Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 178 (2005) 3110–3116

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Synthesis of titanate, TiO_2 (B), and anatase TiO_2 nanofibers from natural rutile sand

Sorapong Pavasupree[a,*], Yoshikazu Suzuki[a], Susumu Yoshikawa[a,*], Ryoji Kawahata[b]

[a]*Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan*
[b]*Iwatani International Corporation, 4-8, Hommachi 3-Chome, Chuo-ku, Osaka 541-0053, Japan*

Received 8 May 2005; received in revised form 9 June 2005; accepted 22 July 2005
Available online 24 August 2005

Abstract

Titanate nanofibers were synthesized by hydrothermal method (150 °C for 72 h) using natural rutile sand as the starting materials. TiO_2 (B) and anatase TiO_2 (high crystallinity) nanofibers with the diameters of 20–100 nm and the lengths of 10–100 μm were obtained by calcined titanate nanofibers for 4 h at 400 and 700 °C (in air), respectively. The samples characterized by XRD, SEM, TEM, SAED, HRTEM, and BET surface area. This synthesis method provides a simple route to fabricate one-dimensional nanostructured TiO_2 from low cost material.

Keywords: Natural rutile sand; Titanate; TiO_2 (B); Anatase TiO_2; Nanofibers

1. Introduction

The synthesis and characterization of one-dimensional (1-D) nanostructured (nanotubes, nanorods, and nanowires) have received considerable attention due to their unique properties and novel application [1–4]. Much effort has concentrated on the important metal oxides such as TiO_2, SnO_2, VO_2, and ZnO [1–8]. Among them, TiO_2 and TiO_2-derived materials are of importance for utilizing solar energy and environmental purification. TiO_2 has been widely used for various applications such as a semiconductor in dye-sensitized solar cell, water treatment materials, catalysts, gas sensors, and so on [9–14]. TiO_2-derived nanotubes and nanowires can be easily fabricated by treating TiO_2 power with highly concentrated NaOH [15–28]. In our previous works, due to high cost of TiO_2 nanoparticles [18,21,22], the use of natural rutile sand via hydrothermal synthesis was investigated [19], however the products in an earlier study were titanate (not TiO_2) nanofibers. By modifying ion-exchanging treatment, TiO_2 anatase nanofiber/nanoparticle composite powder was also prepared [20].

In this study, TiO_2 (B) and anatase TiO_2 nanofibers obtained by hydrothermal and post-heat-treatments from natural rutile sand will be reported.

2. Experimental

2.1. Synthesis

Titanate nanofibers were synthesized by hydrothermal method (150 °C for 72 h) using natural rutile sand (96.0% TiO_2, yielded in Australia, Tiwest Sales Pty. Ltd., Bentley, Australia) as the starting materials [19,20]. It is worth noting that the cost of natural rutile sand used in this study is <US\$1/kg, which is 1/50–1/100 of a commercial rutile or an anatase powder in an ordinary grade [19].

In a typical synthesis, 300 mg of natural rutile sand (without further purification) brown granules were put

---

*Corresponding authors. Fax: +81 774 38 3508.
E-mail address: s-yoshi@iae.kyoto-u.ac.jp (S. Yoshikawa).

0022-4596/\$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.07.022

into a Teflon-lined stainless steel autoclave. Then, the autoclave was added with 50 mL of 10 M NaOH aqueous solution and heated at 150 °C for 72 h with stirring condition. After the autoclave was naturally cooled to room temperature, the obtained product was washed with HCl aqueous solution, distilled water for several times, followed by freezed drying. The samples were calcined for 4 h at 120–1000 °C in air condition.

2.2. Characterization

The crystalline structure of samples was evaluated by X-ray diffraction (XRD, RIGAKU RINT 2100). The microstructure of the prepared materials was analyzed by scanning electron microscopy (SEM, JEOL JSM-6500FE), transmission electron microscopy (TEM, JEOL JEM-200CX), and selected-area electron diffraction (SAED). The Brunauer–Emmett–Teller (BET) specific surface area was determined by the nitrogen adsorption (BEL Japan, BELSORP-18 Plus).

