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Photocatalytic Activity of Anodized Titanium Sheets under Ultra-Violet and Visible Light Irradiation

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Abstract

A commercially pure titanium sheet precipitated TiC in the surface layer was fabricated by anodic oxidation in NH_4NO_3 solution and heat treatment in air. The fabricated sheet showed relatively high photocatalytic activity in 0.1 M KI solution, which was close to the activity level of the P-25 particle made by Degussa Corporation. It exhibited photocatalytic activity in antifungal and anti-virus tests under black light irradiation. The better photocatalytic activity under black light irradiation is considered to be related to the formation of anatase and rutile type titanium dioxides and rough surface. It also showed photocatalytic activity under visible light irradiation, which is considered to be attributable to carbon and nitrogen doping in titanium dioxide.

Keywords

Photocatalysis, Titanium Dioxide, Anodic Oxidation, Visible-Light Response, Carbon-Doping

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. The various methods for making titanium dioxide with high photocatalytic activity have been investigated.

Anodic oxidation of titanium substrate is commercially used to produce colored titanium sheets. The color of

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the anodized titanium substrate can be changed by varying the thickness of surface titanium oxide layer. And colored titanium sheets are mainly used as architectural materials.

Recently, the anodic oxidation method has been applied for making titanium dioxide with enhanced photocatalytic activity under ultra-violet (UV) or visual 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 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 $(NH_4)_2O_5B_2O_3$ and it was identified that S, P and B were incorporated into oxide layers, which affected photocatalytic activity [7].

Concerning visual 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 investigated. The authors have investigated the effects of a TiC precipitated in surface layer of titanium sheet on discoloration of titanium due to the growth of titanium oxide layer and it was found that TiC in surface layer enhanced the growth of titanium oxide layer on the titanium substrate under an atmospheric environment [10] [11]. In this study, based on the prior studies, the effects of TiC precipitated in the surface layer on the photocatalytic activity of anodized titanium sheets were investigated. Concerning an electrolyte, NH_4NO_3 solution was applied based on previous studies by N. Ohtsu *et al*. [7] [9]. Photocatalytic activity of anodized titanium sheets was investigated under black light and visual light irradiation.

2. Experimental

2.1. Materials and Photocatalytic Activity Measurement

Commercially pure (CP) titanium sheets cold rolled to the thickness of 0.4 mm were heat treated in vacuum annealing furnace. The holding temperature and time were 873 K and 6 hours, respectively. And average raising rate was approximately 100 K/hour and cooling rate was nearly 50 K/hour. 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 0.06 M NH_4NO_3 solution for anodic oxidation. The anodic oxidation was controlled by galvanostatically at 15 V, 24 V, 45 V and 80 V for 120 sec at room temperature. After the anodization they were rinsed in distilled water and air-dry. After these treatments, they were 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 136 K/min, following which they were cut into 15 mm × 25 mm and 50 mm × 50 mm samples to be used for measuring photocatalytic activity.

Photocatalytic activity was measured using KI solution [12]. The 15 mm × 25 mm test samples were dipped in 4 cc of 0.1 M KI solution at room temperature and illuminated with black light for 1800 sec or white light emission diode (LED) for 21,600 sec. The intensity of the black light at 365 nm was 1010 μW/cm^2, and the intensity of the white LED was 47,000 lx. After irradiation with black light or LED, the peak intensity of 0.1 M KI solution at 287 nm was measured by absorption spectrophotometer (U2910, HITACHI). In addition, P-25 titanium dioxide particles made by Degussa corp. were also tested. The photocatalytic activity of a tape measuring 15 × 25 mm in size to which P-25 particles were attached was also measured under black light illumination as same method as described above. And I^- is oxidized by dissolved oxygen without a phtocatalyst, thus 0.1 M KI solution without test specimen were also measured as control.

Photocatalytic activity of the anodized Ti samples was also investigated in antifungal and antivirus tests based on Japanese Industrial Standard (JIS) R-1705 (2008) [13] and JIS R-1702 [14] using black light irradiation. The antifungal test was carried out at Japan Food Research Laboratories. Three anodized titanium samples of 50 mm

Table 1. Concentration of impurity elements of Ti sheets tested (mass %).

