

K. LEE*, D. YOO*[‡]**LARGE-AREA SODIUM TITANATE NANORODS FORMED ON TITANIUM SURFACE VIA NaOH ALKALI TREATMENT****WIELKOPOWIERZCHNIOWE NANOPRĘTY TLENKU TYTANU SODU WYTWORZONE NA POWIERZCHNI TYTANU POD WPLYWEM NaOH**

Ti surfaces covered with large sodium titanate nanorods act as efficient electrodes for energy conversion and environmental applications. In this study, sodium titanate nanorod films were prepared on a Ti substrate in a 5M NaOH aqueous solution followed by heat treatment. The morphological characterization and the crystal structures of the sodium titanate nanorods were investigated via scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive spectroscopy (EDS). Thin amorphous sodium titanate layers formed during the alkali-treatment, and sodium titanate nanorods were obtained after heat treatment at a temperature of 700°C. The sodium titanate nanorods obtained at this temperature had a thickness of about 80 nm and a length of 1 μm. The crystal structure of the sodium titanate was identified with the use of Na₂Ti₅O₁₁. The nanorods were agglomerated at a temperature above 900°C, and large-scale nanorods formed on the Ti surface, which may be used for electrodes for energy conversion applications.

Keywords: Sodium titanate, Nanorods, Titanium, Alkali treatment, SEM

1. Introduction

Nanostructured materials have unique electronic, optical, chemical, mechanical, and magnetic properties, and these materials have attracted much attention due to their applicability in a variety of research areas [1]. Such unusual properties make these promising for use in next-generation nanotechnology. In particular, TiO₂-based nanostructured materials have been widely studied due to their potential use for photovoltaic cells, electrochemical sensing, optical emission, catalysis, and photocatalysis [2]. TiO₂ thin films can be prepared through various depositions methods, such as electron-beam evaporation [3], chemical vapor deposition [4], physical vapor deposition [5], dip-coating [6], and spin-coating [7].

Recently, nanostructured TiO₂ prepared through a sol-gel method has also attracted attention. The presence of templates, such as nanospheric nanorods or anodic porous alumina, allows for titanium alkoxide or halide (TiCl₄, TiF₄) to be hydrolyzed [8]. Template synthesis [9] and hydrothermal reactions [10] are the two main approaches that have been used to prepare TiO₂ nanotubes. Although most TiO₂ nanostructures have been obtained in powder form, advanced nanomaterials require novel methods to fabricate well-organized nanostructures. Therefore, new technology that involves minimal steps and also allows for large-scale production should be developed to enable applications involving catalysis, filtration, electrochemical sensing, photovoltaic cells, and high-surface-area electrodes.

In this study, sodium titanate nanorods were fabricated by using an alkali treatment that allows for a low cost and facile fabrication process. Their morphological characteristics and crystal structures were also investigated.

2. Experimental**2.1. Sample preparation**

CP-Ti disks (Grade 2, purity >99.9 wt %, Kobe Steel Co., Japan) were used as starting materials with a diameter of 15 mm and a thickness of 3 mm. The Ti disks were ground with 400-2000 grit silicon carbide papers, and were then polished with Al₂O₃ powder (1 μm). After polishing, the specimens were ultrasonically cleaned in acetone, ethanol, and distilled water for 5 min progressively.

2.2. NaOH alkali treatment

The specimens were immersed in 10 mL of different NaOH solutions at a temperature of 60°C in the oven (Vacuum drying oven, Jisico, Korea) for 24 hours in order to form a sodium titanate layer on the surface of the specimen. The solution was prepared by dissolving analytical-grade reagent (Duksan Co, Korea) with distilled water. The resulting samples were then washed with distilled water and were dried.

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2.3. Heat treatment

All alkali treated samples were annealed at temperatures of 500, 600, 700, 800, and 900°C for 2 hours in a muffle box furnace with a heating rate of 5°C min⁻¹. The furnace was then cooled to room temperature.