3. Results and discussion

3.1. The as-synthesized nanofibers

The as-synthesized nanopowders were white (very slightly yellowish) while as the starting natural rutile was brown-colored [19]. The XRD patterns of the starting natural rutile and the as-synthesized nanofibers are shown in Fig. 1(a). The structure of the as-synthesized nanofibers should be similar to that expected for a layered titanate $H_2Ti_xO_{2x+1}$, probably trititanate ($H_2Ti_3O_7$) [19]. No diffraction peaks of other impurities (such as starting rutile and NaCl) were observed.

SEM image of the starting natural rutile shows the granules size about 75–300 μm (Fig. 2(a)). After hydrothermal treatment, the as-synthesized sample showed fiber-like morphology. The length of the nanofibers ranges from several 10 μm to more than 100 μm (Fig. 2(b)). In order to confirm nanofibers were solid (not hollow), TEM experiment should be investigated. TEM and SAED images of the as-synthesized nanofibers are shown in Fig. 3(a). The as-synthesized nanofibers were solid (not hollow) with diameter about 20–50 nm.

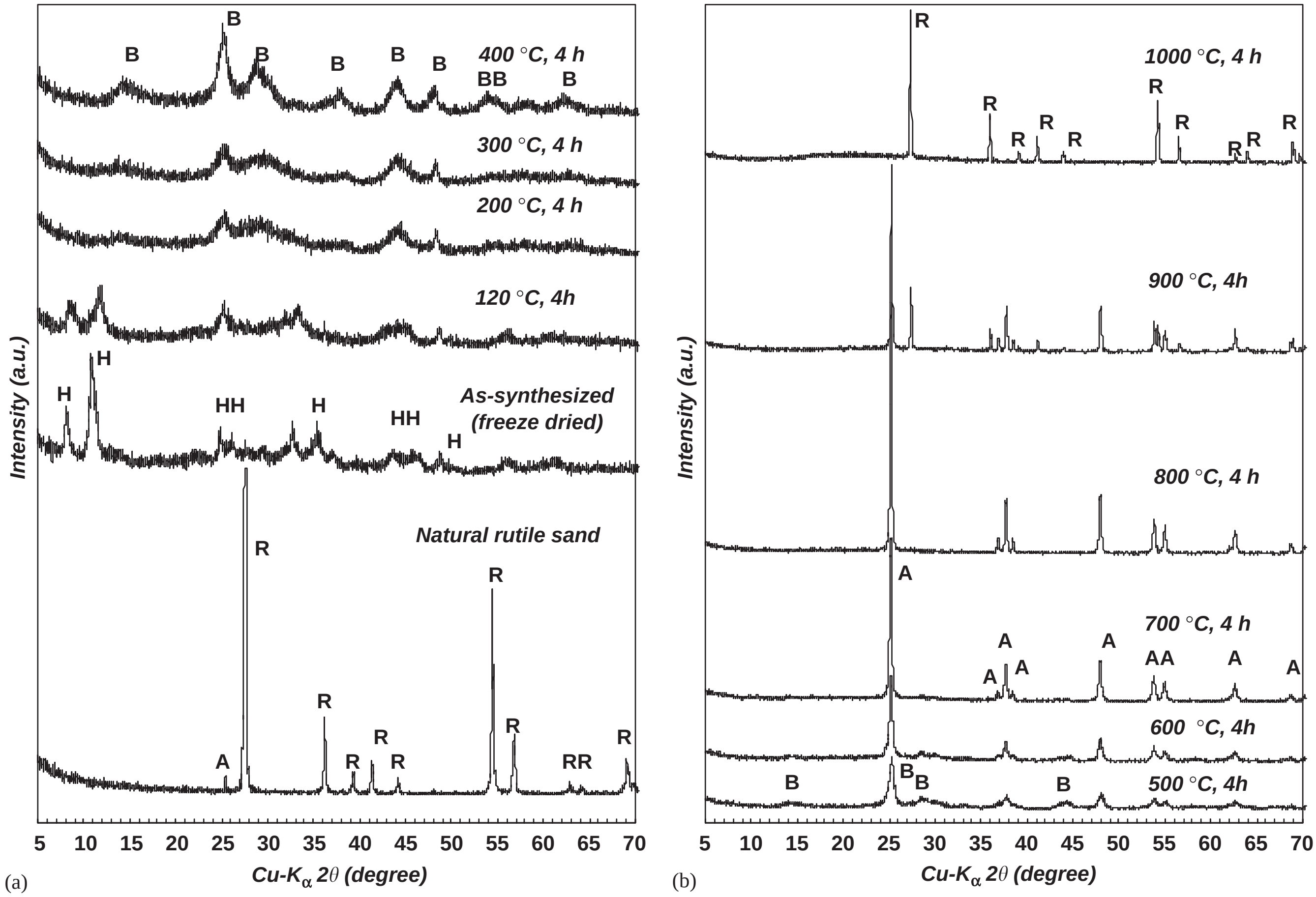

Fig. 1. XRD patterns of the starting natural rutile, the as-synthesized nanofibers, the calcined nanofibers for 4 h at (a) 120–400 °C and (b) 500–1000 °C; A = anatase TiO_2, B = TiO_2 (B), H = hydrogen titanate, and R = rutile TiO_2.

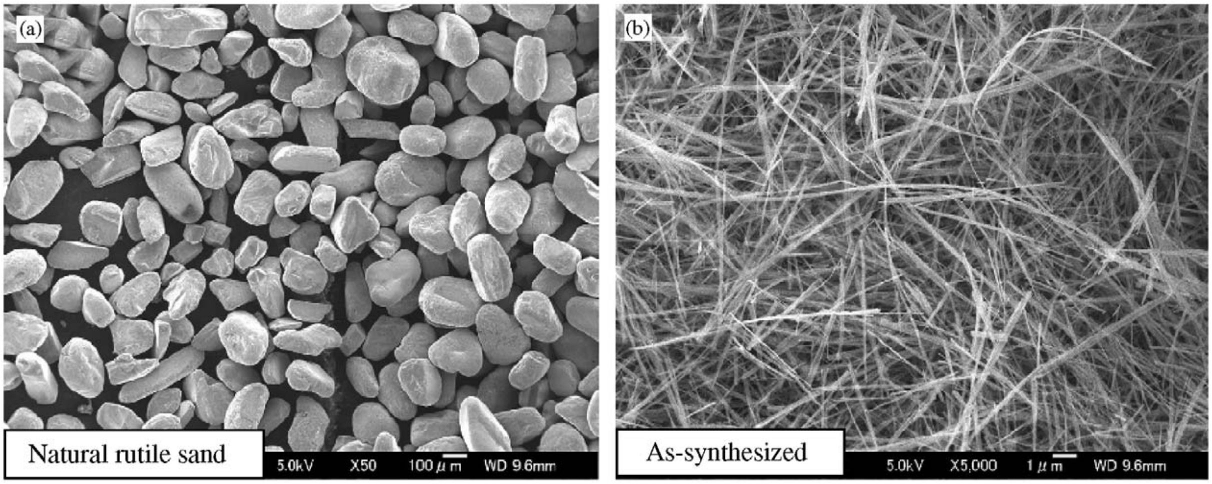

Fig. 2. SEM images of (a) the starting natural rutile and (b) the as-synthesized nanofibers.

