Technical Report

Titanium with High Photocatalytic Activity (ECOTitana™)

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Abstract

Titanium material (ECOTitana™) with high photocatalytic activity has been developed and fabricated. ECOTitana™ is fabricated by anodic oxidation of commercially pure titanium sheets, with TiC precipitated on the surface layer, in NH_4NO_3 solution and heat treatment in air to result in the formation of titanium oxide layers mainly consisting of anatase type TiO_2 with carbon and nitrogen. ECOTitana™ showed photocatalytic activity under visible light irradiation. It also showed high antivirus efficacy, antibacterial efficacy, antifungal efficacy, deodorizing efficacy, and decomposition of volatile organic compounds (VOC) under ultra-violet (UV) irradiation. ECOTitana™ can be easily cut or bent due to good adhesion of the titanium oxide layers to commercially pure titanium substrate and has been applied for air-cleaning machines. As titanium oxides are chemically stable substances and titanium substrate has excellent corrosion resistance, ECOTitana™ can be used for severe corrosive environments in the future.

1. Introduction

Since Honda and Fujishima discovered the capability of titanium oxide (TiO_2) to decompose water under light irradiation,[1)] the use of TiO_2 has been advanced in various fields such as environmental purification[2, 3)] and antibacterial treatment,[4, 5)] and its use is expected to expand even further. According to the Photocatalysis Industry Association of Japan, the market size of photocatalytic products in Japan was 63.8 billion yen (ca. US$ 600 million) as of 2016, and is anticipated to grow to 128 billion yen (ca. US$ 1200 million) by 2030. Various methods have been studied for producing TiO_2 having excellent photocatalytic activity: one of them is the anodizing of titanium, which serves as a substrate. This method has been industrially employed also for manufacturing colored titanium sheets used mainly for building external finishing; we have developed such products having improved resistance to discoloring in outdoor environments by this method.[6)] In parallel, research has been actively conducted in recent years on the production of titanium oxide having excellent photocatalytic activity by the anodizing method using titanium as the substrate. Onoda et al. reported that it was possible to obtain a titanium oxide layer that exhibits excellent photocatalytic activity by anodizing surface-nitrided titanium sheets in a bath of a solution consisting of H_2SO_4, H_3PO_4, and H_2O_2.[7)] Separately from the above, Ohtsu et al. investigated the effects of anionic species in an aqueous solution of $(NH_4)_2SO_4$, $(NH_4)_2PO_4$, and $(NH_4)_2O_5B_2O_3$ used for the anodizing, and reported that S, P, and B were adsorbed in the titanium oxide film, and they exerted influence upon the photocatalytic activity of the film.[8)]

In the meantime, regarding titanium oxide's responsiveness to visible light, Mizukoshi et al. reported study results on the visible light responsiveness of rutile type TiO_2 that is formed on the surface of a titanium substrate by anodizing it and doped with sulfur.[9)] On the other hand, Ohtsu et al. reported that a titanium oxide layer having visible light responsiveness could be obtained by anodizing a titanium substrate in an aqueous solution of nitric acid and then heat-treating it.[10)]

However, there have only been a small number of studies on the influence of the material factors of the titanium substrate upon the photocatalytic activity of the titanium oxide layer formed by the anodizing method. We found that TiC on the surface layer of a titanium substrate increases the thickness of a titanium oxide layer that is formed on its surface in a bath of a weak acid solution.[11, 12)] In addition, based on the results of past studies, we investigated the effects of TiC on the surface layer of titanium substrates upon the photocatalytic activity of the titanium oxide layer formed by anodizing them. In consideration of the study results of Ohtsu et al.,[8, 10)] NH_4NO_3 was selected as the anodizing bath for the study. As a result of examining the influences of the NH_4NO_3 concentration, anodizing voltage, and the condition of the heat treatment in normal atmosphere after anod-

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izing upon the photocatalytic activity of the TiO_2 layer, they identified the optimum condition for obtaining photocatalytic activity,[13] developed a titanium product having excellent photocatalytic activity, ECOTitana™, and brought it into actual use. The present paper reports the capability of ECOTitana™ to decompose viruses, bacteria, molds, malodorous substances, and volatile organic compounds (VOCs), focusing mainly on the results of tests conducted in accordance with the test methods under the Japanese Industrial Standards (JIS), and actual applications of the product.

