JOURNAL OF MATERIALS SCIENCE **39** (2004) 4239–4245

Synthesis of nanotube from a layered $H_2Ti_4O_9 \cdot H_2O$ in a hydrothermal treatment using various titania sources

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In this paper, the synthesis of tubular titania was carried out through a soft chemical hydrothermal reaction of TiO_2 powders in NaOH or KOH aqueous solution systems. It was found that nanotubular products prepared in our studies were identified as $H_2Ti_4O_9{\cdot}H_2O$ by X-ray diffraction analysis with their morphology and crystallinity being dependent on synthetic conditions, i.e. reaction time and temperature of the hydrothermal process. The photocatalytic activity of nanotubular $H_2Ti_4O_9{\cdot}H_2O$ was evaluated in a decomposition test of HCHO at 298 K in an aqueous system using radiation with a mercury lamp. The morphology and yield of these nanotubular products were found to be dependent on the hydrothermal synthetic conditions. © *2004 Kluwer Academic Publishers*

1. Introduction

Since carbon nanotube has been discovered [1], much attention to the synthesis of various nanotubes and nanowires in nanotechnology is observed. Especially, titania based nanotubes and nanowires are one of most promising nanotubes for applications as photocatalysts, sensors, and microelectronic devices [2–4]. For example, O'Regan *et al.* [2] showed that titania nanotubes are expected to be used as materials in high efficient solar cells. Previous results of the synthesis of titania nanotubes prepared by chemical processing, e.g. reaction of TiO_2 particles in a NaOH aqueous solution showed tubular morphology with an average diameter of 5–10 nm and a few micron in length [5–7]. According to Adachi *et al.* [6], the formation mechanism of titania nanotubes is not yet clear and unfortunately their photocatalytic properties are not high. Also, they have synthesized titania nanotube from laurylamine hydrochloride/tetraisopropyl orthotitanate modified with acetylacetone. They showed that those titania nanotubes showed a higher activity in a photocatalytic process in which the formation of I_3^- due to the oxidation of I^- to I_2 in a KI aqueous solution was measured, when compared to P-25 TiO_2 and JRC-4 TiO_2 [6]. Recently, Chen *et al.* reported that these titania nanotubes through reaction of TiO_2 particles in a NaOH aqueous solution consisted of layered trititanate $H_2Ti_3O_7$, and not anatase and rutile [7, 8]. Therefore, to establish a synthesis process of titania nanotubes is now of specific interest.

In this paper, the synthesis of tubular titania has been carried out through a soft chemical hydrothermal reaction of various TiO_2 powders in a NaOH or KOH aqueous solution system. The nanotubular products prepared in our studies were evaluated by XRD and their morphology and cystallinity were observed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The photocatalytic activity of nanotubular products was evaluated in a decomposition test of HCHO at 298 K in an aqueous system. The morphology and yield of nanotubular products were found to be dependent on the synthetic conditions, i.e. reaction time and temperature of the hydrothermal process.

2. Experimental procedure

The starting materials were all commercial TiO_2 powders, i.e. anatase TiO_2 (Kojundo Chem. Co.), TiO_2 (Degussa Co., P-25, a mixture of anatase and rutile = 3 : 1) [9], and rutile-TiO_2 (Kojundo Chem. Co.). Rutile TiO_2 contained a few % of anatase. Anatase TiO_2 had an average particle size of 200 nm. Rutile TiO_2 consisted of large particles of a few microns. However, P-25 TiO_2 was very fine powder having an average particle size of 25–85 nm[9]. TiO_2 powder (1 g) was hydrothermally treated in a 10 mol/1 NaOH or 10 mol/1 KOH aqueous solution at 383 and 423 K during 20 to 168 h (7 days) in a stainless bomb. The products were filtered using a Bucher filter. Subsequently, the residues were carried out by sufficient washing with a dilute HCl solution (0.1 mol/1) and then distilled water. The products were dried at 323 K in an oven. The structural components were determined using X-ray diffraction (XRD). The microstructural features were observed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) at 200 kV. BET of the products was measured with the adsorption equipment (BellSorp-25, Nihon-Bell Co.). Photocatalytic activity was evaluated with the decomposition of an aqueous HCHO solution at 298 K. In brief, 0.5 g of product was added to a 1000 ppm aqueous solution with O_2 gas bubbling using a mercury lamp radiations (100 W) for 2.5 h. The photocatalytic property was evaluated as the fraction of decomposition of an aqueous HCHO solution after 2.5 h radiation with a mercury lamp.