2.4. Characterization

The microstructures were observed using field emission scanning electron microscopy (FE-SEM, S-4700, Hitachi, Japan). The phase structure was analyzed using X-ray diffraction (X'Pert pro, PANalytical, Netherlands) with Cu K α radiation at 45 kV and 35 mA. An incident beam angle of 1° was used on the sample surface. Furthermore, energy dispersive X-ray spectroscopy (EDX, EMAX Energy EX-200, Horiba, Japan) was used to analyze the composition of the sodium titanate nanorod films.

3. Results and discussion

Fig. 1 shows the formation of the alkali titanate layer on the surface of titanium. During the alkali treatment, the corrosive attack of hydroxyl groups partially dissolves the passive TiO₂ layer into an alkali solution.

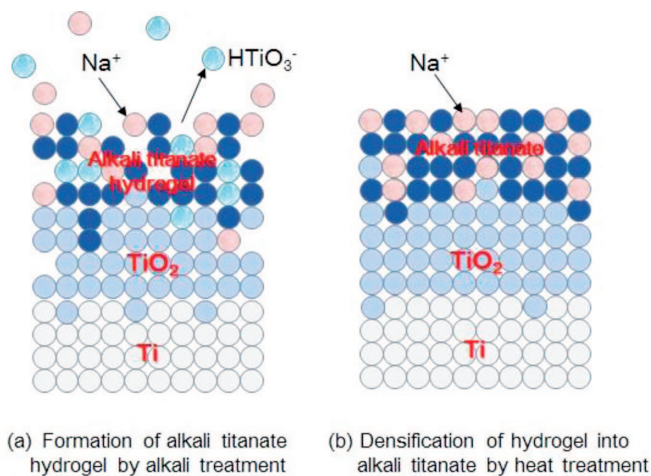
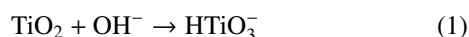
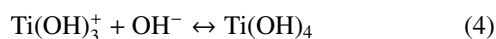
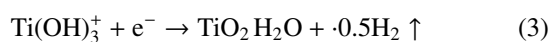
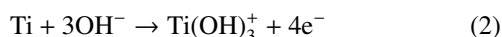


Fig. 1. Schematic representation of the structural changes in the Ti metal surface after alkali and heat treatments



The reaction shown above occurs simultaneously with the following hydration of the Ti metal.



The hydroxyl group further attacks the hydrated TiO₂, which results in negatively charged hydrates on the surface of the substrates [11].



The interaction between the negatively charged species and the alkali ions in the aqueous solution results in the formation of an alkali titanate hydrogel layer. A stable amorphous or crystalline alkali titanate layer is produced when the hydrogel layer is dehydrated and densified during heat treatment.

In Fig. 2, the SEM images show the surfaces of the 5 M NaOH-treated Ti disks with various temperatures for heat treatment. Fig. 2 (a), (b), and (c) show the pore morphology that formed on the surface of the Ti disk, and many researchers have reported that such a morphology can only be obtained when Ti is immersed into an NaOH solution [12, 13]. The increase in temperature during heat treatment densifies the pores and changes them into rod-like features. The change in the morphology occurs at a temperature above 700°C as shown in Fig. 2 (d). A layer of high-density nanorods was observed on the surface of titanium at higher calcination temperatures. The Na₂Ti₆O₁₃ was synthesized using a hydrothermal treatment in an NaOH solution at a temperature of 250°C for 4 hours when spherical titanium dioxide (TiO₂) powders were used as starting material [14]. Kolen'ko et al. [15] observed sodium tri-titanate (Na₂Ti₃O₇) particles with rod-like surface morphology by mixing amorphous TiO₂ · nH₂O gel with an NaOH aqueous solution in an autoclave at temperatures of 110, 160, and 200°C for 20 hours.

