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Layered sodium titanate nanofiber and microsphere synthesized from peroxotitanic acid solution

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Abstract

In this paper, we report titania and titanate nanofiber synthesized by using peroxotitanic acid solution as a titanium source. The peroxotitanic acid solution was mixed with NaOH aqueous solution, followed by the hydrothermal treatment with or without vigorous agitation. In TEM and SEM images for solids obtained by the synthesis with vigorous agitation, nanofibers are observed. On the other hand, microspheres as well as nanofibers were observed in solids obtained by the synthesis without agitation. The microspheres are composed of nanofibers and nanosheets. EDX analysis for the obtained solids detected Ti and Na, indicating that the obtained solids are sodium titanate. As a reference, synthesis by using TiO_2 particles instead of the peroxotitanic acid solution was also performed. The Na to Ti mole ratio for the peroxotitanic acid based solid determined by EDX was 0.55 which is twice the value of 0.26 for the TiO_2 particle based solid. The obtained sodium titanate could be converted into anatase-type titania by the HCl treatment of the sodium titanate and the subsequent calcination.

Keywords: TiO_2; Titanate; Fibers

1. Introduction

One-dimensional nanostructures such as nanowire, nanofiber and nanotube with high aspect ratios attract much attention due to their high potential for applications in fabricating electronic-devices, sensors, etc., where they are expected to have unusual characteristics amplified through their quantum size effects and marked shape-specific effects.[1–5] Especially, various kinds of nanostructured titania are actively reported, since titania and its related materials with the nanostructure are expected to the application to the photocatalyst and the dye-sensitized type solar cell. For example, layered and hexagonal nanostructured titania templated by organic molecules are known to be the excellent photocatalyst.[6,7] Nanofibers and nanotubes of titania and titanate are also synthesized by utilizing the ultrasonic wave[8] and the hydrothermal treatment,[9–16] even if templates such as organic molecules and nanostructured inorganic materials are not used. Particularly, it has been focused that the hydrothermal treatment of TiO_2 particles led to the formation of titania or titanate nanotube and nanofiber. In the hydrothermal process, it has been already appeared that obtained nanostructures of titania and titanate differ depending on the titanium source, but there are no reports on the synthesis using peroxotitanic acid solution as the titanium source. In this paper, we report the titania and titanate nanofiber and microsphere synthesized by using peroxotitanic acid solution.

2. Experimental procedure

Peroxotitanic acid ($Ti_2O_5(OH)_x^{(x-2)-}$; $x > 2$) solution[17,18] abbreviated as PTA solution (P-cat. (assay as TiO_2 1.7–1.8 wt%); Ecoat Co. Ltd.) was used as a precursor for the titanate nanofiber. Ten milliliters of the PTA solution was mixed with 10 ml of NaOH aqueous solution with con-

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centrations of 1–15 mol l^{-1}, followed by the hydrothermal treatment at 100–120 °C for 5–72 h with or without vigorous agitation. The obtained solid was repeatedly centrifuged and washed with distilled water. Volume of the obtained solid phase or gel composed of product and water was measured. As a reference, similar synthesis using rutile-type titania particle (TTO-55(N); ISHIHARA SANGYO KAISHA Ltd.) as a Ti source was also performed. The obtained solid phase or gel was freeze-dried. Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2010 and a Hitachi H-800MU instrument. Scanning electron microscopy (SEM) was performed using a JEOL JSM-5510LV. X-ray micro analysis (XMA) was conducted with a HORIBA EMAX-5770 instrument. Powder X-ray diffraction (XRD) measurement was made on a Shimadzu XRD-6100 instrument with Cu Kα radiation. Thermogravimetric and differential thermal analyses (TG–DTA) were carried with a SEIKO TG/DTA320U. Fourier transform infrared absorption (FT-IR) spectra were measured on a Nippon Bunko FT/IR-300 instrument.

