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Characterization of Surface Oxide Layers on Black-Colored Titanium

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Abstract

Black-colored titanium was obtained by anodic oxidation of a commercially pure grade-1 titanium sheet in a 0.06 M NH_4NO_3 solution, followed by heat treatment at 773 K for 1 h in a vacuum furnace. The resulting oxide layer on the titanium substrate was examined by X-ray photoelectron spectroscopy, X-ray diffraction, glow discharge spectroscopy, and scanning electron microscopy. It was found that the oxide layer on the black-colored titanium sheet was several micrometers thick and mainly consisted of rutile TiO_2 exhibiting a sponge like nanoporous structure. It is considered that the black-colored appearance of the titanium sheet is due to the sponge like nanoporous structure of the oxide layer absorbing the incident light. The photocatalytic activity of the black-colored titanium sheet was examined by observing the decomposition of a methylene blue (MB, $C_{16}H_{18}N_3SCl$) solution under ultraviolet irradiation due to the existence of rutile TiO_2. The sheet also exhibited photocatalytic activity under visible light irradiation. It is believed that the photocatalytic response upon irradiation with white light is due to carbon doping of the titanium oxide layer on the titanium substrate.

Keywords

Titanium, Titanium Oxide, Titanium Dioxide, Rutile, Photocatalyst, Visible Light Response, Nanoporous Structure

1. Introduction

Titanium exhibits good corrosion resistance due to the highly protective titanium oxide layer formed on its surface. Titanium oxides have another important feature: photocatalytic activity under irradiation by ultraviolet (UV) light [1].

The anodic oxidation of titanium in an aqueous solution is a well-known method for producing titanium oxide layers on titanium substrates. Many studies have been conducted on the fabrication of anodized-titanium layers with enhanced photocatalytic activity on titanium substrates [2]. Onoda *et al.* [3] reported that the anodization of a pre-nitrated titanium substrate in a mixed electrolyte composed of H_2SO_4, H_3PO_4, and H_2O_2 resulted in enhanced photocatalytic activity. Ohtsu *et al.* [4] investigated the effects of anions in various ammonium salt electrolytes such as $(NH_4)_2SO_4$, $(NH_4)_2PO_4$, and $(NH_4)_2O_5B_2O_3$ solutions, and it was concluded that S, P, and B were incorporated into titanium oxide layers on the titanium substrates, which affected their photocatalytic activity. Concerning the visible light response, Mizukoshi *et al.* [5] conducted a study on sulfur-doped rutile titanium dioxide photocatalysts. Ohtsu *et al.* [6] reported that a visible-light-responsive titanium dioxide layer was fabricated by anodizing a titanium sheet in aqueous nitric acid solutions, followed by heat treatment.

The authors [7] also conducted studies to develop an anodized titanium sheet with enhanced photocatalytic activity. An anodized titanium sheet that showed high photocatalytic activity under UV irradiation was fabricated by the anodic oxidation of a commercially pure (CP) titanium sheet in a 0.06 M NH_4NO_3 aqueous solution, followed by heat treatment at 803 K for 1 h in air. The anodized titanium sheet also exhibited photocatalytic activity when irradiated with visible light. It was concluded that the enhanced photocatalytic activity under UV irradiation could be attributed to the formation of anatase titanium dioxide and an increase in the surface area. The visible light response of the anodized titanium sheet was believed to be due to C and N doping in the anatase titanium dioxide layer.

On the basis of our previous studies described above, we investigated the effect of heat treatment in a vacuum furnace on the characteristics of anodized titanium sheets. We observed that the color of the anodized titanium sheet turned black after heat treatment in the vacuum furnace. Thus, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), glow discharge spectroscopy (GDS), and scanning electron microscopy (SEM) analyses were conducted to characterize the black-colored titanium sheet. The photocatalytic activity of the black-colored titanium sheet was also examined by observing the decomposition of a methylene blue (MB) solution by irradiation with UV or visible light.

2. Experimental Procedure

2.1. Material Preparation

CP grade-1 titanium sheets cold rolled to a thickness of 0.4 mm were heat treated in a vacuum annealing furnace. The holding temperature and time were 873 K and 6 h, respectively. The average heating rate was approximately 100 K/h, and the cooling rate was nearly 50 K/h. The concentrations of impurity elements in the CP titanium sheets are shown in **Table 1**.

The titanium sheets were rinsed in acetone and immersed in a 0.06 M NH_4NO_3

Table 1. Concentration of impurity elements in CP grade-1 Ti sheet (mass %).