3. Results and discussion

Fig. 1 shows XRD results of products using anatase TiO_2 as a starting material being hydrothermally treated in a NaOH solution at 383 K for 20 to 168 h. After the hydrothermal treatment for 48 to 168 h, some peaks of $H_2Ti_4O_9{\cdot}H_2O$ were identified for samples in which no peak at 2 theta of 25.5° from (101) of anatase TiO_2 was observed. Only samples prepared by a hydrothermal treatment for 20 h showed $H_2Ti_4O_9{\cdot}H_2O$ peaks as well as a small peak from anatase. $H_2Ti_4O_9{\cdot}H_2O$ is a titanate with layered structure, as shown by Feist *et al.* [10] and Uchida *et al.* [11]. In Fig. 2, XRD results of products from anatase TiO_2 after a hydrothermal treatment in a KOH solution at 383 K for 20 h and 48 h are shown (and compared with NaOH). After 20 h, $H_2Ti_4O_9{\cdot}H_2O$ was in part synthesized in the NaOH system, resulting in samples consisting of anatase and $H_2Ti_4O_9{\cdot}H_2O$. On the other hand, in the KOH solution system during 20 h, $H_2Ti_4O_9{\cdot}H_2O$ could not be confirmed by XRD. However, hydrothermal treatments for 48 h in a KOH solution at 383 K resulting in small amount of formation of $H_2Ti_4O_9{\cdot}H_2O$. And it was further found that the use of NaOH enhanced the formation of $H_2Ti_4O_9{\cdot}H_2O$, when compared to the KOH system. These results suggest the possibility that any TiO_2 may be used to prepare $H_2Ti_4O_9{\cdot}H_2O$ as in the presented synthesis process, i.e. in NaOH and KOH solution systems. The XRD results of products synthesized by hydrothermal treatment at 383 and 423 K in the NaOH system for 48 h are shown in Fig. 2e and f, with the existence of $H_2Ti_4O_9{\cdot}H_2O$ at both temperatures. At 423 K, the hydrothermal treatment of anatase also resulted in the formation of $H_2Ti_4O_9{\cdot}H_2O$, although the yield of $H_2Ti_4O_9{\cdot}H_2O$ was similar at 383 K.

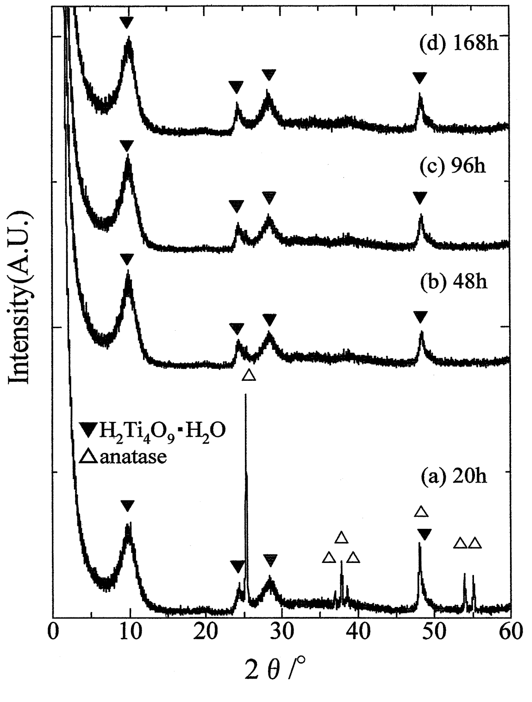

Figure 1 XRD results of products using anatase TiO_2 as starting material being hydrothermally treated in a NaOH solution at 383 K for 20, 48, 96, and 168 h.

