Electrochromism

# Electrochromism of Titanate-Based Nanotubes**

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Wide-bandgap semiconductor nanotubes have potential as components in electronic and optical devices because of their transparency and high energies of excited charge-carriers.[1–3] Among the various semiconductor nanotubes with wide bandgaps, titanate-based nanotubes, which have been synthesized and characterized over the last few years,[4–9] have received a lot of attention because of their cheap fabrication and unique one-dimensional nanostructure. Recently, we reported the synthesis of a novel thin film of titanate nanotubes by an alternate adsorption method and its photochemical properties, in particular its photocatalytic oxidation activity and photoinduced hydrophilicity.[10] Thin-film fabrication of titanate nanotubes enables us to develop a new, functional, transparent device.

Herein, we focus on the electrochromic properties of titanate nanotubes. Electrochromism depends on the crystal structure, and cathodic coloration occurs in transition metal oxide semiconductors such as $TiO_2$, $WO_3$, $MoO_3$, $MnO_2$, and $Nb_2O_5$ that are constructed from $MO_6$ octahedra.[11] Recently, several research groups have reported the electrochemical properties of layered materials made from these oxides;[12,13] however, the electrochromic properties of transparent nanotube thin films have yet to be disclosed. A titanate nanotube is composed of a one-dimensional nanostructure generated from nanosheets of $TiO_6$ octahedra, and therefore unique electrochromic properties are expected. In this study, transparent thin films of titanate nanotubes were deposited on electroconductive substrates by an alternate-layer deposition and their electrochromism was evaluated. The titanate nanotubes were found to exhibit significant electrochromism

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under cathodic polarization in water, and turned brown. This phenomenon arises from the creation of $Ti^{3+}$ centers caused by intercalation of protons in the nanotubes. The color change of these titanate nanotubes is more significant than that of $TiO_2$ anatase because of their layered nanostructure.

Powders of titanate nanotubes were synthesized by a hydrothermal method.[4] After the hydrothermal reaction, the products were immersed in an aqueous $HNO_3$ solution to replace the sodium ions with protons, and were subsequently stirred in an aqueous solution of tetra(*n*-butyl)ammonium hydroxide, which resulted in a translucent, colloidal suspension of titanate nanotubes.[10] Subsequent TEM and XRD analysis revealed that the nanotubes were constructed of scrolled titanate nanosheets, similar to the previous reports.[5–7] The inner cavity diameter, the outer diameter, and the length of the nanotubes were approximately 3.5 nm, 9.0 nm, and several hundreds of nanometers, respectively. The interlayer separation corresponds to a $2\theta$ value of around 9.0° in the XRD patterns obtained with $Cu_{K\alpha}$ radiation;[5,6] the estimated interlayer separation is 0.98 nm.

Electrodes of titanate nanotubes were fabricated by an alternate-layer deposition process.[10,14,15] A zeta-potential analysis revealed that the pH value at the zero-charge point of the titanate nanotubes is 5.5. In the present study, the pH value in solution was adjusted to 9.0. Under these conditions the titanate nanotubes act as negatively charged particles, while poly(ethyleneimine) (PEI) or poly(diallyldimethylammonium chloride) (PDDA) are polycations. Alternate adsorption of titanate nanotubes and polycations is a result of the Coulomb force. Transparent electroconductive glass plates (F-doped $SnO_2$-coated glass: Asahi Glass Co. Ltd.) were used as the substrates and one-third of the $SnO_2$ area was covered with masking tape to prevent coating. The substrates were dipped into PEI solution and rinsed with pure water (first step), then dipped into a solution of titanate nanotubes and rinsed with water (second step), and finally dipped into PDDA solution and rinsed with water (third step). A multilayered film, substrate/PEI/(nanotube/PDDA)$_5$/nanotube, was created by repeating the second and third steps six times. As in our previous report, the inserted polycations were removed by a photocatalytic oxidation process under UV irradiation using a 200 W Hg–Xe lamp (Hayashi Watch Works Co. Ltd., Japan).[10] This procedure resulted in thin films of polymer-free titanate nanotubes deposited on transparent electroconductive substrates. A copper wire was attached to the uncoated $SnO_2$ surface with silver paste and the attached part and the uncoated $SnO_2$ area were then covered with an epoxy resin so that only the surface of the titanate nanotubes was exposed (size of the exposed area: 15 × 25 mm). $TiO_2$ anatase electrodes with the same size were also fabricated by a dip coating method with a titanium tetraisopropoxide solution (NDH-510C, Nihon Soda Co. Ltd., Japan). The coated substrates were annealed at 500 °C for 30 min to give a polycrystalline $TiO_2$ anatase electrode.

Figure 1 shows the SEM images of the electrodes observed from a tilted angle (30°). Titanate nanotubes and $TiO_2$ anatase films are coated on columnar crystallites of $SnO_2$. Both films are optically transparent. Their thicknesses were investigated by taking cross-sectional SEM images at several points, and, as a result, the average thicknesses of the titanate nanotube and anatase layers were calculated to be 60 nm and 80 nm, respectively. As for the titanate nanotube thin films, the thickness for each adsorption cycles is about 10 nm, which corresponds to the diameter of the nanotubes. These results demonstrate that the self-assembled alternate absorption method results in the growth of titanate nanotubes layer-by-layer. The diameter of $TiO_2$ anatase particles ranges from 20 to 30 nm.

