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Syntheses of TiO_2(B) nanowires and TiO_2 anatase nanowires by hydrothermal and post-heat treatments

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Abstract

TiO_2(B) nanowires and TiO_2 anatase nanowires were synthesized by the hydrothermal processing in 10 M NaOH aq. at 150 °C followed by the post-heat treatment at 300–800 °C. As-synthesized Na-free titanate nanowires (prepared by the hydrothermal treatment and repeated ion exchanging by HCl (aq.) were transformed into TiO_2(B) structure with maintaining 1-D morphology at 300–500 °C, and further transformed into anatase structure at 600–800 °C with keeping 1-D shape. At 900 °C, they transformed into rod-shaped rutile grains. Microstructure of these 1-D TiO_2 nanomaterials is reported.

Keywords: Hydrothermal process; TiO_2(B) nanowire; Anatase nanowire; Microstructure

1. Introduction

One-dimensional TiO_2-related materials, such as nanotubes, nanowires, and nanofibers have attracted particular interest because of their unique microstructure and promising functions. After the pioneer work on TiO_2-related nanotubes preparation by Kasuga et al. [1,2] the hydrothermal method in alkali solution has become one of the most powerful techniques to prepare a wide range of TiO_2-related 1-D nanomaterials. In their original work [1,2] single crystal nanotubes (firstly reported as TiO_2-anatase) with small diameter of ca.10 nm were obtained by the hydrothermal treatment of TiO_2 powder in 10 M NaOH aqueous solution, without using any templates.

Many groups have tried to modify the processing or to analyze the structure of the nanotubes, and have reported that the synthetic mechanism should be the sheet folding [3–5]; the nanotubes are composed of a layered titanate rather than TiO_2 anatase, that is, reported as $H_2Ti_3O_7 \cdot xH_2O$ [6–8], $Na_xH_{2-x}Ti_3O_7$ [9], $H_2Ti_4O_9 \cdot H_2O$ [10], $H_2Ti_2O_4(OH)_2$ [11], and so on.

The hydrothermal method has been expanded to prepare other TiO_2-related 1-D nanomaterials, such as $K_2Ti_6O_{13}$ nanowires [12], $H_2Ti_3O_7$–$H_2Ti_6O_{13}$ nanofibers [13], and TiO_2(B) nanowires [14]. 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. 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 [8,15,16]. To maintain the 1-D nanostructure at higher temperature (typically at 500–800 °C), the solid nanowire form should be more favorable.

As mentioned above, Armstrong et al. have recently synthesized TiO_2(B) nanowires via hydrothermal treatment and post-heat treatment [14]. TiO_2(B) is a metastable polymorph formed by the dehydration of layered or tunnel-structured hydrogen titanate first

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synthesized in 1980 [17–20], and also called as monoclinic TiO_2 [21]. Owing to its low density and tunnel structure, TiO_2(B) can be a promising Li intercalation host material [14,22]. Although some properties of hydrothermally synthesized TiO_2(B) nanowires have been reported [14,23], further studies are required to put them into actual applications.

In this paper, synthesis of TiO_2(B) nanowires by hydrothermal and post-heat treatments will be reported in detail. Furthermore, synthesis of TiO_2 anatase nanowires by the similar processing (obtained by post-heat treatment at higher temperature) will be also reported. As is reported earlier by Brohan et al., TiO_2(B) transforms into anatase above ~550 °C [24]. Thus, by optimizing the post-heat treatment temperature, TiO_2 anatase nanowires are successfully obtained.

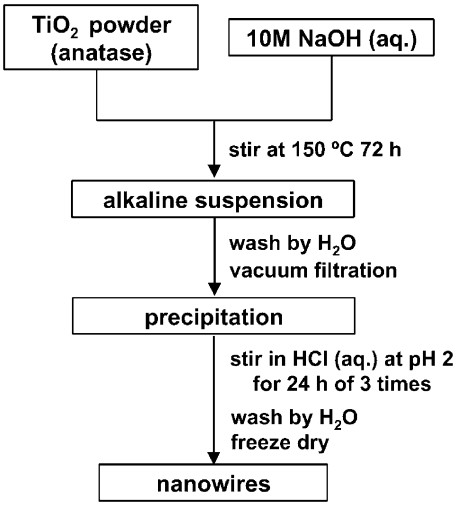

Fig. 1. Schematic representation for experimental procedure.

