

Formation of Sodium Titanate Nanotube Films by Hydrothermal Transcription

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Since Kasuga et al.¹ reported the synthesis of titania nanotubes by the hydrothermal method with regard to titania^{1,2} and titanate³ nanotubes (hereafter referred to as TNT), several application studies⁴ on electrochromism,⁵ bone regeneration,⁶ proton conduction,⁷ photoinduced hydrophilicity,⁸ catalysts,⁹ hydrogen storage,¹⁰ and dye-sensitizing solar batteries¹¹ have been conducted all over the world. For the effective utilization and maximization of TNT characters, it is important to ensure the prevention of nonuniform aggregation and the uniform and organized arrangement of TNT in terms of size and morphology at larger than micrometer or centimeter size, respectively. In particular, a film form is considered to have wide applications. For the formation of TNT films on various substrates, methods of painting a dispersion liquid of TNT particles on a substrate¹² and coating TNT using the alternate-layer deposition process⁸ have been reported. However, there are limitations with respect to the formation of only thin films and film formation on a surface of three-dimensional and complex forms; therefore, a film formation technique for TNT needs to be developed. Recently, we reported that by hydrothermally

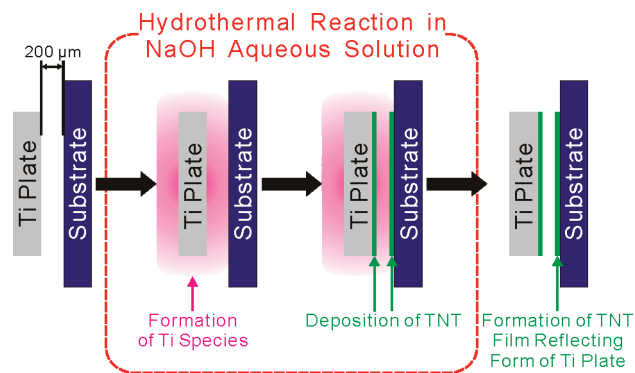


Figure 1. Schematic representation of a reaction process by the hydrothermal transcription method.

treating titanium metal, the size and form of which were controlled at larger than micrometer or centimeter size, in aqueous NaOH solution, TNT was formed on titanium metal retaining these forms.¹³ In the report, we discussed that by the hydrothermal treatment of titanium metal in NaOH solution, titanium species¹⁴ such as TiO_3^{2-} , $\text{TiO}_2(\text{OH})_2^{2-}$, and $\text{Ti}_n\text{O}_{2n+m}^{2m-}$ were formed near the surface of the titanium metal plate and that the titanium species were redeposited on the titanium plate as TNT. On the other hand, in the present study, we devised a “hydrothermal transcription method” for forming TNT films on various substrates, as shown in Figure 1. In this method, TNT is produced by redepositing or transcribing the titanium species formed near the surface of the titanium plate on other substrates by hydrothermal treatment in aqueous NaOH solution, which grow to form dense films on several substrates as well as on the titanium plate.¹³ By this method, TNT film can be formed even on a substrate with three-dimensional and complex morphologies and adheres strongly and chemically to the substrate compared with the two film formation methods^{8,12} described above; in these methods, the long axis of TNT is painted almost parallel to the substrate. In this paper, we report the formation of TNT films on several substrates by hydrothermal transcription.

The experiment was conducted as follows. As shown in Figure 1, a titanium metal plate and a substrate were placed adjacently with a gap of about 200 μm and fixed using titanium wires or SUS316 wires. For the substrate, a Co–Cr alloy disk, SUS316L plate, SUS430 plate, tantalum plate, and silicon plate were used. These were immersed in 10 mol/L NaOH aqueous solution and treated hydrothermally for 20 h at 160 $^\circ\text{C}$. After the reaction, the samples were removed from the container and dried. Then, by washing with water following heat treatment at 300 $^\circ\text{C}$, excessive NaOH adhered on the substrate was removed. Experimental details are provided in the Supporting Information, part 1.