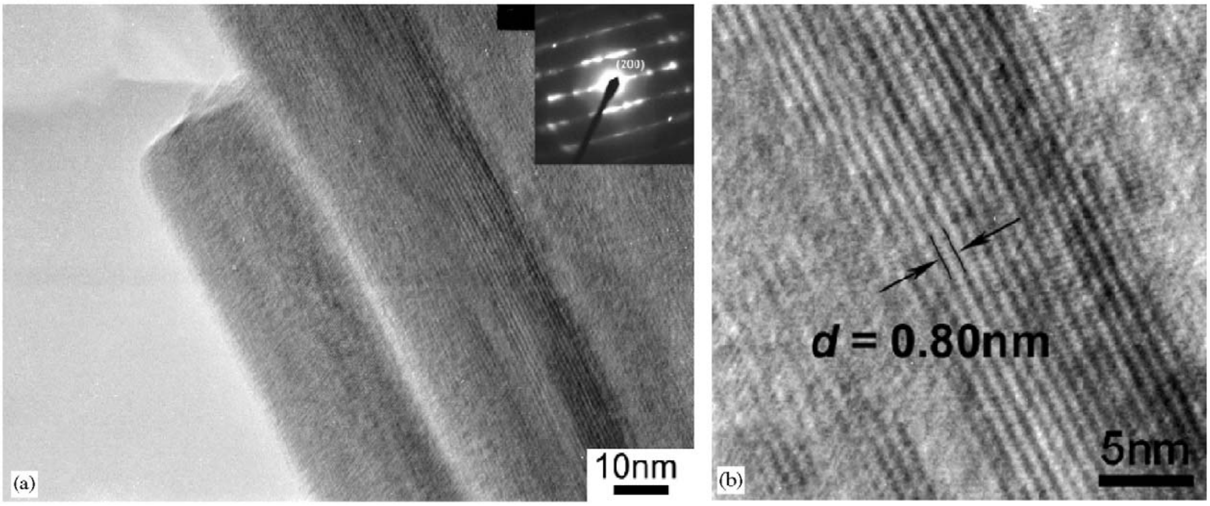

Fig. 3. (a) TEM, (the inset of (a)) SAED, and (b) HRTEM images of the as-synthesized nanofibers.

Nanofibers tend to form bundles, thus some of the nanofibers looked thicker than others. HRTEM image (Fig. 3(b)), the distance between two stripes ($d = 0.80\,\mathrm{nm}$) correspond to (200) plane of trititanate [19]. The BET surface area of the as-synthesized nanofibers (without pre-heating for BET measurement) were about $45\,\mathrm{m^2/g}$, while the BET surface area of the starting natural rutile sand was about $0\,\mathrm{m^2/g}$ (Table 1). Although the nanotube structure is attractive due to its high surface area, titanate nanotubes with free-alkali ions are usually unstable at high temperatures (at ~500 °C) and convert into anatase particles [18,21]. To maintain the 1-D nanostructure at higher temperature (typically at 500–800 °C), the solid nanowires or nanofibers form should be more favorable. In general, hydrothermal treatment at a slightly higher temperature (~150 °C or higher) or in stronger alkali solution (conc. NaOH(aq.)or KOH(aq.)) results in the formation of solid nanowires (or even long nanofibers) rather than scrolled nanotubes, because the normal unidirectional crystal growth becomes preferential at these conditions. This phenomenon can be explained by following mechanism. The natural rutile granules were coarse so that they slowly dissolved into NaOH solution, which suppressed the nucleation and assisted preferential crystal growth along with the 0 1 0 direction of trititanate [19]. In addition, for the current study, impurity element in natural rutile source might act as a catalyst for the fibrous crystal growth [19].

3.2. The TiO_2 (B) nanofibers

Fig. 1(a) also shows the XRD patterns of the nanofibers calcined for 4 h at 120, 200, 300, and

Table 1
Summarized results of the samples

Conditions	Morphology	Crystalline structure	BET surface area (m^2/g)
Starting material	Micrograules (75–300 μm)	TiO_2 (rutile)	0
As-synthesized	Nanofibers (20–50 nm)	$H_2Ti_xO_{2x+1}$ ($H_2Ti_3O_7$)	45
Calcined at 400 °C, 4 h	Nanofibers (20–70 nm)	TiO_2 (B)	20
Calcined at 700 °C, 4 h	Nanofibers (20–100 nm)	TiO_2 (anatase)	10
Calcined at 1000 °C, 4 h	Submicron rod-like (200 nm–1 μm)	TiO_2 (rutile)	2

