Effects of Additives on Microstructures of Titanate Based Nanotubes Prepared by the Hydrothermal Process

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Silica-containing TiO₂-derived titanate nanotubes were prepared by the addition of a small amount of tetraethyl orthosilicate (TEOS) to TiO₂-derived titanate nanotubes prepared by the hydrothermal process and a subsequent heat-treatment at 473 K in air. The microstructure and thermal behavior of synthesized silica containing TiO₂-derived titanate nanotubes were investigated by various methods such as X-ray diffraction (XRD), X-ray absorption fine structure (XAF), and X-ray photoelectron spectroscopy (XPS). As a result, the addition of a small amount of TEOS led to the improvement of the thermal stability for TiO₂-derived titanate nanotubes. XPS results revealed that Si was combined onto the surface of TiO₂-derived titanate nanotubes, forming partial Si-O-Ti chemical bonds. Therefore, it was inferred that the thermal stability could be modified by forming partial Si-O-Ti chemical bonds at interface of silica and TiO₂-derived titanate nanotubes.

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1. Introduction

Oxide nanotubes, nanowire, and nanofiber constitute a promising new class of materials having uniform dimensions and well-developed morphologies. In particular, since the discovery of carbon nanotubes,¹⁾ the syntheses of micro- and nanotubes of TiO₂ have been attempted by various methods such as template methods^{2–4)} Kasuga *et al.* treated TiO₂ at 383 K in 10 M NaOH aqueous solutions without the replication or template and nanotubes with 8 nm in diameter and 100 nm in length were obtained by their experiments.⁵⁾ These TiO₂-derived nanotubes are notable nanoscale-materials because of their nanotubular structures and high surface areas. Therefore, several application studies on such as electrochromism,⁶⁾ bone regeneration,⁷⁾ proton conduction,⁸⁾ photoinduced hydrophilicity,⁹⁾ photocatalysts,^{10–12)} and dye-sensitizing solar batteries¹³⁾ have been conducted by many researchers, although discussion about the structure and formation mechanism are in problems.^{14–20)} Furthermore, preparations of thin film and bulk for these nanotubes have been attempted extensively.^{21–23)} On the contrary, these TiO₂-derived nanotubes can not keep nanotubular structures at high heat (573 K ~).^{24,25)} For that reason, it is considered that these TiO₂-derived nanotubular materials are restricted in their practical application because of their poor thermostability. So, the synthesis of silica-supported TiO₂-derived nanotubes was attempted to improve their thermal stability for nanotubular structures in this study. Moreover, the composite with silica is also expected to provide functions such as an adsorptive capacity, leading to the modification of the photocatalytic activity. In fact, as for TiO₂ nanoparticles, the effectiveness of the addition of silica for enhancement of the phase stability^{26–29)} and the photocatalytic activity^{30,31)} has been reported in large numbers.

In the present work, silica-containing TiO₂-derived nanotubes were prepared by hydrothermal treatments of anatase-

type TiO₂ in NaOH aqueous solutions and a subsequent addition of tetraethyl orthosilicate (TEOS) to these nanotubes in water/ethanol system. The microstructure and thermal behavior of synthesized silica-containing TiO₂-derived nanotubes were investigated in detail. In special, the effect of the additive TEOS on the local structure around Ti atom was investigated by Ti K-edge XAFS. Furthermore, the surface states of silica-containing TiO₂-derived nanotubes were also investigated by XPS.

2. Experimental Procedure

The synthesis of TiO₂-derived nanotubes was attempted via the hydrothermal process. Commercial anatase-type TiO₂ powder (3 m²/g, Kojundo Chem., Japan) was used as a starting material. 2 g of anatase powder was added in 10 M NaOH aqueous solutions (20 ml). Then the specimen was treated under a hydrothermal reaction at 383 K for 96 h. The obtained product after the hydrothermal treatment were sufficiently washed with de-ionized water and dilute HCl aqueous solution (0.1 M) and was subsequently separated from the washing solution by filtration. This treatment was repeated until the washing water showed pH < 7. The final pH value of the washing water was 6.8. This was dried at 323 K for more than 12 h in an oven. The obtained nanotubular product (1 g) was mixed with TEOS (0.1, 0.3, and 0.5 ml) in water/ethanol system and then heat-treated at 473 K for 6 h in air. The obtained silica-containing samples were heated at 573 and 673 K for 2 h in air. For comparison with silica containing products, the sample without the addition of TEOS was also heated at 573 and 673 K for 2 h in air.

