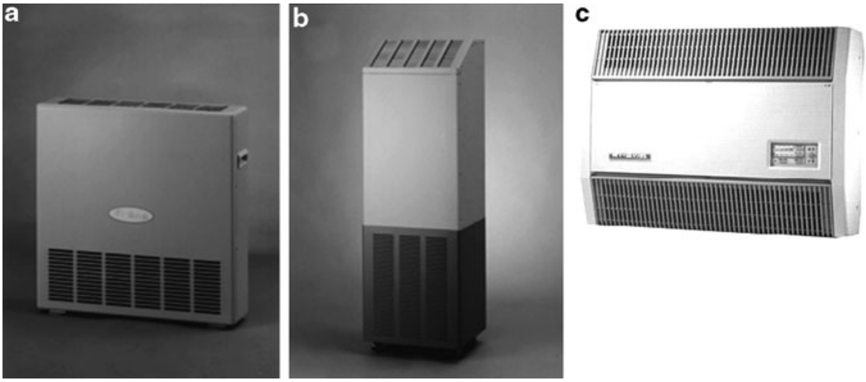

Fig. 8 Air purification systems applying the rectangular column-structured TiO_2 photocatalysts, Air purifier for Sick House Syndrome, Model (BF-H102A), Air purifier for Industrial Use, Model (BF-S103A), Air purifier for Walls, Model (BF-H201A)

BF-H102A) and Fig. 8b shows the air purifier for "Industrial Use" (Model BF-S103A). The inner structures of these purifiers are rather simple, consisting of anchored rectangular column-structured TiO_2 photocatalyst sheets, a UV light source, and a fan for air circulation.

The photocatalytic performance of these air purifiers for the complete oxidation reaction of contaminants such as formaldehyde into CO_2 compared with that of other TiO_2 photocatalytic systems is shown in Fig. 9. Evaluations of the photocatalytic reactivity for decomposition reactions were carried out in a 1 m^3 box. The efficiency of air purifiers using activated carbon or absorbents, Systems A and B, respectively, were seen to decrease gradually and reach zero as the absorbents and activated carbons became saturated with various contaminants such as formaldehyde. In contrast, the air purifier (BF-H102) applying the rectangular column-structured TiO_2 showed high and constant efficiency in decomposing formaldehyde, with the concentration decreasing rapidly to below the guideline limits issued by the Ministry of Health, Labor and Welfare of Japan.

Trial operations were carried out in a home specifically made with materials that can cause sick house syndrome, as shown in Fig. 10. The test conditions were as follows: Two air purifiers (BF-H102A) were operated for 90 min in a room of about 31.3 m^3 size. After air purification, the air in the room was collected and analyzed by gas chromatography and mass spectrometry (GC/MS). Analysis was carried out by solid phase adsorption/thermal desorption-GC/MS methods. Before air purification, a number of organic compounds were detected in the room, i.e.,acetaldehyde, methanol, toluene, styrene, α-pinene, etc. However, after operating our air purifier systems, the peaks attributed to these compounds were seen to decrease dramatically, indicating the complete oxidation of these compounds into CO_2 and H_2O. Such field experiments could establish the actual efficiency and stability of air purifiers incorporating rectangular column-structured TiO_2 sheets for the decomposition of organic compounds outside the laboratory in the living environment.

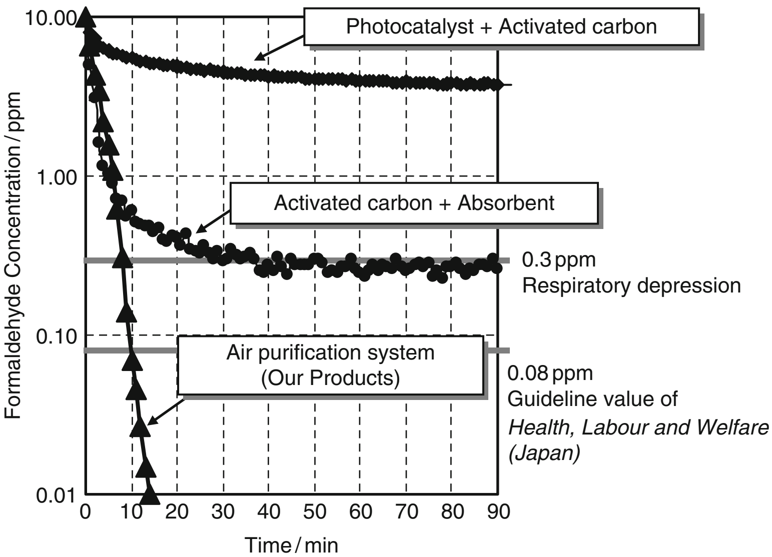

Fig. 9 Comparison of the capacity for formaldehyde decomposition with different purification systems