2. Manufacturing Method of ECOTitana™ and Characteristics of Its Surface Structure

Since the details of the manufacturing method of ECOTitana™ and the results of various surface analyses have already been reported,[13] only their essential points are briefly explained below.

ECOTitana™ is manufactured by anodizing substrates of commercially pure titanium in an aqueous solution of NH_4NO_3 and then heat-treating them in normal atmosphere. The main characteristics of ECOTitana™ are that the titanium oxide layer formed on the surface of the substrates has a large specific surface area (or surface irregularities) as a result of the anodizing in an aqueous solution of NH_4NO_3 (see **Photo 1**), and that mainly anatase type TiO_2 excellent in photocatalytic activity is formed through the heat treatment in normal atmosphere (see **Photo 2** and **Fig. 1**). What is indicated by “a” in Fig. 1 is presumed to be the anatase type TiO_2, “b” rutile type TiO_2, and “c” titanium carbide or titanium carbonitride; “m” is metallic titanium. Note here that titanium sheets having precipitates of titanium carbide (or titanium carbonitride) deposited on the surface layer, micrometers in thickness, are used as the substrates in order to obtain good visible light responsiveness, and for this reason, “c” is presumed to be titanium carbide or titanium carbonitride not anodized but remaining at the interface between the titanium oxide layer and the metallic titanium. In addition, by using an aqueous solution of NH_4NO_3 containing nitrogen as the anodizing solution, it is intended to have carbon and nitrogen adsorbed in the titanium oxide layer.[13] **Figure 2** schematically shows a sectional view of ECOTitana™ based on the above analysis results.

