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The design of highly active rectangular column-structured titanium oxide photocatalysts and their application in purification systems

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Abstract

The development of highly active TiO_2 photocatalysts anchored onto a stable substrate have been investigated using a wet or dry process. The results of this study led to the development of highly active rectangular column-structured titanium oxide photocatalysts which could be anchored onto silica sheets. These highly active photocatalysts were then applied to develop an effective air purification system.

Keywords: TiO_2 photocatalyst; Anchored TiO_2; Rectangular column-structured TiO_2; Silica sheet; Air purifier

1. Introduction

In recent years, environmental pollution on a global scale has resulted in many serious health and environmental concerns caused by toxic chemical substances, bacteria and viruses. To address these problems, investigations into the development of environmental purification systems using highly active and efficient photocatalysts have been actively carried out by academia, research institutes and industry [1–4]. In line with such work, titanium oxide (TiO_2) semiconductor powdered photocatalysts have been found to be one of the most stable and highly active. Photocatalytic reactions could be initiated on the surface of TiO_2 photocatalysts under UV light irradiation by the formation of active oxygen radical species of O_2^- superoxide anion radicals and OH radicals through the reaction of the photo-formed electrons with O_2 and the photo-formed holes with the OH^- groups on the surface, respectively. These active oxygen radical species were seen to react with various organic compounds such as aldehydes and aromatics to oxidize them into CO_2 and H_2O by a complete oxidation reaction [5]. Such photocatalytic reactions to oxidize toxic organic compounds into CO_2 and H_2O can be applied for the remediation of the polluted global environment, especially for the purification of polluted air and water as well as the development of materials coated with TiO_2 thin film photocatalysts which exhibit efficient antibacterial, self-cleaning and anti-fogging properties.

The development of TiO_2 photocatalysts for environmental purification systems are presently being carried out at Andes Electric Co. on a commercial scale. Powdered TiO_2 photocatalysts such as the commercially available P-25 was first considered for use in our purification systems. However, powdered TiO_2 was not easy to use and various binder materials had to be combined to fix or immobilize a powdered photocatalyst on substrate materials. The binder materials, however, dramatically 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.

The purpose of the present study is to design highly active TiO_2 photocatalysts directly on substrate surfaces with strong chemical bonds by the combination of an anchoring method to form Ti-oxide seeds on the substrate surface and the preparation of titanium oxide crystalline photocatalysts on these seeds by a

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sol–gel method. Our investigations have led to the successful development of highly active rectangular column-structured TiO_2 photocatalysts anchored onto silica sheets with –Si–O–Ti– chemical bonds for application in an effective air purification system [6–8]. In this work, the preparation method is described along with a characterization of these rectangular column-structured TiO_2 photocatalysts. Their photocatalytic reactivity and, significantly, their performance in air purification systems are also introduced.

2. Brief background in the development of rectangular column-structured TiO_2 photocatalysts and their practical applications

The development of efficient TiO_2 photocatalysts anchored on various supports is greatly desired for applicable photofunctional systems [9,10]. Anpo et al. have reported that TiO_2 photocatalysts with a well-defined and highly dispersed Ti-oxide species anchored onto supports such as silica glass, silica and zeolites could be developed by applying a facile reaction of $TiCl_4$ with the surface OH groups on the supports [11,12]. A high photocatalytic reactivity and selectivity for such anchored titanium oxides was obtained as compared with bulk TiO_2 semiconducting powders and this was attributed to dramatic modifications of the electronic and reactive properties of TiO_2 by the small particle size, size quantization, high dispersion and support effects [13–17]. Additionally, in such anchored systems, the titanium oxide photocatalysts exhibited high mechanical strength due to the formation of –Si–O–Ti– bonds on the substrate surfaces.

Here, we have constructed highly active rectangular column-structured TiO_2 semiconducting photocatalysts directly on silica sheets using a highly dispersed Ti-oxide species as seeds for crystallization or nucleation to form TiO_2 with high crystallinity. This unique method has led to the design of highly active TiO_2 photocatalysts for practical applications in environmental remediation such as the purification of polluted air and water.