O	H	C	Fe	N
0.0473	0.0022	0.008	0.025	0.004

× 50 mm size were used. Same size glass sheets were used as control. *Aspergillus niger* NBRC 105649 was used in the test. Intensity of black light was 0.8 mW/cm^2 and irradiation time was 24 hour. And the antivirus test was conducted at Kitasato Research Center for Environmental Science. Anodized titanium sample of 50 mm × 50 mm size were used and glass sheets of the same size were used as a control. Influenza A virus was used in the test and the intensity of the black light was 0.1 mW/cm^2 and the irradiation time was 8 hour.

2.2. Surface Analysis

Anodic oxidation layers on the titanium substrate were analyzed by X-ray diffraction (XRD; RINT1500, RIGAKU) measurement. For XRD measurement, incident angle of X-ray beam to surface was 1 degree to obtain structure of anodized oxidized layer on titanium substrate. Surface morphology of the anodized titanium sample was observed by scanning electron microscope (SEM; JIS-7000F, Jeol). Glow Discharge Spectroscopy (GDS; GD Profiler2, HORIBA Jobin Yvon) with Ar ion sputtering was conducted to investigate content of elements in oxide layers. X-ray photoelectron spectroscopy (XPS; Physical Electronics Quantum 2000 Scanning ESCA Microprobe, ULVAC-PHI Inc.) with Ar ion sputtering was conducted using monochromatized Al Kαradiation (1486.6 eV) to investigate the chemical states of O, C and N in anodized titanium oxide layer on titanium substrate.

3. Experimental Results and Discussion

3.1. Photocatalytic Activity under Blacklight Illumination

Figure 1 shows applied voltage vs. current density of CP titanium sheets in 0.06 M NH_4NO_3 solution. Current density of CP titanium sheet in NH_4NO_3 solution was almost same below 20 V, however it increased largely above 20 V and it was increased with applied voltage. And above 20 V, surface of anodized titanium sheets became rough. Based on the results shown in **Figure 1**, phtocatalytic activity for anodized titanium samples at 15 V, 24 V, 45 V and 80 V and heat treated at 803 K were evaluated in KI solution. Obtained results were shown in **Figure 2**.

The sample "Blank" was a control performed by irradiating a 0.1 M KI solution containing no samples with black light for the prescribed time. As shown in **Figure 2**, Blank showed about 0.2 of absorbance at 287 nm. It was considered that I^- was oxidized by dissolved oxygen without phtocatalyst. For the sample anodized at 15 V, an absorbance value slightly increased but large. But above 20 V, absorbance values increased largely with applied voltages. And anodiezed samples at 45 V and 80 V showed about 5 times higher that of Blank, which were close to that of the P-25 particle. It is considered that thicker titanium oxide layer and rough surface might enhance photocatalytic activity above 20 V of applied voltage.

In order to investigate crystal structure and surface morphogy of anodized titanium samples, XRD measurement and SEM observation were carried out for the titanium sample anodized at 45 V.

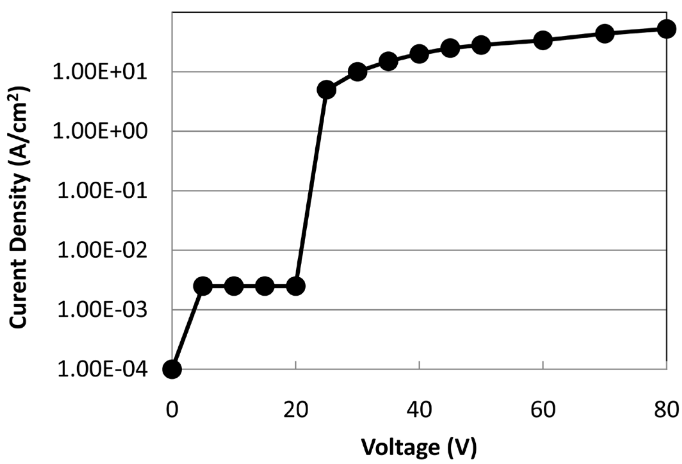


Figure 1. Applied voltage vs. current density of titanium sheet in 0.06 M NH_4NO_3 solution.

