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Photocatalytic Activity of Titanium Dioxide Powder Fabricated from an Anodized Titanium Sheet under Ultra-Violet and Visible Light Irradiation

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Abstract

A commercially pure titanium sheet with titanium carbide (TiC) precipitated in its surface layer was anodized in NH_4NO_3 aqueous solution and heat treated in air. The photocatalytic activity of titanium dioxide powder collected from the surface of the anodized titanium sheet was evaluated under ultra-violet and visible light irradiation. It showed relatively high photocatalytic activity in 0.1 mol/l potassium iodide solution, which was almost equal to the activity level of TiO_2 powder (P-25) manufactured by Degussa Corporation. The better photocatalytic activity under ultra-violet irradiation is considered to be related to the formation of anatase type titanium dioxide. Photocatalytic activity under visible light irradiation was also observed, which was considered to be attributable to impurity doping, (carbon), in the titanium dioxide powder.

Keywords

Photocatalysis, Titanium, Titanium Dioxide Powder, Anodic Oxidation, Ultra-Violet, Visible-Light Response

1. Introduction

Since Honda and Fujishima discovered the electrolysis of water by titanium dioxide under irradiation [1], the interest in titanium dioxide has been widened to environmental purification [2] [3] antibacterial [4] [5] and other uses. Various methods for fabricating titanium dioxide with high photocatalytic activity have

been investigated. Moreover, anodic oxidation is one of the methods to produce titanium dioxides on titanium substrate and is commercially used to produce colored titanium materials. The color of the anodized titanium substrate can be changed by varying the thickness of surface titanium oxide layer. Colored titanium sheets are mainly used as architectural materials.

Recently, the anodic oxidation method has been applied for fabricating titanium dioxide with enhanced photocatalytic activity under ultra-violet or visible light irradiation. K. Onoda *et al.* reported that the anodization of a pre-nitridated titanium substrate in a mixed electrolyte composed of H_2SO_4, H_3PO_4 and H_2O_2 resulted in high photocatalytic activity [6]. Furthermore, N. Ohtsu *et al.* investigated the effects of anions in various ammonium salts electrolytes and reported on titanium substrate anodized in ammonium salts such as $(NH_4)_2SO_4$, $(NH_4)_2PO_4$ and $(NH_4)_2O_5B_2O_3$, it was identified that S, P and B were incorporated into oxide layers, which affected photocatalytic activity [7].

Concerning visible light response, Y. Mizukoshi *et al.* conducted research on the visible light response of sulfur-doped rutile titanium dioxide photocatalysts fabricated by anodic oxidation [8]. N. Ohtsu *et al.* reported that the visible-light-responsive titanium dioxide layer was fabricated by anodizing a titanium plate in aqueous nitric acid solutions, followed by annealing [9].

However, a few studies for effects of material factors on photocatalytic activity of anodized titanium substrate have been conducted. The authors have investigated the effects of TiC precipitated in the surface layer of the titanium sheet on the photocatalytic activity of anodized titanium sheets. It was observed that a commercially pure titanium sheet precipitated TiC in the surface layer fabricated by anodic oxidation in NH_4NO_3 solution at 45 and 80 V and the heat treatment in air at 803 K showed relatively high photocatalytic activity in 0.1 mol/l potassium iodide (KI) solution which was close to the absorbance value of the P-25 powder, *i.e.* titanium dioxide powder manufactured by Degussa corporation. The better photocatalytic activity under black light irradiation of the anodized titanium sheet is considered to be related to the formation of anatase type titanium dioxide and rough surface. The sample also showed photocatalytic activity under visible light irradiation. It is considered that visible light response is caused by doping of carbon and nitrogen in titanium dioxide [10] [11].

In this study, the photocatalytic activity of titanium dioxide powder collected from the surface of an anodized and heat-treated titanium sheet was investigated under ultra-violet and visible light irradiation. The photocatalytic activity of the titanium oxide powder was evaluated in 0.1 mol/l KI solution under ultra-violet and visible light irradiation. And the photocatalytic activity of the titanium oxide powder was discussed in terms of crystal structure, size and chemical content of the titanium oxide powders.