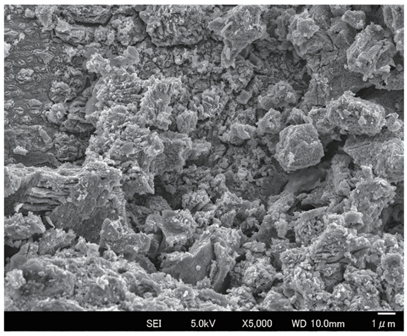

Photo 1 SEM observation of surface of ECOTitana™

Photo 2 Cross-sectional TEM microphotograph of ECOTitana™

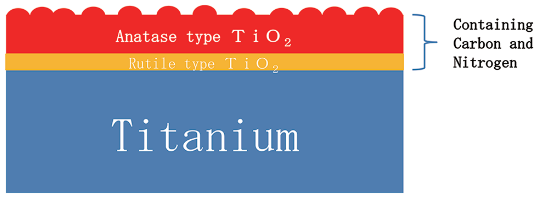

Fig. 2 Schematic diagram of cross-section of ECOTitana™

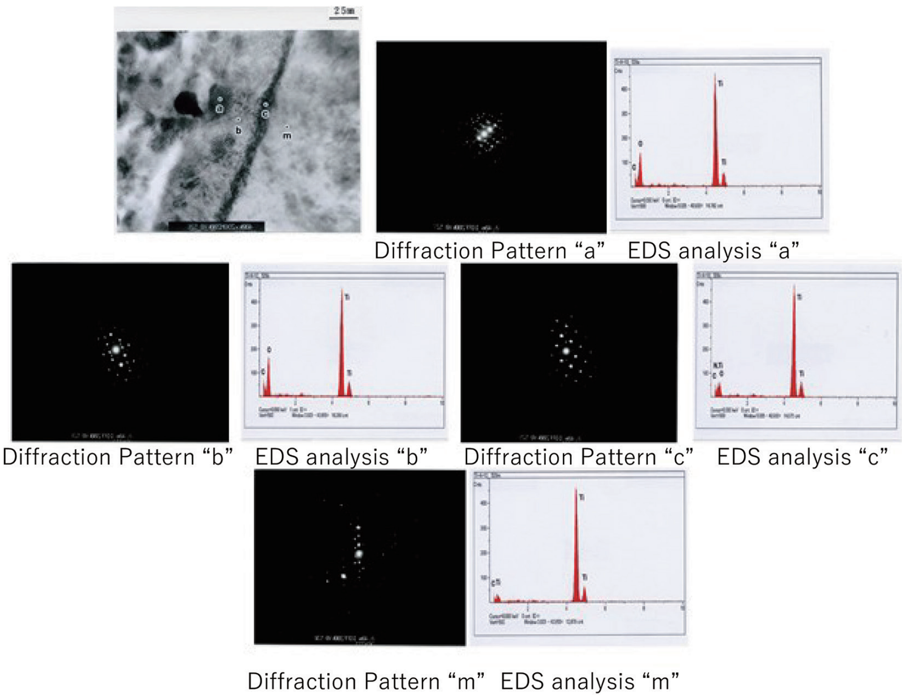

Fig. 1 TEM-EDS analysis of cross-section of ECOTitana™

3. Test Results and Discussion

3.1 Antiviral capability

To examine the antiviral capability of ECOTitana™, a photocatalytic antiviral test was conducted according to JIS R 1702: 2006 "Fine Ceramics—Antibacterial test method and antibacterial effect of photocatalytic antibacterial processed products under light irradiation." Antiviral capability against the following two virus species was tested: influenza A virus, H1N1, A /PR/8/34, (hereinafter referred to as influenza A virus) and poliovirus 1, Sabin strain (Lsc, 2ab) (hereinafter referred to as poliovirus). For all the tests described in this Section, glass plates were used as comparative specimens, and Black Light FL20SBLB-A made by Toshiba Lighting & Technology Corp. was used as the source of ultraviolet (UV) rays.

Figure 3 shows the results of the anti-influenza virus ability test under irradiation of UV rays. The graph shows that the viral infectivity of ECOTitana™ specimens fell to below the detection limit after UV irradiation for 8 h; the rate of decrease after the virus inoculation was 99.999% or more. **Figure 4** shows the results of the anti-poliovirus ability test. Similar to the case of influenza A virus, the viral infectivity of ECOTitana™ specimens was reduced after the UV irradiation for 8 h to 99.994% of what it was immediately after the inoculation. Note here that both the influenza A virus and the poliovirus used in the present test have an envelope (lipid bilayer membrane). It has been reported that, when light having an energy equal to or greater than the band gap of TiO_2 is irradiated, active oxygen species are formed by photocatalysis, they oxidize and decompose the outer membrane (envelope or capsid) of the virus, which suppresses its activity (infectivity). In the case of ECOTitana™, which is composed mainly of anatase type TiO_2, outer membranes of influenza A virus and poliovirus are presumed to be oxidized and decomposed by the same mechanism, effectively lowering their infectivity. There is a report to the effect that, in the case of influenza virus in particular, the outermost components (hemagglutinin (HA) and neuraminidase (NA)) of the membrane are degenerated, and as a result, the virus is inactivated.[14]

3.2 Antibacterial capability

An antibacterial test of ECOTitana™ was conducted in accordance with JIS R 1702: 2006 "Antibacterial test method for photocatalytic antibacterial processed products and light irradiation film adhesion method." The species of bacteria used in the test were Escherichia coli NBRC3972 (hereinafter referred to as colon bacilli) and staphylococcus aureus NBRC 12732. According to JIS R 1702: 2006, antibacterial effect is defined as a condition under which the growth of bacteria on the surface of the test subject product is suppressed.

Figure 5 shows the results of the test using colon bacilli. The number of the bacteria on the surface of ECOTitana™ was lower than that on the glass plates by nearly four orders of magnitude. It has to be noted in relation to JIS R 1702: 2006 that the Photocatalysis Industry Association of Japan judges that a test specimen has effective photocatalytic activity when its antibacterial activity value (R_L = log (average number of bacteria on a glass plate divided by the same on the test subject product)) is 2 or more. When the value is calculated from Fig. 5, R_L (colon bacilli) of ECOTitana™ is 3.9, and it is judged that its photocatalytic activity is effective. **Figure 6** shows the results of the antibacterial test using staphylococcus aureus. In this case as well, the number of bacteria on ECOTitana™ was significantly lower than the same on the glass plates, the value being below the detection limit of 10. Assuming that the average number of bacteria on all the ECOTitana™ specimens after the test is 10, its antibacterial activity value (R_L) is calculated at 3.7, and it is judged

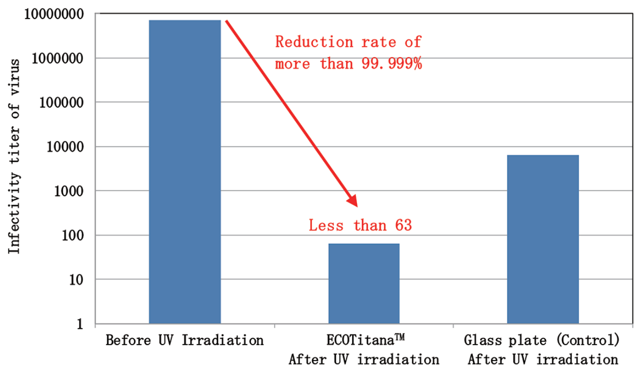

Fig. 3 Anti-virus test results (Influenza A virus)