3. Results and discussion

The effect of the reaction time was investigated by reacting 10 ml of PTA solution and 10 ml of NaOH (15 mol l^{-1}) with reaction times of 5 h, 20 h and 72 h. The volume of the solid phase obtained after water washings and centrifugations was measured. The solid phase are composed of product and water. The volume of the solid phase immediately after mixing the PTA solution and the NaOH solution was 3.9 ml. The volumes were 3.8 ml, 6.0 ml and 14.6 ml at reaction times of 5 h, 20 h and 72 h, respectively. It was revealed that the volume increased remarkably as the reaction time increased, though the same number of moles of Ti is in the product. The increase in volume suggests that 3D network structure develops as the reaction temperature increases to form a gel structure. It is expected that the 3D network structure develops more in the gel with the larger volume. Furthermore, it is also prospected a larger specific surface area is generated after water is removed from a gel by the freeze drying. It is supposed that they are promising materials for photocatalysts and dye sensitizing solar cells. The solid **1** obtained at a reaction time of 72 h was thus characterized in detail. As shown in a TEM image in Fig. 1a for **1**, fibers with widths from several tens to 200 nm were observed. Therefore, it is supposed that the volume increases as the reaction temperature increases, because the 3D network structure is formed by tangled nanofibers. A further enlarged image of the nanofibers shown in Fig. 1b indicates that finer nanofibers gather along the long axis to form the fibrous structure. In a SEM image of Fig. 2a for the solid with a reaction time of 20 h, clear long fibrous substance was not observed, but short nanofibers were observable. On the other hand, clear fibrous patterns were observed in a SEM image (Fig. 2b) of the solid with a reaction time of 72 h. The nanofibers became thicker and longer with an increase of the reaction time. XRD measurements were also performed on the solids. All solids showed several peaks at almost the same positions. The peaks were broad in a solid obtained immediately after mixing the PTA solution and the NaOH solution (Fig. 3a). On the other hand, the peaks were the sharpest and largest in the solid at a reaction

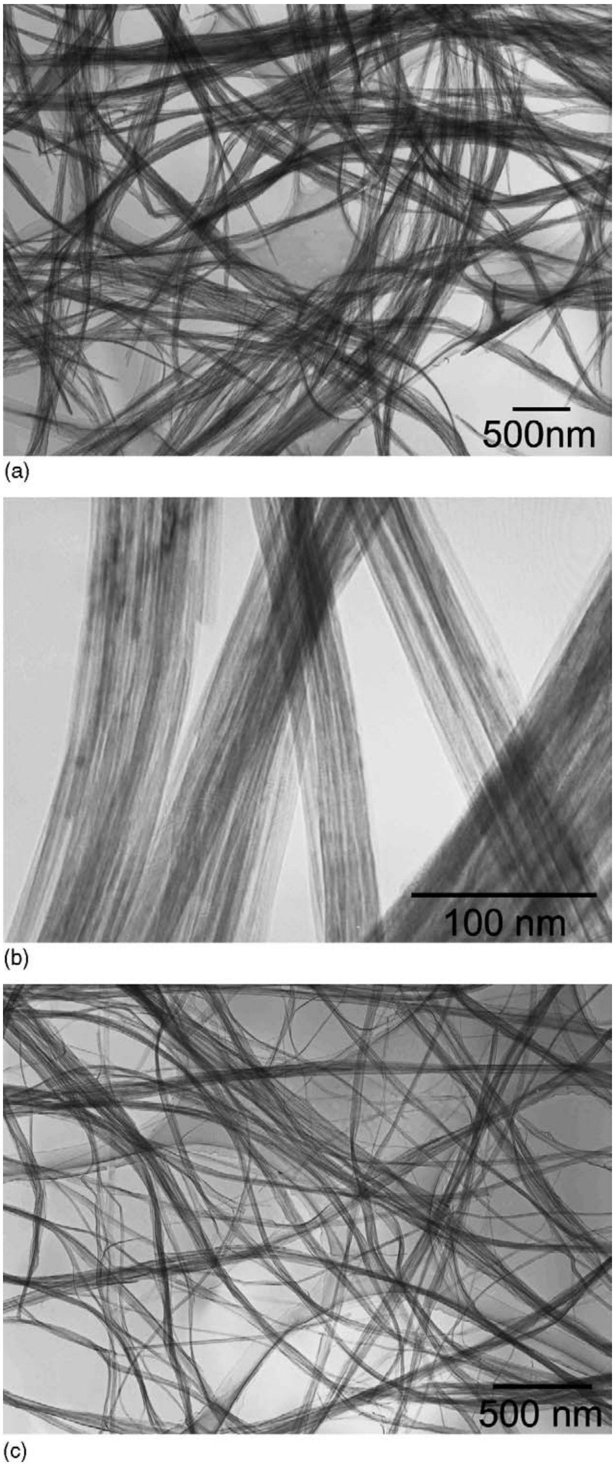

Fig. 1. TEM images for the solids synthesized with vigorous agitation at a reaction time of 72 h using PTA solution (a and b) and titania particle (c). Part (b) is an enlarged image of the nanofiber in **1**.