2. Experimental Procedure

2.1. Material and Preparation

A commercially pure (CP) titanium sheet cold rolled to a thickness of 0.4 mm

was heat treated in a vacuum annealing furnace. The holding temperature and time were 873 K and 6 hours, respectively. The average raising rate was approximately 100 K/hour and cooling rate was almost 50 K/hour. The concentrations of impurity elements in the CP titanium sheets are shown in Table 1. Carbon content of titanium sheet was as low as 80 ppm; however, TiC was formed in the surface layer of the titanium sheet derived from lubricants during cold rolling and heat treatment. The formation mechanism of TiC has been already described elsewhere [12].

The titanium sheet was rinsed in acetone and immersed in 0.06 mol/l NH_4NO_3 solution for anodic oxidation. The anodic oxidation was galvanostatically controlled at 80 V for 120 sec at room temperature. After the anodization, it was rinsed in distilled water and air-dried. Subsequently, it was heated in air at 803 K for 3600 sec and air cooled. The average raising rate was 315 K/min and the average cooling rate was 136 K/min. Also, powders formed on the anodized titanium sheet were collected for measuring photocatalytic activity.

2.2. Photocatalytic Activity Measurement

The photocatalytic activity was measured using KI solution [10] [11] [13]. Tapes measuring 15 × 25 mm in size, to which the corrected powder was attached, were dipped in 4 cc of 0.1 mol/l KI solution at room temperature and illuminated with black light as ultra-violet light for 1800 sec with intensity of 1 mW/cm^2 or fluorescent light of 15 W. For the irradiation of the fluorescent light, an ultra-violet ray-shielding sheet was applied to irradiate only visible light to the sample. After irradiation with black light or the fluorescent light, a peak intensity of 0.1 mol/l KI solution at 287 nm was measured by an absorption spectrophotometer (U2910, HITACHI) for measuring I_3^- formed by the photocatalytic reaction. I_3^- is slightly formed by dissolved oxygen without a phtocatalyst, thus, 0.1 mol/l KI solution without test specimen were also measured as control [10] [11] [13]. The photocatalytic activity of the P-25 powder was also measured by the same method described above under the ultra violet and visible light irradiation.

2.3. Analysis

Anodic oxidation layers on the titanium substrate were analyzed by a cross sectional transmission electron microscopy with EDS (TEM; HF2000, HITACHI). The collected and the P-25 powders were analyzed by X-ray diffraction (XRD; RINT1500, RIGAKU) measurement. The size of the corrected powder from the anodized titanium sample was observed by scanning electron microscope (SEM; JIS-7000F, JEOL). BET specific surface areas of the corrected and the P-25 powders were also measured by a surface area analyzer (Flowsorb2300, Micro-

Table 1. Concentration of impurity elements in commercially pure titanium sheet (mass%).

	O	H	C	Fe	N
Gr.1	0.047	0.0022	0.008	0.025	0.004

meritics Instrument Corporation). A field emission electron probe micro-analyzer (JXA-8500F, JEOL), (EPMA), was applied to analyze the chemical content of titanium powder corrected from the anodized titanium sheets. Moreover, an ultraviolet-visible (UV-vis) near infrared spectrophotometer (V570, JASCO Corp) was applied to investigate absorbance of the collected powder from the anodized titanium sheet and the P-25 powder.

3. Experimental Results and Discussion

3.1. Photocatalytic Activity under Ultra-Violet Illumination

Figure 1 shows photocatalytic activity test results of the collected and P-25 powders under ultra-violet irradiation. The sample "Blank" was a control performed by irradiating a 0.1 mol/l KI solution containing no samples with ultra-violet irradiation for the prescribed time. As shown in Figure 1, Blank exhibited approximately 0.2 of absorbance at 287 nm. It was considered that I_3^- was formed by dissolved oxygen without a phtocatalytic reaction. The collected powder from the anodized and heat-treated titanium sheet exhibited approximately 8 times higher than that of Blank, which was almost equal to that of the P-25 powder. It was observed that the collected powder from anodized and heat-treated titanium sheet exhibited better phtocatalytic activity.

Figure 2 shows the XRD measurement result of the collected powders. All observed peaks were attributable to anatase and rutile-type TiO_2. The highest peak at 24˚ was from the anatase-type TiO_2. It is clear that anatase-type TiO_2 is the predominant titanium oxide. Figure 3 shows the XRD measurement result of the P-25 powder. It is also clear that anatase-type TiO_2 is the predominant titanium oxide for the P-25 powder. It is generally accepted that anatase-type TiO_2 shows the highest photocatalytic activity among three types of titanium dioxides. These results are in good agreement with better photocatalytic activity for both the collected and P-25 powders.