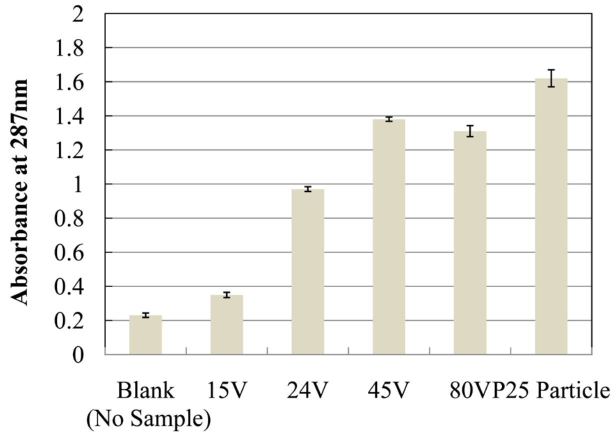


Figure 2. Photocatalytic activity test results using 0.1 M KI solution under black light irradiation.

As **Figure 3** shows result of the XRD measurement, strong peaks from anatase type TiO_2 were observed. And peaks from rutile type TiO_2 were also observed. Weak peaks of titanium metal were from titanium substrate. It is generally accepted that TiO_2 in anatase type shows the highest photocatalytic activity.

On the other hand, it has been considered that dual phase of anatase and rutile had better photocatalytic activity [15] [16]. As shown in **Figure 3**, anodized CP titanium sheets followed by heat treatment had dual phase of anatase and rutile. Dual phase might contribute better photocatalytic activity of anodized CP titanium sample.

Next a surface morphology of the anodized and heat treated titanium sample was observed by SEM. **Figure 4** shows SEM photographs of the titanium sample, and as can be seen in the photographes, the surface of the sample was relatively rough. In addition to the formation of dual phase of anatase and rutile TiO_2, surface roughness on titanium surface is also considered to enhance photocatalytic activity.

In order to investigate the photocatalytic activity of the anodized titanium sample at 45 V and heat treated in regards to fungal growth, an antifungal test was carried out. The obtained results were shown in **Figure 5** and **Figure 6**. The spore count on the glass sheet used as a control changed little during the test. On the other hand, spore count of the titanium sample remarkably decreased to below 10. As shown in **Figure 6**, it is clear that the titanium sample under black light irradiation effectively terminates *Aspergillus niger* NBRC 105649. From **Figure 5** and **Figure 6**, it was found that the anodized titanium sheets had better photocatalytic activity in relation to fungal growth. Next, antivirus test was carried out.

Figure 7 shows the antivirus test results for a glass sheet as a control and titanium sample. After the test, the infectivity titer of the virus for the glass sheet was over 6000. On the other hand, it was undetectable for the titanium sample. Thus, it was also found that the anodized titanium sample had better photocatalytic activity in relation to the influenza A virus. These results are in good agreement with the results shown in **Figure 2**.

3.2. Photocatalytic Activity under Visual Light Irradiation

Next, photocatalytic activity under visible light such as white color LED light was investigated by using 0.1 M KI solution. The results obtained are shown in **Figure 8**.

The absorbance of Ti sample was clearly higher than blank (no sample), which indicates photocatalytic activity under visual light irradiation. Thus, a surface analysis of the titanium sample before and after anodization was carried out by GDS. **Figure 9** shows GDS analysis of titanium sample before anodization.

As shown in **Figure 8**, the anodized titanium sample showed photocatalytic activity under visual light irradiation. Concerning visible light response, R. Asahi *et al.* indicated that doping of anions such as carbon, nitrogen, fluorine and sulfur to titanium dioxide was effective for enhancing visual light response [17].