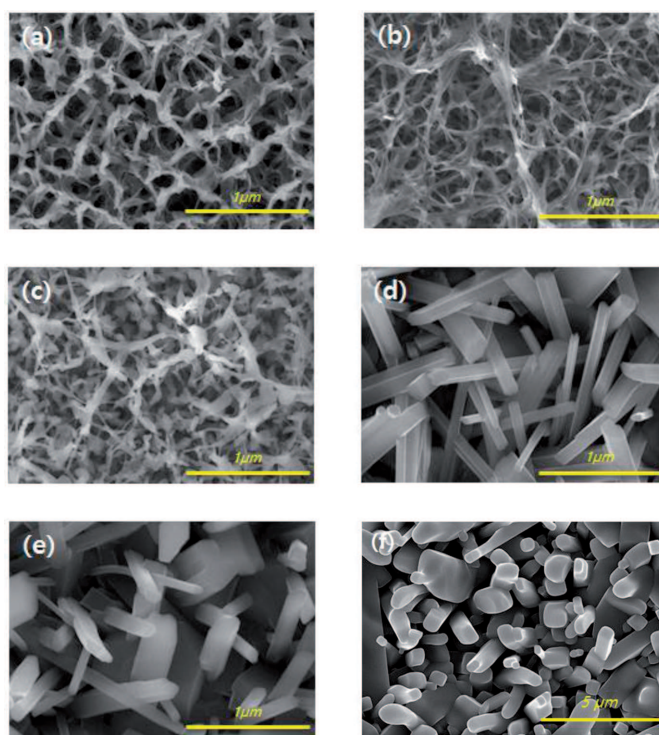


Fig. 2. FE-SEM images of the samples treated with 5 M NaOH at various temperatures: (a) room temperature, (b) 500°C, (c) 600°C, (d) 700°C, (e) 800°C, and (f) 900°C

Fig. 3 shows cross sectional FE-SEM images of the samples in which a diamond pencil was used to produce micro-cracks on the surface. The samples were alkali-treated in 5 M NaOH solution and subjected to heat treatments at various temperatures. A needle-shaped structure is observed in Fig. 3 (a), (b), and (c) is associated with that shown in Fig. 2 (a), (b), and (c). Changes in the structure of the rod-like morphology occurred at a temperature above 700°C. However,

agglomerated shapes were observed followed by heat treatment at a temperature of 900°C.

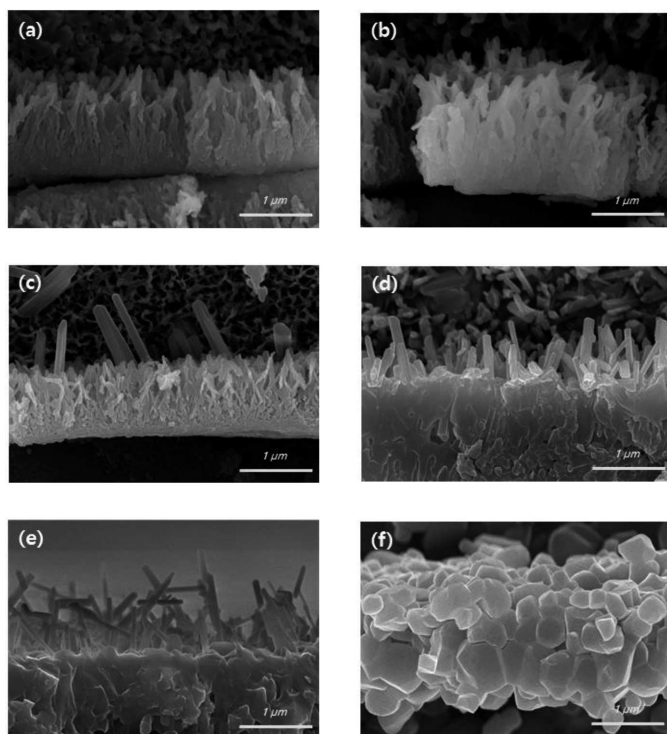


Fig. 3. Cross-sectional FE-SEM images of the samples treated with 5 M NaOH at various temperatures: (a) room temperature, (b) 500°C, (c) 600°C, (d) 700°C, (e) 800°C, and (f) 900°C