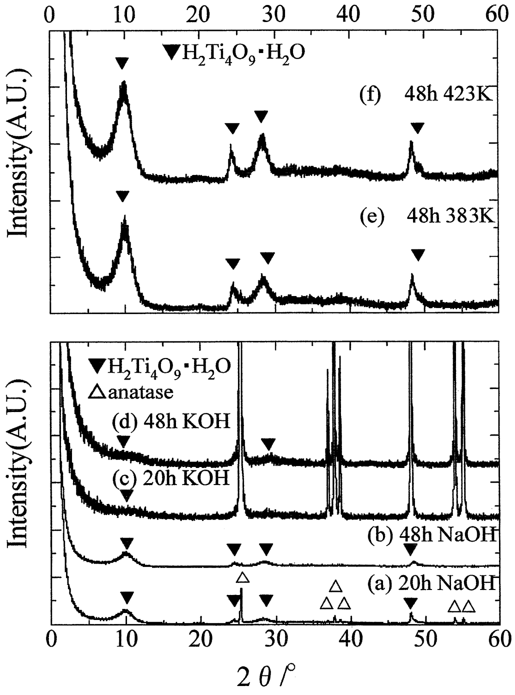

Figure 2 XRD results of products from anatase TiO_2 after a hydrothermal treatment at 383 K in a NaOH solution for 20 h (a) and 48 h (b) and in a KOH solution for 20 h (c) and 48 h (d). XRD results of products synthesized by hydrothermal treatment at 383 K (e) and 423 K (f) in a NaOH solution for 48 h.

After the hydrothermal treatment of P-25 TiO_2 as starting material in a NaOH solution at 383 K, the XRD results are shown in Fig. 3. P-25 TiO_2 is the mixture of anatase and rutile (3:1) [9]. The XRD peaks found are similar to those of $H_2Ti_4O_9{\cdot}H_2O$ as shown in Fig. 1. However, even after 20 h of hydrothermal treatment at 383 K, $H_2Ti_4O_9{\cdot}H_2O$ was only confirmed without anatase being found. In case of P-25 TiO_2, products hydrothermally-treated in a NaOH solution at 383 K for 20 to 168 h were identified as $H_2Ti_4O_9{\cdot}H_2O$. Fig. 4 shows the XRD patterns after hydrothermal treatments of rutile TiO_2 as starting material. A very weak peak around 10° from $H_2Ti_4O_9{\cdot}H_2O$ is observed. The main peak of rutile, (110) at 2 theta of 27.5°, decreased with hydrothermal reaction time. Also, products after the hydrothermal treatment for 20 h had a small peak at 2 theta of 25.5° from (101) of anatase phase in addition of rutile. This peak of anatase decreased with hydrothermal reaction time and diminished after 96 h. Consequently, it was found that the formation of $H_2Ti_4O_9{\cdot}H_2O$ from P-25 TiO_2 was faster than from anatase TiO_2 or rutile TiO_2 as starting material. This difference of the formation of $H_2Ti_4O_9{\cdot}H_2O$ is suggested to result from the particle size of the starting powders, as P-25 TiO_2 was

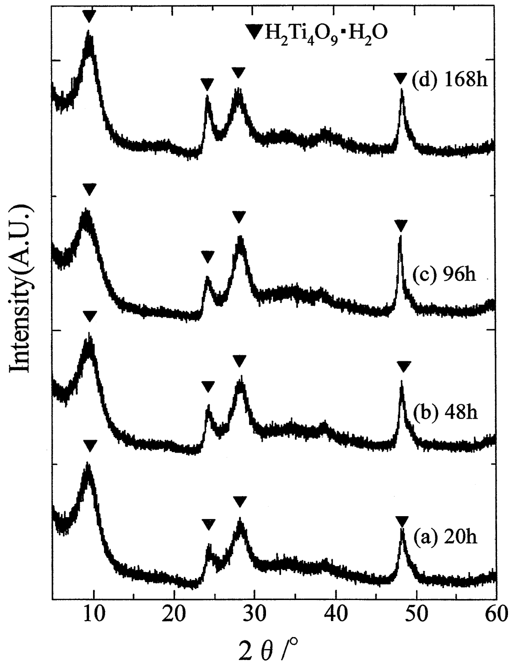

Figure 3 XRD results after a hydrothermal treatment of P-25 TiO_2 as starting material in a NaOH solution at 383 K.

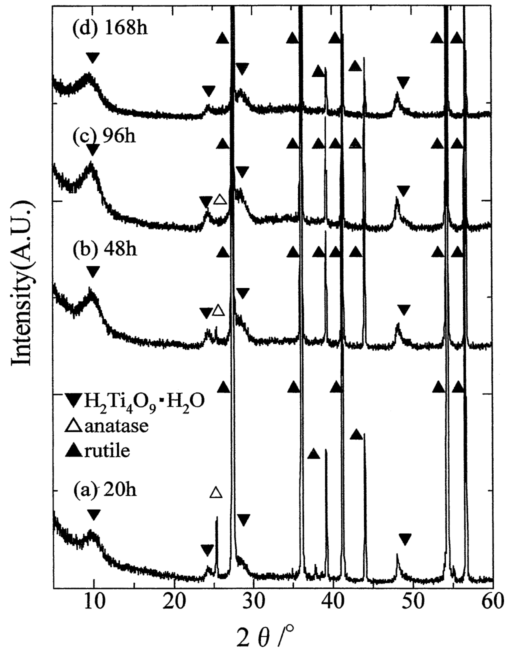

Figure 4 XRD patterns after a hydrothermal treatment from rutile TiO_2 as starting material in a NaOH solution at 383 K.

the powder with the smallest particles. Therefore, XRD results suggest that the formation of $H_2Ti_4O_9{\cdot}H_2O$ after a hydrothermal treatment depends on the reaction time, temperature and starting materials in NaOH and KOH solution systems.