First, the Co–Cr alloy disk (see the Supporting Information, part 2) was used as a substrate. As shown in Figure 2a

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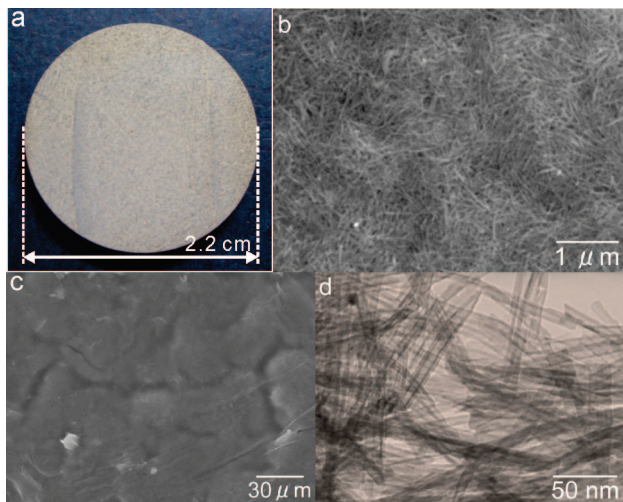


Figure 2. (a) Digital camera, (b, c) SEM images, and (d) TEM image for the obtained thin film formed on the surface of the Co–Cr alloy that was counter to the titanium metal.

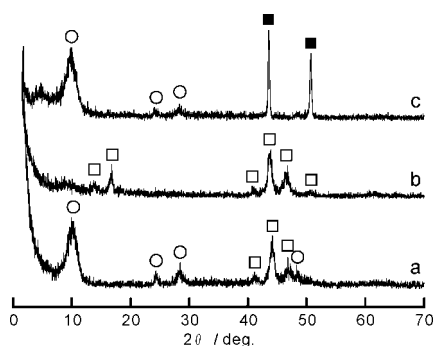


Figure 3. XRD patterns for (a) the Co–Cr alloy disk surface counter to the titanium metal, (b) the Co–Cr alloy disk surface not counter to the titanium metal, and (c) the surface of the SUS316L plate counter to the titanium metal. Peak assignment: ○, TNT; □, Co–Cr alloy; ■, SUS316L.

and the Supporting Information, part 3, after the reaction, the formation of a white film whose base color was similar to that of the Co–Cr alloy along the square form of the counter titanium plate on the face counter to the titanium plate was observed. This white film strongly adhered to the Co–Cr alloy plate. By examining SEM images (images b and c in Figure 2), the uniform and dense formation of fibrous substances was identified. In addition, by TEM observation of fibrous substances, nanotubes with an outer diameter of about 8 nm were identified (Figure 2d). The thickness of this film was about 5 μm , which was less than the thickness of the TNT film formed on the titanium plate (20 μm) when reacted separately.¹³ If TNT particles produced from the titanium plate spread and physically attach to the Co–Cr alloy plate, it can be assumed that TNT particles were aggregated into irregular-shaped TNT aggregates by capillary force, when removed from the reaction solution and dried, and that uniform and dense TNT films, as shown in images b and c in Figure 2, were not present. Therefore, in this experiment, it can be assumed that TNT was grown from the surface of the Co–Cr alloy to form a TNT film. As shown in the XRD pattern of the Co–Cr alloy surface counter to the titanium plate (Figure 3a), a diffraction peak characteristic of titanate nanotubes near $2\theta = 10^\circ$ as well

