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In Situ TEM Observation of Double-Wall TiO₂ Nanotube Arrays at High Temperature

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Double-wall TiO₂ nanotube arrays were prepared using an anodization method in a glycerol-containing electrolyte. *In situ* TEM observation of these samples at high temperature was carried out with and without oxygen injections. With injection of oxygen gas, an improved thermal stability of nanotubes at high temperature was observed. It may provide more detailed information about the calcinations process of TiO₂ nanotubes and assist its morphology and structure modulation.

Titanium dioxide (TiO₂) nanotube arrays demonstrate their effective applications in various fields such as hydrogen generation,^{1,2} gas sensing,³ dye-sensitized solar cell,⁴ photocatalysis,⁵ as well as biomedical applications.⁶ In order to realize their efficient performance, high temperature annealing is necessary to convert amorphous TiO₂ nanotube arrays into crystalline forms.⁷ Thus, the evolution of crystal phase and the increase of the surface area of TiO₂ nanotube arrays attract much attention for the improvement of their properties. For example, anatase phase of TiO₂ is preferred for photo-catalytic applications whereas rutile phase is widely accepted as gas sensing materials.^{8,9} Magnéli phase of substoichiometric titanium oxides, which can be obtained by thermal treatment under reductive condition, shows a high conductive property.¹⁰ Fang et al. profoundly investigated the growth mechanisms of multilayered TiO₂ nanotubes by anodization.¹¹ The stability of the nanotube structure, which maintains a large surface area even under high temperature conditions, is also essential for effective applications.

In situ TEM (transmission electron microscopic) observation at high temperature is a powerful tool to monitor the calcination process in a real time during heating. It provides a detailed information on the morphological changes and evolution of crystalline phase.¹² Kamino and Saka introduced filament type heating sample holder in order to observe morphological and crystal changes of nanomaterials at high temperature.¹³ So far, we have used *in situ* TEM observation for understanding the sintering process of copper fine particles^{14,15} and other nanoparticles.^{16,17} In our system as Kamino-Saka system, oxygen gas can be introduced to TEM column during *in situ* TEM observation and we can control the gas pressure around the samples.¹²⁻¹⁷ The morphological changes of TiO₂ nanotubes at high temperature would be varied with the atmosphere, *that is*, with oxygen gas and under high vacuum without oxygen. In this study, thermal annealing of TiO₂ nanotubes prepared in a glycerol-containing electrolyte was performed in TEM column with and without injection of oxygen, and its morphological changes were observed.

The anodization of a Ti foil was carried out in a two-electrode system using a DC power supply (Kikusui KX-100H, Japan). A counter electrode used was a Pt foil, and a Ti foil (10 mm×15 mm, thickness 250 μm, 99.6% purity, Nilaco, Japan) was used as an anode. Anodization voltage and time were 60 V and 24 h, respectively. An electrolyte contains 96.5 wt% glycerol (Junsei), 3 wt% H₂O (purified by Organo/ELGA Purelabo system, >18 MΩ), and 0.5 wt% NH₄F (Wako). The surface of the prepared samples was washed carefully with purified water for several times and dried under air. A JEOL-JSM 6701F field emission scanning electron microscope (FE-SEM) was used to observe the surface morphology of the obtained samples. TEM imaging including *in-situ* observation was conducted using a Hitachi H-9500 (300 kV). The behavior of TiO₂ nanotube samples upon heating was observed by using a filament-type specimen heating holder (see TOC Figure).¹²⁻¹⁷ Oxygen gas was introduced from an oxygen gas cylinder under a regulated pressure.

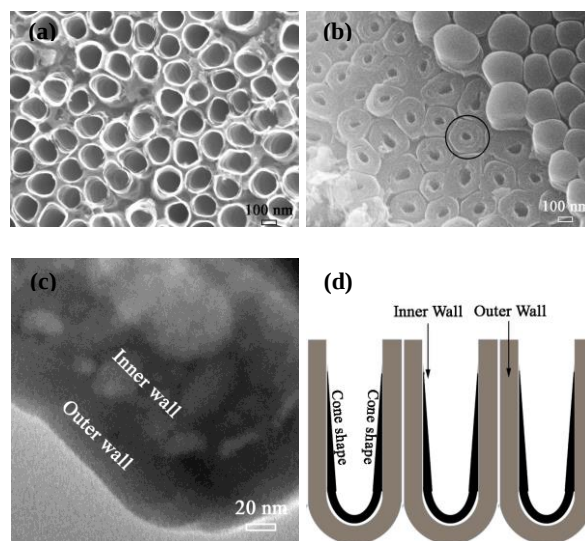


Figure 1. (a) SEM image of the surface, (b) SEM image of the bottom, (c) cross-sectional TEM image of the root segments and (d) schematic illustration of the cross section of the obtained double wall TiO₂ nanotube arrays by anodization.