3. Experimental

3.1. Synthesis 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 or silica fibers obtained from Advantec MFS [6–8] in the following ways: first, the TiO_2 crystal nuclei were formed on the silica sheet by a sputtering or spray method. A dc magnetron sputtering method was used to prepare the TiO_2 crystal nuclei using a Ti plate as the sputtering target and Ar/O_2 as the sputtering gas. The spraying materials consisted of titanium tetraisopropoxide and alcohol. The synthetic materials consisting of titanium tetraisopropoxide, alchohol 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.

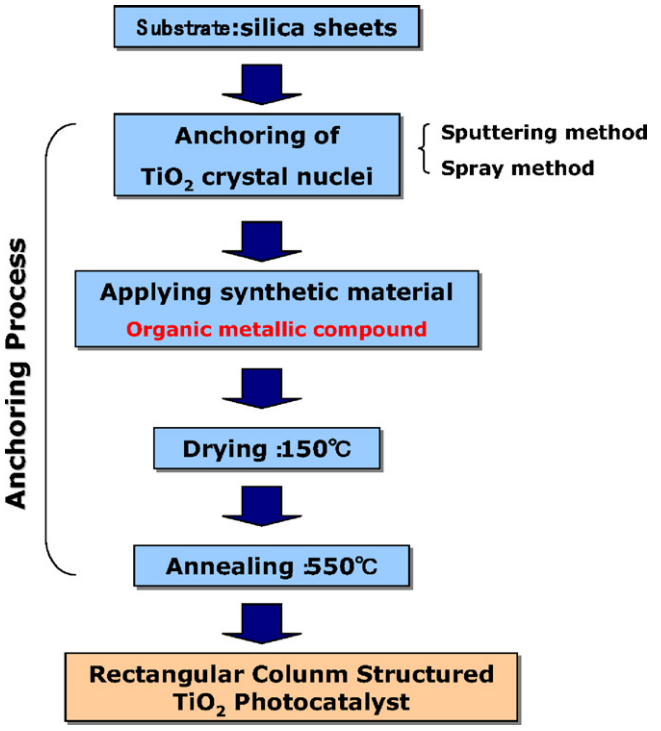

Fig. 1. Synthesis method of the rectangular column titanium oxide photocatalysts anchored onto a silica sheet.

3.2. Characterizations

The surface morphology of the synthesized 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 of the synthesized samples were recorded with a JEOL JDX-3530 X-ray diffraction system using Cu Kα radiation (40 kV and 30 mA) and a scan speed of $1^\circ\ min^{-1}$ in 2θ.

3.3. Evaluation of the photocatalytic reactivity for the complete oxidation of CH_3CHO into CO_2 and H_2O

To evaluate the photocatalytic reactivity of the synthesized rectangular column-structured TiO_2 photocatalysts, complete oxidation of the organic compounds into CO_2 and H_2O in a gas phase reaction system was investigated. Complete oxidation of gaseous acetaldehyde (CH_3CHO) was examined by measuring the gas concentrations of CH_3CHO as well as CO_2 and H_2O 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 mm × 60 mm). The reaction was carried out at 25 ± 3 °C under humidity of 60 ± 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 the acetaldehyde concentration and the complete oxidation reaction of acetaldehyde into CO_2 and H_2O were monitored by a photo-acoustic multi-gas monitor (Model 1312-5, INNOVA).

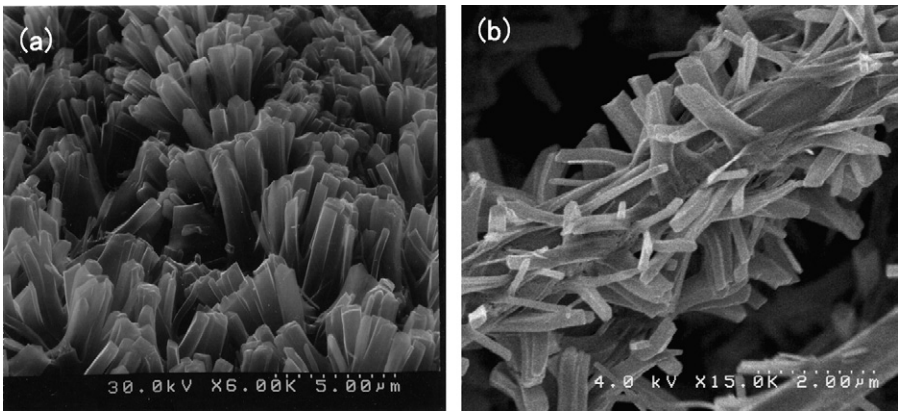

Fig. 2. SEM images of the rectangular column-structured titanium oxide photocatalysts anchored onto a silica sheet: (a) 6000×; (b) 15,000×.