The phase identification was carried out by XRD (Rint 2100, Rigaku Co., Ltd, Japan) method using CuK α radiation at 40 kV and 20 mA. The XRD profiles were collected between 5 to 60° of 2 θ angles with a step interval of 0.02° and scanning rate of 1°/min. Various microstructural analyses were performed by scanning electron microscope (SEM,

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S-4500, Hitachi, Japan) with accelerating voltage of 15 kV and transmission electron microscope (TEM, JEM2010/SP, JEOL, Japan) with accelerating voltage of 200 kV. The concentration of sodium in prepared samples was analyzed by energy dispersive X-ray (EDX) analysis. The Si/Ti molar ratio was measured by X-ray fluorescence spectrometry (XRF, XRF-1700, SHIMADZU, Japan) using $\text{CuK}\alpha$ radiation at 40 kV and 95 mA. Nitrogen adsorption isotherms at 77 K were obtained by automatic gas adsorption measurement apparatus (BELSORP 18PLUS-SPL, Japan-BEL, Japan). Some products were pretreated at 403 K for 10 h.

Ti K-edge XAFS was recorded at room temperature at BL01B1 beamline of SPring 8 in Japan. Ti K-edge XAFS data for this study was corrected with transmission mode using the Si (111) double crystal monochromator ($2d = 0.627 \text{ nm}$). The data were collected with the ionization chambers filled with gas (I_0 chamber: $\text{He}/\text{N}_2 = 7/3$, I chamber: N_2). For the XAFS measurements, the samples were prepared as pellets with the thickness varied to obtain a 0.5–1 jump at the Ti K absorption edge. Ti metallic foil was used to carry out for the energy calibration. X-ray absorption near-edge structure (XANES) was analyzed by subtracting a linear background computed by least-square fitting from the pre-edge region and normalized. Extended X-ray absorption fine structure (EXAFS) was analyzed by using standard methods. The pre-edge region was subtracted, and then the EXAFS spectrum was extracted by fitting the absorption coefficient with a cubic spline method. Fourier transformation of the k^3 -weighted EXAFS oscillation from k (k is the photoelectron wavenumber) space to r space was performed over the range $0.25\text{--}1.05 \text{ nm}^{-1}$ to obtain radial distribution function (FT-EXAFS). The analysis of EXAFS data conducted using the commercial software “REX2000” (Rigaku Co. Ltd., Japan).

The XPS analysis was performed in an ultrahigh vacuum (less than $1.33 \times 10^{-6} \text{ Pa}$) using an ULVAC-PHI 5500MT system, with Mg $\text{K}\alpha$ ($h\nu = 1253.6 \text{ eV}$) X-ray source operated at 15 kV. Binding energies were referenced to C 1s level of residual graphitic carbon.

3. Results and Discussion

Figure 1(A) shows a typical TEM image of the product prepared by the hydrothermal treatment of anatase-type TiO_2 at 383 K at 96 h in 10 M NaOH aqueous solutions. As shown in Fig. 1(A), the obtained product possessed nanotubular structures with about 10 nm in outer diameter and 5 nm in inner diameter and a few hundred nm in length, and they were open-end with several wall layers on both sides. The measured interlayer spacing was about 0.90 nm. Figure 1(B) shows XRD patterns of the obtained nanotubular product before and after heat treatments at 573 and 673 K in air. In the XRD pattern of the nanotubular product before the heat-treatment, the broad reflection peaks were observed at 2θ of approximately 9° , 24° , 30° , 48° and 62° . The XRD pattern of the synthesized nanotubular product in this study was consistent with TiO_2 -derived nanotubes prepared in other previous literatures.^{6–9,11,12,19,20} In particular, the peak at $2\theta = \text{ca. } 9^\circ$ ($d = 0.95 \text{ nm}$) was corresponding to the interlayer spacing value measured by TEM observation,