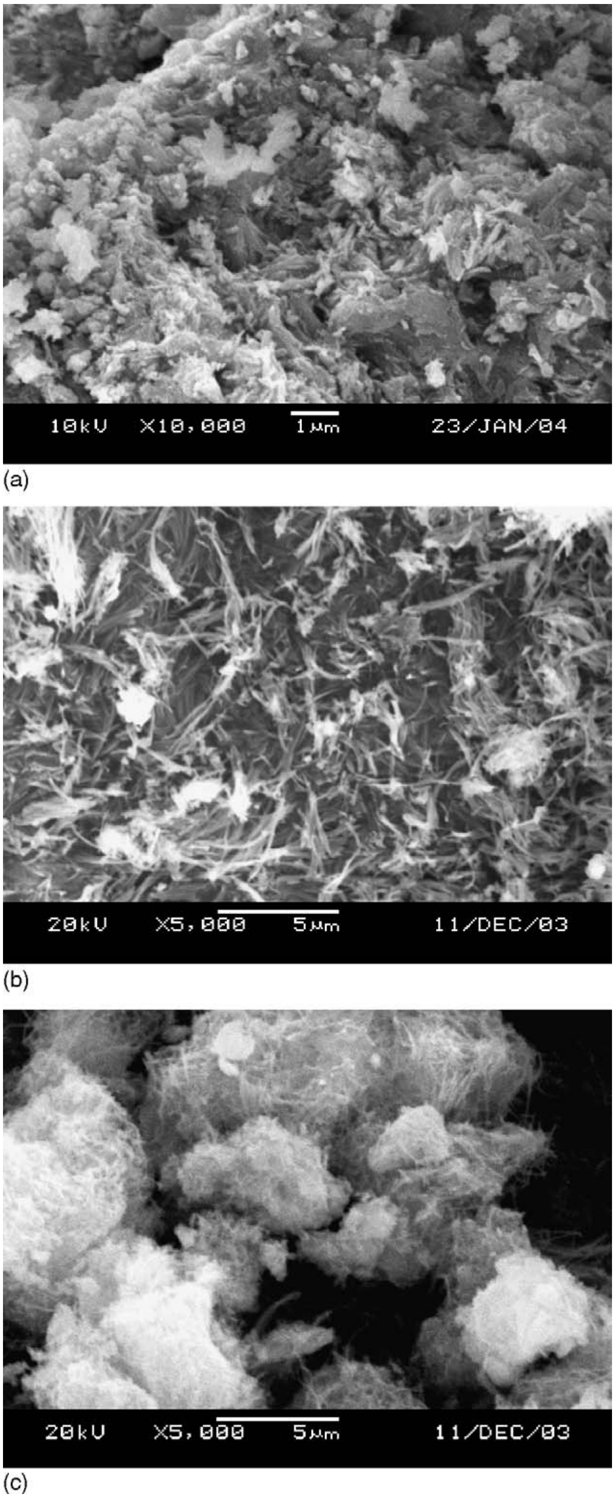

Fig. 2. SEM images for the solids synthesized by using PTA solution (a and b) and titania particles (c) with vigorous agitation at reaction times of 20 h (a) and 72 h (b and c).