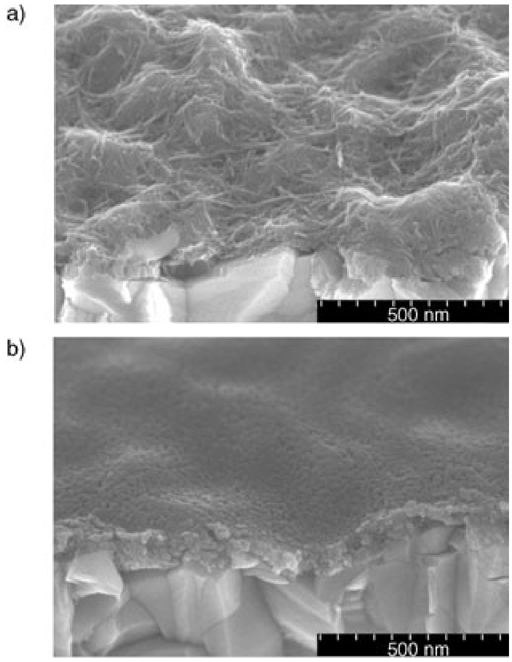


***Figure 1.*** SEM images of the electrodes: a) titanate nanotube; b) $TiO_2$ (anatase).

Electrochemical measurements were conducted in a standard buffer solution (pH 6.8) containing 0.1 M $Na_2SO_4$ as an electrolyte, in the dark with a potentiostat (HSV-100, Hokuto Denko Co. Ltd., Japan). The working electrode, the counterelectrode, and the reference electrode were titanate nanotube electrode, platinum wire, and Ag/AgCl/saturated KCl(aq), respectively. Figure 2 shows the cyclic voltammograms for electrodes of the titanate nanotube and the $TiO_2$ (anatase) at various scan rates. Changes in the current were observed under cathodic polarization for both electrodes, but not under anodic polarization. These results indicate that both titanate nanotubes and $TiO_2$ anatase are n-type semiconductors. In addition, oxidation waves were observed between −1.0 V and −0.5 V for both electrodes. Previous studies have reported that cathodic polarization causes electrons to accumulate in the semiconductor film; thus, charge compensation is accomplished by proton intercalation [Eq. (1)].[16,17]

$$Ti^{4+} + e^- + H^+ \rightarrow Ti^{3+}H^+ \qquad (1)$$

This reaction is reversible; therefore, an oxidation current is observed when the voltage is scanned in a positive mode. The current at the oxidation peaks increases linearly as the square root of the scan rate increases for both films. These

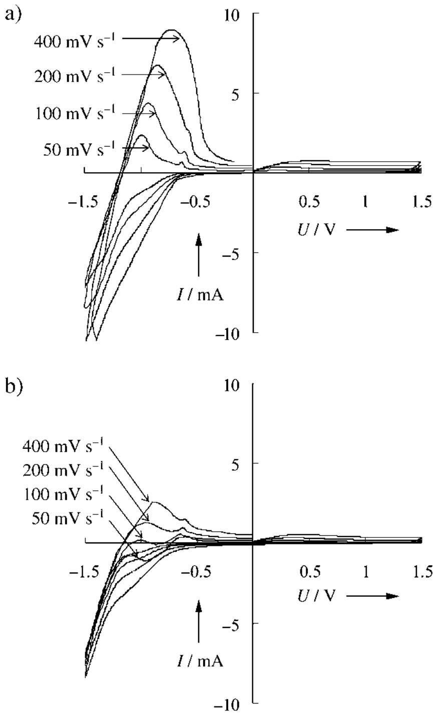


***Figure 2.*** Cyclic voltammograms of the electrodes, at various scan rates, in a standard buffer solution (pH 6.8) containing 0.1 M $Na_2SO_4$: a) titanate nanotube; b) $TiO_2$ (anatase).

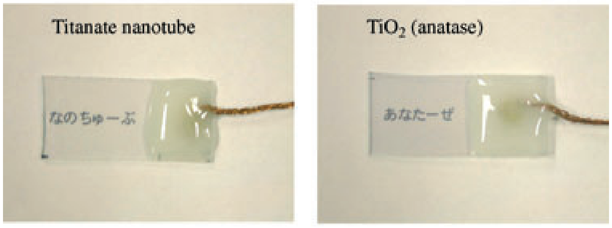
results are consistent with the Nernst equation, thus indicating that the redox process proceeds with proton diffusion. It is noteworthy that the oxidation peak current of the titanate nanotube is higher than that of $TiO_2$ (anatase), although the thickness of the titanate nanotube (60 nm) is less than that of $TiO_2$ (80 nm). These results indicate that proton diffusion in the titanate nanotube is faster than in $TiO_2$.