Fig. 5A–C show the microstructures of products after a hydrothermal treatment of anatase TiO_2 as starting material by SEM and TEM observations. Tubular and fibrous products with 10–20 nm in diameter and some hundred nm in length are observed after the hydrothermal treatment for 20 and 96 h at 383 K. These products further grew with reaction time of the hydrothermal treatment. Fig. 6A and B further shows the microstructure of products after a hydrothermal treatment from anatase TiO_2 as starting material in both KOH and NaOH solutions for 20 h at 383 K. According to TEM and SEM observations, products prepared from NaOH and KOH solution both showed tubular and fibrous morphologies with 10–20 nm in diameter and some hundred nm in length (TEM images not shown here). It is found that the products in the KOH system have the same tubular morphology as the ones in a NaOH system after hydrothermal treatment for 20 h at 383 K, although the XRD results did not show the formation of $H_2Ti_4O_9{\cdot}H_2O$ after a hydrothermal treatment in a KOH solution for 20 h at 383 K. Furthermore, Fig. 6C and D show SEM images of the products prepared in a NaOH solution for 48 h at 383 and 423 K. TEM observations show that these products from hydrothermal treatment in NaOH and KOH solution were tubular (not shown here). And even at 423 K, fibrous and tublar products were observed. Therefore, it is suggested that tubular and fibrous products can be prepared at 233 to 423 K in NaOH and KOH solutions in these hydrothermal treatments.

The products after a hydrothermal treatment of P-25 TiO_2 were observed by SEM for various reaction times. Fig. 7A–C show SEM images and TEM images of products of P-25 TiO_2 after hydrothermal treatment for 20 and 96 h. SEM observation shows the fibrous morphology for all products after the hydrothermal treatments. Fig. 7C shows TEM results of microstructural observations of product after 96 h under hydrothermal treatment through P-25 TiO_2 as a starting material, with both of these products being fine and tubular. However, after 168 h, tubular products were obtained (data not shown). Fig. 7D–F show SEM images and TEM image of products after a hydrothermal treatment from rutile TiO_2 as starting material for various reaction times. As shown in Fig. 7F, tubular morphology was confirmed by TEM results of microstructural observations of product after hydrothermal treatment of rutile for 96 h. Although until 96 h, fine tubular products were observed, the hydrothermal treatment from rutile TiO_2 during 168 h resulted in a product having a larger diameter (whisker and rod-like) than the ones below 96 h. As for anatase TiO_2, however, such thick tubular products diameter (whisker and rod-like) were not obtained after 168 h (not shown here). Furthermore, products from anatase TiO_2 and P-25 TiO_2 after a hydrothermal treatment for 168 h were found to be finer tubular-shaped. Therefore, it is suggested that the microstructures of hydrothermally treated products depend on the crystal structure of the starting TiO_2 material. And, according to TEM observations, a long-term hydrothermal treatment reduced the formation of fine tubular products in case of rutile TiO_2 as starting material.

Fig. 5C and D show the results of microstructural observations and electron diffraction by TEM of tubular products from anatase TiO_2 after a hydrothermal treatment for 96 h in a NaOH solution. According to analysis of the pattern of electron diffraction in Fig. 5D, (220) and (602) of $H_2Ti_4O_9{\cdot}H_2O$ were identified. Additionally, the hexagonal streak in the pattern of electron diffraction is thought to be due to the interlayer of nanotublar $H_2Ti_4O_9$. From these analysis, it was thought