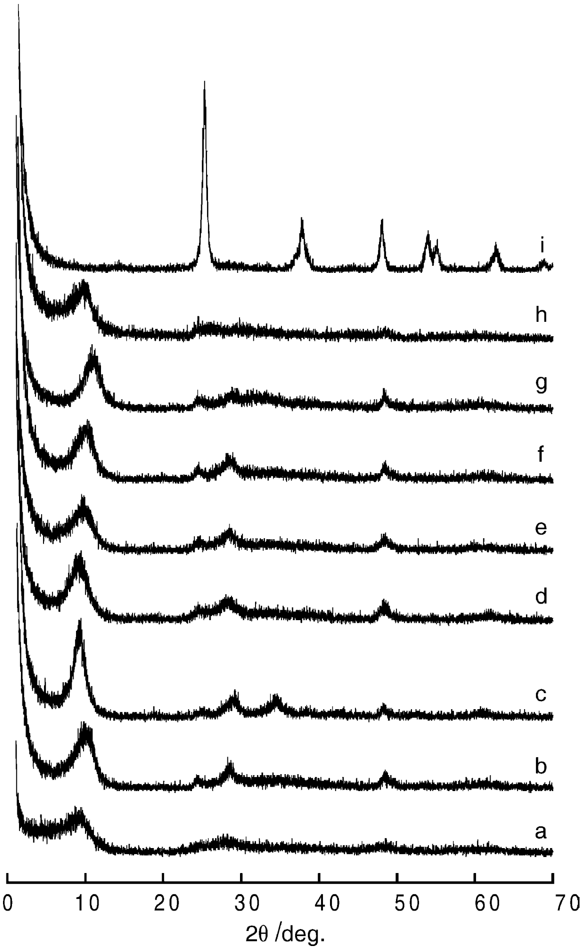

Fig. 3. XRD patterns for the solids: (a) the solid obtained immediately after mixing PTA solution and NaOH solution; (b and c) the solids synthesized with vigorous agitation from PTA solution at reaction times of 20 h (b) and 72 h (c); (d) the solids synthesized with vigorous agitation from titania particles at reaction times of 72 h; (e and f) the solids synthesized without vigorous agitation from PTA solution at reaction times of 20 h (e) and 72 h (f); (g) the 500 °C calcined solid of **1**; (h) the HCl treated solid of **1** and (i) the 500 °C calcined solid of the HCl treated solid.

time of 72 h or **1** (Fig. 3c). It is clear that the peak intensity increased as the reaction time increased as shown in Fig. 3a–c. The peaks were like those of titanate with a layered structure, being consistent with the TEM image shown in Fig. 1b. In this case, *d* value or 0.95 nm calculated from a peak at 2θ = ca. 10° corresponds to an interlayer spacing of the layered titanate. From the results shown above, it is clear that crystallization of solids proceeded to develop fibrous morphologies with an increase of the reaction time. EDX measurement of **1** revealed that the Na to Ti molar ration was 0.55.

Subsequently, synthesis was performed using titania powders as a source of titanium with a reaction time of 72 h for comparison in the same condition to obtain a solid **2**. As shown in Figs. 1c and 2c for **2**, nanofibers similar to those of **1** were observed. XRD pattern for **2** is also similar to that for **1**, as shown in Fig. 3d. However, the mole ratio of Na to Ti in the product was 0.26 which is the half of 0.55 for **1**. Thus, it is clear that compounds with larger amounts of Na^+ ion can be obtained by the syntheses using the PTA solution as a source of titanium. The color of the solids obtained from the PTA solution was yellowish white. On the other

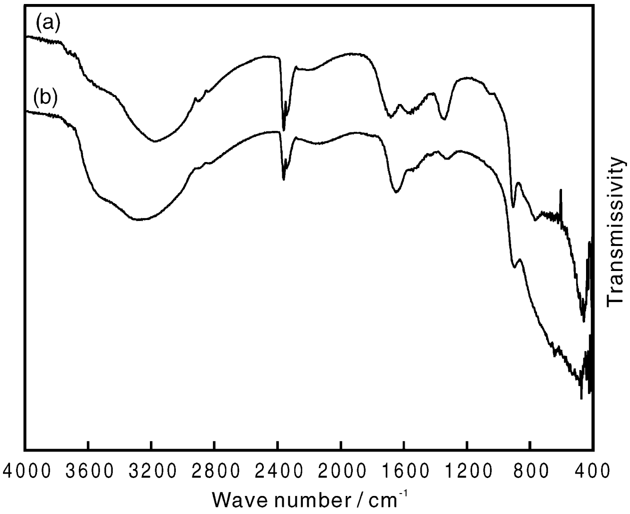

Fig. 4. FT-IR spectra for **1** (a) and **2** (b).

hand, the color of **2** was white. The yellowish color due to titanium oxyhydroxide containing peroxo group[17,18] for the solids faded to be white as the reaction time increased. It is thus suggested that peroxo group in the inorganic framework or titanate sheet decreased as the polycondensation with an increase of the reaction time proceeded. Therefore, it is suggested that products including a large amount of Na^+ ion were obtained because the titanate framework partially containing peroxo group as $(Ti_2O_5)_q(OH)_y{}^{(y-2q)-}$ [17,18] has negative charge formed by using the PTA solution as a titanium source. Figs. 4 and 5 show FT-IR spectra and TG curves, respectively, for **1** and **2**. Several peaks in Fig. 4 are shown at almost the same wave numbers, but are different in intensity. In Fig. 5, the weight loss over 100 °C attributable to desorption of water adsorbed in the interlayer space and formed by condensation of hydroxyl groups in the titanate framework for **1** is larger than that for **2**, although the weight losses for the solids below 100 °C due to desorption of adsorbed water on the surface of the solids were almost same. These results suggest that morphologically same but structurally different various nanofibers can be obtained by appropriate selecting of the titanium source.