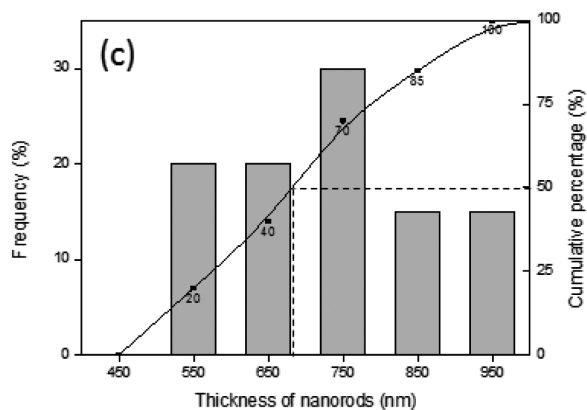
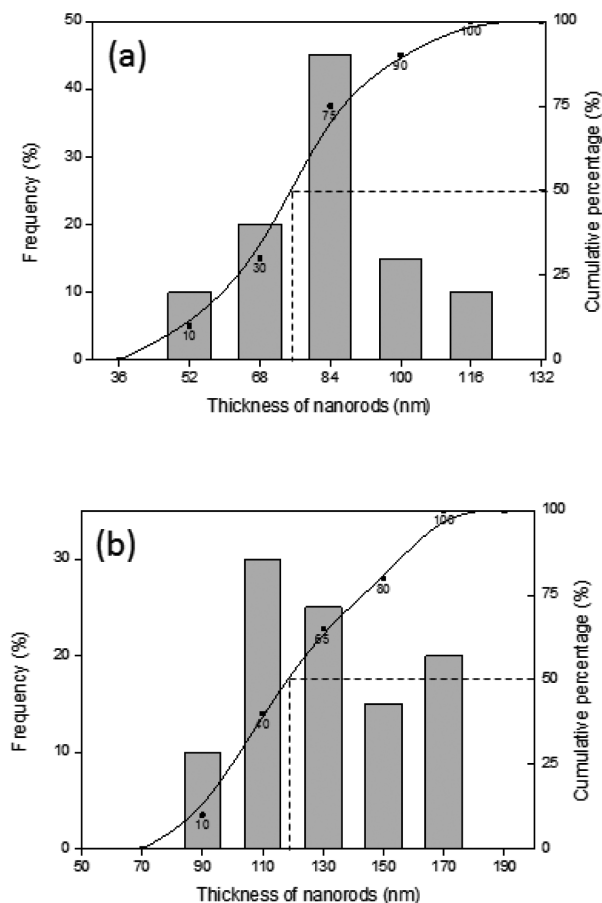


Fig. 4. Average of the nanorod thicknesses immersed in 5 M NaOH followed by heat treatment at temperatures of (a) 700°C, (b) 800°C, and (c) 900°C

The average thickness of the nanorods, shown in Fig. 4, was determined from Fig. 2 (d), (e), and (f). The nanorods changed from a porous to a rod-like shape at a temperature above 700°C. Fig 4 (a), (b), and (c) exhibit nanorods with thicknesses of approximately 90-110 nm, 110-140 nm, and 700-800 nm, respectively. The results indicated that the thickness of the nanorods increased as the heat treatment temperature increased.