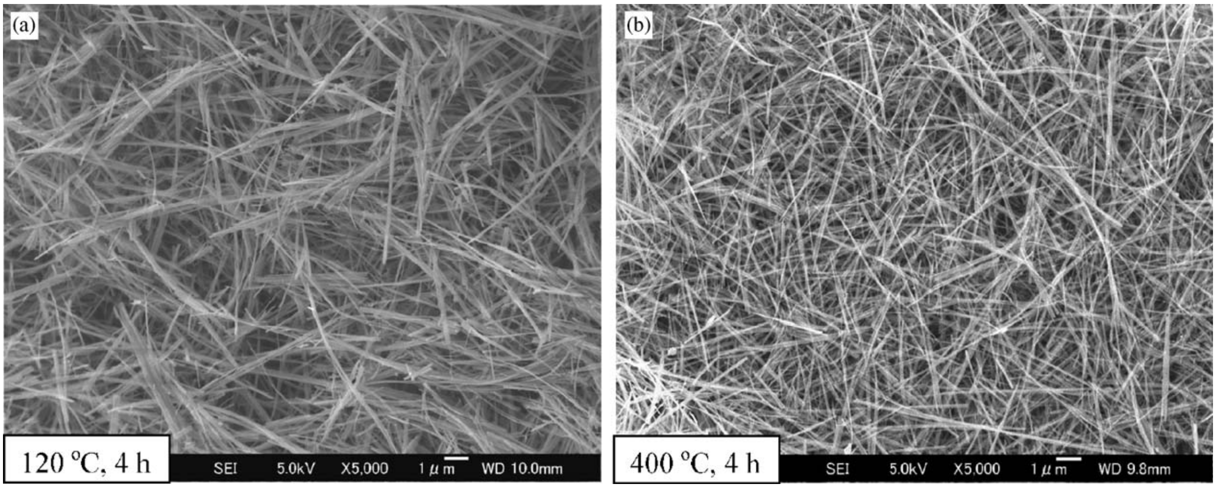

Fig. 4. SEM images of the calcined nanofibers for 4 h at (a) 120 °C and (b) 400 °C.

400 °C, respectively. After calcination at the temperature range of 200—400 °C, the nanofibers are dehydrated and re-crystallized into the metastable form of TiO_2 (B) [18–22]. Annealing a sample of the acid-washed wires at 400 °C for 4 h in air produces a material which gave the powder diffraction pattern of TiO_2 (B) [17]. However, TiO_2 (B) nanofibers derived from natural rutile sand have not been extensively reported.

Fig. 4 shows SEM images of the nanofibers calcined for 4 h at 120 and 400 °C, respectively. From SEM images, the nanofibers calcined for 4 h at 120–400 °C seem to be not quite different in the length of nanofibers. TEM and SAED images of the nanofibers calcined at 400 °C for 4 h show in Fig. 5(a). Individual nanofibers with diameter around 35 nm were observed and the diffraction patterns can be indexed as TiO_2 (B). We can also observe lattice fringes of the nanofibers (HRTEM image, Fig. 5(b)) with the distance about 0.62 and 0.36 nm, which corresponding to (001) and (110) planes (angels between planes: 85°), allowing for the identification of the monoclinic phase [30]. The BET surface area of the nanofibers calcined at 400 °C for 4 h were about 20 m^2/g (Table 1).

3.3. The anatase TiO_2 nanofibers

XRD patterns of the nanofibers calcined for 4 h at 500, 600, 700, 800, 900, and 1000 °C are shown in Fig. 1(b), respectively. The nanofibers calcined for 4 h at 500–600 °C consisted of a mixture of TiO_2 (B) and anatase TiO_2. The peak intensity corresponding to the TiO_2 (B) decreased as the calcination temperature was increased and almost disappeared at 700–800 °C, whereas that corresponding to anatase TiO_2 increased. The peaks corresponding to rutile TiO_2 appeared at 900 °C and the intensity increased with increasing temperature (1000 °C).

Fig. 6 gives SEM images of the nanofibers calcined for 4 h at 500, 700, 900, and 1000 °C, respectively. The nanofibers calcined for 4 h at 500–900 °C maintained nanofiber morphology. Normally, the TiO_2-derived nanotubes after heat-treatment at 400 °C (anatase phase) were destroyed and change into particles [21,23] and the phase transformation from anatase phase TiO_2 to rutile phase TiO_2 begins to appear at 600–700 °C [14,29]. However, anatase TiO_2 nanofibers, prepared by this method, are stable at 700–800 °C. Therefore,