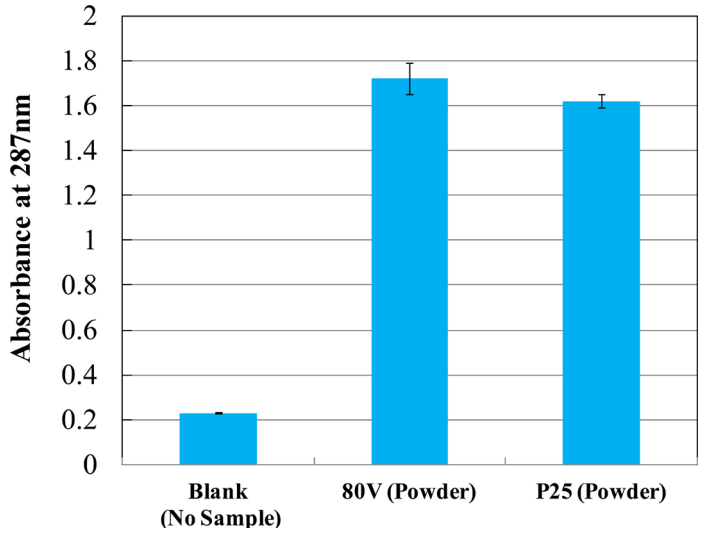

Figure 1. Photocatalytic activity of the corrected powder and P-25 in 0.1 mol/l KI solution under ultra-violet irradiation.