2. Experimental procedure

2.1. Synthesis of titanate nanowires by hydrothermal synthesis

A commercial, fine TiO_2 (anatase) powder (Ishihara Sangyo Ltd., ST-01, ~300 m^2/g) was used as a starting material. A total of 2 g of TiO_2 powder and 25 mL of 10 M NaOH aqueous solution were put into a Teflon-lined stainless autoclave (the rate of TiO_2 powder and NaOH aq. is 0.08 g/mL). The autoclave was heated and stirred at 150 °C for 72 h. After it was cooled down to room temperature, it was washed by H_2O and filtered in the vacuum. The obtained precipitation was put into 500 mL of HCl aqueous solution at pH2 and stirred for 24 h. After 24 h, the solution was centrifuged and the precipitation was obtained. This HCl treatment was repeated 3 times in order to remove residual Na ions [16]. After HCl treatment the obtained precipitation was washed by distilled water and dried by freeze dryer. The as-synthesized titanate powder was composed of nanowires with no residual Na ions. The experimental procedure is shown in Fig. 1.

2.2. Post-heat treatment of TiO_2-related nanowires

Titanate nanowires, obtained by the above-mentioned method, were heated in an air atmosphere at 100–900 °C for 2 h. Crucibles containing as-synthesized nanowires were put into a preheated oven of 100–900 °C. After 2 h heat-treatment, they were taken out from the oven and cooled down to the room temperature.

2.3. Characterization

The microstructures of the as-synthesized and the heat-treated samples were observed by scanning electron microscopy (SEM; JEOL, JSM-6500FE) and transmission electron microscopy (TEM; JEOL, JEM-200CX). The powder X-ray diffraction (XRD) patterns of the samples were obtained by Rigaku RINT-2100 diffractometer (Cu$K\alpha$ radiation, operated at 40 kV and 40 mA). The dehydration and transformation behavior of as-synthesized nanowires was also analyzed by thermogravimetry-differential thermal analysis (TG-DTA; SHIMADZU, DTG-50 H).

3. Results and discussion

3.1. As-synthesized nanowires

Fig. 2 shows the SEM images, TEM images and nitrogen adsorption isotherms of the samples prepared by hydrothermal method for 72 h at (a–c) 120 °C and (d–f) 150 °C, respectively. Both samples were H_2O washed, acid treated at pH2 for 24 h, 3 times, and then freeze-dried. As described in introduction part, the 120 °C-treated sample was composed of titanate nanotubes and the 150 °C-treated one was composed of titanate nanowires. From the SEM images, both diameter and length of nanowires were larger than those of nanotubes; the diameter and length of nanowires were about 10–50 nm and several μm, respectively. TEM images and nitrogen adsorption isotherms clearly indicated the difference of nanotubes and nanowires. The 150 °C-treated sample was solid (not hollow) (Fig. 2(e)) and did not contain mesopores (Fig. 2(f)). Although mesopores in nanotubes (Fig. 2(c)) are attractive to obtain a high-surface area material, they destabilize 1-D nanostructure at ~500 °C [16]. The hydrothermal temperature to obtain solid nanowires in our study, 150 °C, was 20 °C lower than Armstrong et al. [14]. This slight difference can be attributable to the use of hot-stirrer during the hydrothermal processing.