Figure 3 shows photographs of the electrodes before and after cathodic polarization at −1.5 V for three minutes. Both films are optically transparent before cathodic polarization, whereas they are brown after cathodic polarization. The color change of titanate nanotubes is more striking than that of $TiO_2$ (anatase). We also evaluated electrochromism on the bare electroconductive $SnO_2$-coated substrate. This bare electrode, however, did not turn brown under cathodic polarization. Thus, the color change originates in the titanate nanotube or $TiO_2$ anatase films.

Figure 4 shows the UV/Vis spectra for the electrodes. The absorbance value in the visible light region is higher after cathodic polarization. The increase in the absorbance value in the titanate nanotube is more significant than that in $TiO_2$. As mentioned earlier, cathodic polarization forms $Ti^{3+}$ species by proton intercalation. A previous study has reported that the $Ti^{3+}$ bands are located between 0.75 and 1.18 eV, which is below the minimum conduction-band level of $TiO_2$.[18] Therefore, the $TiO_2$ containing $Ti^{3+}$ centers absorbs a broad range of visible light and is generally darker.

In the present study, titanate nanotubes exhibit a faster proton diffusion and higher proton capacity than $TiO_2$ (anatase). The significant electrochromism of the titanate nanotube is attributed to its layered nanostructure. In an earlier work, the crystal structure of nanotubes was considered to be anatase.[4] However, it was later realized that the crystal structure is not anatase, but contains protonated titanate.[5–7] Chen et al. have reported that the nanotubes are composed of scrolled trititanate ($H_2Ti_3O_7$) sheets.[5,6] On the other hand, Ma et al. have reported that the nanotubes are constructed from lepidocrocite ($H_xTi_{2-x/4}\square_{x/4}O_4$, $x \approx 0.7$, $\square$: vacancy) sheets.[7] The exact crystal structure is therefore still

a) before cathodic polarization



b) after cathodic polarization

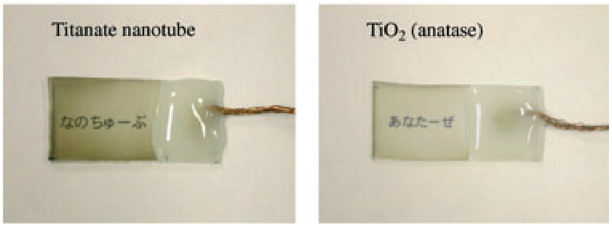


***Figure 3.*** Photographs of the electrodes before (a) and after (b) three minutes of cathodic polarization at −1.5 V.

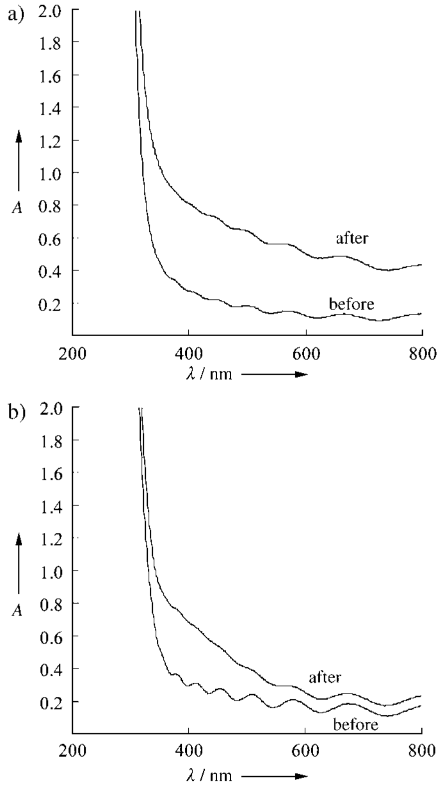


***Figure 4.*** UV/Vis spectra for the electrodes before and after three minutes of cathodic polarization at −1.5 V: a) titanate nanotube; b) $TiO_2$ (anatase).

unknown, although both these reports indicate that the titanate nanotubes are composed of scrolled $TiO_2$ sheets separated by $H^+$ ions. Our X-ray diffraction pattern for a dried powder formed from the colloidal solution is similar to these reports and indicates that the nanotubes are composed of scrolled nanosheets of protonated titanate. In this arrangement, a large surface area acts as $H^+$ host as a result of its one-dimensional, open-pore nature. Therefore, it is reasonable to suppose that protons can diffuse more easily into the layered nanostructure than into a densely packed polycrystalline $TiO_2$ particle.

In summary, new nanotube-based devices can be created from a stable, colloidal solution of titanate nanotubes and a thin film fabricated by an alternate-layer deposition process. The transparent titanate nanotube electrode demonstrates an intriguing electrochromism because of its layered nanostructure. Although the film thickness is only 60 nm, the color change in the titanate nanotubes is significant. An alternate-layer deposition process does not need an annealing step, therefore titanate nanotubes can be coated on various plastic substrates. This unique material has potential applications in various industrial components such as displays, sensor devices, and smart windows.

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