O	H	C	Fe	N
0.0473	0.0022	0.008	0.025	0.004

solution for anodic oxidation. The anodic oxidation was conducted at 80 V for 120 s at 298 K. After anodization, the sheets were rinsed in distilled water and air-dried. After these treatments, the sheets were heated to 773 K in a vacuum furnace for 1h, held at a pressure of 1×10^{-3} Torr, and subsequently furnace cooled. The sheets were then cut into 25 mm × 25 mm × 0.4 mm and 15 mm × 25 mm × 0.4 mm samples for various analyses and photocatalytic activity measurements, respectively.

2.2. Characterization of the Titanium Sheet after Anodization and Vacuum Heat Treatment

The color of the specimen was quantitatively evaluated by colorimetry using L*, a* and b* coordinates. L*, a* and b* are darkness-brightness, green-red and blue-yellow, respectively [8]. In addition, ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy was conducted to measure the reflection ratio (%) of the titanium specimen at wavelengths from 250 nm to 2500 nm. The incident angle of the UV-Vis-NIR light to the sample surface was 8˚. XPS was conducted using monochromatized Al Kαradiation (1486.6 eV) combined with Ar ion sputtering to investigate the chemical states of Ti and C in the anodized titanium oxide layer on the titaniumsubstrate. The anodic oxide layer was also analyzed by XRD to investigate its structure. For the XRD measurements, the incident angle of the X-ray beam to the sample surface was 1˚. The surface and cross-sectional morphology of the titanium sample after anodization and vacuum heat treatment was observed by SEM. GDS was conducted to measure the thickness and elemental content of the whole oxide layer.

2.3. Photocatalytic Activity Test

Photocatalytic activity was measured using a methylene blue (MB) solution. A regent grade methylene blue trihydrate was dissolved into distilled water to make 3.13×10^{-5} M MB solution. Test samples of the titanium sheet before and after anodization and vacuum heat treatment—15 mm × 25 mm × 0.4 mm in size—were separately dipped in 4 cm^3 of a 3.13×10^{-5} M MB solution at 298 K and illuminated with a black-light UV source for 1800 s. The intensity of the black light at 365 nm was 1010 $\mu W/cm^2$. After the irradiation with black light, the absorbance of the MB solution at 664 nm was measured by absorption spectrophotometry to evaluate the decomposition of MB by photocatalytic reaction.

In addition to black-light irradiation, white light-emitting diode (LED) irradiation was conducted to evaluate the visible light response of the titanium sheet after anodization and vacuum heat treatment. The intensity of the white LED illumination was 47,000 lx. After irradiation with white LED light, the absorbance of the MB solution at 664 nm was measured by absorption spectrophotometry.

3. Experimental Results and Discussion

Figure 1 shows three titanium sheets: 1) titanium sheet without anodization and heat treatment, 2) titanium sheet anodized in a 0.06 M NH_4NO_3 solution, and 3) titanium sheet after anodization and vacuum heat treatment. Although the color of the anodized specimen was gray, it turned black after heat treatment in the low-vacuum furnace. Table 2 shows measured L*, a* and b* values for samples (1) and (3) shown in Figure 1. As shown in Table 2, the value of L* decreased significantly and both a* and b* decreased to near zero. These changes in L*, a*, and b* correspond exactly to the change in color from metallic silver to black. Figure 2 shows UV-Vis-NIR spectroscopy results from the black-colored titanium sheet. It was found that incident light of wavelengths from 200 nm to 2500 nm was effectively absorbed by the black-colored titanium sheet.

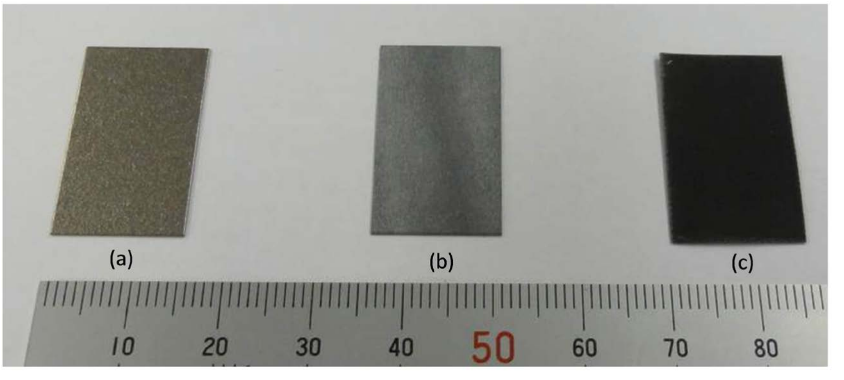


Figure 1. Outward appearance of titanium sheets: (a) Titanium sheet without anodization and heat treatment, (b) Titanium sheet anodized in a 0.06 M NH_4NO_3 solution, and (c) Titanium sheet anodized and heat-treated in a low-vacuum furnace.