Fig. 1 (A) Typical TEM images of the product prepared by the hydrothermal treatment of anatase at 383 K for 96 h and the subsequent washing treatment with $\text{H}_2\text{O}/\text{HCl}$. (B) XRD patterns of the nanotubular products before and after heat treatments at 573 and 673 K for 2 h in air.

indicating that this product might be composed of layered titanate structure. Sodium hardly could be detected in the nanotubular product according to surface analytic methods such as EDX and XPS. Therefore, it was indicated that sodium could be removed from the product by the $\text{H}_2\text{O}/\text{HCl}$ washing treatment and that the product might be mainly composed of the H-type of titanate. The Brunauer-Emmett-Teller (BET) surface area value obtained by N_2 -adsorption measurement for TiO_2 -derived titanate nanotube was *ca.* $250 \text{ m}^2/\text{g}$.

As shown in Fig. 1(B), in XRD pattern of the sample after a heat-treatment at 573 K, diffraction peaks derived from anatase-type TiO_2 were slightly observed. Particularly, in the case of a heat-treatment at 673 K, TiO_2 -derived titanate nanotubes mostly transferred to anatase-type TiO_2 . Moreover, SEM result shows that this sample prepared by a heat-treatment at 673 K possessed non-tubular structures, and this sample was mainly composed of spherical particles (Fig. 2).

Silica-containing TiO_2 -derived titanate nanotubes were attempted to synthesize by the addition of TEOS (0.1, 0.3, and 0.5 ml) to TiO_2 -derived titanate nanotubes in water/

Fig. 2 Typical SEM image of TiO_2 -derived titanate nanotubes heat-treated at 673 K for 2 h in air.

ethanol and a subsequent heat-treatment at 473 K in air. According to XRF measurements, Si/Ti molar ratios of samples prepared by additions of 0.1, 0.3, and 0.5 ml of TEOS were 0.013, 0.026, and 0.033, respectively. Figure 3 shows XRD patterns of these silica-containing samples before and after heat-treatments. XRD patterns of silica-containing samples before heat-treatments were similar with that of TiO_2 -derived titanate nanotubes. In XRD patterns of samples after heat-treatments, the peaks intensity derived from anatase-type TiO_2 decreased with an increase in the amount of additive TEOS. Though typical SEM images of silica-containing samples (TEOS additive amount: 0.5 ml) before and after heat-treatments are shown in Fig. 4, silica-containing sample heat-treated at 673 K had nanowisker-like morphologies and possessed high BET value ($174 \text{ m}^2/\text{g}$), indicating that this sample mostly maintained nanotubular structures after a heat-treatment at 673 K. Thus, the small additive TEOS had any effect on thermal behavior of TiO_2 -derived titanate nanotubes, leading to the modification of their thermal stability for nanotubular structures. The effect of the additive TEOS on the local structure around Ti atom was investigated by Ti K-edge XAFS.

Figure 5 shows Ti K-edge XANES spectra for TiO_2 -derived titanate nanotubes and silica-containing TiO_2 -derived titanate nanotubes (TEOS additive amount: 0.5 ml). The edge region in the absorption spectra provides much information on the environment geometry and electronic structure of the absorption atom. In Ti K-edge XANES, the characteristic pre-edge peaks were also observed at 4960–4970 eV. These pre-edge features are widely used to derive information on the coordination environment of Ti atom.^{20,32–35} As shown in Fig. 5, the edge energy position of silica-containing TiO_2 -derived titanate nanotubes was very close to that of TiO_2 -derived titanate nanotubes, and their pre-edge features illustrated similar features each other. Therefore, the symmetry of the Ti environment in TiO_2 -derived titanate nanotubes has hardly changed with the addition of a small amount of TEOS.