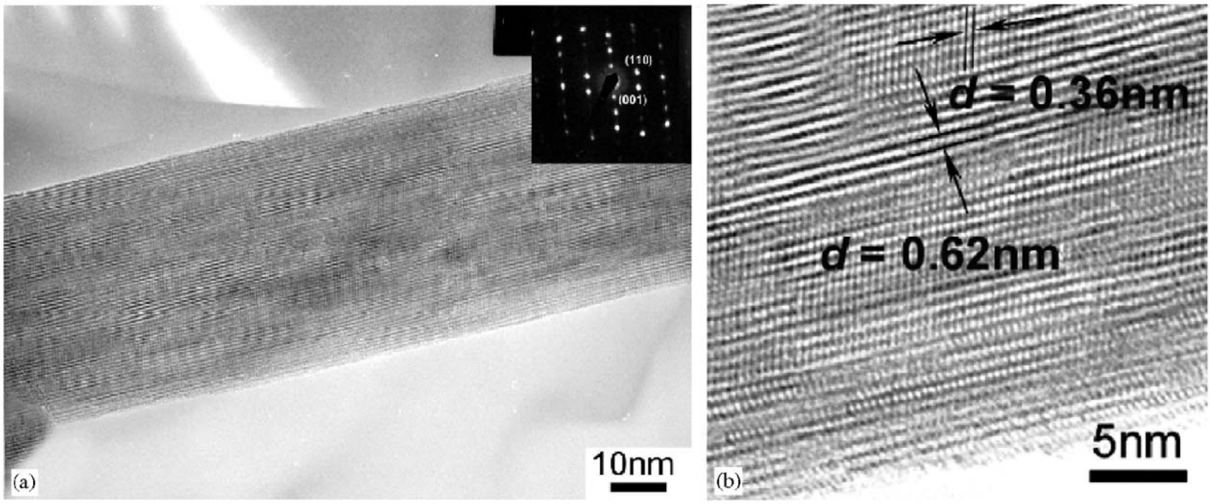

Fig. 5. (a) TEM, (the inset of (a)) SAED, and (b) HRTEM images of the nanofibers calcined at 400 °C for 4 h, indicating TiO_2 (B) structure.