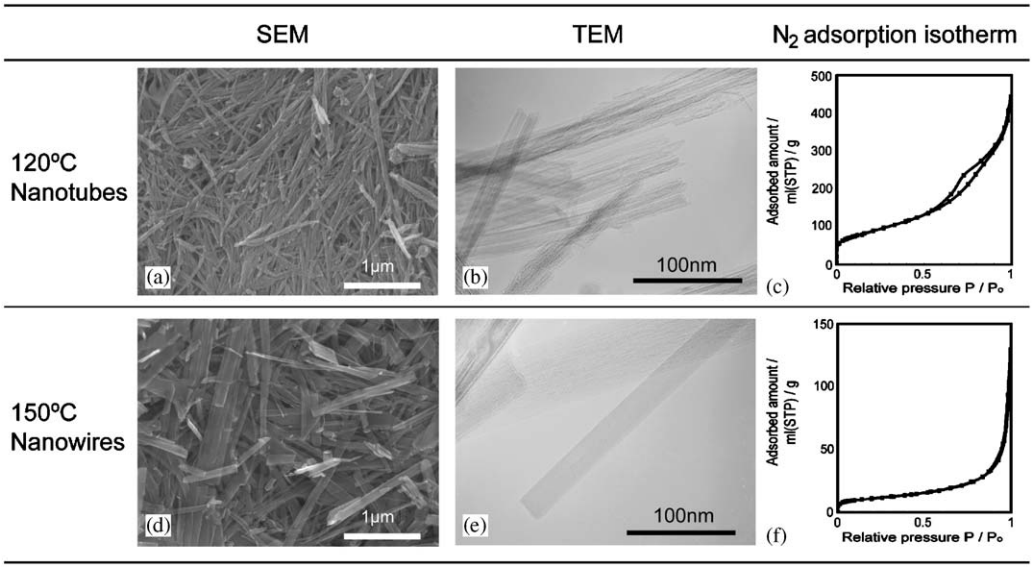

Fig. 2. SEM, TEM images and N_2 adsorption isotherms of the samples prepared by hydrothermal method for 72 h: (a–c) at 120 °C; (d–f) at 150 °C. After the hydrothermal treatment, samples were washed by H_2O and subsequently HCl treated at pH2 for 3 times, respectively; IUPAC type-IV pattern (indicating the mesopores) was observed in Fig. 2(c) but not in Fig. 2 (f).

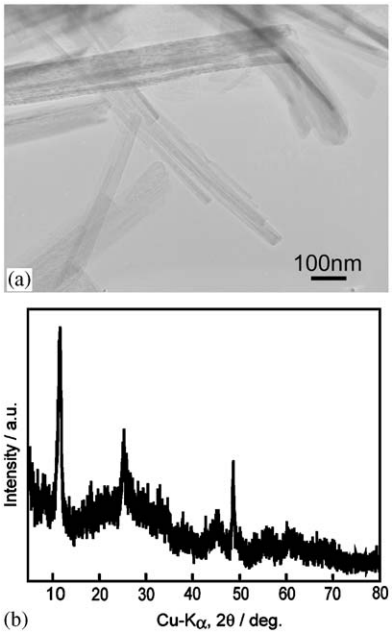

Fig. 3. TEM image and XRD pattern of the titanate nanowires prepared by hydrothermal method at 150 °C for 72 h and H_2O wash and subsequent HCl treatment pH2 for 3 times.

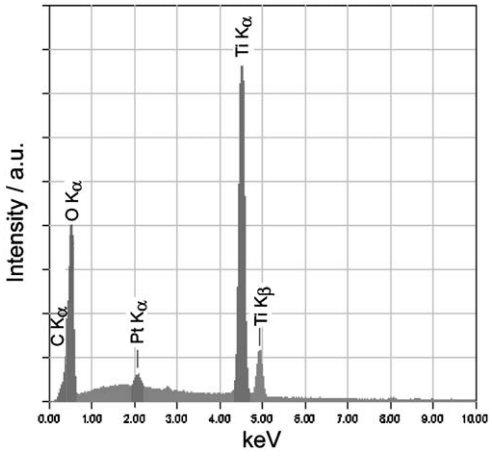

Fig. 4. EDS spectrum of the TiO_2-related nanowires prepared by hydrothermal method at 150 °C for 72 h and H_2O wash and subsequent HCl treatment pH2 for 3 times. Pt peaks are arisen from the coating for SEM observation and sample stages.

For the following experiments, titanate nanowires were used as precursor to obtain TiO_2(B) and TiO_2 anatase nanowires. Fig. 3 shows a TEM image and an XRD pattern of the titanate nanowires, prepared by the hydrothermal method at 150 °C at 72 h. The diameter of each titanate nanowire was 10–50 nm, and some nanowires formed bundles of ~100 nm in diameter. The XRD pattern resembled that in Ref. [14], indicating layered or tunnel-structured titanate structure, $H_2Ti_nO_{2n+1} \cdot xH_2O$. Further electron diffraction study will be needed to clarify the as-synthesized nanowires.