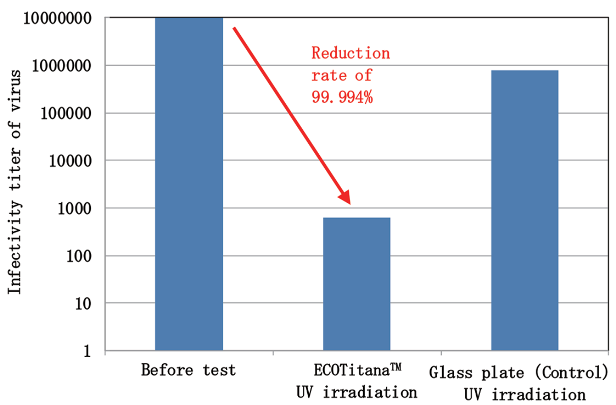

Fig. 4 Anti-virus test results (Poliovirus 1)

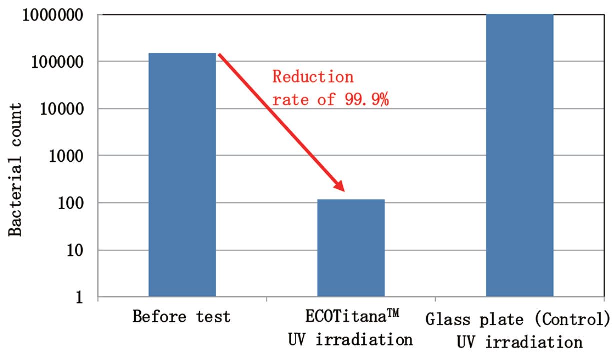

Fig. 5 Anti-bacterial test results (Escherichia coli)

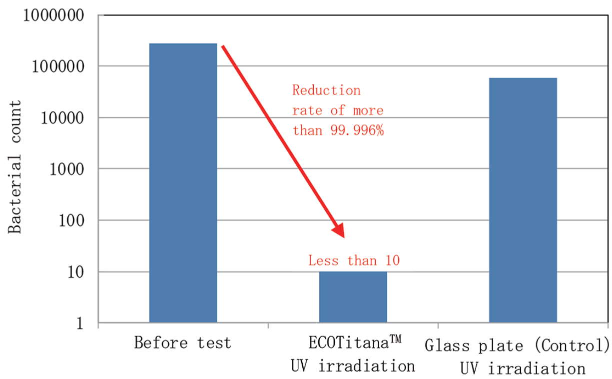

Fig. 6 Anti-bacterial test results (Staphylococcus aureus)

that photocatalytic antibacterial activity is effective against staphylococcus aureus. It is considered that the antibacterial effect of titanium oxide results from active radicals destroying the membrane structure of the bacteria cell surface by the strong oxidizing power, their penetration into the cells to destroy the membrane structure inside the bacteria cells, and consequent inactivation of the bacteria and the loss of their infectivity.[15] It is presumed possible that a similar mechanism works when UV rays are irradiated to ECOTitana™. The following has to be noted in this relation: Sunada et al. studied the oxidative decomposition of the surface endotoxin layer and the inner peptidoglycan layer of the outer membrane of colon bacilli by the photocatalytic effect of titanium oxide; calculated the chronological change of their survival rate; and from the fact that the colon bacilli died before the complete oxidative decomposition of their outer membrane, they concluded that hydroxyl radicals were instrumental to the antibacterial capability of titanium oxide.[16]

In addition, Nakata et al. examined the change in the survival rate of colon bacilli in detail, found that the change consisted of two stages, a slow reaction and a quick reaction to the time of UV irradiation, and concluded that the cause of the change was the cell wall of colon bacilli (gram-negative bacteria), which is to say, the first stage of the bactericidal process against colon bacilli was the destruction of the outer layer of the cell wall, and the second stage was the structural change and functional destruction of the cytoplasmic membrane.[17]