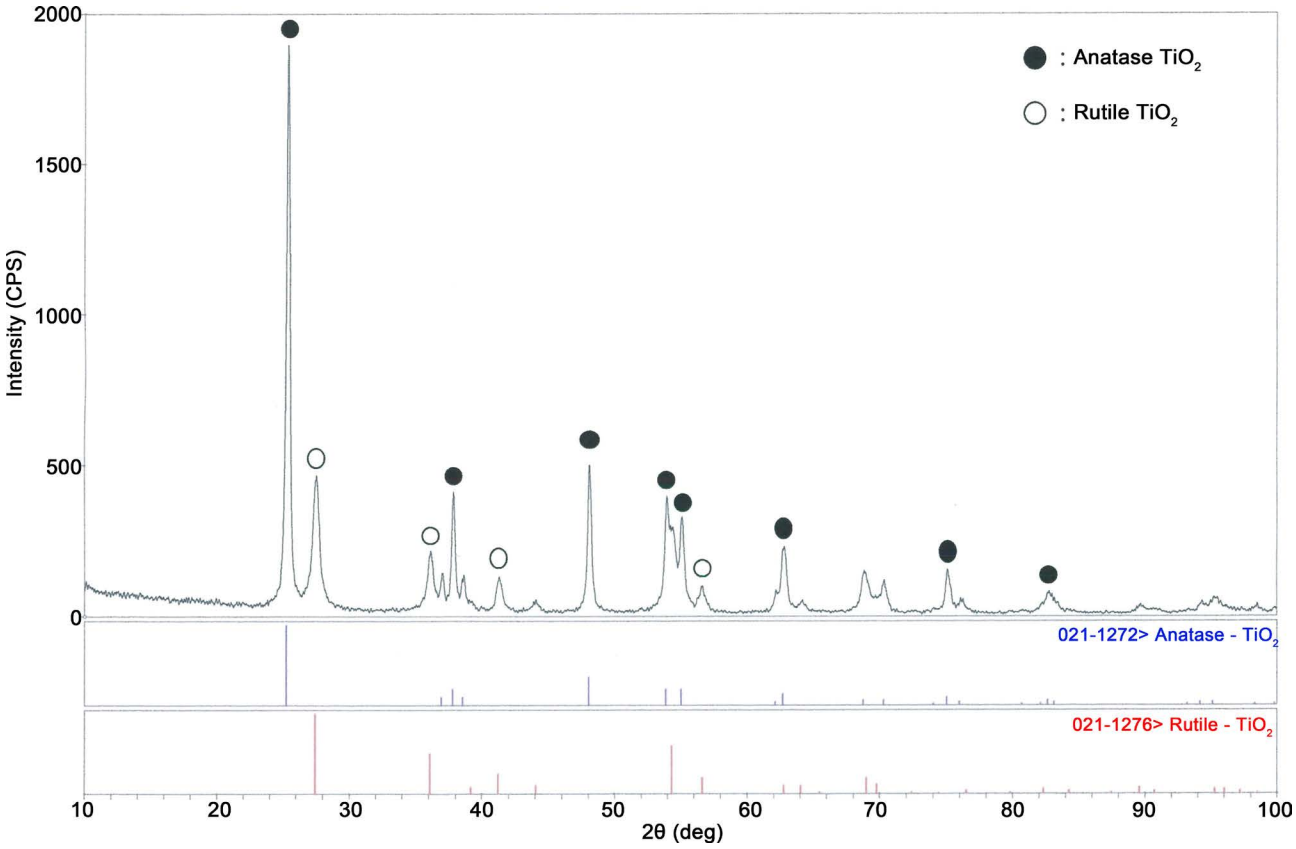

Figure 2. XRD measurement result of the collected powder from the anodized and heat-treated titanium sheet.

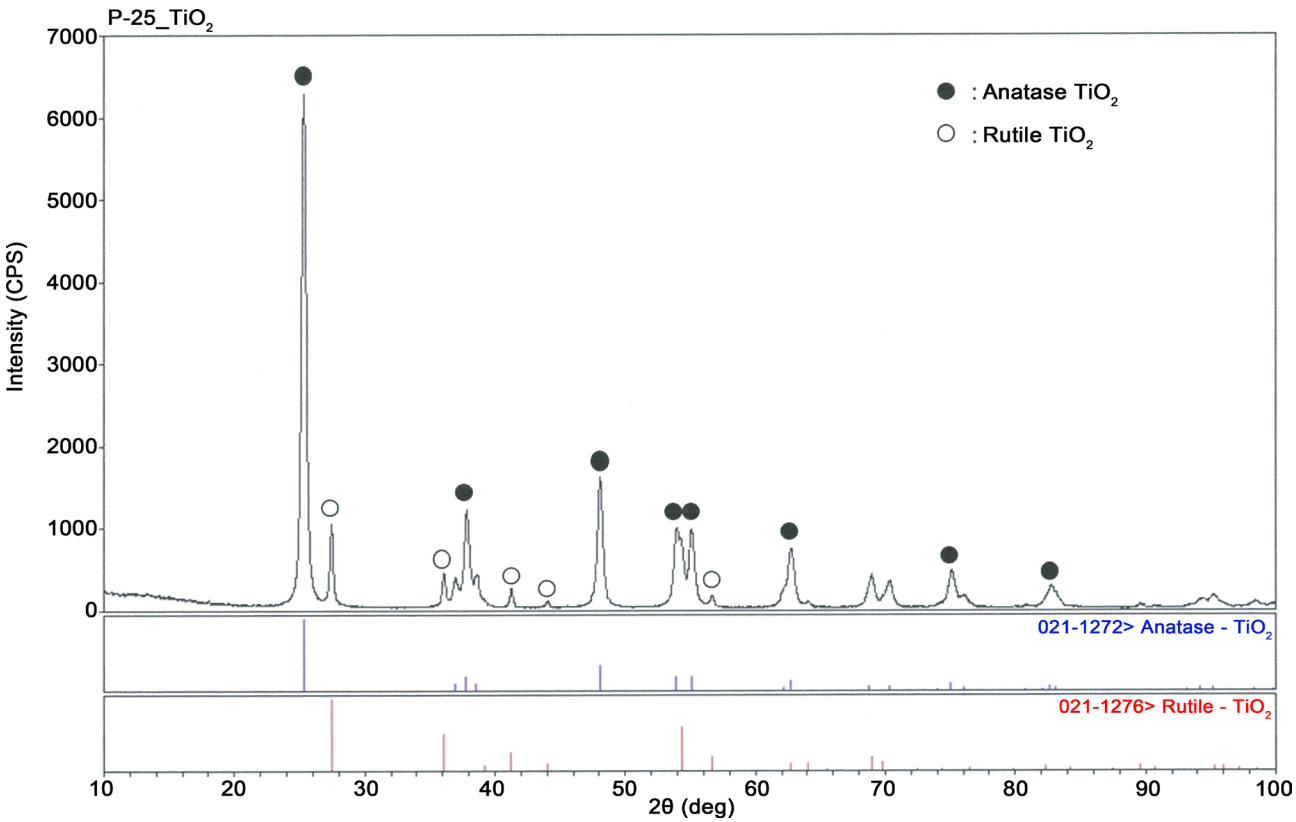

Figure 3. XRD measurement result of the P-25 TiO_2 powder.