As shown in **Figure 9** carbon is enriched in the surface layer of titanium sheets which forms TiC. Formation mechanism of TiC has been described elsewhere [10]. **Figure 10** shows GDS analysis result for a titanium sample anodized at 45 V and heat treated. As shown in **Figure 10**, carbon existing in the titanium oxide layer which is considered to be derived from TiC and is attributable to visual right response. In **Figure 10** nitrogen was also observed in the titanium oxide later, although the concentration was lower than that of carbon.

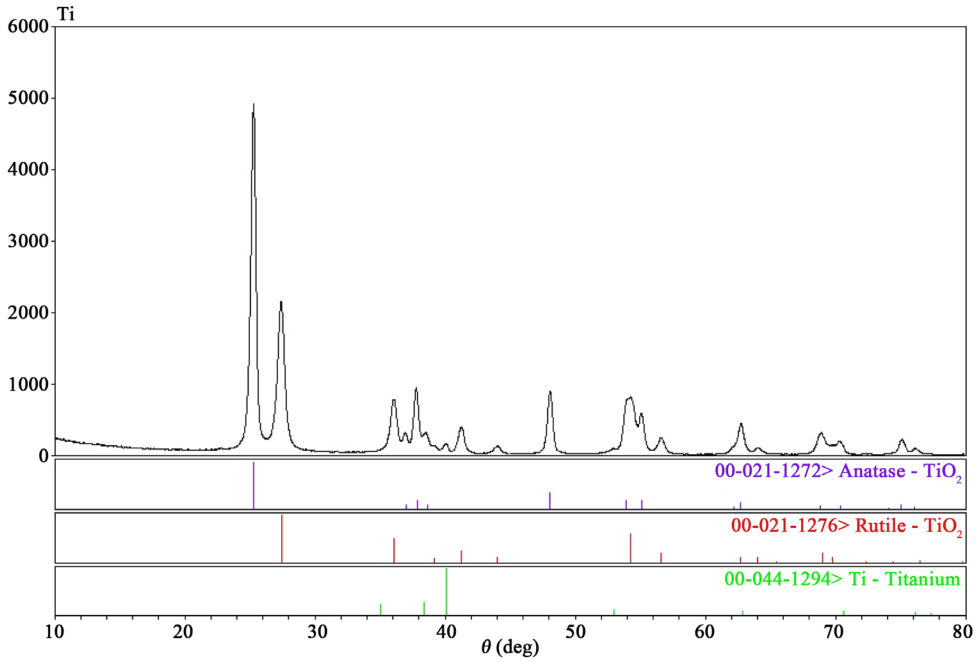


Figure 3. XRD pattern of the titanium sample anodized at 45 V and heat treated.

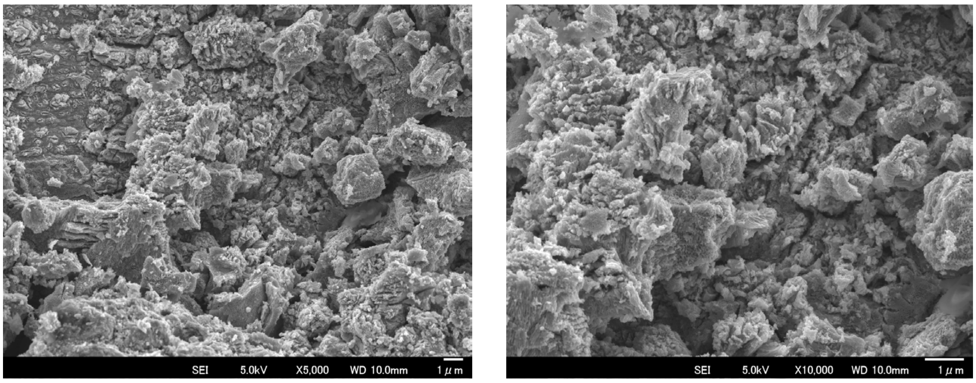


Figure 4. SEM microphotographs of titanium sample anodized at 45 V and heat treated.