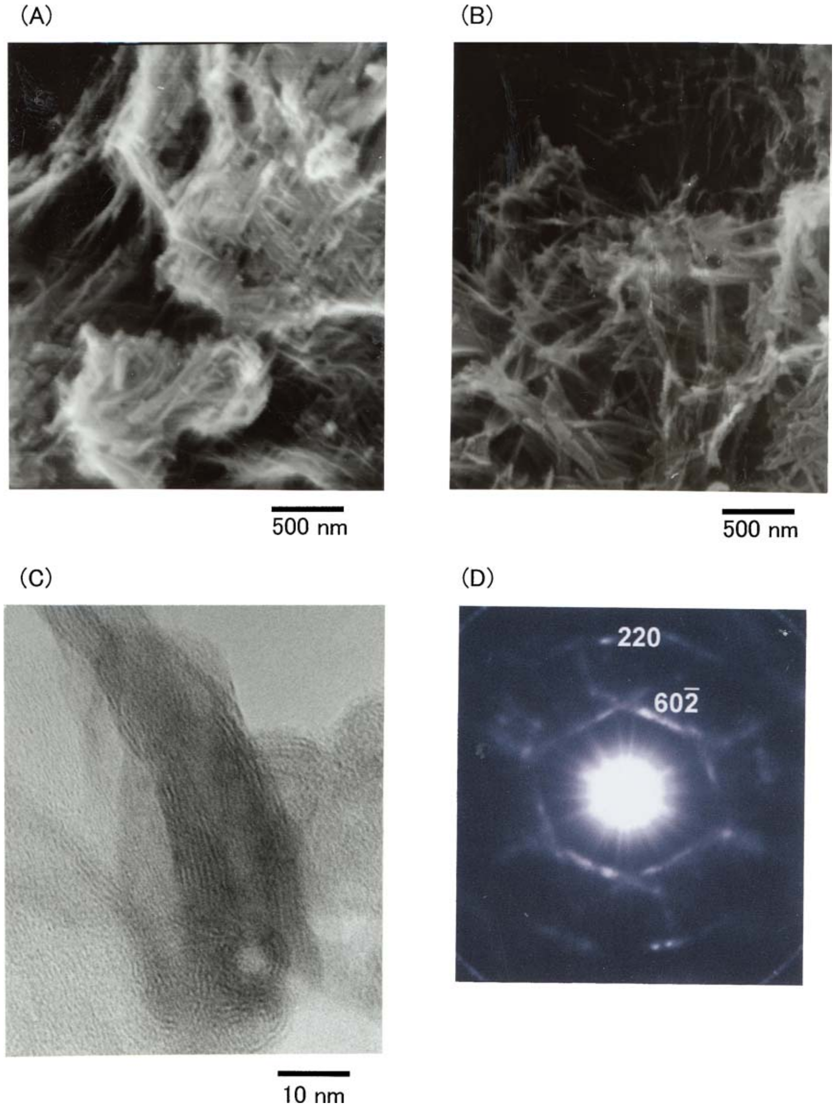

Figure 5 SEM and TEM images of products after hydrothermal treatment from anatase TiO_2 as starting material under various hydrothermal time. (A) SEM after hydrothermal treatment for 20 h, (B) SEM after hydrothermal treatment for 96 h, (C) TEM after hydrothermal treatment for 96 h, and (D) electron diffraction of (C) after hydrothermal treatment for 96 h.

that these nanotubular products were identified to be $H_2Ti_4O_9{\cdot}H_2O$. Furthermore, the TEM image with a low magnification shows agglomeration of a very fine string product. High magnification TEM image of the string product shows the tubular morphology with a diameter smaller than 10 nm. These nanotubular products contained some layers resembling crystalline tubes with multiple shells like a carbon nanotube. The shell spacing of these nanotubular products was found approximately 0.9 nm. Further electron diffraction patters show the nanotubular products are crystalline. Results of diffraction analysis suggest that nanotubular products are titanate, $H_2Ti_4O_9{\cdot}H_2O$, being consistent with the previous found X-ray diffraction results. Kasuga *et al.* reported that their obtained nanotube could be assigned to anatase [5]. Du *et al.* [7] showed that the electron diffraction patterns of their obtained nanotube being synthesized by following the same procedure as Kasuga *et al.* [5] was assigned as $H_2Ti_3O_7$. Nanotubular products synthesized in the present study in a hydrothermal process were identified as $H_2Ti_4O_9{\cdot}H_2O$ according to both TEM and XRD results. Therefore, it is suggested that the hydrothermal treatment of TiO_2 at 383 K results in nanotubular products consisting of $H_2Ti_4O_9{\cdot}H_2O$.