as the peaks attributed to the Co–Cr alloy of the raw material were observed. From EDX analysis, it was found that the film contained Na, Ti, O, Co, Cr, and Si and that the molar ratio of the film was Na:Ti:O:Co:Cr:Si = 0.322:1:2.401:0.112:0.052:0.045. Therefore, sodium titanate nanotube⁴ film is thought to be formed on the Co–Cr alloy disk. The elements Co, Cr, and Si dissolved in the Co–Cr disk and were incorporated into the titanate framework and/or the interlayer spacing of the titanate. Next, the face of the Co–Cr alloy plate, which was not placed counter to the titanium plate, was also analyzed in detail. In the XRD pattern shown in Figure 3b, the peak near $2\theta = 10^\circ$ attributed to the titanate was scarcely observed. In the SEM image, a small amount of fibrous substance was observed, suggesting the existence of nanotubes. It can thus be considered that the nanotubes did not form easily on the Co–Cr alloy disk surface that was not counter to the titanium metal. As mentioned above, the white TNT film reflecting the square form of the titanium plate was observed on the Co–Cr alloy disk that was counter to the titanium plate (Figure 2a and the Supporting Information, part 3). Thus, it can be concluded that the titanium species capable of forming TNT were present near the surface of the titanium, and that the TNT pattern reflecting the form of the titanium plate was formed on the surface of the Co–Cr disk counter to the titanium plate. The above results suggest that by using several forms of the titanium plate as the titanium source, different patterns of TNT can be formed on heterogeneous substrates. On the other hand, when only the Co–Cr alloy disk was hydrothermally treated in 10 mol/L NaOH aqueous solution, the surface of the reacted Co–Cr alloy plate changed to dilute black, and blocklike images were observed in the SEM image (see the Supporting Information, part 4). In the XRD pattern, only the peaks attributed to the Co–Cr alloy were observed. It is thus concluded that amorphous oxyhydroxides of Co or Cr form on the surface. Therefore, it is considered that by hydrothermally reacting the titanium plate and the Co–Cr alloy disk along with countering, before the dissolution/redeposition reaction of the Co–Cr alloy progresses excessively, copious amounts of titanium species originating from the titanium plate spread into the solution and reached the surface of the Co–Cr alloy. These species were immediately redeposited and they grew as TNT through the OH group produced on the surface of the Co–Cr alloy. As a result, it is considered that excessive reaction of the Co–Cr alloy surface counter to the titanium plate in NaOH aqueous solution was remarkably suppressed.

When the same experiment was conducted with the SUS316L plate (see the Supporting Information, part 5) instead of the Co–Cr alloy disk, it was found that, as in the case of the Co–Cr alloy, diluted white film was formed on the surface of the SUS316L plate that was counter to the titanium plate, as shown in Figure 4a and the Supporting Information, part 6. From the SEM image of this film (Figure 4b), a surface covered with several domes was observed, which differed from the smooth surface of the raw SUS316L. These domes were composed of uniform fibrous substances, as shown in Figure 4c. From the TEM image of the film

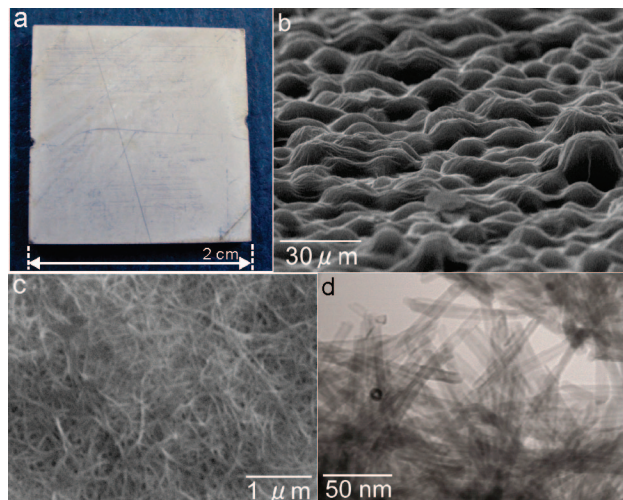


Figure 4. (a) Digital camera, (b, c) SEM images, and (d) TEM image for the obtained thin film formed on the surface of the SUS316L counter to the titanium metal.