3.3 Antifungal capability

The test of the antifungal capability of ECOTitana™ was conducted in accordance with JIS R 1705: 2008 "Fine ceramics—Antifungal test method for photocatalytic antifungal processed products under light irradiation." According to this standard, antifungal effect is defined as a condition in which the activities of germination and growth of fungal spores are suppressed on the surface of the test object product. Two types of molds were used in the test, aspergillus niger NRBC 105649 (hereinafter referred to as black mold) and penicillium pinophilum NBRC 6345 (hereinafter referred to as white mold). **Figure 7** shows the results of the antifungal test on the black mold. Whereas the number of black mold spores on the comparative glass plates after the black light irradiation was virtually unchanged from that before the irradiation, the same on the ECOTitana™ specimens decreased to below the detection limit of 10 after the irradiation, which demonstrated excellent antifungal properties of ECOTitana™. **Photo 3** shows the appearances of the ECOTitana™ and the comparative glass plate specimens before and after the black mold test under UV irradiation. It is clear that there was no black mold on ECOTitana™ after the test. **Figure 8** shows the results of the test of resistance to white mold. Similar to the case of the anti-black mold test, the number of spores on ECOTitana™ decreased to below the detection limit.

While many points remain unclear about the antifungal properties of photocatalysts, Sunada et al. reported that photocatalysts act directly on mold spores to destroy them.[16] Although it is still unclear after the present study whether or not the radicals that formed on the surface of ECOTitana™ under UV irradiation directly destroyed the spores of black mold, it is highly likely that radicals that formed on the surface of anodized titanium sheets directly destroyed the black mold spores as reported by Sunada et al..

3.4 Capability to remove formaldehyde, toluene, methyl mercaptan, and nitrogen oxides

Next, tests of the capability of ECOTitana™ to remove the following substances were conducted: formaldehyde, which is defined under the Building Standards Law of Japan as a substance that causes sick building syndrome; toluene, a VOC; methyl mercaptan, one of the components of excrement and garbage odors and defined under the Malodor Prevention Law as a specific malodorous substance; and nitrogen oxide (NOx), an air pollutant.

The formaldehyde removal performance was tested in accordance with Part 4 "Formaldehyde removal performance" of JIS R 1701-4: 2008 "Fine ceramics—Air purification performance test method for photocatalytic materials," the toluene removal performance in accordance with Part 3 "Toluene removal performance" of JIS R 1701-3: 2008 "Fine ceramics—Air purification performance test method for photocatalytic materials," the methyl mercaptan re-

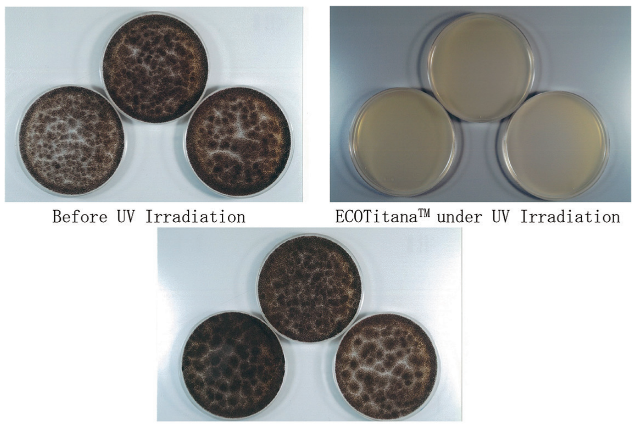

Photo 3 Antifungal test results (Aspergillus niger)

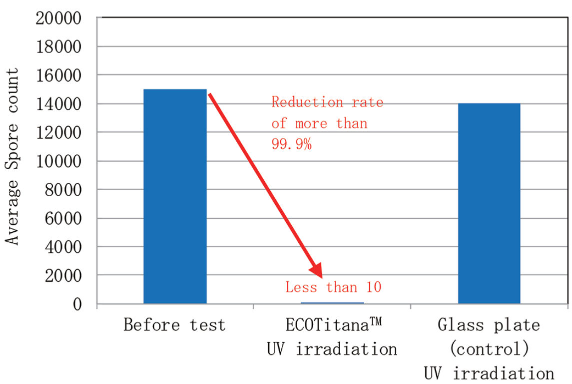

Fig. 7 Antifungal test results (Aspergillus niger)