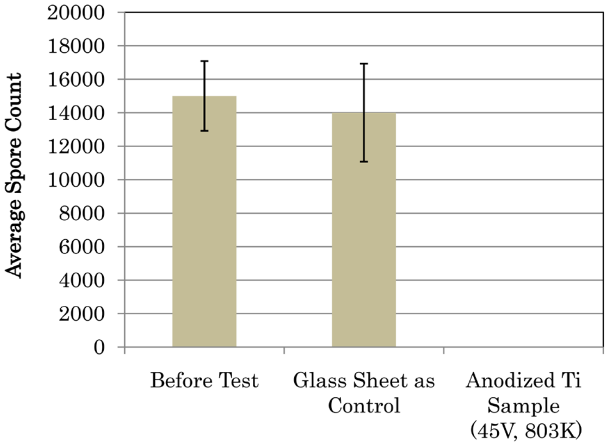


Figure 5. Antifungal test results of glass sheet and titanium sample anodized at 45 V and heat treated.

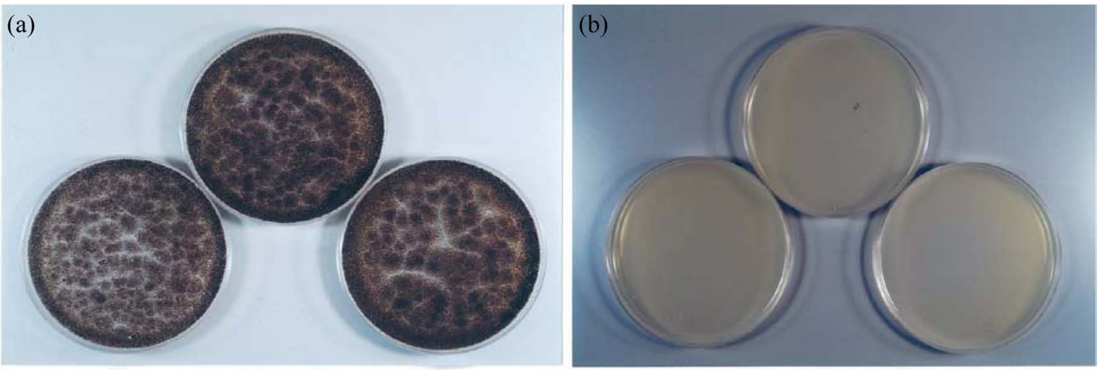


Figure 6. Appearance after antifungal test of glass sheet (a) and titanium sample anodized at 45 V and heat treated (b).

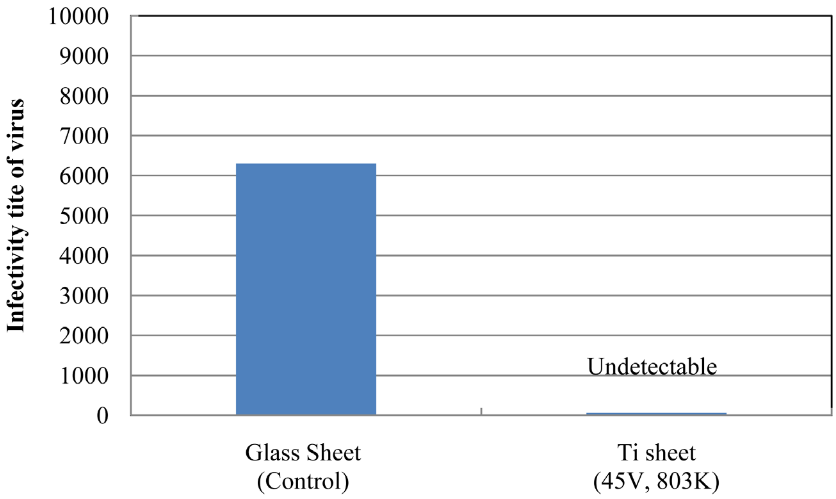


Figure 7. Antivirus test results of glass sheet and the titanium sample anodized at 45 V and heat treated.