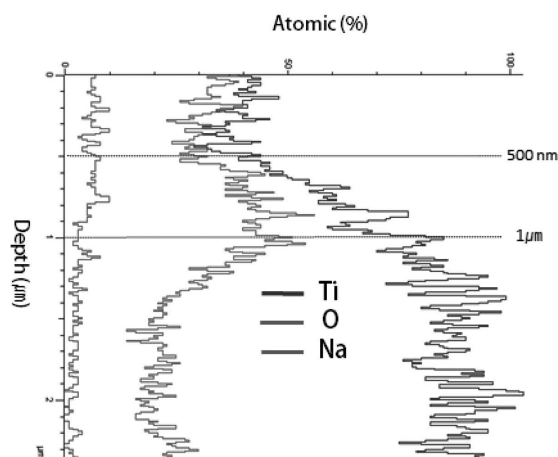
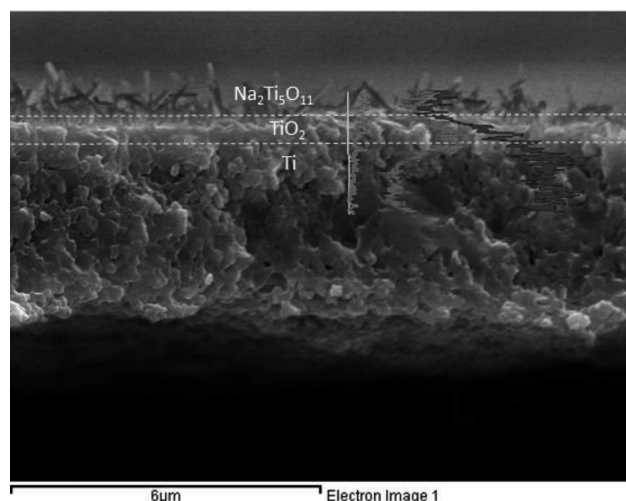


Fig. 5. EDX profiles of the cross sections of the samples heat treated at a temperature of 800°C

Fig. 5 shows cross sectional FE-SEM images and the EDX line profile of the samples subjected to NaOH treatment followed by heat treatment at a temperature of 800°C. The EDX line profile indicates that the Na content gradually decreased as the depth increased. Ti and O content decreased up to a depth of 400 nm. The Ti content gradually increased after 1 μm . However, the oxygen content decreased as the depth continued to increase after 1 μm , indicating that the sodium titanate progressively changed into TiO_2 at the boundary between the sodium titanate layer and the Ti substrate.

Fig. 6 shows the XRD patterns of the samples heated at various temperatures after alkali treatment in 5 M NaOH at 60°C. In Fig. 6 (a), only the titanium peaks were indexed. This alkali-treated sample was processed without heat treatment, and the amorphous alkali titanate hydrogel resulted in only titanium peaks in the absence of a heat treatment. The broad diffraction peaks first appeared at around 24–29° when the temperature was above 500°C. These peaks were attributed to the presence of the sodium titanate ($\text{Na}_2\text{Ti}_5\text{O}_{11}$) hydrogel layer, confirmed by Kim et al. [11]. The hydrogel layer begins to crystallize at a temperature above 700°C, and fully crystallizes at a temperature above 800°C, as shown Fig. 3 (d). The titanium, $\text{Na}_2\text{Ti}_5\text{O}_{11}$ and rutile- TiO_2 peaks were observed until 700°C. However, titanium peaks disappeared at a temperature above 800°C.