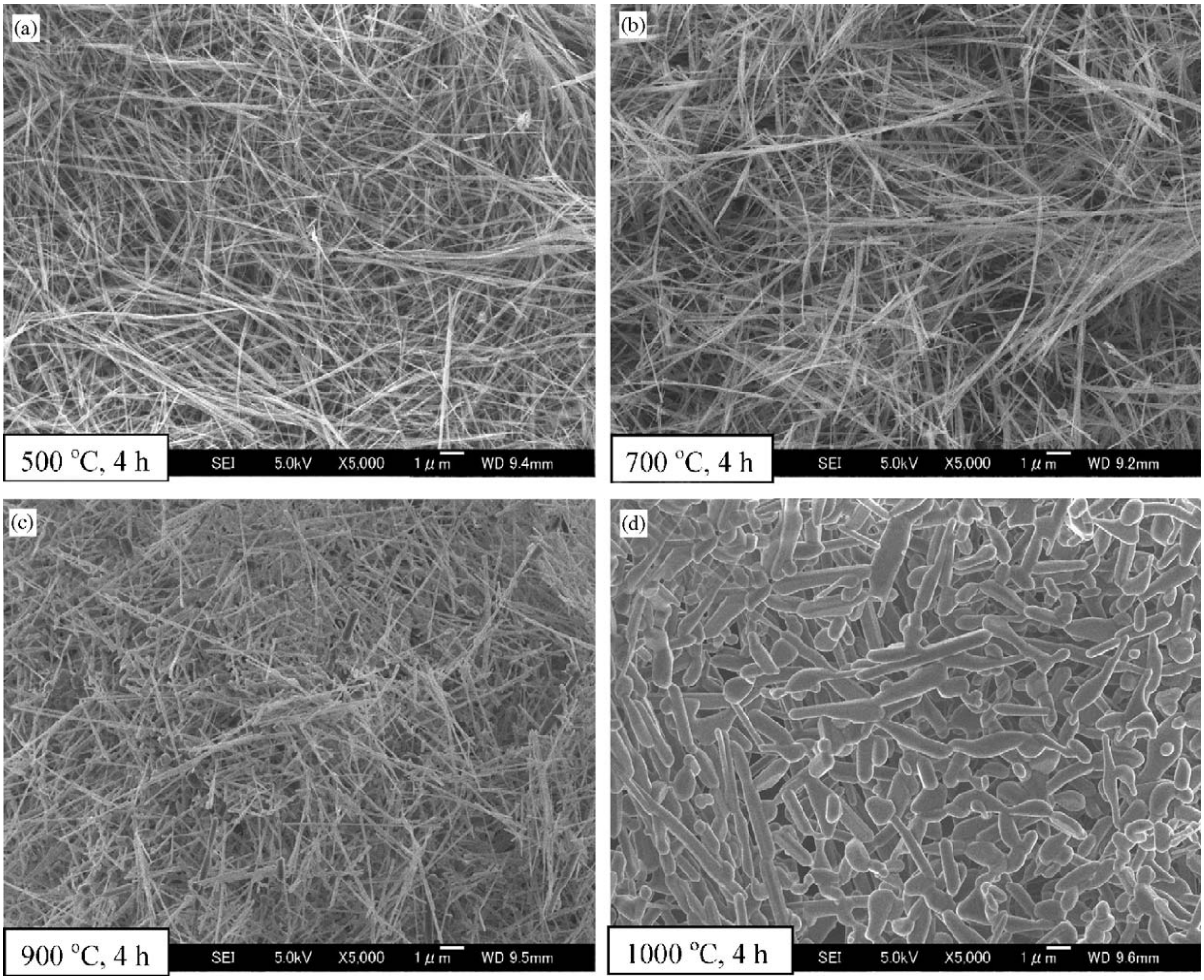

Fig. 6. SEM images of the calcined nanofibers for 4 h at (a) 500 °C, (b) 700 °C, (c) 900 °C, and (d) 1000 °C, respectively.

anatase TiO_2 nanofibers can be used at high temperatures. The nanofibers calcined at 1000 °C for 4 h show submicron rod-like structure of rutile TiO_2 (Fig. 6(d)). TEM and SAED images reveal that nanofibers calcined at 700 °C for 4 h (with diameter about 25 nm) compose of anatase phase TiO_2 (Fig. 7(a)). The lattice fringes of

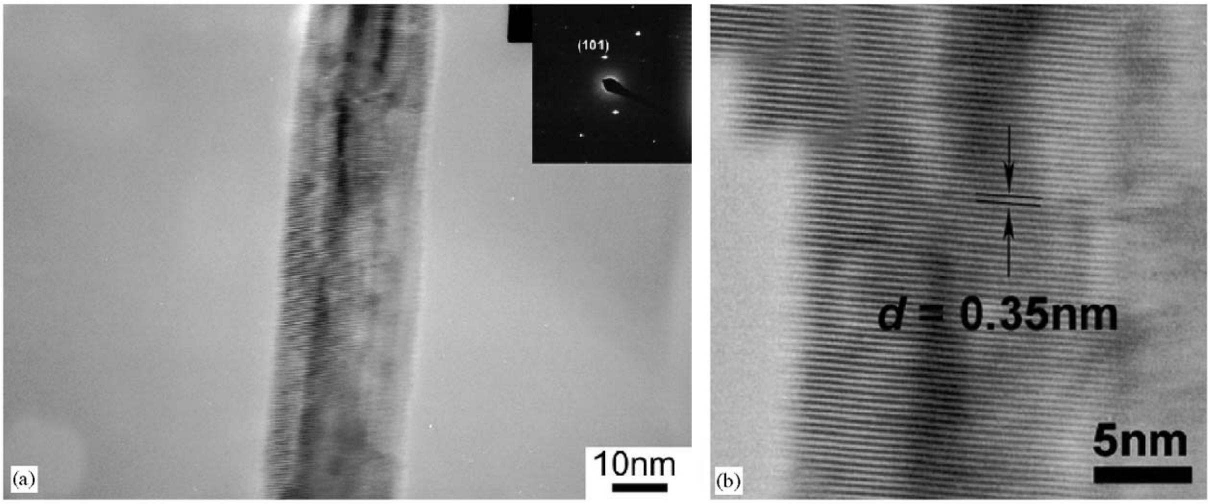

Fig. 7. (a) TEM, (the inset of (a)) SAED, and (b) HRTEM images of the nanofibers calcined at 700 °C for 4 h, indicating anatase TiO_2 structure.

the nanofibers (HRTEM image, Fig. 7(b)) show the distance about 0.35 nm, which corresponding to (101) plane of the anatase phase [31]. HRTEM images of nanorods with clear lattice fringes, again confirming its high crystallinity. The BET surface area of the nanofibers calcined for 4 h at 700 and 1000 °C were about 10 and 2 m^2/g, respectively (Table 1).

4. Conclusions

In summary, titanate nanofibers were synthesized by hydrothermal method (150 °C for 72 h) using natural rutile sand as the starting materials. TiO_2 (B) and anatase TiO_2 (high crystallinity) nanofibers with the diameters of 20–100 nm and the lengths of 10–100 μm were obtained by calcined titanate nanofibers for 4 h at 400 and 700 °C (in air), respectively. At higher temperature than 900 °C, they begin to change into rutile-type TiO_2 rod-like structure. The operation of this synthesis method is a simple hydrothermal method and all the reactions of the synthetic process are carried out in aqueous solution.