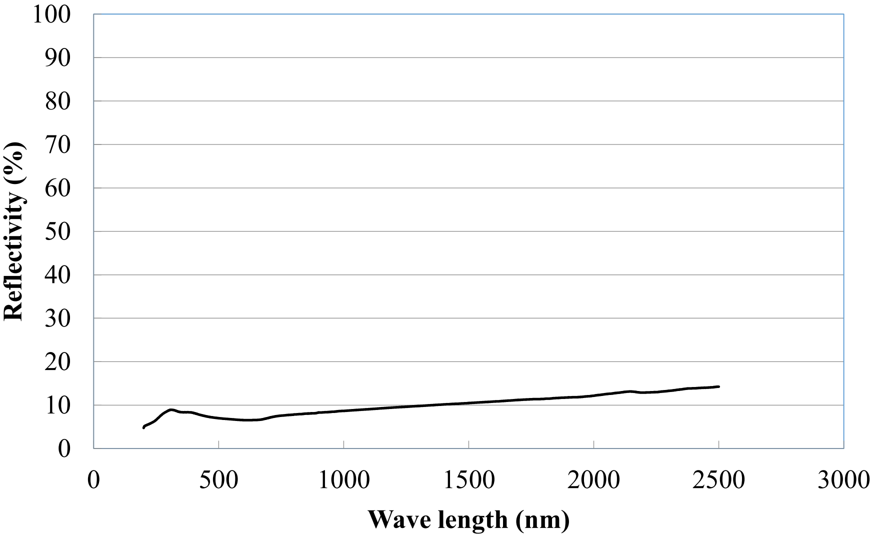


Figure 2. UV-Vis-NIR reflectivity of the titanium sheet after anodization and low-vacuum heat treatment.

Table 2. L*, a*, and b* values of the two samples shown in Figure 1(a) and Figure 1(c).

Samples	L*	a*	b*
Sample (a) in Figure 1	68.26	1.41	5.06
Sample (c) in Figure 1	28.91	0.50	0.22

It has been reported that $Ti_nO_{(2n-1)}$ (n = 2 - 4) exhibits a black color [9]. Additionally, H. Matsunaga *et al.* [10] investigated the effect of anodization, followed by vacuum heat treatment on the color of a titanium sheet, in order to fabricate black-colored titanium sheets by forming low-valence titanium oxide, such as TiO or Ti_2O_3. As a result, a relatively black-colored titanium sheet was obtained by anodic oxidation at 150 V in a mixed solution of 0.3 M H_3PO_4, 0.4 M H_2SO_4, and 0.3 M H_2O_2 followed by vacuum heat treatment at 673 K for 8h at a pressure of 1×10^{-3} Torr; however, there is no report on whether low-valence titanium oxides were formed or not. In addition, H. Jun-xiang *et al.* reported that plasma electrolytic oxidation of Ti-6Al-4V alloy or pure titanium was carried out and the black appearance can be attributed to the presence of Ti^{2+} and Ti^{3+} [11].

The vacuum pressure used during the heat treatments in this study was lower than that used by Matsunaga *et al.*; therefore, the formation of low-valence titanium oxides is plausible. Thus, XPS analysis was carried out to investigate the valence state of titanium oxide from the outersurface to a depth of 1047.1 nm. The obtained results are shown in **Figure 3**. Clearly, TiO_2 was formed on the surface layer of the titanium substrate. Low-valence Ti peaks were observed inside the titanium oxide layer; however, Ti^{4+} might be reduced during Arion sputtering.

Therefore, XRD measurements were conducted, and the obtained results are shown in **Figure 4**. Other than the diffraction peaks from metallic titanium, the strongest diffraction peaks are attributable to rutile TiO_2, and weak peaks from anatase TiO_2 were detected. No peaks from low-valance titanium oxides were observed. This clearly indicates that the black-colored appearance is not due to the formation of low-valence titanium oxides.

Consequently, the surface and cross-sectional morphology of the black-colored titanium sheet was examined by SEM. **Figure 4** shows SEM images of the surface of the black-colored titanium sheet. As shown in **Figure 5**, the surface is quite rough with many holes as small as a few tens of nanometers. **Figure 6** shows cross-sectional SEM images of the black-colored titanium sheet. As shown in **Figure 6**, the thickness of the oxide layer is several micrometers and the layer has the small holes with their width of several tens nanometers and several hundred nanometers in length. Based on these observations, it is considered that the black color induced by anodization and subsequent vacuum heat treatment is attributable to a sponge like nanostructure that might strongly absorb visible light.