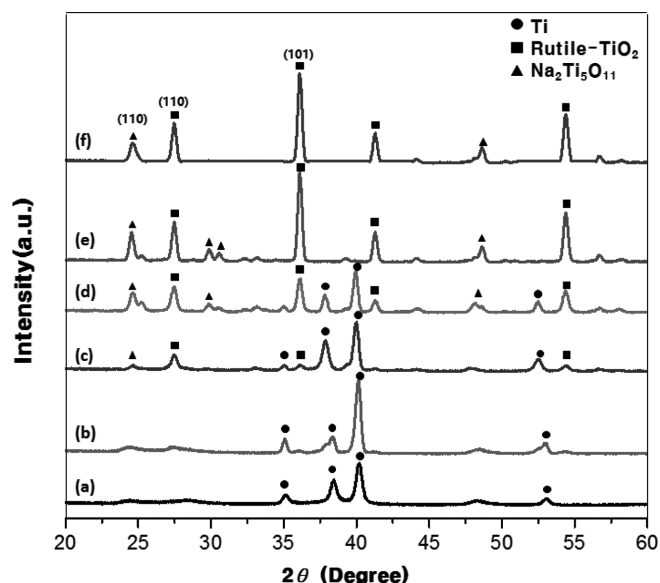


Fig. 6. X-ray diffraction of the 5 M NaOH treated samples at various temperatures: (a) room temperature, (b) 500°C, (c) 600°C, (d) 700°C, (e) 800°C, and (f) 900°C

4. Conclusions

Sodium titanate nanorods formed at temperatures above 700°C after alkali treatment in 5M NaOH solution. The morphology of the nanorods further changed into an agglomerated structure when the temperature reached 900°C. The thickness of the nanorods increased as the temperature of heat treatment increased. The crystal structure of the sodium titanate nanorod showed both $\text{Na}_2\text{Ti}_5\text{O}_{11}$ and rutile- TiO_2 phases. The EDS analysis confirmed that the nanorods were composed of sodium titanate on the surface of the TiO_2 layer.

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REFERENCES

- [1] X. Peng, J. Wang, D.F. Thomas, A. Chen, *Nanotechnology* **16**, 2389 (2005).
- [2] S. Liu, A. Chen, *Langmuir* **21**, 8409 (2005).
- [3] T.-S. Yang, C.-B. Shiu, M.-S. Wong, *Surf. Science* **548**, 75 (2004).
- [4] M.C. Marco de Lucas, F. Fabreguette, S. Collin, S. Bourgeois, *Int. J. Inorg. Mater.* **2**, 255 (2000).
- [5] D. Dumitriu, A.R. Bally, C. Ballif, P. Hones, P.E. Schmid, R. Sanjinés, F. Lévy, V.I. Pârvescu, *Appl. Catal. B* **25**, 83 (2000).
- [6] X.-P. Wang, Y. Yu, X.-F. Hu, L. Gao, *Thin Solid Films* **371**, 148 (2000).
- [7] K. Kato, A. Tsuzuki, H. Taoda, Y. Torii, T. Kato, Y. Butsugan, *J. Mater. Sci.* **29**, 5911 (1994).
- [8] S. Uchida, R. Chiba, M. Tomiha, N. Masaki, M. Shirai, *Electrochemistry*. **70**, 418 (2002).
- [9] Y. Zhang, G. Li, Y. Jin, Y. Zhang, J. Zhang, L. Zhang, *Chem. Phys. Lett.* **365**, 300 (2002).
- [10] M. Adachi, I. Okada, S. Ngamsinlapasathian, Y. Murata, S. Yoshikawa, *Electrochemistry* **70**, 449 (2002).
- [11] H.-M. Kim, F. Miyaji, T. Kokubo, T. Nakamura, *J. Biomed. Mater. Res. A* **32**, 409 (1996).
- [12] C. Kim, M.R. Kendall, M.A. Miller, C.L. Long, P.R. Larson, M.B. Humphrey, A.S. Madden, A.C. Tas, *Mater. Sci. Eng. C Mater. Biol. Appl.* **33**, 327 (2013).
- [13] S.-I. Tanaka, M. Aonuma, N. Hirose, T. Tanaki, *J. Electrochem. Soc.* **149**, D167 (2002).
- [14] D.-S. Seo, H. Kim, J.-K. Lee, *J. Cryst. Growth* **275**, e2371 (2005).
- [15] Y.V. Kolen'ko, K.A. Kovnir, A.I. Gavrilov, A.V. Garshev, J. Frantti, O.I. Lebedev, B.R. Churagulov, G. Van Tendeloo, M. Yoshimura, *J. Phys. Chem. B* **110**, 4030 (2006).