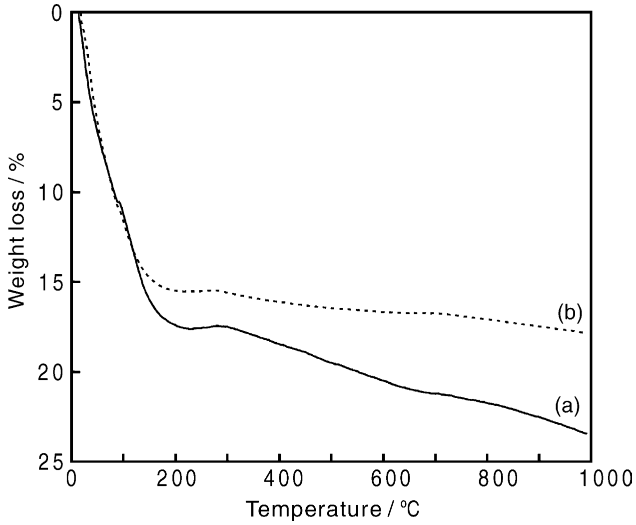

Fig. 5. TG curves for **1** (a) and **2** (b).

The effect of the reaction temperature was then investigated. Syntheses were performed by the same material ratio at a reaction time of 20 h. The volumes of the obtained solid phases were 1.6 ml, 2.5 ml and 6.0 ml at the reaction temperatures of 100 °C, 110 °C and 120 °C, respectively. It was revealed that the volume increases significantly as the reaction temperature increases, indicating that fibrous morphology developed with an increase of the reaction temperature. Similar XRD patterns were obtained in all reaction temperatures.

Then, the effect of the concentration of NaOH was investigated. Ten milliliters of the PTA solution and 10 ml of NaOH solutions with varied concentrations were reacted in the reaction temperature of 120 °C and reaction time of 20 h. The volume of the solid phase was 2.2 ml when the concentration of NaOH was 1 mol l^{-1}. The volume of the solid phase changed into 2.4 ml (5 mol l^{-1}), 4.0 ml (10 mol l^{-1}) and 6.0 ml (15 mol l^{-1}). The volume of the solid phase increased as the concentration of NaOH solution increased. Therefore, it is supposed that the fibrous structure developed as the concentration of NaOH increased. The yellowish color faded and whiteness degree increased as the concentration of NaOH solution increased. It is supposed that the amount of peroxo group or $(Ti_2O_5)_q(OH)_y{}^{(y-2q)-}$ [17,18] species in the titanate framework decreases as the concentration of NaOH solution increases.

The effect of the agitation of the reaction mixture was also investigated. Ten milliliters of the PTA solution and 10 ml of NaOH (15 mol l^{-1}) were reacted at 120 °C without agitating with reaction times of 20 h and 72 h. As shown in the XRD patterns of Fig. 3e for the 20 h solid and Fig. 3f for the 72 h solid, similar XRD patterns were observed regardless of the reaction time, being different from the results obtained by the XRD patterns (Fig. 3b and c) for the solids synthesized with vigorous agitating. It reveals that solids with the similar crystalline structure can be obtained regardless of the reaction time in the synthesis without agitation. In a SEM image for the solid obtained with a reaction time of 20 h (Fig. 6a), spherical particles or microspheres with a diameter of 2–3 μm were observed along with the similar nanofibers that were observed in **1** or solids synthesized with agitation. An enlarged image of the spherical particles indicates that the spherical particles or microspheres were composed of aggregations of nanofibers or nanosheets (Fig. 6b). Similar spherical particles in size are also observed in the solid with a reaction time of 72 h, as shown in Fig. 6c and d. Since the mechanical agitation was not carried out, each chemical species such as titanium oxyhydroxide cluster and hydroxide ion could not be mixed and then the condition suitable for the self-organization of titanate species seemed to locally occur to form the spherical particles. In