Next, the photocatalytic activity of the black-colored titanium sheet was examined by observing the decomposition of MB under black-light irradiation.

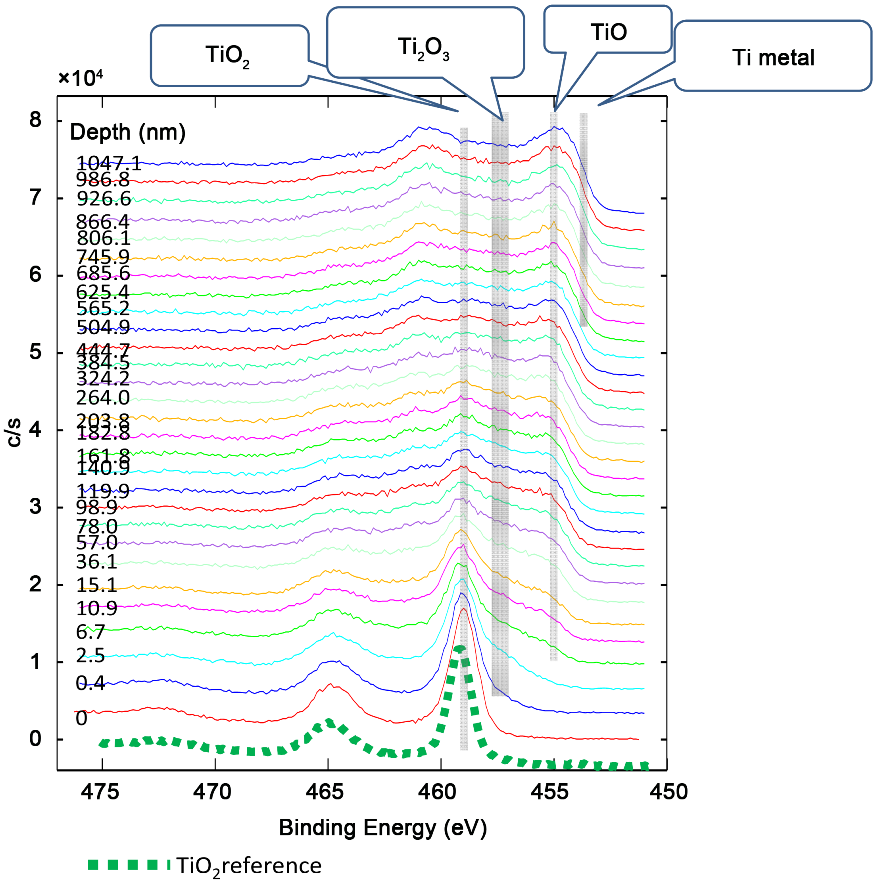


Figure 3. XPS analysis of Ti (1 s) from surface to interior of the oxide layer formed on the titanium sheet after anodization and low-vacuum heat treatment.