As described in our previous work [16], Na concentration in the NaOH-treated samples can be minimized by repeated ion-exchanging treatment by HCl. Fig. 4 shows an EDS spectrum of the nanowires. Na concentration in the sample was less than the EDS lower limit of detection.

3.2. Nanowires with post-heat treatment (100–500 °C)

Figs. 5 and 6 show the SEM images and XRD patterns of the as-synthesized titanate nanowires and the heat-treated samples: (a) is the as-synthesized nanowires

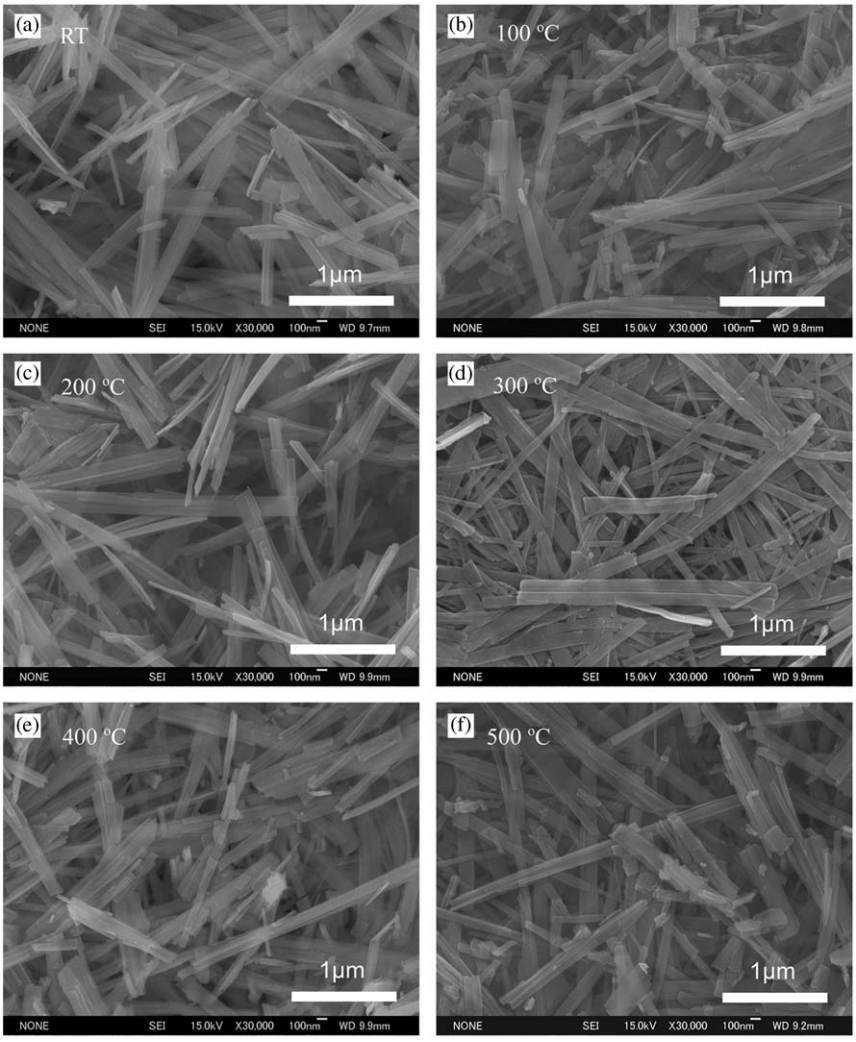

Fig. 5. SEM images of TiO_2-related nanowires (prepared for 72 h at 150 °C), (a) as-synthesized, and calcined for 2 h; (b) at 100 °C; (c) at 200 °C; (d) at 300 °C; (e) at 400 °C; (f) at 500 °C.