(Figure 4d), the fibrous substances were confirmed as nanotubes. From the EDX analysis, it was found that the film contained Na, Ti, O, Fe, Mn, Cr, and Si, and that the molar ratio for the film was Na:Ti:O:Fe:Mn:Cr:Si = 0.407:1:2.432:0.188:0.001:0.057:0.022. In the XRD pattern (Figure 3c) of the film, diffraction peaks attributed to the titanate nanotubes and SUS316L were observed, and diffraction peaks resulting from iron compounds such as iron hydroxide, iron oxyhydroxide, and iron oxide were not observed. Therefore, sodium titanate nanotube⁴ film is thought to be formed. The elements Fe, Mn, Cr, and Si dissolved in the SUS316L plate and were incorporated into the titanate framework and/or the interlayer spacing of the titanate. Thus, it is considered that TNT grew on the surface of the SUS316L plate that was counter to the titanium plate to form the TNT film with several domes. The surface morphology of the TNT film formed on the SUS316L plate differed from that of the relatively flat TNT film obtained in the experiment with the Co–Cr alloy. The obtained results suggest that the surface morphology of the TNT film can be controlled by a substrate.

On the other hand, when the same reaction was performed using the SUS430 plate instead of the Co–Cr alloy disk, brown and black iron compounds were formed on the SUS430 plate, although white TNT film was formed in part (see the Supporting Information, part 7). SUS430 is an industrial-grade stainless alloy, whereas SUS316L is a stainless alloy used in implants that has exceptionally high corrosion resistance; the results obtained reflected this corrosion resistance. When the same reaction was performed with the tantalum plate instead of the Co–Cr alloy plate, copious amounts of white products were produced on the tantalum plate (see the Supporting Information, part 7), and particles other than nanotubes were observed. In addition, when the same experiment was performed using a silicon plate instead of the Co–Cr alloy disk, the silicon plate was completely dissolved by the hydrothermal reaction. Considering the differences in the responsiveness of the substrates

observed in the above experiments, it is inferred that the dissolution rate of the titanium plate and substrates and the redeposition rate of the chemical species that arose from the dissolved titanium plate and substrates should be considered. In particular, in this experimental system, it is considered that the dissolution rate of the substrates has a large effect on the results of the experiments. The dissolution rate, as in this study, can be explained by the ionization tendency, i.e., oxidation–reduction potential. Because titanium has a large ionization tendency than hydrogen existing in the solution, it is considered that titanium dissolves into titanium ions (Ti^{4+}) and hydrogen ions transform into H_2 ; these dissolved ions immediately form chemical species¹⁴ such as TiO_3^{2-} , $\text{TiO}_2(\text{OH})_2^{2-}$, and $\text{Ti}_m\text{O}_{2n+m}^{2m-}$, which are redeposited as TNT. When a substrate whose ionization tendency is smaller than that of titanium, particularly materials such as SUS316L and Co–Cr alloy with ionization tendencies smaller than hydrogen, is simultaneously hydrothermally treated with titanium, the dissolution rate of titanium is higher than that of the substrate. In this reaction, the titanium species were immediately produced following the dissolution of titanium and are spread and redeposited on the substrate as the TNT film, which predominated the dissolving reaction of the substrates. As a result, the surface of the substrate was covered by the TNT film, and the dissolution of the substrate was further suppressed (although minimally). On the other hand, it is considered that when substrates with ionization tendencies larger than that of titanium, i.e., substrates such as silicon and tantalum, were hydrothermally treated at the same time as titanium, the dissolution reaction of the substrates predominate the dissolution reaction of titanium. TNT film was thus not obtained on the substrates.

In this study, we have reported the novel growth of the TNT film on substrates such as Co–Cr alloy and SUS316L and the formation of simple patterns of the TNT. Because these substrates have superior mechanical properties and corrosion resistance, they are frequently used in implants such as artificial joints. Therefore, we are investigating the application of the obtained TNT/substrate composites as implants. We believe that these composites can be used in sensors or catalysts. We also think that the hydrothermal transcription method could be applied to the formation and patterning of various compounds on a variety of substrates. Currently, we are investigating the detailed observation of TNT–substrate interfaces, the patterning of TNT film, and the formation of the TNT film on several ceramic substrates such as Al_2O_3 and ZrO_2 with high corrosion resistance using the same technique.

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Supporting Information Available: Experimental details, SEM images, and photographs (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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