Figure 1 shows the representative SEM and TEM images of the double wall TiO₂ nanotube arrays prepared by anodization. From the top surface (Fig 1a), nanotubes demonstrate only single wall structures with inner diameter of 200-250 nm. The tube walls are very thin (< 30 nm). However, from the bottom (Fig. 1b), the tube walls became thicker (>

100 nm), and the inner diameter decreased to 90-100 nm. Judging from these SEM and TEM images, it can be concluded that the inner side of the tubes has a cone like structure as illustrated in Fig. 1d. This unique structure is probably derived from the excessive etching of the top of tubes. In addition, tube wall also split to a double layered structure as can be observed in the inset circle area in Fig. 1b. The cross-sectional TEM image of the root segments of the nanotubes (Fig. 1c) confirms their double wall structure. Similar situation was reported in the case of anodization using polyol electrolyte.^{18,19} These nanotubes shall be considered as amorphous at room temperature, which is previously reported in the case of single wall titanium oxide nanotubes with a thicker side wall.⁷ Selected area electron diffraction (SAED) measurement for our sample unfortunately destroyed their structures during the observation according to the beam focusing.

In situ TEM observation at high temperatures was carried out with the obtained nanotube array samples. Figure 2 shows the morphological changes of the nanotube array at high temperature with introduction of oxygen gas. The pressure of the TEM column was kept at 10^{-4} Pa. The temperature profile up to 820 °C during this experiment is shown in Fig. 2a. At room temperature, a nanotube structure was clearly identified. As the temperature increased step by step to 600 °C and after heating at this temperature for 12 min, the contrast of the image (Fig. 2c) became shaper than that at room temperature (Fig. 2b). Many protrude ends were still observed and no structural collapse was observable (Fig. 2c). According to another *in situ* TEM annealing of single wall TiO₂ nanotube,⁷ this contrast change should because of the crystallization at high temperature. On the other hand, structural changes of flower like structures with small titanium oxide nanoparticles in the upper right area (Figs. 2b and 2c) changed their arrangements. These changes can also be attributed to the crystallization of titanium oxide. Next step, after the heating the sample at 820 °C for around 5 min, a clear structural collapse of the nanotubes was observed (Fig. 2d). The tube transformed to a coral like structure. This

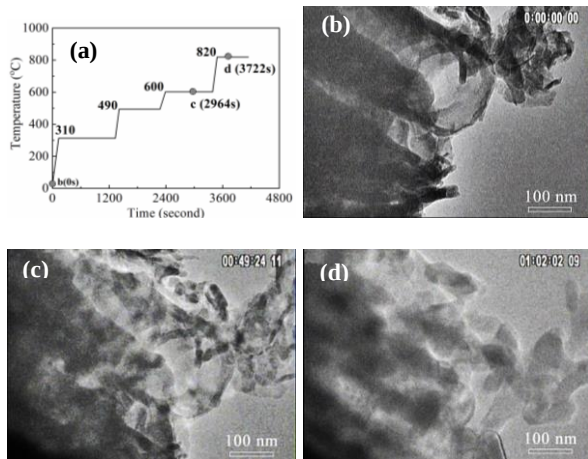


Figure 2. (a) Temperature profile of *in-situ* TEM observation with introduction of oxygen (Pressure of the TEM column: 10^{-4} Pa) and (b), (c), (d) *in-situ* TEM images of TiO₂ nanotube under oxygen atmosphere at various temperatures. (b) at room temperature, (c) at 600 °C, and (d) at 820 °C (Images collected at the points shown in (a)).

transformation is presumably derived from the coalescence of crystal grains and sintering at 820 °C.

As shown in Fig. 3, without oxygen injection, *in situ* TEM observation of TiO₂ nanotubes at high temperature also performed. The pressure of the TEM column was 2×10^{-5} Pa. Some crystalline fringes, which were not observed in TiO₂ nanotubes at r. t. can be observed in a high resolution TEM image of the nanotubes at 320° C. They suggest that crystallization of our TiO₂ nanotubes, which were amorphous at r. t., proceeded at high temperatures (Fig. 4).