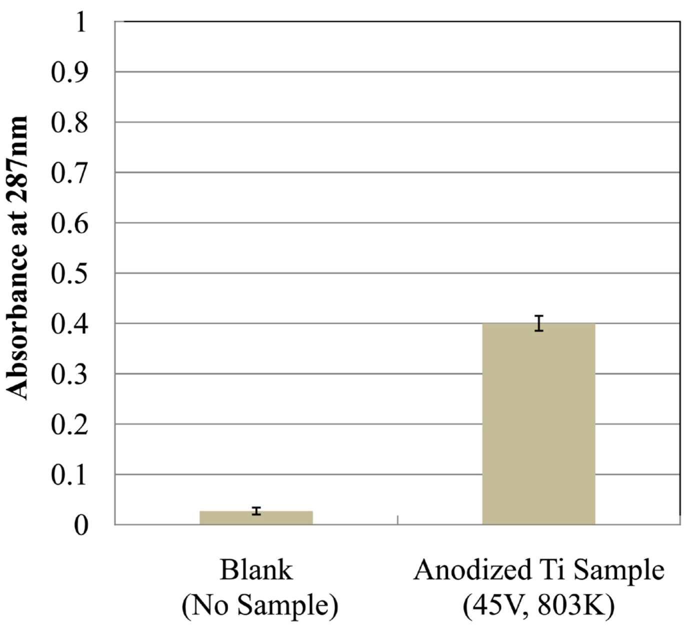


Figure 8. Photoactivity test results under white color LED irradiation.

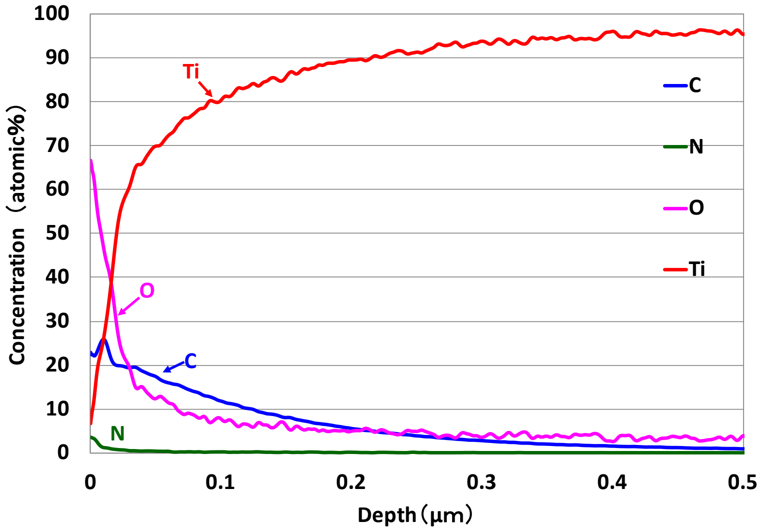


Figure 9. GDS analysis result for titanium sample before anodization.