From TEM observations, curved sheet-like products could frequently be observed. Therefore, the formation mechanism of this nanotubular $H_2Ti_4O_9{\cdot}H_2O$ is thought to be related to the formation of layered $H_2Ti_4O_9{\cdot}H_2O$, being constructed from layered trititanate $H_2Ti_3O_7$, and not anatase and rutile. Chen *et al.* [8] proposed that this sheet of layered titanate may be constructed by coiling a sheet of $H_2Ti_3O_7$. As Feist *et al.* [9] pointed out, this layered titanate material is able to undergo a quantitative exchange with alkali metal cations like Ag^+ and Tl^+. Also, Uchida *et al.* [11] reported the synthesis of intercalation of layered $H_2Ti_4O_9$ with some metal and their properties. Therefore, these titanate nanotubes are expected to be applicable in photochemistry as catalysts. Additionally, hydrothermal processing is a simple method that can be easily modified to develop novel titanate nanotubes with metal ions. Chen *et al.* [8] have reported the structure of $H_2Ti_3O_7$ by TEM observations and simulation and proposed that this sheet of a layered titanate might be constructed by the coiling of a sheet of $H_2Ti_3O_7$. We frequently

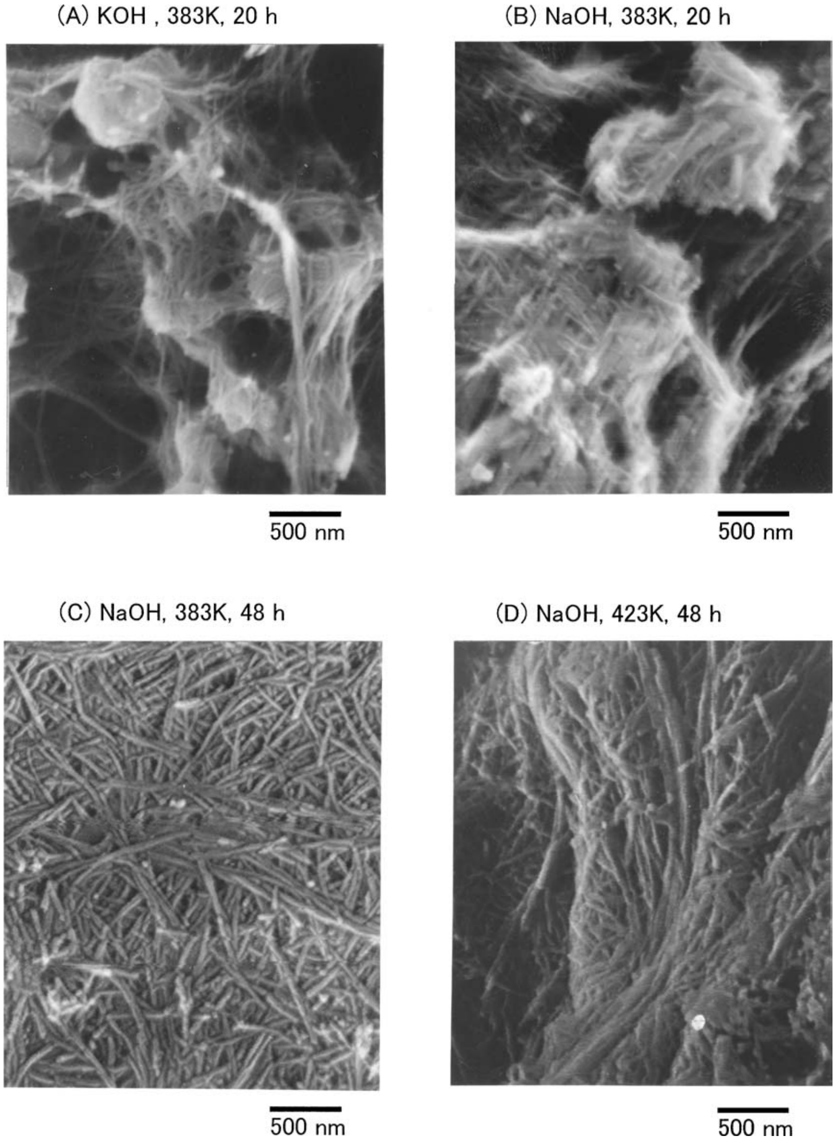

Figure 6 SEM images of products after hydrothermal treatment from anatase TiO_2 as starting material in KOH (A) and NaOH (B) solution for 20 h at 383 K. SEM images of the products prepared in a NaOH solution for 48 h at 383 K (C) and 423 K (D).