Figures 6(A) shows k^3 -weighted EXAFS oscillations for TiO_2 -derived titanate nanotubes and silica-containing TiO_2 -derived titanate nanotubes (TEOS additive amount: 0.5 ml). For EXAFS oscillations, as shown in Fig. 6(A), a marked

Fig. 3 XRD patterns of TiO_2 -derived titanate nanotubes with addition of TEOS before and after heat-treatments at 573 and 673 K for 2 h in air. Amount of addition of TEOS to titanate nanotube (1 g): (A) 0.1 ml, (B) 0.3 ml, and (C) 0.5 ml.

difference between these samples could not be confirmed. Figure 6(B) also shows FT-EXAFS for these samples. They represent radial distribution function plots around the Ti atom, and the first peak was indicated as the coordination number corresponding to the Ti-O bond distance. The magnitudes of the second peak and subsequent ones were further small in FT-EXAFS for TiO_2 -derived titanate nanotubes. This indicated that TiO_2 -derived titanate nanotubes

Fig. 4 Typical SEM images of silica-containing TiO_2 -derived titanate nanotubes before and after a heat treatment at 673 K for 2 h in air.

Fig. 5 Ti K-edge XANES spectra for (a) TiO_2 -derived titanate nanotubes and (b) silica containing TiO_2 -derived titanate nanotubes (TEOS additive amount: 0.5 ml).

had only periodic structures in short order. Furthermore, in order to the structural parameters, the curve fitting of the Ti-O shell within the range of 0.06–0.2 nm was performed by inverse FT. The later each value was obtained from the simulation of the experimental spectrum using the theoretical curves calculated by Mckale *et al.*³⁶⁾ For TiO_2 -derived titanate nanotubes, the nearest Ti-O distance and its average coordination number obtained by the curve fitting were 0.192 nm and 5.2, respectively. In our previous study, the local structure of TiO_2 -derived titanate nanotubes prepared by the hydrothermal process has been investigated by XAFS, and the result detail has been reported.²⁰⁾ As shown in Fig. 6(B), the radial distribution function plot around the Ti atom for silica-containing TiO_2 -derived titanate nanotubes was very similar to that of TiO_2 -derived titanate nanotubes. In particular, the nearest Ti-O peak geometries of these samples were almost the same, and the nearest Ti-O distance and its average coordination number were 0.192 nm and 5.25, respectively. This result indicated that TiO_x polyhedra in TiO_2 -derived titanate nanotubes has hardly changed due to the addition of a small amount of TEOS, and this EXAFS result also agrees with XANES result. Thus, Ti K-edge XAFS results revealed that the addition of a small amount of TEOS did not have much effect on local structures around Ti atom.

The surface states of silica-containing TiO_2 -derived titanate nanotubes were also investigated by XPS analysis

Fig. 6 (A) k^3 -weighted EXAFS oscillations and (B) FT-EXAFS for TiO_2 -derived titanate nanotubes and silica containing TiO_2 -derived titanate nanotubes (TEOS additive amount: 0.5 ml).

in this study. Figure 7 shows Si 2p XPS of silica-containing TiO_2 -derived titanate nanotubes (TEOS additive amount: 0.5 ml). The peak derived from Si^{4+} in silica was located at around 103 eV.³⁷⁾ In fact, the binding energy of Si 2p peak for commercial silica quartz was also located at 103.2 eV in this measurement. For silica-containing TiO_2 -derived titanate nanotubes, the binding energy of Si 2p peak was located at 102.5 eV, 0.7 eV lower than Si 2p peak for commercial silica. Therefore, it was considered that the state of Si species in silica-containing TiO_2 -derived titanate nanotubes could be different from that of Si species in commercial silica.

Fig. 7 Si 2p XPS for (a) commercial silica and (b) silica containing TiO_2 -derived titanate nanotubes (TEOS additive amount: 0.5 ml).

Fig. 8 (A) O 1s and (B) Ti 2p XPS for TiO_2 -derived titanate nanotubes and silica containing TiO_2 -derived titanate nanotubes (TEOS additive amount: 0.5 ml).