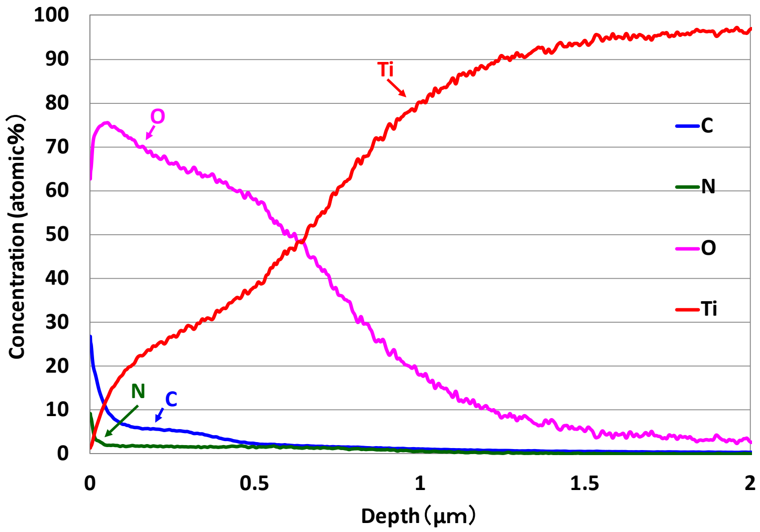


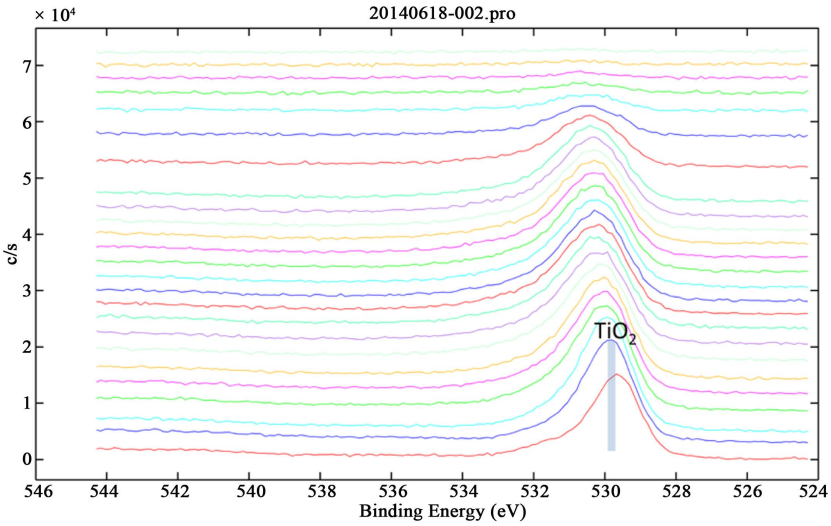
Figure 10. GDS analysis result for anodized titanium sample at 45 V, followed by heat-treatment.

Figure 11 shows XPS analysis of surface layers of the anodized titanium sample at 45 V and followed by heat treatment. From the **Figure 11(a)**, titanium oxide exists at 37 nm and 230.5 nm in depth from the outmost surface. And chemical states of carbon were analyzed at the depth above. Obtained results were shown in **Figure 11(b)** and **Figure 11(c)**. In **Figure 11(b)** (C-H)n bonding was observed which was presumably caused by a contamination. However, a weak peak other than (C-H)n was also observed which indicated carbide. And a weak peak from carbide was also observed in depth of 230.5 nm. Concerning a chemical state of nitrogen, a peak from nitride was observed from only near the outmost surface layers.

As R. Asahi *et al*. reported that doping of carbon and nitrogen into titanium oxide induced visible light response [17]. Thus, it is believed that doped carbon and nitrogen in anodized titanium oxide layer induced visible light response. Nitride in titanium oxide layer is considered to derive from electrolyte, NH_4NO_3 solution, for anodic oxidation.

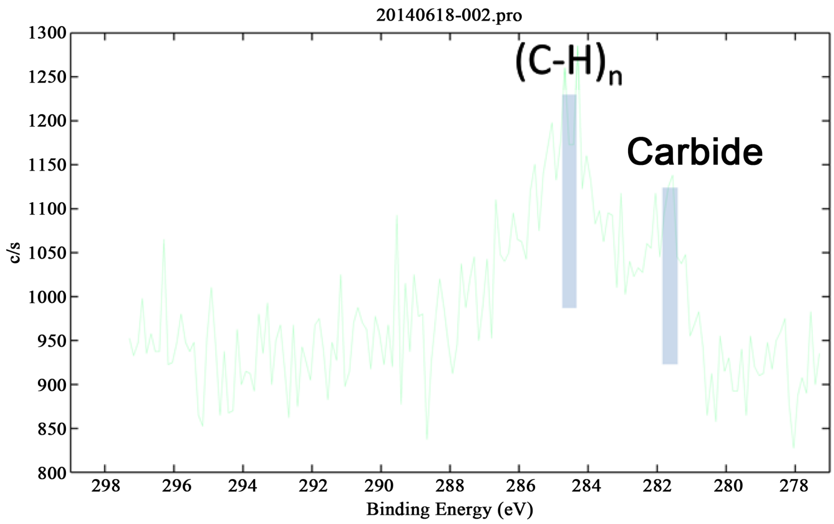
4. Conclusion

A commercially pure titanium sheet precipitated TiC in the surface layer fabricated by anodic oxidation in