Phtotocatalytic activity is considered to be affected by the size of the powders, thus the P-25 powder and the collected powder from the anodized titanium sheet were observed by SEM. Figure 4 and Figure 5 show SEM images of the P-25 powder and the corrected powder from the anodized titanium sheet, respectively. As shown in Figure 4 and Figure 5, the size of the corrected powder is much larger than that of the P-25 powder. It presumably indicates that a specific surface area of the P-25 is larger than that of the corrected powder, however, the BET specific surface area of the corrected powder was almost the same as that of the P-25 powder as shown in Table 2. It is considered that rough surface of the collected powder might increase BET specific surface. The result shown in Table 2 is also in agreement with the result shown in Figure 1.

Subsequently, to investigate the formation process of the TiO_2 powders on the

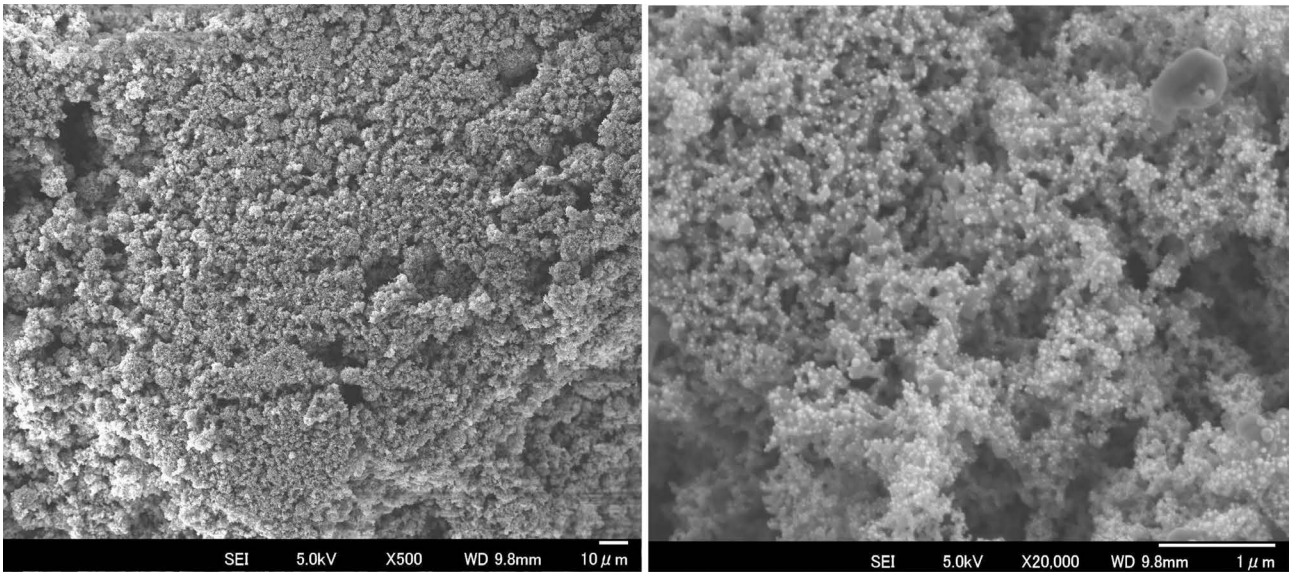

Figure 4. SEM images of P-25 powder.