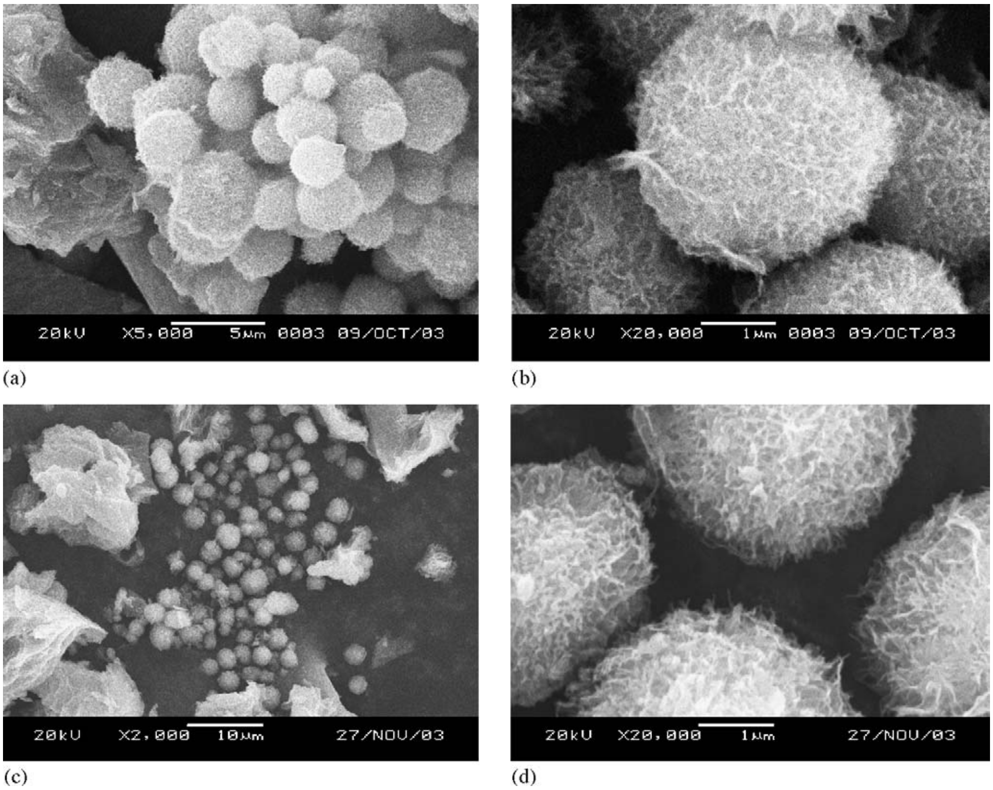

Fig. 6. SEM images for the solids synthesized without agitation from PTA solution at reaction times of 20 h (a and b) and 72 h (c and d); (a and c) microspheres, (b and d) enlarged images of microspheres.

addition, crystal growth with an increase of the reaction time observed in the synthesis with agitation also did not seem to occur in the synthesis without agitation. These spherical particles were not observed in the syntheses using titania particles as a titanium source in the same condition. These results indicate that the spherical particles appear to be a unique nanostructure self-organized only in the syntheses using PTA solution as a source of titanium without agitating.

Finally, the changes in structures and morphologies of the nanofibers and spherical particles by the calcination were investigated. The samples were calcined in air at 500 °C for 3 h. As a typical case, results of **1** were described. In the XRD pattern of the calcined **1** shown in Fig. 3g, the peak on the lowest angle shifted from $d = 0.95$ nm (before the calcination) to $d = 0.81$ nm. It is supposed that the shift occurred because the interlayer spacing became smaller by the removal of absorbed water between the sodium titanate layers. Then, Na^+ ions in the solid were attempted to be exchanged with H^+ ions by adding 0.06 g of the solid into 40 ml of the hydrochloric acid solution ($0.1\ \mathrm{mol\,l^{-1}}$) and then agitating for 3 h. In the XRD pattern of **1** treated with HCl (Fig. 3h), peaks almost the same in position as the sample before the HCl treatment (Fig. 3c) was observed. But the peak intensity decreased by the HCl treatment. EDX measurement was performed to be determined that Na that was detected before the treatment by HCl was not detected at all. Thus, it has been confirmed that the Na^+ ion in the solid shows the ion exchange property and that Na^+ ions are completely exchanged with H^+ ions with the layer structure retained. The HCl treated solid was then calcined at 500 °C for 3 h. As shown in Fig. 3i, anatase-type titanium dioxide was generated. No morphologic change was observed after the treatments by HCl and calcination.