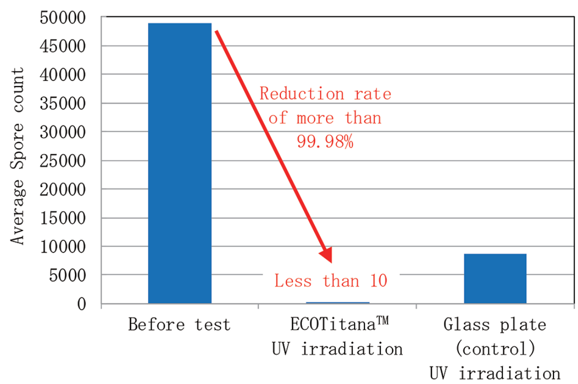

Fig. 8 Antifungal test results (Penicillium pinophilum)

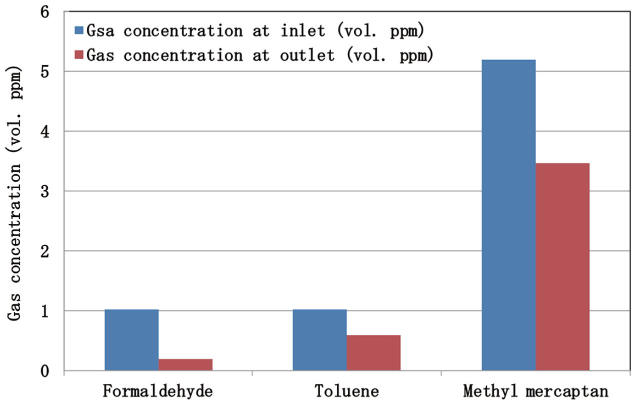

Fig. 9 Removal test results of formaldehyde, toluene, and methyl mercaptan

Table 1 Removal test result for nitrogen oxides

Material tested	Removal test result for nitrogen oxides	Criterion for photocatalytic activity by Photocatalysis Industry Association of Japan (UV irradiation)
ECOTitana™	2 μmol/L/min	More than 0.5 μmol/L/min

moval performance in accordance with Part 5 "Removal performance of methyl mercaptan" of JIS R 1701-5: 2008 "Fine ceramics—Air purification performance test method for photocatalytic material," and the nitrogen oxide removal performance in accordance with Part 1 "Nitrogen oxide removal performance" of JIS R 1701-1: 2008 "Fine ceramics—Air purification performance test method for photocatalytic materials."

Figure 9 shows the results of the performance test of ECOTitana™ to remove formaldehyde, toluene, and methyl mercaptan. The graph shows that ECOTitana™ removes all these types of compounds. It has to be noted, for example, that the threshold value of formaldehyde removal performance set out by the Photocatalysis Industry Association of Japan is 0.17 μmol/L/min or more, and from Fig. 9, the photocatalytic performance of ECOTitana™ to remove formaldehyde is calculated at 2.0 μmol/L/min, more than 10 times the threshold value.

Table 1 shows the results of the NOx removal performance test of ECOTitana™ and the threshold value of the NOx removal performance set out by the Photocatalysis Industry Association of Japan. It is clear that the NOx removal performance of ECOTitana™ is four times the threshold value. Whereas the bonding energy in the molecules of organic compounds composed of carbon, hydrogen, nitrogen, etc. is roughly 100 kcal/mol, active oxidative species (hydroxyl radicals, for example) formed by photocatalytic reactions have an energy of roughly 120 kcal/mol,[18] and they are considered to be capable of easily cutting the interatomic bonds of organic compounds to break them down.

3.5 Visible light responsiveness

The visible light responsiveness of ECOTitana™ was examined in accordance with Part 2 "Wet decomposition performance" of JIS R 1703-2 "Fine ceramics—Self-cleaning performance test method for photocatalytic materials," except that a fluorescent lamp and a UV cutting film were used as the light source instead of the black light. The test results are shown in **Table 2**. The measured activity index of methylene blue decomposition, 8.25 μmol/L/min, was higher than the judgement criterion, 5 μmol/L/min, specified by the Photocatalysis Industry Association of Japan, and consequently, ECOTitana™ is regarded as having visible light responsiveness. In relation to this, Asahi et al. reported that visible light responsiveness was developed by doping titanium oxide with carbon, nitrogen, fluorine, and/or sulfur.[19] By doping with these elements, the band gap of titanium oxide is narrowed and visible light responsiveness is expressed.