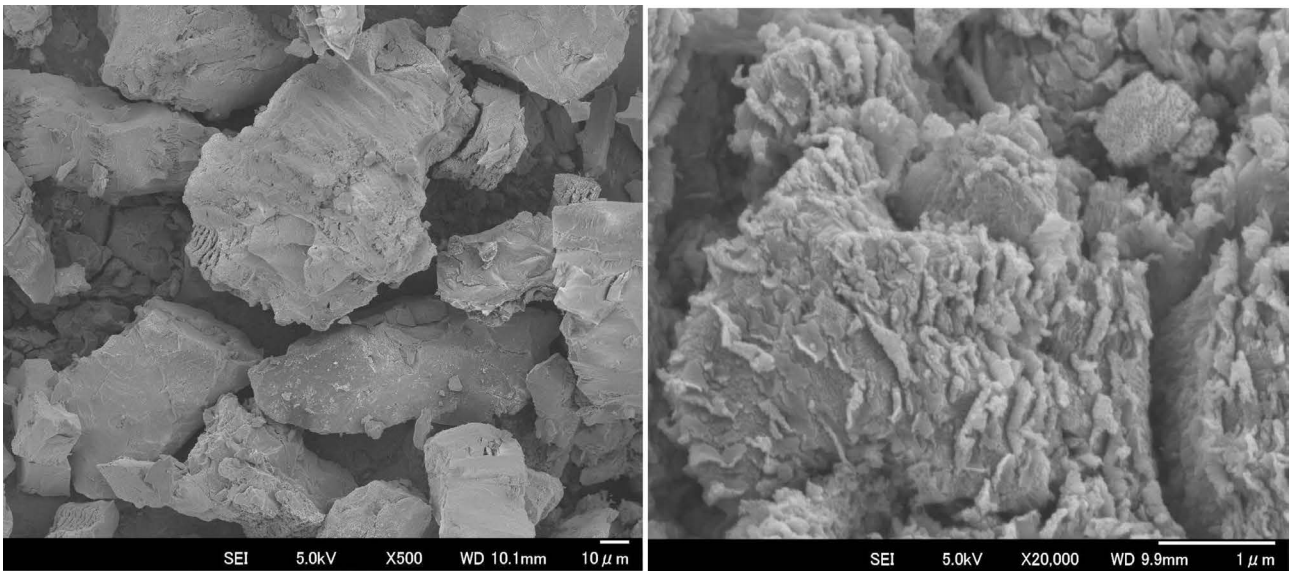

Figure 5. SEM images of the corrected powder from the anodized and heat-treated titanium sheet.

Table 2. BET specific surface areas of the collected and P-25 powders.

The collected Powder from the Anodized and heat-treated Titanium Sheet	51.976	51.976	51.874
The P-25 TiO_2 Powder	52.664	52.576	52.576

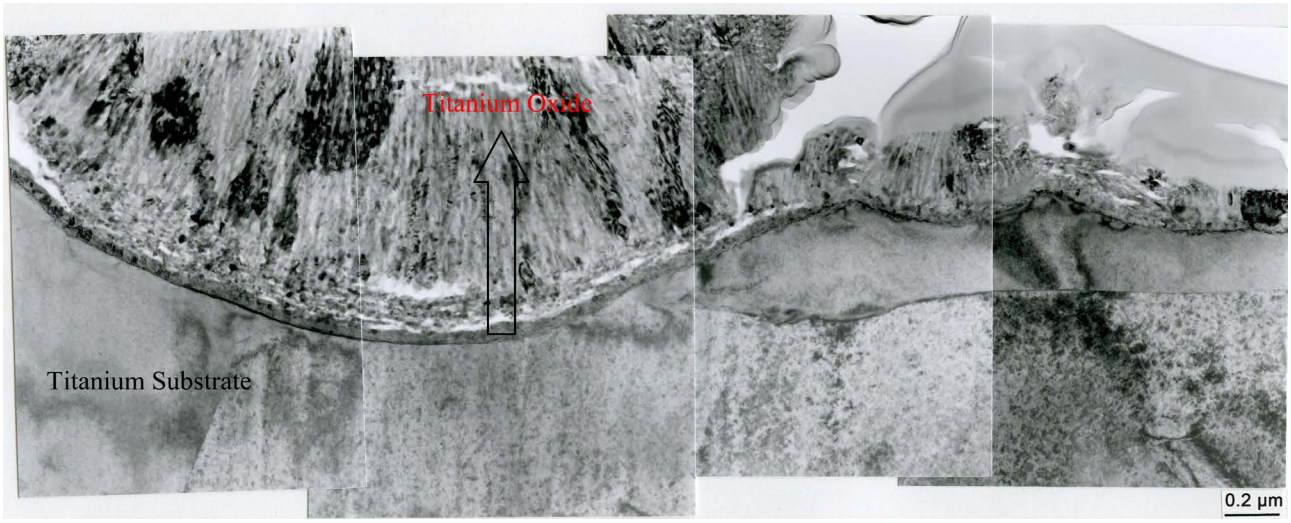

Figure 6. Cross-sectional TEM observation of the anodized and heat-treated titanium sheet.

titanium sheet, cross-sectional TEM analysis was conducted for the anodized and heat-treated titanium sample. Figure 6 shows the cross-sectional TEM image of the anodized titanium and heat-treated sample. The surface of the titanium substrate was coated with a titanium oxide layer with a thickness of approximately 0.1 μm and a relatively large size of titanium oxide powders exfoliating from the substrate was observed. As already described [10], anodization of the CP substrate occurred very radically owing to a high applied voltage, (80 V), thus, the thickness of titanium oxide increased to a large extent, and particles were formed by exfoliation from the titanium substrate.