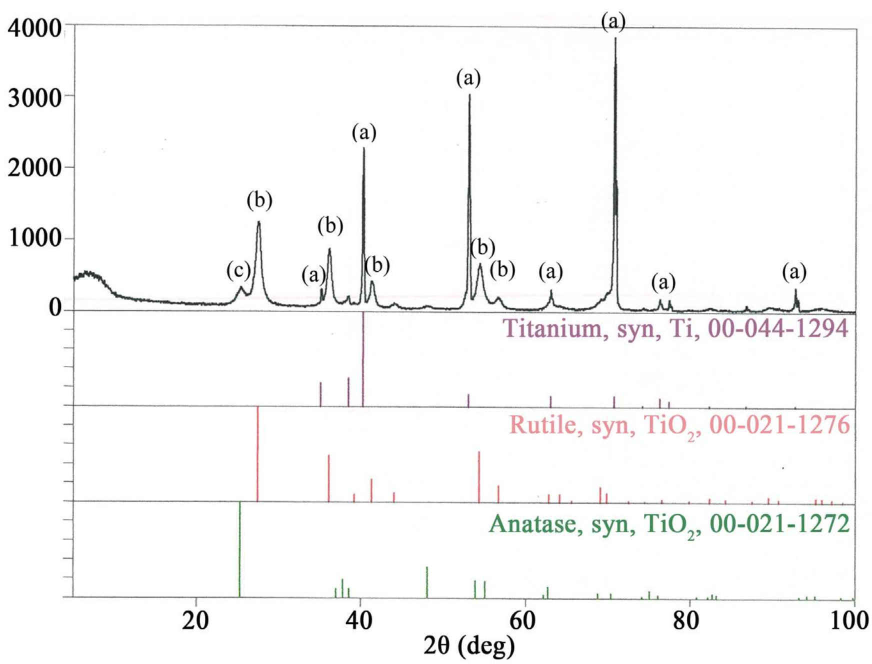
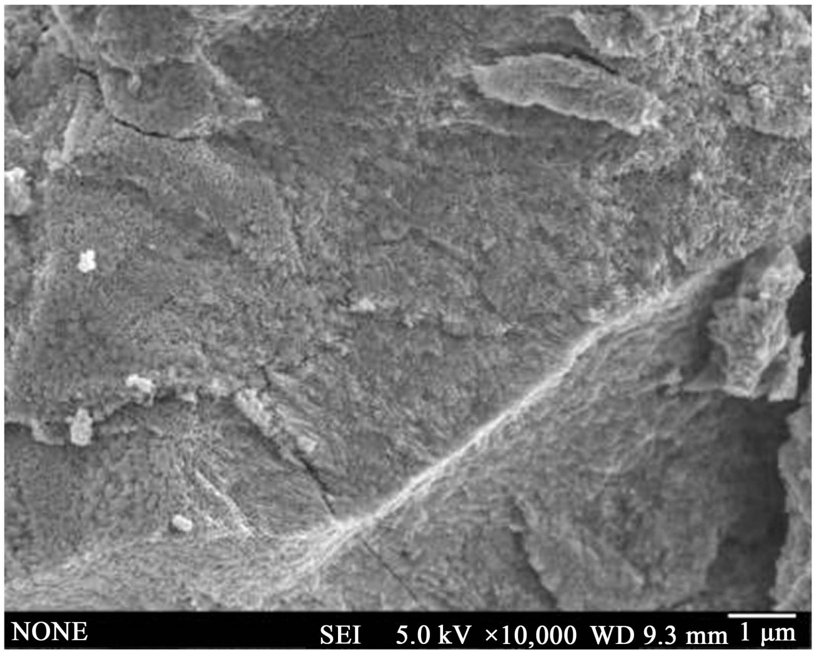


Figure 4. XRD patterns of titanium sheet after anodization and low-vacuum heat treatment, (a) Metallic titanium; (b) Rutile TiO_2; and (c) Anatase TiO_2.



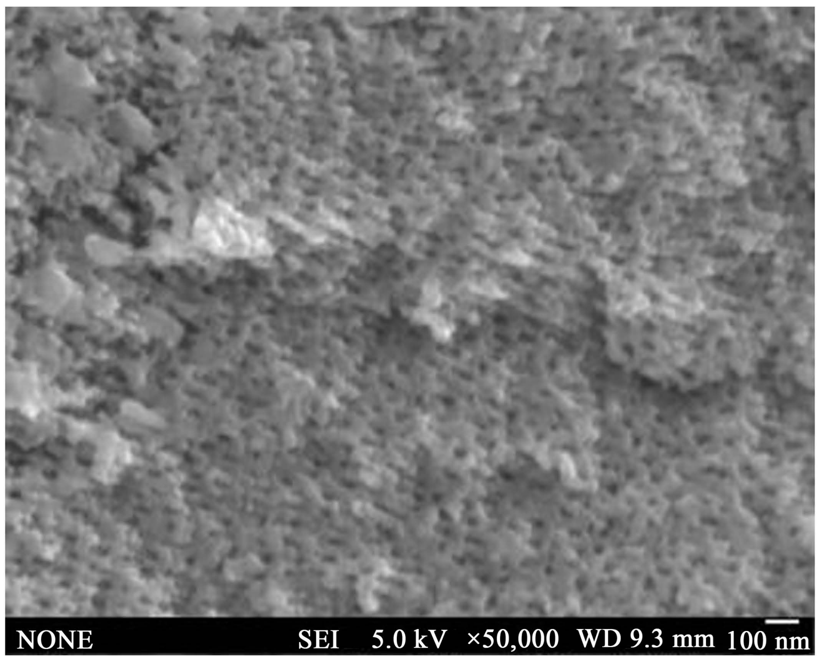


Figure 5. SEM images of the surface of titanium sheet after anodization and low-vacuum heat treatment.

Figure 7 shows the photocatalytic-activity test results under the black-light irradiation. The absorbance of the anodized and vacuum heat-treated titanium sheet was almost half that of the untreated titanium sheet due to the decomposition of MB under black-light irradiation. As shown in **Figure 4**, rutile TiO_2 is the main component of the titanium oxide layer. The photocatalytic activity of the black-colored titanium sheet was therefore considered to be due to the presence of rutile TiO_2.