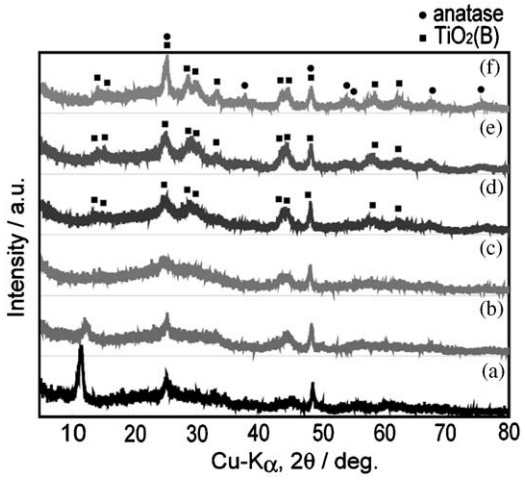

Fig. 6. XRD patterns of TiO_2-related nanowires (prepared for 72 h at 150 °C), (a) as-synthesized, and calcined for 2 h; (b) at 100 °C; (c) at 200 °C; (d) at 300 °C; (e) at 400 °C; (f) at 500 °C.

(hydrothermally synthesized at 150 °C for 72 h, and ion-exchanged by repeated acid treatment), and (b)–(f) are samples heated for 2 h at 100, 200, 300, 400 and 500 °C, respectively. Apparently, the SEM images of heat-treated samples are almost identical to that of the as-synthesized nanowires. The samples of (a)–(f) are composed of almost only nanowires.

In the XRD patterns of (a) and (b), drastic change was not observed. However, the reflection peak at $2\theta \sim 10^\circ$ shifts to higher angle and becomes broader. This reflection peak corresponds to the interlayer (or tunnel–tunnel) spacing of titanate. Thus, this peak shift means the decrease of the interlayer spacing. This can be explained by dehydration of H_2O molecules [13,15], contained in the as-synthesized nanowires. The 300 °C-calcined sample had very broad XRD pattern (Fig. 6(c)). At around 300 °C, phase transformation from titanate to TiO_2(B) seems to proceed. The XRD patterns

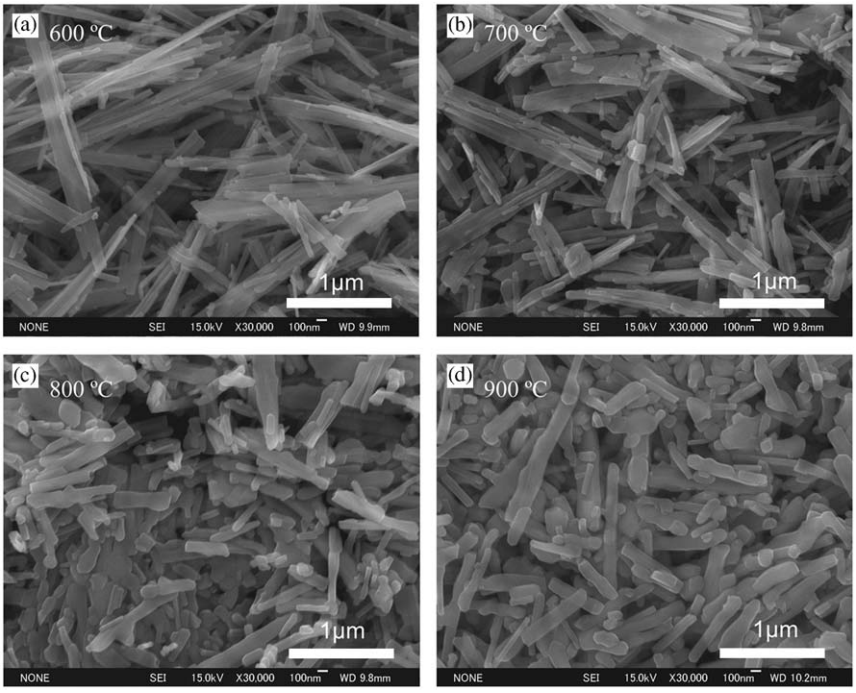

Fig. 7. SEM images of TiO_2-related nanowires (prepared for 72 h at 150 °C) calcined for 2 h (a) at 600 °C; (b) at 700 °C; (c) at 800 °C; (d) at 900 °C.

of (d)–(f) can be indexed as TiO_2(B). In our conditions, TiO_2(B) nanowires were synthesized by heat treatment of titanate nanowires at 300–500 °C for 2 h. Recent reports on the synthesis of TiO_2(B) nanowires showed similar formation temperature range of 300–600 °C [14] or at 400–600 °C [25]. Some differences can be attributed to the synthesis conditions of precursor nanowires, and kinetics effect (Note that TiO_2(B) is a metastable phase).