Figure 7 shows magnified cross-sectional TEM image and EDS analysis of the anodized and heat-treated titanium substrate. A thin oxide layer existed on the titanium substrate and the particles were formed on the oxide layer. Thus, the diffraction pattern and EDS analysis of the particle was conducted. Diffraction pattern was matched to that of anatase type TiO_2. It is in good agreement with the XRD measurement as shown in Figure 2. Moreover, it contained a small amount of carbon as shown in Figure 7. It is reported that doping of anions such as carbon into titanium dioxide was plausible for enhancing visible light response [14].

3.2. Photocatalytic Activity under Visible-Light Illumination

Next, the photocatalytic activity under visible light irradiation was investigated using 0.1 mol/l KI solution for the collected powder. The results obtained are shown in Figure 8. The absorbance of Ti sample was approximately 12 times higher than the Bank, which clearly indicates photocatalytic activity under visual light irradiation. Thus, EPMA analysis for the corrected powder was conducted

and the obtained result is shown in Table 3. In addition to Ti and O, 10 mass% of carbon was detected by EPMA. Figure 9 shows UV-vis reflectivity measurements for the corrected powder and P-25 titanium oxide. As for the P-25 powder, reflectivity decreased below a wavelength of approximately 400 nm, in the UV region. Conversely, the collected powder absorbed visible light with a wavelength below approximately 500 nm.

Regarding visible light response for titanium dioxide, R. Asahi *et al.* indicated that doping of anions such as carbon, nitrogen, fluorine and sulfur to titanium

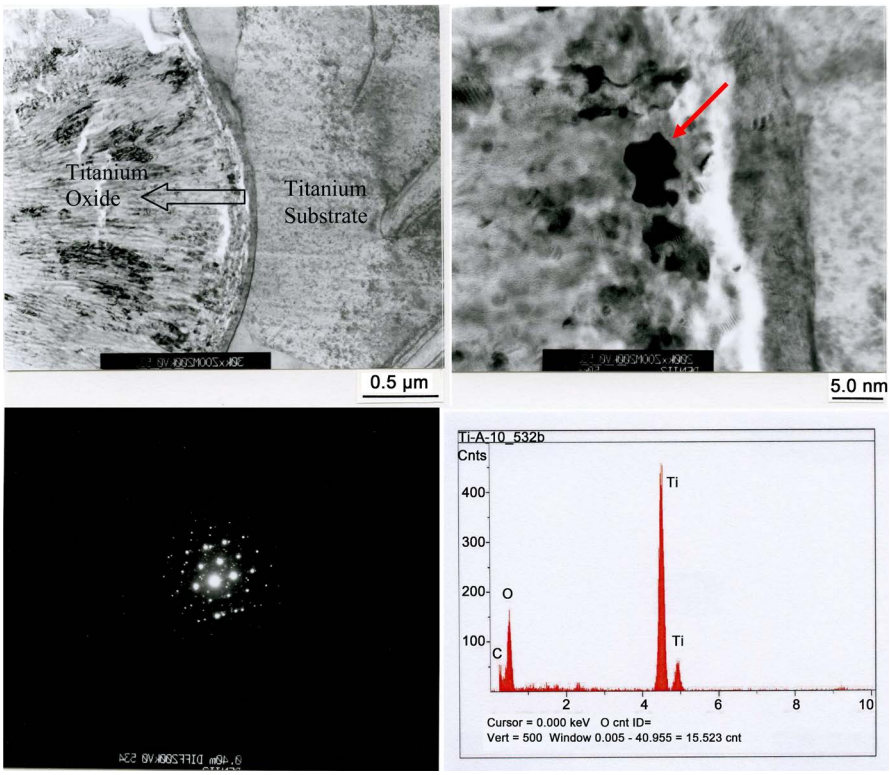

Figure 7. Cross-sectional TEM observation, diffraction pattern and EDS analysis of the anodized and heat-treated titanium sheet.