observed curved sheets of nanotubular products upon a hydrothermal treatment. Suggesting the possibility that sheet formation during a hydrothermal treatment is related to the formation of nanotubular $H_2Ti_4O_9{\cdot}H_2O$. Also, Kasuga *et al.* [5] have reported that nanotubes obtained in their experiments were formed during the washing process of treated TiO_2 with a HCl solution. Du *et al.* [7], however, suggested that a washing effect was not confirmed in their nanotubes synthesis. In our study, the treatment with a HCl aqueous solution was not found critical for the formation of nanotubular $H_2Ti_4O_9{\cdot}H_2O$, since after a hydrothermal treatment, both products obtained by washing with H_2O instead of 0.1 mol/1 HCl solution and products prepared by washing with a 0.5 mol/1 HCl solution showed the formation of $H_2Ti_4O_9$ by XRD and nanotubular morphology by SEM (not shown here), in which washing with both a HCl solution or H_2O led to nanotubular $H_2Ti_4O_9$. It is suggested that the Na-Ti-O structure after a hydrothermal treatment being washed with a HCl solution or H_2O, results in a proton exchange ($Na^+ \rightarrow H^+$) to form this Na-Ti-O structure.

TABLE I Results of photocatalytic property at 298 K after 2.5 h radiation with a mercury lamp and BET for nanotubular $H_2Ti_4O_9{\cdot}H_2O$ prepared by a hydrothermal treatment in a NaOH solution from anatase TiO_2 as starting material in a NaOH solution at 383 K for 96 h

Treatments	BET (m^2/g)	Decomposition ratio (%)
Non-treatment (anatase TiO_2)	3	37
20 h, 383 K	135	55
48 h, 383 K	185	60
96 h, 383 K	155	65
168 h, 383 K	140	60
48 h, 383 K*	200	30
48 h, 383 K**	160	70
P-25 TiO_2***	49	53

*Nanotubular products prepared by washing with a 0.5 mol/1 HCl solution.

**Nanotubular products prepared by washing with H_2O instead of 0.1 mol/1 HCl solution.

***As-received P-25 TiO_2.

Table I shows the results of photocatalytic property at 298 K after 2.5 h radiation with a mercury lamp and