4. Results and discussions

4.1. Microstructure

Highly efficient photocatalysts that could be anchored onto a substrate, i.e., ''rectangular column-structured TiO_2 photocatalysts'' anchored onto a silica sheet were synthesized by the method shown in Fig. 1. Fig. 2a and b shows the SEM images of the synthesized TiO_2 photocatalysts. These rectangular column-structured crystals, having a width of 100–500 nm and a length of 1000–5000 nm, were observed to be anchored perpendicularly to the substrate in a very dense state, having a 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 possible to prepare them in a similar way with the spray method. On the other hand, 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. Without such titanium oxide seeds, even with 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 an important factor for the silica fibers, TiO_2 crystal nuclei and rectangular column-structured TiO_2 crystals to be chemically combined to synthesize a stable photofunctional material.

The fine structure of the rectangular column-structured TiO_2, in which the column crystals have a width of between 100 and 500 nm and length of 1000 and 5000 nm, is shown in Fig. 4. However, rectangular columnar crystals were observed to consist of additional fine crystallites of 10–30 nm and also had open structures of less than 10 nm.

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. 5. The thickness of the shell was observed to be around 50 nm. Fig. 6 shows the cross-sectional SEM image of the TiO_2 crystal. It can be clearly seen that 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 surface area of about 70 m^2/g. Moreover, XRD

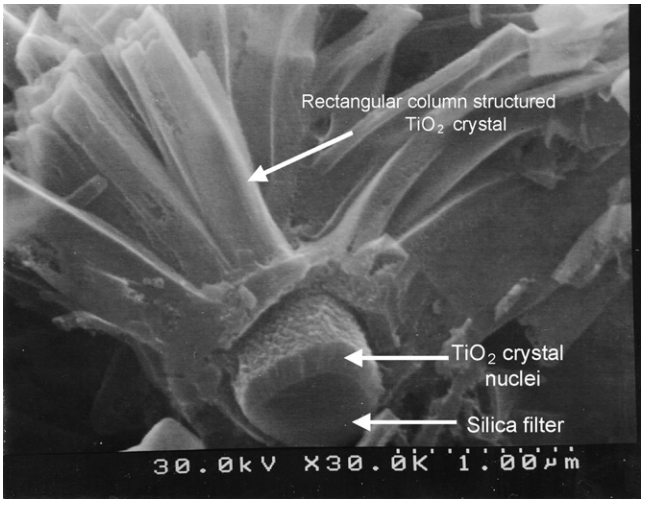

Fig. 3. Cross-sectional SEM image of the rectangular column-structured titanium oxide photocatalysts anchored onto a silica fiber.

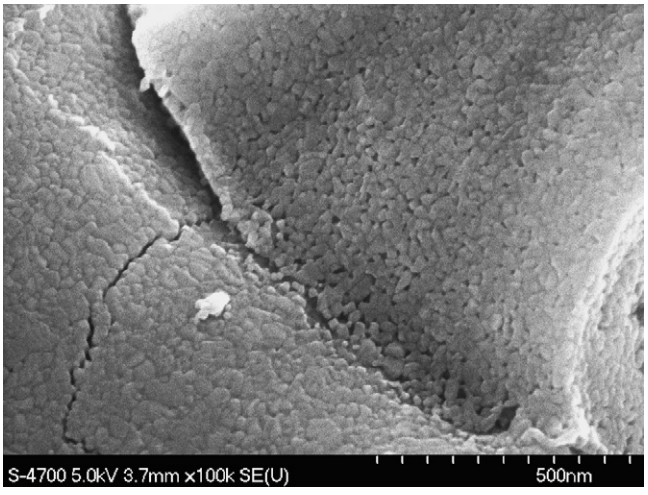

Fig. 4. The fine structure of the rectangular column-structured titanium oxide crystals.