O 1s and Ti 2p XPS of TiO_2 -derived titanate nanotubes and silica-containing TiO_2 -derived titanate nanotubes are also shown in Fig. 8. As shown in Fig. 8(A), the binding energy of O 1s peak for TiO_2 -derived titanate nanotubes was mainly located at 530 eV. On the other hand, the binding energy of O 1s peak for silica-containing TiO_2 -derived titanate nanotubes was mainly located at 530.5 eV. Thus, the binding energy of Si 2p peak slightly shifted to higher binding energy by the addition of a small amount of TEOS. In Ti 2p XPS, the binding energy of Ti $2p_{3/2}$ peak for TiO_2 -derived titanate nanotubes was 458.3 eV (Fig. 8(B)). Ti $2p_{3/2}$ peak for silica-containing TiO_2 -derived titanate nanotubes

was 458.9 eV, 0.6 eV higher than that for TiO_2 -derived titanate nanotubes. From these XPS results, for silica-containing TiO_2 -derived titanate nanotubes, it is speculated that Si is combined onto the surface of TiO_2 -derived titanate nanotubes, forming partial Si-O-Ti chemical bonds. Because the electronegativity of Si is greater than that of Ti, O 1s peak for TiO_2 -derived titanate nanotubes is thought to have a chemical shift of +0.5 eV. Moreover, a chemical shift in Ti $2p_{3/2}$ XPS can be also derived from forming these Si-O-Ti chemical bonds. The decrease of the electron density around Ti atom results from the greater electronegativity of Si via O acting on Ti. The shielding effect is weakened, and then the binding energy is increased.³⁸⁾

Consequently, the addition of a small amount of TEOS led to the improvement of the thermal stability for TiO_2 -derived titanate nanotubes prepared by the hydrothermal process. According to XPS, it was speculated that the thermal stability was modified by forming partial Si-O-Ti chemical bindings at interface of silica and TiO_2 -derived titanate nanotubes. Si-O-Ti bonds were investigated in studies on TiO_2 - SiO_2 composites prepared by the sol-gel process.^{39–42)} According to these researches, thermodynamically there was no possibility of Si-O-Ti bonds breakage at low temperatures. For instance, Izutsu *et al.* has confirmed the presence of Si-O-Ti bonds at 1073 K. Therefore, it is expected that Si-O-Ti bonds at interface of silica and TiO_2 -derived titanate nanotubes could not also break up on heating. Thus if Si-O-Ti bonds could be stable at high heat, Si atoms might be inserted to titanate matrix during the heat-treatment, and there is a possibility that this insertion of Si atoms could retard the titanate-to-anatase phase transformation. The detailed analyses for the state of Si, Ti, and O in silica-containing TiO_2 -derived titanate nanotubes and their stabilization mechanism are further investigation by using high resolution TEM (HRTEM) coupled with electron energy loss spectroscopy (EELS).

4. Conclusions

In this study, TiO_2 -derived titanate nanotubes with about 10 nm in outer diameter and 5 nm in inner diameter and a few hundred nm in length were attempted by the hydrothermal treatment at 383 K for 96 h of anatase-type TiO_2 in 10 M NaOH aqueous solutions and subsequent washing treatments with $\text{H}_2\text{O}/\text{HCl}$. The obtained TiO_2 -derived titanate nanotubes (1 g) was mixed with TEOS (0.1, 0.3, and 0.5 ml) in water/ethanol system and then heat-treated at 473 K for 6 h in air. The microstructure and thermal behavior of synthesized silica containing TiO_2 -derived titanate nanotubes were investigated by various methods such as XRD, XAFS, and XPS. As a result, the addition of a small amount of TEOS led to the modification of the thermal stability for TiO_2 -derived titanate nanotubes. From Ti K-edge XAFS analysis, the addition of a small amount of TEOS could not have much effect on local structures around Ti atom for TiO_2 -derived titanate nanotubes themselves. In contrast, according to XPS, the surface states of silica-containing TiO_2 -derived titanate nanotubes were different from those of TiO_2 -derived titanate nanotubes, and it was considered that Si could be combined onto the surface of TiO_2 -derived titanate nanotubes, forming

partial Si-O-Ti chemical bonds. It was indicated that the thermal stability was modified by forming partial Si-O-Ti chemical bonds at interface of silica and TiO₂-derived titanate nanotubes.

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