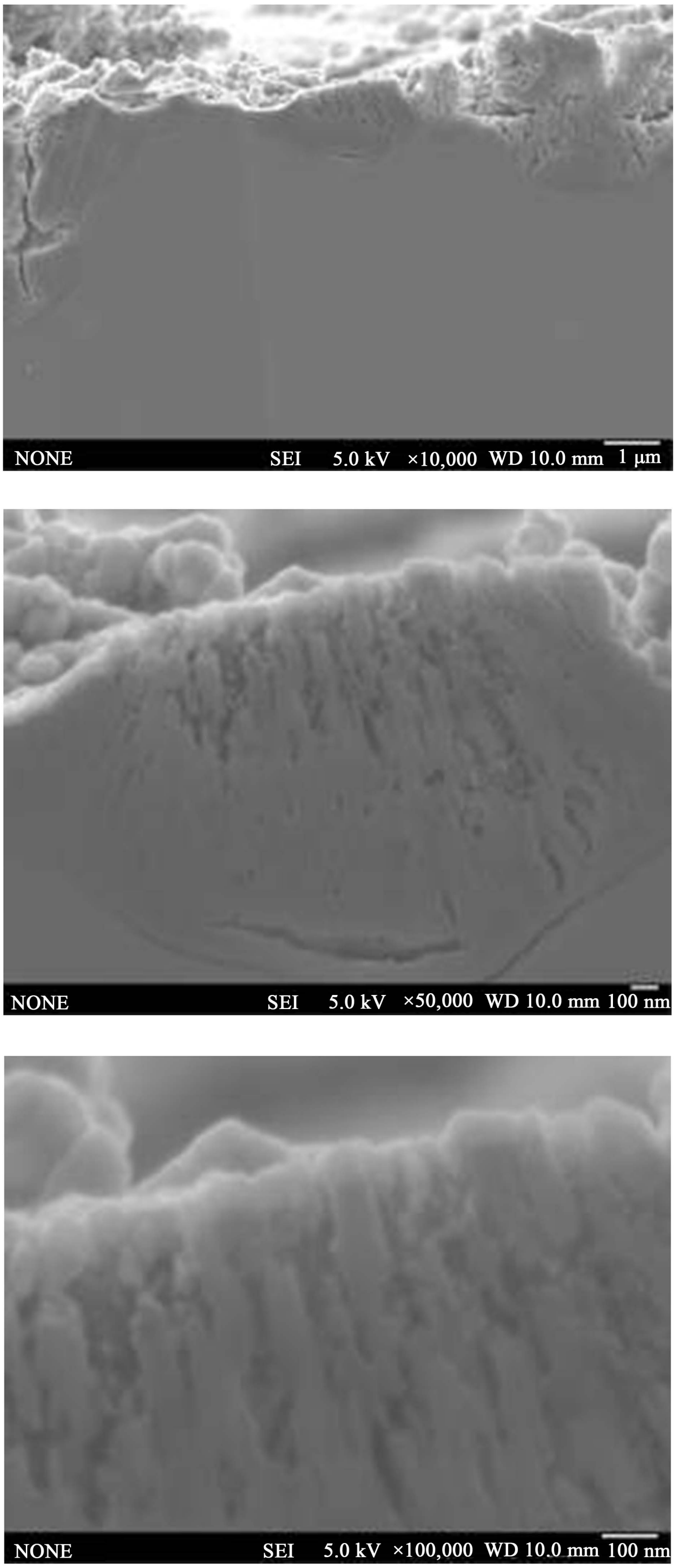


Figure 6. Cross-sectional SEM images of titanium sheet after anodization and low-vacuum heat treatment.

In addition to the black-light irradiation, the photocatalytic activity under visible light irradiation was also examined. As shown in **Figure 8**, the black-colored titanium sheet exhibited photocatalytic activity under irradiation with white LED light. However, both rutile and anatase TiO_2 do not show photocatalytic activity when irradiated with visible light. Therefore, impurity elements, specifically carbon and nitrogen, inside the titanium oxide layer on the titanium substrate were examined by GDS. The results of the GDS analysis are shown in **Figure 9**. The concentration of nitrogen was very low. A large amount of carbon was observed in the titanium oxide layer; however, the state of the carbon in the titanium oxide layer was not clarified by GDS. The chemical state of carbon in