20140618-002.pro
× 10⁴
c/s
Binding Energy (eV)
TiO_2

(a)



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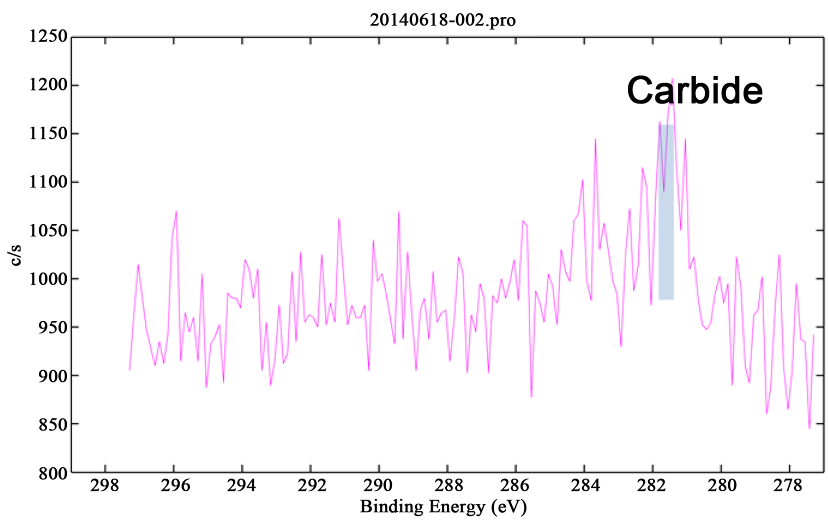
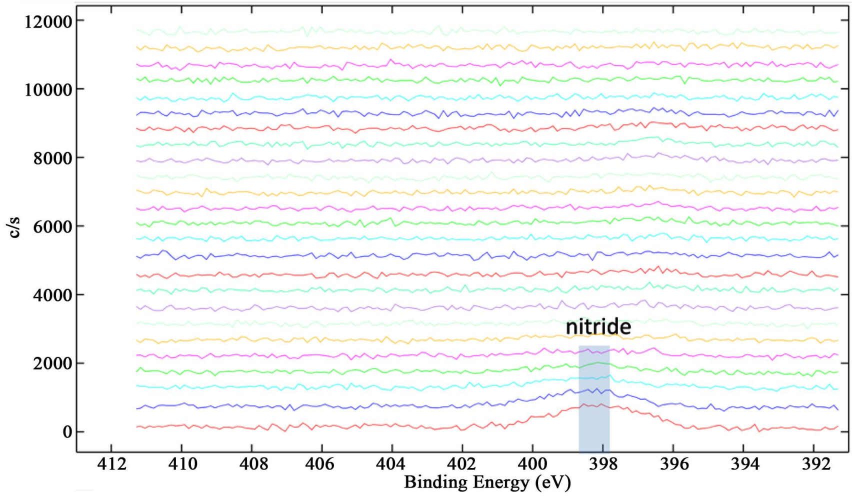
c/s
Binding Energy (eV)
$(C-H)_n$
Carbide

(b)



20140618-002.pro
c/s
Binding Energy (eV)
Carbide

(c)



(d)

Figure 11. XPS analysis of anodized titanium sheet at 45 V and followed by heat treatment: (a) O1s; (b) C1s at 37 nm; (c) C1s at 230.5 nm; (d) N1s.

NH_4NO_3 solution at 45 V and 80 V and heat treatment in air at 803 K showed relatively high photocatalytic activity in 0.1 M KI solution which was close to the absorbance value of P-25 particle. The anodized sample at 45 V and heat treated, showed good photocatalytic activity in antifungal and antivirus tests under black light irradiation. The better photocatalytic activity under black light irradiation is considered to be related formation of dual phase of anatase and rutile type titanium dioxide and rough surface. It also showed photocatalytic activity under visual light irradiation. It is considered that visible light response was caused by doping of carbon and nitrogen in titanium dioxide.

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