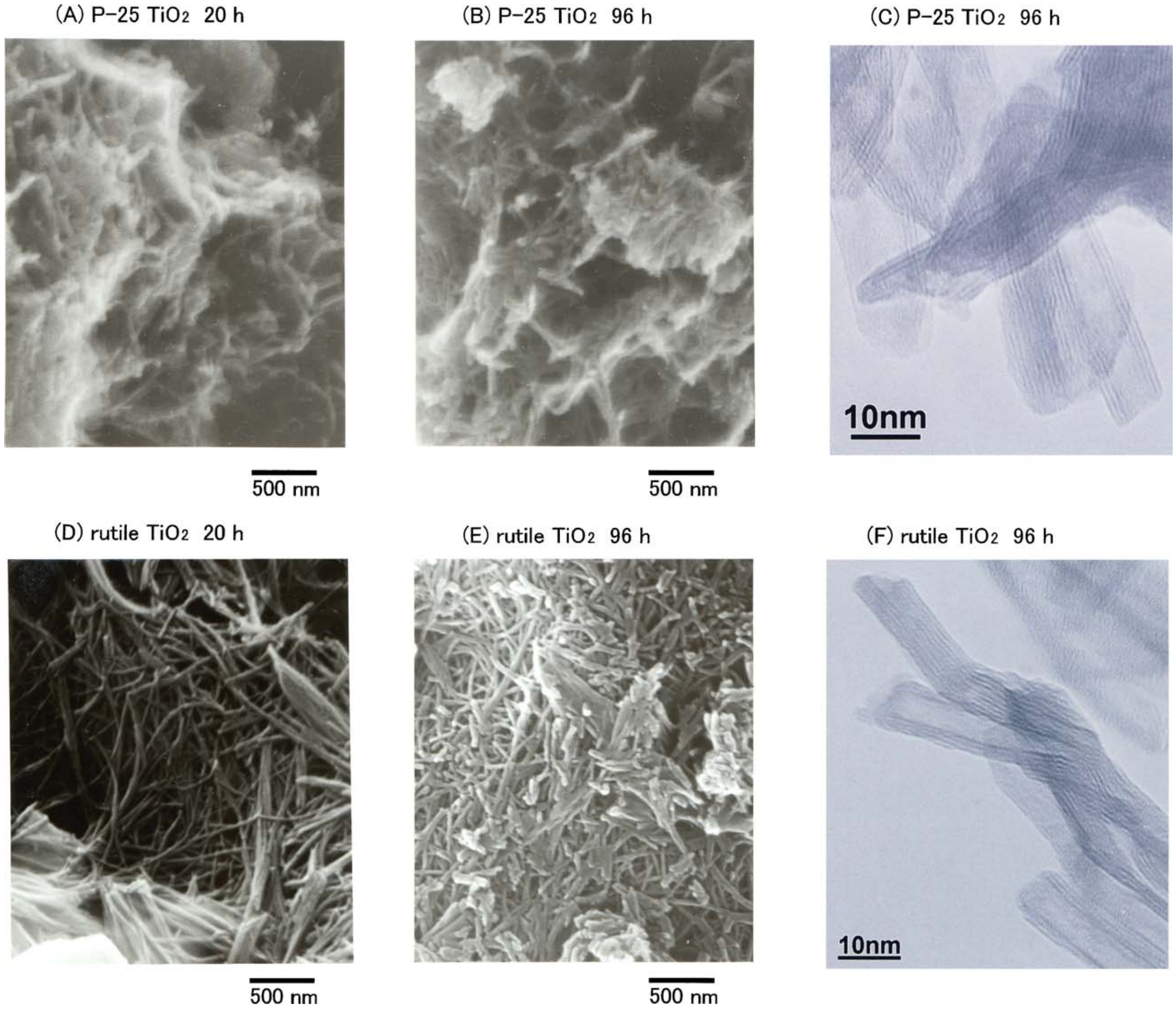

Figure 7 SEM and TEM images of products after hydrothermal treatment: P-25 TiO_2 for SEM after hydrothermal treatment for 20 h (A), SEM after hydrothermal treatment for 96 h (B), TEM after hydrothermal treatment for 96 h (C), rutile TiO_2 for SEM after hydrothermal treatment for 20 h (D), SEM after hydrothermal treatment for 96 h (E), TEM after hydrothermal treatment for 96 h (F).

BET for nanotubular $H_2Ti_4O_9{\cdot}H_2O$ products prepared by a hydrothermal treatment in a NaOH solution from anatase TiO_2 as starting material in a NaOH solution at 383 K for 96 h. As a reference material, photocatalytic properties of P-25 TiO_2 were measured at 298 K after 2.5 h radiation with a mercury lamp and its results were also shown in Table I. P-25 TiO_2 showed a decomposition ratio of 53%. The photocatalytic property was evaluated as the fraction of decomposition of an aqueous HCHO solution after 2.5 h radiation with a mercury lamp (100 W). Non-treated anatase TiO_2 (as-received powder) resulted in a 37% decomposition of the initial HCHO concentration (1000 ppm). The nanotubular products showed a higher decomposition ratio of about 60%, compared to the non-treated one. Using nanotubular products obtained by washing with H_2O instead of 0.1 mol/1 HCl solution possess a much higher decomposition capacity at approximately 70%. However, nanotubular products prepared by washing with a 0.5 mol/1 HCl solution showed lower decomposition ratio. This high decomposition of an aqueous HCHO solution using nanotubular products prepared by this hydrothermal treatment may be caused by a high BET value and a nanotubular structure, compared to P-25 TiO_2. However, the photocatalytic property strongly depends on the synthetic condition of hydrothermal treatments. Consequently, the detailed mechanism of high decomposition capacity for these nanotubular $H_2Ti_4O_9{\cdot}H_2O$ synthesized in this study is now under investigation.

4. Conclusions

Nanotubular $H_2Ti_4O_9{\cdot}H_2O$ could be synthesized by a hydrothermal treatments in a 10 mol/1 NaOH and 10 mol/1 KOH aqueous solution for anatase TiO_2, P-25 TiO_2, and rutile TiO_2 under various conditions. The use of any of these starting materials led to tubular products in a hydrothermal treatment under optimized conditions. The morphology and yield of nanotubular $H_2Ti_4O_9{\cdot}H_2O$ strongly varied with the structure of starting material, hydrothermal reaction time, and temperature in the hydrothermal treatments and washing conditions. Nanotubular $H_2Ti_4O_9{\cdot}H_2O$ prepared by a hydrothermal treatment from anatase TiO_2 in a NaOH solution at 383 K for 96 h possess a much higher decomposition capacity at approximately 60 to 70%.

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Received 15 April 2003
and accepted 8 March 2004