Fig. 5. TEM image of the rectangular column-structured titanium oxide crystals.

analysis revealed that the TiO_2 crystals have an anatase polycrystalline structure.

4.2. Photocatalytic reactivity

The photocatalytic reactivity of the photocatalysts was examined for the decomposition of gaseous acetaldehyde and trimethylamine by measuring the changes in the gas

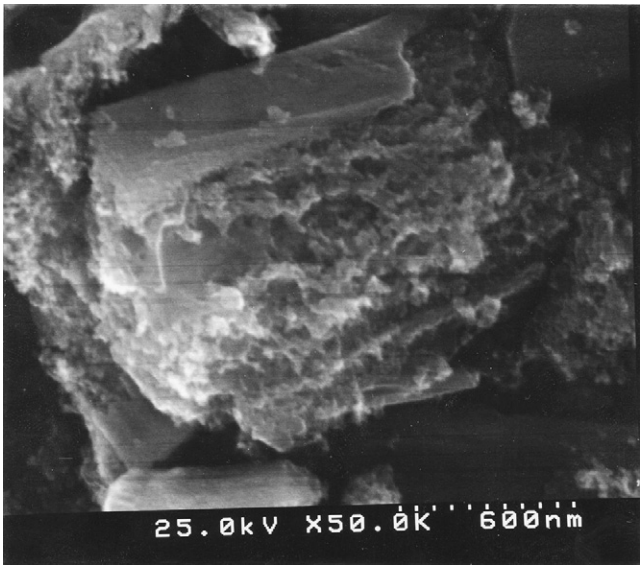

Fig. 6. Internal structure of the rectangular column-structured titanium oxide crystals.

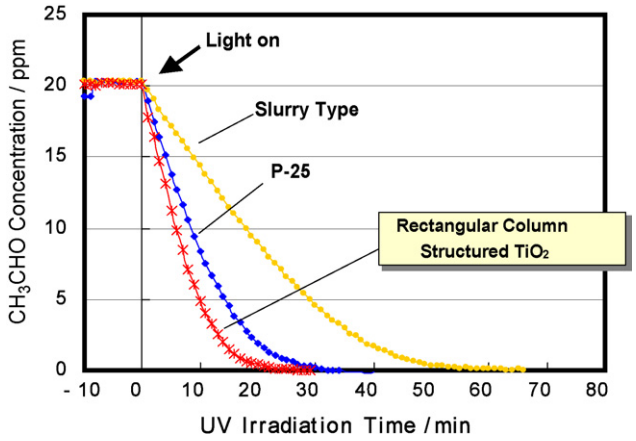

Fig. 7. Comparative study of the reaction time profiles for the photocatalytic decomposition of CH_3CHO using various TiO_2 photocatalysts.

concentration as a function of the irradiation time under UV light. The reaction time profiles of the complete oxidation of acetaldehyde (CH_3CHO) as compared with the most efficient marketed powdered photocatalysts (P-25) are shown in Fig. 7 and it can be seen that the acetaldehyde concentration decreased rapidly under UV light irradiation. Particularly, 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 and binder materials. Investigations on the complete oxidation reaction of acetaldehyde using the rectangular column-structured TiO_2 showed a high performance equivalent to or even higher than the standard powdered P-25 TiO_2 photocatalyst. Acetaldehyde was considered to diffuse into the pores on the rectangular column-structured TiO_2 crystals, as shown in Fig. 4. The unique structure allowed the efficient diffusion of the reactant molecules inside the pore structures of TiO_2 aggregates, providing an ideal reaction space for acetaldehyde oxidation.