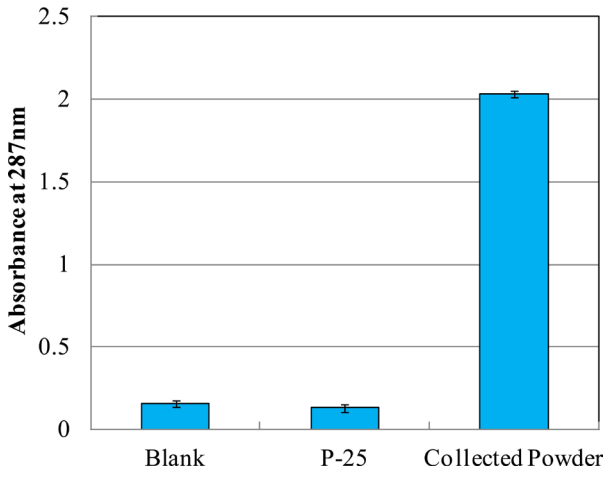

Figure 8. Photocatalytic activity of the collected powder in 0.1 mol/l KI solution under visible light irradiation.

Table 3. Chemical Composition of the collected powder (mass%).

Ti	O	C
51.6	38.4	10

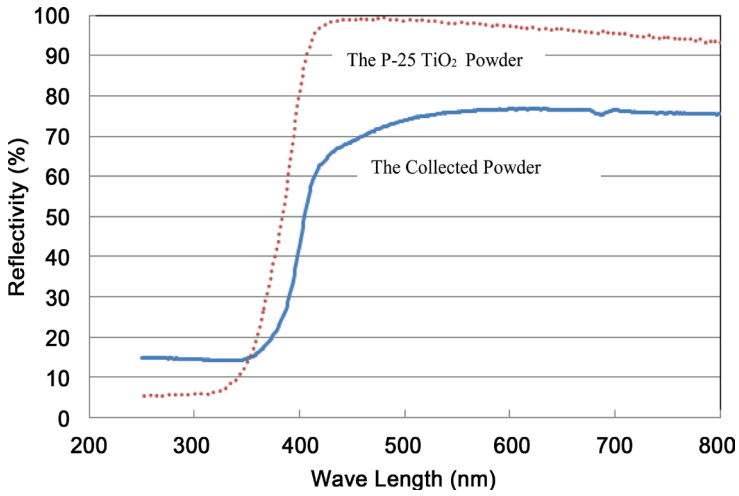

Figure 9. UV-vis reflectivity measurements for the P-25 titanium oxide and the collected powders.

dioxide was effective for enhancing visible light response [14]. De-en Gu *et al.* reported a C-doped titanium dioxide powder with exhibiting photocatalytic activity under visible light irradiation [15]. Micro-mesoporous carbon-doped TiO_2 was fabricated by applying chemical treatment for TiC powder. TiC was dipped in a nitric acid solution with ethanol and was oxidized to titanium oxide by the strong oxidation ability of nitric acid. They ascribed that most of the carbon consisted of TiC dissolved as CO_2 but some carbon was incorporated into the lattice in the form of Cs-o, exchange of oxygen site, and carbonate species. Moreover, they considered that it was a cause for visible light response. We did not use nitric acid but performed anodic oxidation in NH_4NO_3 solution for commercially pure titanium sheet with TiC precipitated in the surface layer. By anodic oxidation TiC in the surface layer of the titanium substrate dissolved as CO_2 but some carbon might remain in titanium dioxide. In our study, the form of carbon in the titanium dioxide has not been clarified yet. However, in terms of the UV-vis reflectivity measurement result, the collected powder clearly shows absorbance below approximately 500 nm. De-en Gu *et al.* reported that a fundamental optical absorption threshold of their fabricated C-doped was 453 nm, which was almost equal to the value to our collected powder.

4. Conclusion

A commercially pure titanium sheet with TiC precipitated in its surface layer was anodized in NH_4NO_3 aqueous solution and heat treated in air. The photocatalytic activity of the titanium dioxide powder collected from the surface of anodized and heat-treated titanium sheets was evaluated under ultra-violet and visible light irradiation. It showed relatively high photocatalytic activity in 0.1 mol/l

potassium iodide solution, which was almost equal to the activity level of the TiO_2 powder (P-25) fabricated by Degussa Corporation. The better photocatalytic activity under ultra-violet irradiation is considered to be related to the formation of the anatase type titanium dioxide. Photocatalytic activity under visible light irradiation was also observed, which was considered to be attributable to impurity doping, (carbon), in the titanium dioxide powder.

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