4. Conclusion

We have succeeded in obtaining sodium titanate nanofibers and spherical particles by reacting PTA solution and NaOH solution. Sodium titanate obtained from PTA solution partially includes peroxo group in the titanium oxyhydroxide framework. Therefore, they can contain a larger amount (about two times) of Na^+ ion than the solid synthesized by using titania powder and has more ion exchange sites. It is supposed that the large number of potential ion exchange sites is very effective for chemical modification in titania and titanate for photocatalysts and dye sensitizing solar cells. Further, anatase-type titania nanofibers and microspheres are obtained by the protonation of the nanostructured sodium titanate and the subsequent calcinations. It is expected that the 3D structure made of inter-tangled nanofibers and microspheres are very effective for actively inducing various surface reactions.

Acknowledgements

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References

1. Patzke, G. R., Krumeich, F. and Nesper, R., Oxidic nanotubes and nanorods—anisotropic modules for a future nanotechnology. *Angew. Chem. Int. Ed.*, 2002, **41**, 2446–2461.
2. Rao, C. N. R., Deepak, F. L., Gundiah, G. and Govindaraj, A., Inorganic nanowires. *Prog. Solid State Chem.*, 2003, **31**, 5–147.
3. Rao, C. N. R. and Nath, M., Inorganic nanotubes. *Dalton Trans.*, 2003, 1–24.
4. Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., Gates, B. *et al.*, One-dimensional nanostructures: synthesis, characterization, and applications. *Adv. Mater.*, 2003, **15**, 353–389.
5. van Bommel, K. J. C., Friggeri, A. and Shinkai, S., Organic templates for the generation of inorganic materials. *Angew. Chem. Int. Ed.*, 2003, **42**, 980–999.
6. Fujii, H., Ohtaki, M. and Eguchi, K., Synthesis and photocatalytic activity of lamellar titanium oxide formed by surfactant bilayer templating. *J. Am. Chem. Soc.*, 1998, **120**, 6832–6833.
7. Stone Jr., V. F. and Davis, R. J., Synthesis, characterization, and photocatalytic activity of titania and niobia mesoporous molecular sieves. *Chem. Mater.*, 1998, **10**, 1468–1474.
8. Zhu, Y., Li, H., Koltypin, Y., Hacohen, Y. R. and Gedanken, A., Sonochemical synthesis of titania whiskers and nanotubes. *Chem. Commun.*, 2001, 2616–2617.
9. Kasuga, T., Hiramatsu, M. and Hoson, A., Formation of titanium oxide nanotube. *Langmuir*, 1998, **14**, 3160–3163.
10. Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T. and Niihara, K., Titania nanotubes prepared by chemical processing. *Adv. Mater.*, 1999, **11**, 1307–1311.
11. Chen, Q., Zhou, W., Du, G. and Peng, L.-M., Trititanate nanotubes made via a single alkali treatment. *Adv. Mater.*, 2002, **14**, 1208–1211.
12. Yuan, Z.-Y., Zhou, W. and Su, B.-L., Hierarchical interlinked structure of titanium oxide nanofibers. *Chem. Commun.*, 2002, 1202–1203.
13. Uchida, S., Chiba, R., Tomiha, M., Masaki, N. and Shirai, M., Application of titania nanotubes to a dye-sensitized solar cell. *Electrochemistry*, 2002, **70**, 418–420.
14. Masaki, N., Uchida, S., Yamane, H. and Sato, T., Characterization of a new potassium titanate $KTiO_2(OH)$ synthesized via hydrothermal method. *Chem. Mater.*, 2002, **14**, 419–424.
15. Tian, Z. R., Voigt, J. A., Liu, J., Mckenzie, B. and Xu, H., Large oriented arrays and continuous films of TiO_2-based nanotubes. *J. Am. Chem. Soc.*, 2003, **125**, 12384–12385.
16. Tokudome, H. and Miyauchi, M., Titanate nanotube thin films via alternate layer deposition. *Chem. Commun.*, 2004, 958–959.
17. Ichinose, H., Terasaki, M. and Katsuki, H., Synthesis of peroxo-modified anatase sol from peroxo titanic acid solution. *J. Ceram. Soc. Jpn.*, 1996, **104**, 715–718.
18. Ichinose, H., *Development and application of the microstructure-controlled photocatalyst materials*, Annual Report of Saga Ceramics Research Laboratory, 2004, pp. 67–70 (in Japanese).