The reaction time profiles of the repeated and continuous oxidation of acetaldehyde in concentrated amounts are shown in Fig. 8. The complete oxidative decomposition of CH_3CHO

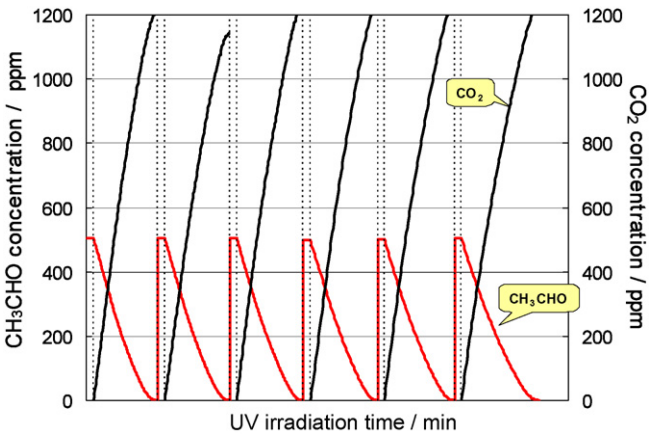

Fig. 8. The reaction time profiles of the photocatalytic decomposition of CH_3CHO into CO_2 and H_2O on the rectangular column-structured titanium oxide photocatalyst anchored onto a silica sheet at 295 K.

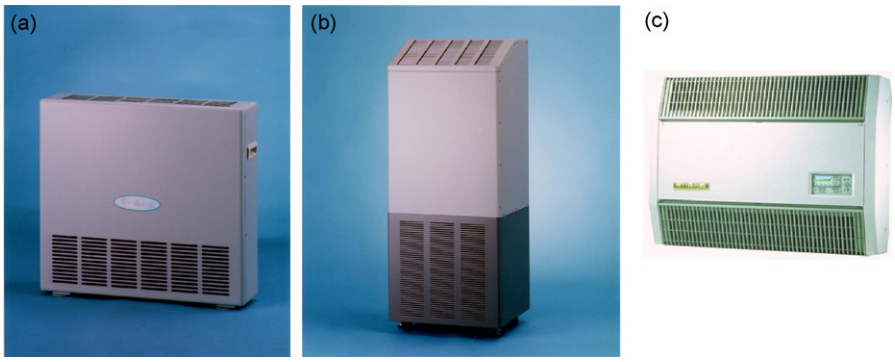

Fig. 9. Air purification systems applying the rectangular column-structured TiO_2 photocatalysts: (a) air purifier for sick house syndrome, Model (BF-H102A); (b) air purifier for industrial use, Model (BF-S103A); (c) air purifier for wall hanging, Model (BF-H201A).

into CO_2 and H_2O was carried out six consecutive times in high concentration atmosphere to study the stability and efficiency of the photocatalysts. As can be seen in Fig. 8, these rectangular column-structured TiO_2 exhibited a constant and high reactivity for the complete oxidation of concentrated amounts of acetaldehyde into CO_2 and H_2O, showing 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.

4.3. Applications for rectangular column-structured TiO_2 photocatalysts

The air purifying system incorporating the rectangular column-structured titanium oxide photocatalysts are shown in Fig. 9. Fig. 9a shows the air purifier which addresses the noxious fumes which cause ‘‘sick house syndrome’’ (Model BF-H102A) and b shows the air purifier to be applied for ‘‘Industrial Use’’ (Model BF-S103A). The inner structure of these air 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 the air purifiers equipped with rectangular column-structured TiO_2 photocatalysts for the complete oxidation reaction of contaminants such as formaldehyde into CO_2 and H_2O as compared with other TiO_2 photocatalytic systems is shown in Fig. 10. Evaluations of the photocatalytic reactivity for decomposition were carried out in a 1 m^3 box. The efficiency of the air purifiers using activated carbon or absorbents, systems A and B, respectively, were seen to gradually decrease and reach zero as the absorbents and activated carbons were saturated with various contaminants such as formaldehyde. In contrast, the air purifier (BF-H102) applying the rectangular column-structured TiO_2 showed high efficiency in decomposing formaldehyde, the concentration decreasing rapidly to below the guideline limits issued by the Ministry of Health, Labour and Welfare of Japan.

Trial operations were carried out in a home specifically made with materials which can cause sick house syndrome, as shown in Fig. 11. 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 system, 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 efficiency and stability of air purifiers incorporating rectangular column-structured TiO_2 sheets for the decomposition of organic compounds outside the lab in the actual environment.