Table 2 Decomposition test result of methylene blue under visible light irradiation

Material tested	Decomposition test results of methylene blue (Visible light irradiation)	Criterion for photocatalytic activity by Photocatalysis Industry Association of Japan (UV irradiation)
ECOTitana™	8.25 μmol/L/min	More than 5 μmol/L/min

TiC is intentionally made to precipitate on the surface layer of the titanium sheets used as the substrates of ECOTitana™, and it is likely that when TiC is turned into TiO_2 during anodizing, the TiO_2 was doped with carbon. In glow discharge optical emission spectrometry (GDS) of ECOTitana™, the results of which have already been reported,[13] carbon was detected in the titanium oxide layer, as was nitrogen, albeit in a smaller concentration than that of carbon. It is considered that the carbon in the titanium oxide layer comes from TiC on the surface layer of the titanium substrate, and that carbon doping causes the development of visible light responsiveness. Regarding nitrogen, on the other hand, since its concentration is so low it is impossible to tell whether or not it also causes visible light responsiveness, but it is likely. The nitrogen in the titanium oxide layer presumably originates from the aqueous solution of NH_4NO_3 used as the anodizing bath, or from titanium carbonitride on the surface layer of the substrate. According to the results of analysis of ECOTitana™ by X-ray photoelectron spectroscopy (XPS), which have also been reported,[13] in the C1s measurement at depths of 37 and 230.5 nm, where there is titanium oxide, a peak of (C-H)n bonds possibly due to contamination and another considered attributable to Ti-C bonds were detected at a depth of 37 nm. In deeper regions, the peak of (C-H)n bonds was not detected at a depth of 230.5 nm, whereas only a peak suspected to be that of Ti-C bonds was. Regarding nitrogen, a peak considered to be that of Ti-N bonds was detected in the region near the outermost surface of the titanium oxide layer. It is presumed from the XPS results that carbon originating from TiC was doped onto the titanium oxide layer, nitrogen from the aqueous solution of NH_4NO_3 was doped onto its outermost part, and owing to these two elements, visible light responsiveness was evident.

4. Examples of Application of ECOTitana™ to Air Purifier

This paper has explained the excellent capabilities of ECOTitana™ to decompose viruses, bacteria, molds, and harmful or malodorous substances in the air. To confirm those functions, we assembled air purifiers in which ECOTitana™ and UV irradiation were combined. One of them was installed in an exhibition room of penguins in an aquarium, and the concentrations of ammonia and methyl mercaptan in the room were found to have decreased. Another unit was set in a breeding room of guinea pigs of a zoo, and improvement of the odor level (from a complaint-worthy level to weak odor) and a reduction of ammonia concentration were confirmed. In addition, four units were placed in a breeding room of

Photo 4 Outward appearance of air purification machine equipped with ECOTitana™ and example of usage in breeding room for guinea pigs

aseptic flies, and the level of odor measured with a smell sensor decreased to less than a quarter of what it was before. **Photo 4** shows the appearance of the air purifier and the unit installed in the breeding room of guinea pigs.

5. Conclusions

- ECOTitana™, a photocatalytic titanium product having visible light responsiveness and exhibiting good photocatalytic activity under UV irradiation has been developed and put into practical use. It is produced by using titanium sheets having TiC deposited on the surface layer as the substrates, anodizing them in an aqueous solution of NH_4NO_3, and then heat-treating them in normal atmosphere.
- The excellent capability of ECOTitana™ to decompose viruses, bacteria, molds, malodorous substances, and volatile organic compounds in the air was confirmed through tests conducted in accordance with test methods specified in JIS.
- ECOTitana™ exhibited visible light responsiveness at a methylene blue decomposition test using visible light as a light source. The visible light responsiveness is considered to result from doping of the titanium oxide layer with carbon and nitrogen.
- Air purifiers were built using ECOTitana™ and light sources of UV rays, installed in breeding rooms of an aquarium and a zoo and another of aseptic flies, and decrease in the concentrations of ammonia and methyl mercaptan and a deodorizing effect were confirmed.
- Titanium oxide is extremely stable chemically, and titanium sheets used as the substrates are excellent in corrosion resistance. For this reason, ECOTitana™ is expected to be effectively used in the future for air purifying, antibacterial, antiviral, antifungal and other purposes in widely varied environments where ordinary materials are likely to corrode.

Acknowledgements

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