3.3. Nanowires with post-heat treatment (600–900 °C)

Figs. 7 and 8 show the SEM images and XRD patterns of the heat-treated samples: (a)–(d) are samples heated for 2 h at 600, 700, 800 and 900 °C, respectively. The SEM images of (a) and (b) show almost only nanowires. Those of (c) and (d) show both nanowires and small amount of particles. Over 800 °C, the surfaces of nanowires became smooth because of the progress of surface diffusion. (At >800 °C, they may be preferably called as "submicron wires" due to the size enlargement.) The XRD patterns of (a)–(c) are indexed as TiO_2 anatase phase. The diffraction peaks of (a)–(c) became very sharp, indicating high crystallinity. In the XRD pattern of (d), the formation of TiO_2 rutile phase is confirmed. Thus, the nanowires transform from TiO_2(B) to anatase at ~600 °C and to rutile at ~900 °C.

Generally, anatase phase of TiO_2 becomes unstable and transforms into rutile phase at the temperature higher than 700 °C. However, the anatase nanowires, prepared by this work, were stable at even 800 °C. So,

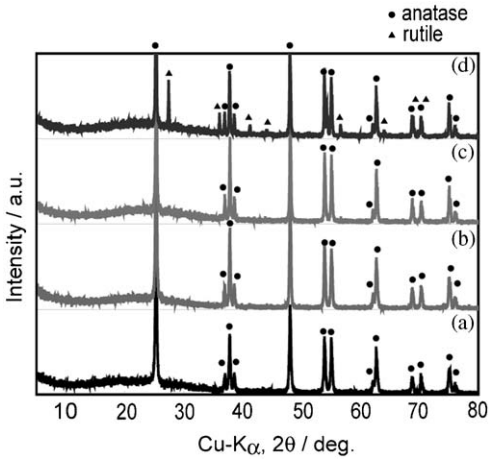

Fig. 8. XRD patterns of TiO_2-related nanowires (prepared for 72 h at 150 °C) calcined for 2 h (a) at 600 °C; (b) at 700 °C; (c) at 800 °C; (d) at 900 °C.

the anatase nanowires might have an advantage for high temperature applications of anatase phase.

3.4. TG-DTA analysis

Fig. 9 shows the TG-DTA diagrams for as-synthesized nanowires. The endothermic peak at 140 °C and weight loss correspond to the dehydration of interlayer (or inside tunnel) water and the start of phase transformation from a titanate to TiO_2(B). The exothermic peaks at 530 and 760 °C can be attributable to the phase transformation from TiO_2(B) to anatase

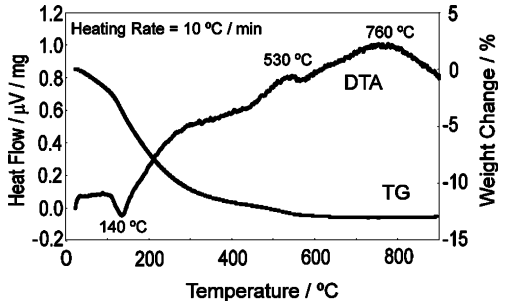

Fig. 9. TG-DTA diagrams for TiO_2-related nanowires.

and that from anatase to rutile, respectively. The results of the TG-DTA curves are in good agreement with that of XRD patterns.

3.5. TEM observation of a nanowire

A TEM image of a nanowire (obtained by the calcination at 700 °C for 2 h) and its enlargement are given in Fig. 10(a) and (b), respectively. The diameter of the nanowire was about 50 nm, and faceted surface was observed (Fig. 10(a)). By a high-resolution image (Fig. 10(b)), two lattice fringes (5.0 and 3.6 Å) were observed. The lattice fringe with 5.0 Å was parallel to the nanowire surface, and the angle between two fringes was 110°.