The structure of the nanotubes was not highly stable even at 610 °C. The structural collapse was confirmed on the top of the tube. Comparing the square areas in Figs. 3b and 3c, we can find that the tip on top of tube disappeared after the *ca.* 12 min heating at 610 °C. This result suggests that the tube already began to lose its structure at 610 °C. It is different from the behavior of TiO₂ nanotubes under oxygen, where no obvious structural failure was observed at *ca.* 600 °C (Fig. 2c). Around 800 °C, nanotube architecture collapsed dramatically (Fig. 3d). The nanotubes completely decomposed and became a dense stone like structure after about 5 min. This structure is

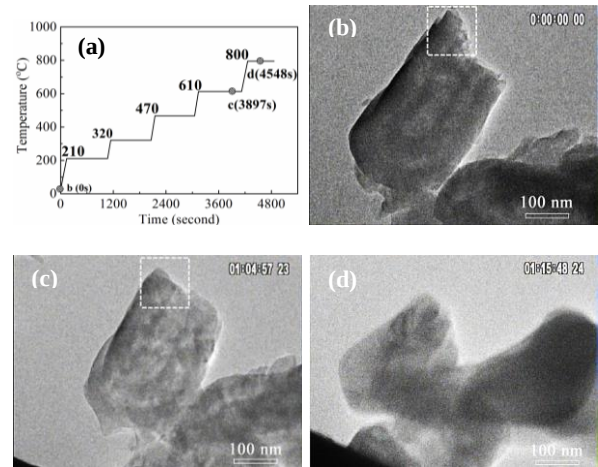


Figure 3. (a) Temperature profile of *in-situ* TEM observation without introduction of oxygen gas (Pressure of the TEM column: 2×10^{-5} Pa) and (b), (c), (d) *in-situ* TEM images of TiO₂ nanotube without oxygen gas introduction at various temperatures. (b) at room temperature, (c) at 610 °C, and (d) at 800 °C. (Images collected at the points shown in (a); A tip on top of tube was shown in square areas).

highly different from the coral like structure consisted of

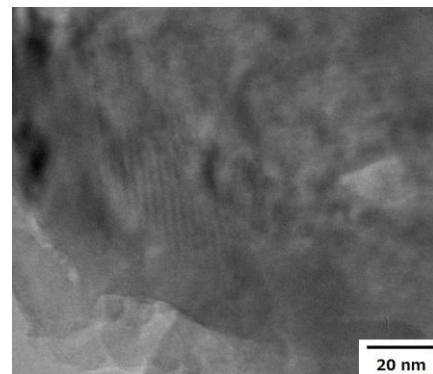


Figure 4. High resolution TEM image of TiO₂ nanotube heated without oxygen at 320 °C. Lattice fringes can be observed at the center and they indicate the crystalline structure of TiO₂.

inter-columnar pores under existence of oxygen (Fig. 2d).

These systematic *in situ* TEM experiments as shown in Figs. 2 and 3 indicate that morphological changes of TiO₂ nanotube occur faster under high vacuum without oxygen. In the presence of oxygen gas, a higher structure stability of TiO₂ nanotubes was achieved. For example, at ca. 600 °C, the tubes showed a higher stability with oxygen gas. The XP spectrum of our as prepared TiO₂ nanotubes showed the atomic ratio of Ti : O is 1 : 2.07. Our TiO₂ nanotubes are almost stoichiometric. Under oxygen atmosphere, these stoichiometric TiO₂ nanotubes, slower and smaller structural change of TiO₂ with the crystallization of amorphous TiO₂ is reasonable to be observed as shown in Fig. 2. Other researchers also claimed the high stability of oxygen rich titania at high temperature.²⁰ Inversely, at a high vacuum without oxygen, morphological changes were observed. Previous literature, oxygen molecules adsorbed on anatase TiO₂ desorbed at ca. 140 °C under high vacuum.²¹ In the previous literature, oxygen ion diffusion is considered as the rate-determining step in the sintering of TiO₂.²² During *in situ* TEM annealing process without oxygen, oxygen vacancy will favor the diffusion according to the general vacancy diffusion mechanism. Thus, a sintering of TiO₂ was accelerated under high vacuum as shown in Fig. 3 and a slower sintering of TiO₂ is reasonable to happen if a low concentration of oxygen vacancy as shown in Fig. 2.

In summary, we performed *in situ* TEM annealing of double wall TiO₂ nanotubes. Double wall TiO₂ nanotube array was prepared by anodization in a fluorinated glycerol electrolyte. *In situ* TEM annealing of TiO₂ nanotube at high temperature was successfully performed with and without oxygen. Under oxygen partial atmosphere, no obvious morphological changes were observed up to ca. 600 °C, but crystallization of nanotubes occurred around 300 °C. According to the general vacancy diffusion mechanism, we concluded that the difference in structural changes at high temperature was due to the existence of oxygen gas molecule, that can stabilize the TiO₂ structure.

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