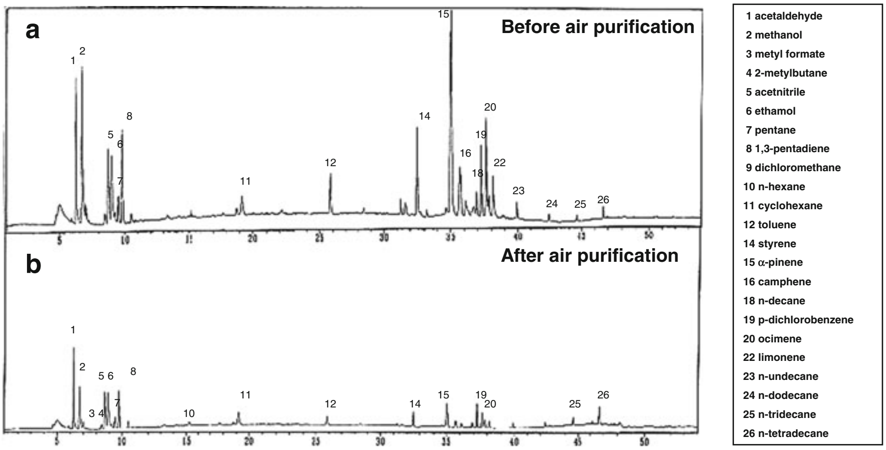

Fig. 10 GC/MS peaks before and after air purification (BF-H102A)

- Study institution: Research Center for Medical Environment, The Kitasato Institute
- Study No.: 00228 March 19, 2003
- Test method (virus): Cytopathic effect method (CPE)
- Test method (bacteria): Nutrient agar plate cultivation
- Tested model: Air purifier (BF-H201A)

Table 16.1 Elimination capacity of air purifier using TiO_2 photocatalysts (BF-H201A)

Tested bacteria	Elimination effects (%)
Influenzavirus A	99
Escherichia coli	99.95
MRSA (methicillin resistant *Staphylococcus aureus*)	99.94

Significantly, in the photocatalytic complete oxidation reaction, the bacteria was not only deactivated but also decomposed so that the anti-bacterial properties could be retained even with constant exposure to the bacterial shells. Table 1 shows the anti-bacterial properties of a wall-hanging type air purifier incorporating the TiO_2 photocatalyst (BF-H201A) in a demonstration of a one-pass operation. A "one-pass operation" allows air to pass through the air purifier from the air inlet port to the outlet port only once to evaluate the direct effectiveness of the purifier on the air (Research Center for Medical Environment, Kitasato Institute). Bacteria elimination of more than 99 % was observed even under such a one-pass operation, as shown in Table 1. These results clearly established that air purifiers employing the rectangular column-structure TiO_2 photocatalyst showed effective and high performance for bacteria elimination in air.

4 Conclusions

Investigations in the synthesis of highly active TiO_2 photocatalysts that can be directly anchored onto silica sheets were carried out in order to develop an effective and stable air purification system. The results obtained from the present study are as follows.

Highly active "rectangular column-structured TiO_2 crystals" which could be anchored onto silica sheets were developed. The rectangular column-structured TiO_2 crystals could be anchored perpendicularly onto a silica fiber substrate in a very dense state with stable chemical bonds. The TiO_2 crystals had a width of 100–500 nm and length of 1,000–5,000 nm, with anatase TiO_2 nanoparticles of 10–30 nm. Moreover, the rectangular columnar crystals were observed to have a hollow structure. Investigations on the complete oxidation reaction of acetaldehyde into CO_2 with these rectangular column-structured TiO_2 photocatalysts showed a high performance equivalent to or even higher than the most efficient standard P-25 powdered photocatalysts. Thus, effective and stable air purifying systems could be successfully developed with the incorporation of these TiO_2 photocatalyst sheets for the complete oxidation of organic compounds and bacteria in the gas phase.

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