In an early study by Brohan et al. [24], the transformation from TiO_2(B) to anatase was explained by the shear of $(\bar{2}01)_{TiO_2(B)}$ plane to form $(10\bar{3})_{anatase}$ plane, along with the $[\bar{2}0\bar{3}]_{TiO_2(B)}$ direction. The lattice spacings of $(\bar{2}01)_{TiO_2(B)}$ and $(10\bar{3})_{anatase}$ are 5.08 and 2.43 Å (almost half of the former), respectively [26,27]. In addition, those of $(110)_{TiO_2(B)}$ and corresponding $(101)_{anatase}$ are 3.57 and 3.52 Å, respectively. Considering these data, the observed nanowire in Fig. 10 can be attributed to a remnant TiO_2(B) nanowire at 700 °C, with the indication of transforming into anatase phase (see the surface steps, implying the possible shear into anatase phase). Observed angle of 110° was then well-explained by the $(\bar{2}01)_{TiO_2(B)}$ and $(110)_{TiO_2(B)}$ plane, which can be calculated using the following equation for monoclinic system:

$$\phi = \cos^{-1}\left[\frac{d_1 d_2}{\sin^2\beta}\left(\frac{h_1 h_2}{a^2} + \frac{k_1 k_2 \sin^2\beta}{b^2} + \frac{l_1 l_2}{c^2} - \frac{(l_1 h_2 + l_2 h_1)\cos\beta}{ac}\right)\right],$$

where each character has its usual crystallographic meaning.

3.6. Possible applications of nanowires

As is very recently reported, TiO_2(B) nanowire is a promising Li-storage material [14,28], which can be

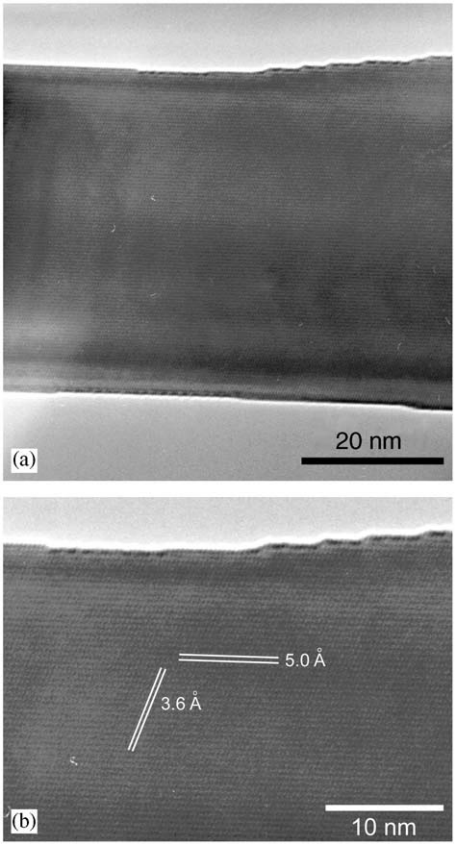

Fig. 10. TEM micrographs of (a) a TiO_2 nanowire (obtained by the calcination at 700 °C for 2 h) and (b) its enlargement.

expected from the earlier reports on the TiO_2(B) phase [17,22]. Other possible applications of TiO_2(B) nanowires are photocatalysts and dye-sensitized solar cells (DSC). Since the currently prepared TiO_2(B) nanowires (with typical surface area of 20 m^2/g) did not have sufficient surface area for these proposes, our preliminary results were not satisfactory: (e.g., DSC solar energy conversion efficiency using TiO_2(B) nanowires was only 0.57% [23]) Decreasing the size of nanowires (like in a very recent paper [29]) is an effective strategy to improve various properties.

4. Conclusions

Na-free titanate nanowires were prepared by the hydrothermal synthesis of 150 °C for 72 h and repeated HCl treatment. The apparent 1-D morphology of TiO_2-related nanowires was thermally stable at any post-heat treatment temperature in this study. At about 300 °C, they began to change into TiO_2(B) nanowires, and at about 600 °C, transformed into anatase-type TiO_2 nanowires. At higher temperature than 900 °C, they begin to change into rutile-type TiO_2 rod-like grains.

Acknowledgments

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