Significantly, with the photocatalytic complete oxidation reaction, the bacteria was not only deactivated but also decomposed so that such 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) demonstrated in 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

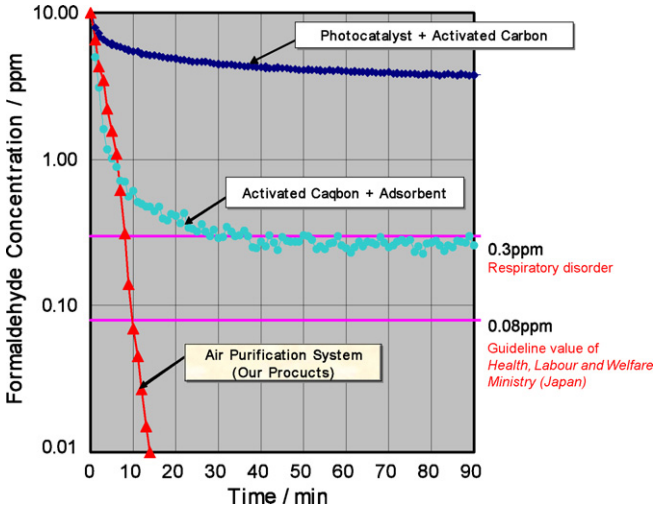

Fig. 10. Comparison of the capacity for formaldehyde decomposition with other purifiers using different systems.

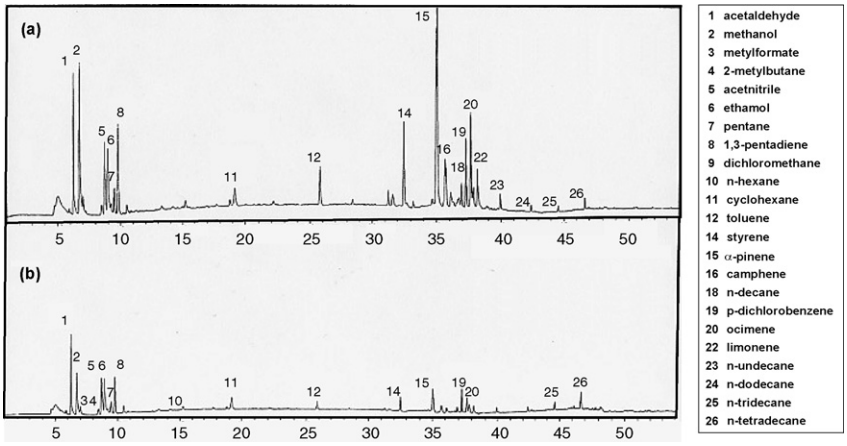

Fig. 11. GC/MS peaks (a) before and (b) after air purification (BF-H102A).

Table 1
Elimination capacity of air purifier using TiO_2 photocatalysts (BF-H201A)

Tested microorganism	Elimination effects (%)
Influenzavirus A	99.00
Escherichia coli	99.95
Methicillin resistant *Staphylococcus aureus* (MRSA)	99.94

Study institution: Research Center for Medical Environment, The Kitasato; institute study no.: 00228, 19 March 2003; test method (virus): cytopathic effect method (CPE); test method (bacteria): nutrient agar plate cultivation; tested model: air purifier (BF-H201A).

effectiveness of the purifier on the air (Research Center for Medical Environment, Kitasato Institute). Bacteria elimination of more than 99% was demonstrated 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 high performance for bacteria elimination in air.

5. Conclusions

The development of highly efficient TiO_2 photocatalysts that can be directly anchored onto a substrate through chemical bonds such as –Si–O–Ti– was 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 1000–5000 nm, consisting of 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 and H_2O showed a high performance for such rectangular column-structured TiO_2 photocatalysts equivalent to or even higher than the most efficient standard P-25 powdered photocatalyst. Effective and stable air purifying systems could be successfully developed by applying these TiO_2 photocatalyst sheets for the complete oxidation of organic compounds and bacteria in the gas phase.

Acknowledgements

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