Acknowledgments

The authors would like to express gratitude to Prof. S. Isoda and Prof. H. Kurata, Institute for Chemical Research, Kyoto University for the use of TEM apparatus Prof. T. Yoko, Institute for Chemical Research, Kyoto University for the use of XRD equipment. We acknowledge the anonymous reviewer for the helpful discussion to improve the manuscript.

References

[1] C.N.R. Rao, M. Nath, Dalton Trans. 1 (2003) 1.
[2] G.R. Patzke, F. Krumeich, R. Nesper, Angew. Chem. Int. Ed. 41 (2002) 2446.
[3] M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science 292 (2001) 1897.
[4] Z.W. Pan, Z.R. Dai, Z.L. Wang, Science 291 (2001) 1947.
[5] L. Miao, S. Tanemura, S. Toh, K. Kaneko, M. Tanemura, Appl. Surf. Sci. 238 (2004) 175.
[6] C. Xu, Y. Zhan, K. Hong, G. Wang, Solid State Commun. 126 (2003) 545.
[7] B. Cheng, J.M. Russell, W. Shi, L. Zhang, E.T. Samulski, J. Am. Chem. Soc. 126 (2004) 5972.
[8] S. Pavasupree, Y. Suzuki, A. Kitiyanan, S. Pivsa-Art, S. Yoshikawa, J. Solid State Chem. 178 (2005) 1948.
[9] M. Grätzel, Nature 414 (2001) 338.
[10] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C 1 (2000) 1.
[11] S. Ngamsinlapasathian, T. Sreethawong, Y. Suzuki, S. Yoshikawa, Sol. Energy Mater. Sol. Cells 86 (2005) 269.
[12] S. Pavasupree, Y. Suzuki, S. Pivsa-Art, S. Yoshikawa, Ceram. Int. 31 (2005) 959–963.
[13] S. Pavasupree, Y. Suzuki, S. Pivsa-Art, S. Yoshikawa, J. Solid State Chem. 178 (2005) 128.
[14] T. Sreethawong, Y. Suzuki, S. Yoshikawa, J. Solid State Chem. 178 (2005) 329.
[15] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Langmuir 14 (1998) 3160.
[16] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Adv. Mater. 11 (1999) 1307.
[17] A.R. Armstrong, G. Armstrong, J. Canales, P.G. Bruce, Angew. Chem. Int. Ed. 43 (2004) 2286.
[18] Y. Suzuki, S. Yoshikawa, J. Mater. Res. 19 (2004) 982.
[19] Y. Suzuki, S. Pavasupree, S. Yoshikawa, R. Kawahata, J. Mater. Res. 20 (2005) 1063.
[20] Y. Suzuki, S. Pavasupree, S. Yoshikawa, R. Kawahata, J. Am. Ceram. Soc., in contribution.
[21] R. Yoshida, Y. Suzuki, S. Yoshikawa, Mater. Chem. Phys. 91 (2005) 409.
[22] R. Yoshida, Y. Suzuki, S. Yoshikawa, J. Solid State Chem. 178 (2005) 2179.

[23] C.-C. Tsai, H. Teng, Chem. Mater. 16 (2004) 4352.
[24] Y.X. Zhang, G.H. Li, Y.X. Jin, Y. Zhang, J. Zhang, L.D. Zhang, Chem. Phys. Lett. 365 (2002) 300.
[25] Z.-Y. Yuan, B.-L. Su, Colloids Surf. A 241 (2004) 173.
[26] H.Y. Zhu, Y. Lan, X.P. Gao, S.P. Ringer, Z.F. Zheng, D.Y. Song, J.C. Zhao, J. Am. Chem. Soc. 127 (2005) 6730.
[27] X.-D. Meng, D.-Z. Wang, J.-H. Liu, S.-Y. Zhang, Mater. Res. Bull. 39 (2004) 2163.
[28] A. Thorne, A. Kruth, D. Tunstall, J.T.S. Irvine, W. Zhou, J. Phys. Chem. B 109 (2005) 5439.
[29] K.C. Song, S.E. Pratsinis, J. Colloid Interface Sci. 231 (2000) 289.
[30] ICDD-JCPDS database, #46-1238 (TiO_2 (B)).
[31] ICDD-JCPDS database, #21-1272 (anatase TiO_2).