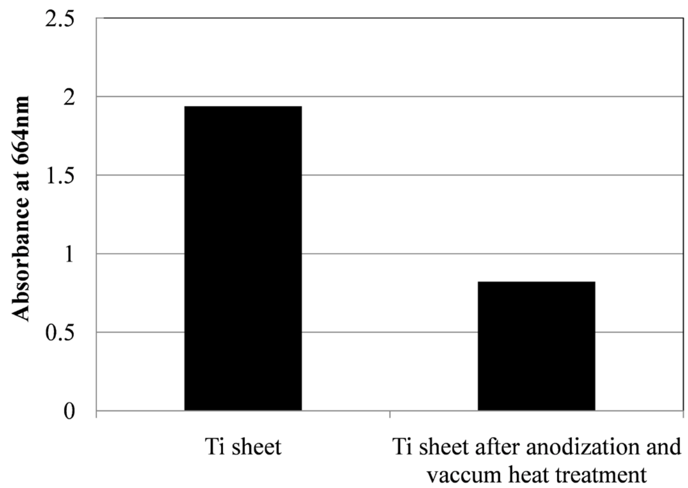


Figure 7. Photocatalytic activity test results under black-light irradiation.

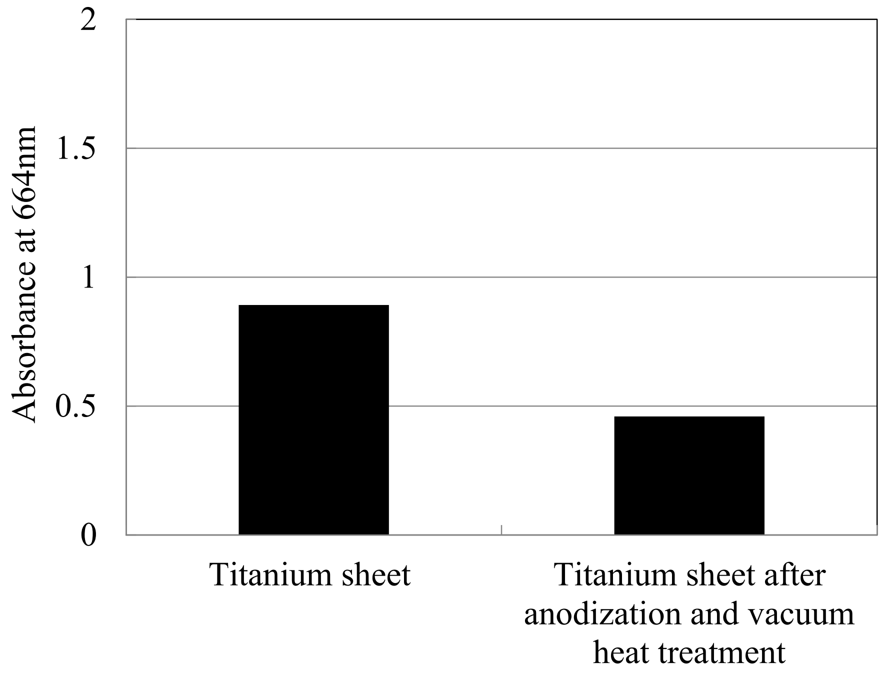


Figure 8. Photocatalytic activity test results under white LED-light irradiation.

the titanium oxide layer was therefore examined by XPS.

Figure 10 shows the chemical state of carbon in the titanium oxide layer as determined by XPS. From the data in Figure 10, $(C–H)_n$ bonding was observed,

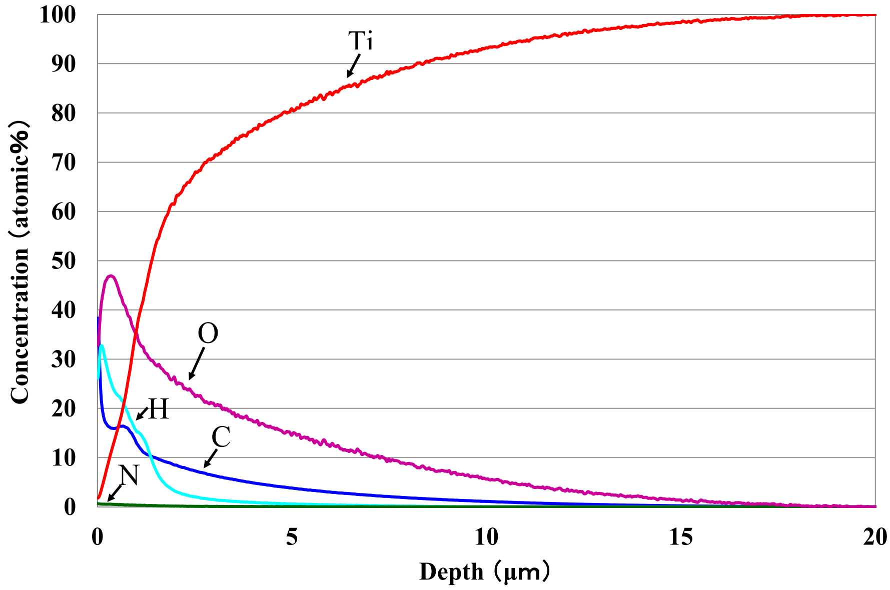


Figure 9. GDS analysis of the titanium sheet after anodization and low-vacuum heat treatment.

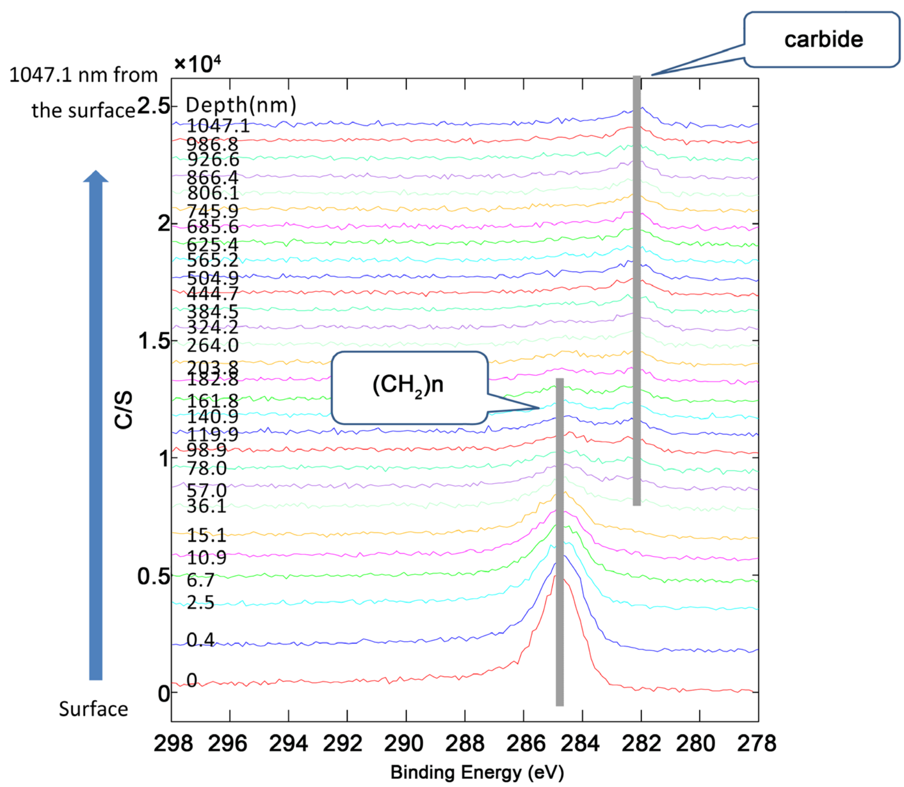


Figure 10. XPS analysis of C (1 s) from surface to interior of the oxide layer formed on the titanium sheet after anodization and low-vacuum heat treatment.

which was presumably caused by contamination; however, a peak other than $(C–H)_n$ was also observed, which indicates the presence of carbides deeper than 57.0 nm. As R. Asahi *et al.* reported the doping of carbon and nitrogen into titanium oxide could induce a visible light response [12]. Thus, it is believed that carbon doping of the titanium oxide layer induced a visible light response. The mechanism of carbon doping into the titanium oxide layer has been described elsewhere [7].

4. Conclusion

A black-colored titanium sheet was obtained by the anodic oxidation of CP grade-1 titanium sheet in a 0.06 M NH_4NO_3 solution followed by heat treatment at 773 K for 1 h in a low-vacuum furnace. The resulting oxide layer on the titanium substrate was examined by XPS, XRD, GDS, and SEM. It was found that the thickness of the oxide layer was more than a few micrometers, and mainly consisted of rutile TiO_2 with a sponge-like nanoporous structure. It is considered that the black-colored appearance of the titanium sheet is due to the sponge likenanoporous structure of the titanium oxide layer. The photocatalytic activity of the black-colored titanium sheet was examined by monitoring the decomposition of a methylene blue (MB) solution under UV irradiation due to the existence of rutile TiO_2. The sheet also exhibited photocatalytic activity under visible light irradiation. It is strongly suggested that the photocatalytic response under irradiation with white LED light is due to carbon doping in the titanium oxide layer on the titanium substrate.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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