# Synthesis and Characterization of Highly Crystalline Anatase Nanowire Arrays

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We developed a novel synthesis strategy of titania nanowire arrays by employing simple hydrothermal reaction and ion-exchange reaction techniques. Hydrothermal reactions of metallic titanium powder with $H_2O_2$ in a 10 M NaOH solution produced a new sodium titanate compound, $Na_2Ti_6O_{13} \cdot xH_2O$ (x~4.2), as arrays of nanowires of lengths up to 1 mm. Acid-treatment followed by calcination of this material produced arrays of highly crystalline anatase nanowires as evidenced by x-ray diffraction, Raman spectroscopy, and transmission electron microscopy studies. In both cases of sodium titanate and anatase, the nanowires have exceptionally large aspect ratios of 10,000 or higher, and they form arrays over a large area of $1.5 \times 3$ cm$^2$. Observations on the reaction products with varied conditions indicate that the array formation requires simultaneously controlled formation and crystal growth rates of the $Na_2Ti_6O_{13} \cdot xH_2O$ phase.

**Key Words :** Nanowire array, Anatase, Titanate, Hydrothermal synthesis

## Introduction

Arrays of one-dimensional (1D) materials are a recent research focus for their potentials in nano-scale electronic and photonic devices.[1-22] However, although a large number of 1D nanomaterials have been synthesized,[23] fabrication of well-aligned nanowire arrays still is a paramount challenge. Various methods have been reported for this end including vapor-liquid-solid or vapor-solid growth techniques[1-8] and methods employing templates such as porous aluminum oxides[9-18] or lyotropic liquid crystals.[19] The vapor techniques generally need special equipments and high temperatures, and the template method often encounters difficulties of pre-fabrication and post-removal of the templates and usually results in impurities. The nanowire arrays by above-mentioned methods are usually in the lengths of several to tens of microns and aligned over a small area supported by substrates or templates, for which aspects further development of synthetic methods is required. Substantial recent studies have indicated that hydrothermal route is a powerful and promising strategy for preparing 1-D nanomaterials, such as nanowires and nanotubes,[24-31] but mostly without any orientational order. Because of its many advantages such as simple procedure and low cost, it would be desirable to use hydrothermal reactions for the synthesis of arrayed nanowires if ever possible. Recently, this technique has been successfully applied to the synthesis of ZnO nanorod arrays that exhibit an interesting optical property.[22] Unfortunately, ZnO appears to be the only example of arrayed nanowires or nanorods from hydrothermal reactions.[32]

In this study, we have synthesized titania (anatase) nano-wire arrays for the first time employing the hydrothermal technique. Titania is a wide band gap semiconductor having important applications in environmental protection, photo-catalysis, chemical sensing and solar energy conversion. Titania nanotubes and nanowires have been prepared by sol-gel or electro-deposition methods within the tunnels of porous alumina or polycarbonate.[21,33-42] The typical products of these methods are mixtures of titania phases in poly-crystalline forms. On the contrary, our strategy is to combine the well-known anisotropic morphologies of alkali titanate compounds and their facile conversion into titania by ion-exchange and thermal treatments.[43] As a result, we have obtained freestanding arrays of nearly single crystalline anatase nanowires of very high aspect ratios up to 20,000.

## Experimental Section

**Synthesis of arrayed nanowires of $Na_2Ti_6O_{13} \cdot xH_2O$ (x~4.2).** The precursor for titania nanowires was prepared by a hydrothermal treatment of metallic Ti powder in an aqueous sodium hydroxide medium using $H_2O_2$ as the oxidant. In a typical procedure, 0.2 g Ti powder (100 mesh, Aldrich) was added in a 20 mL Teflon vessel followed by the addition of a 15 mL 10 M NaOH solution without stirring. Then 1mL $H_2O_2$ (35 wt%) was injected. The hydrothermal reaction was carried out statically at 220 °C for 48 hours. The reaction produced a new sodium titanate compound ($Na_2Ti_6O_{13} \cdot xH_2O$, x~4.2) as precipitated white masses and floccules suspended in the solution. The precipitates were isolated by decanting the solution, washed with water for several times, and dried at room temperature. Analyses on this material showed that it was composed of sodium titanate nanowires aligned almost parallel to one another.

**Ion-exchange and thermal conversion of $Na_2Ti_6O_{13} \cdot xH_2O$ (x~4.2) into anatase.** The arrayed sodium titanate

nanowires were directly submerged into a 1.2 M HCl solution for 4days with the solution refreshed every 24 hours for the ion-exchange of $Na^+$ with $H^+$. The acid treated precursor was washed with distilled water until the pH value became higher than 6 and dried at room temperature. Calcination at 500 °C for 3 hours in air produced pure anatase ($TiO_2$) phase as arrayed nanowires.

**Characterization.** Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2200 Ultima diffractometer equipped with a monochromated $CuK_\alpha$ radiation (2 kW). Thermogravimetric (TG) analyses were performed on a TA4000/SDT2960 thermogravimetric ana-lyzer from room temperature to 500 °C at a heating rate of 5 °C/min in an air flow of 100 mL/min. Scanning electron macroscopic (SEM) images were obtained on a Philips XK30-FEG model operating at a maximum accelerating voltage of 30 kV. Transmission electron microscopic (TEM) studies were performed on a JEM-3011 model operating with a 300 keV electron beam. The sample for TEM was prepared by sonicating the arrays in ethanol for 20 minutes and dipped on carbon-coated copper grid. Raman spectra were recorded on an inVia Raman Microscope from Renishaw plc with 514 nm excitation radiation operating at 0.5 mW.

## Results and Discussion

The hydrothermal reaction of Ti powder with $H_2O_2$ in a 10 M NaOH solution produced fluffy white masses of sizes as wide as up to $1.5 \times 3$ $cm^2$ (Figure 1a). The SEM images show that these are composed of aligned nanowires of up to 1 mm in length (Figure 1b). The XRD pattern does not match any known titania or titanate phases, indicating that it is a new compound (Figure 2). The EDX elemental analysis resulted in the Ti:Na ratio of 3, and the TG data showed a 12.2% weight loss below 350 °C. When heat-treated at 500 °C, this material converted into $Na_2Ti_6O_{13}$ phase [44] as confirmed by XRD (Figure 2). The same Ti : Na ratios before and after the heat-treatment indicate that the weight loss from the TG is due to the loss of water and, thus, the composition of the precursor phase may be formulated as $Na_2Ti_6O_{13} \cdot xH_2O$ (x~4.2). From a similar hydrothermal reaction of NaOH and $TiO_2$, Li *et al*. have found an unidentified sodium titanate phase also.[8] However, their titanate showed a different XRD pattern from ours, suggesting that our sodium titanate is a yet new phase. In addition, their titanate did not show a structural change up to 700 °C and converted into a mixture of $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ at higher temperatures, contrary to the water loss and accompanying structural change below 350 °C of our titanate.

Upon proton exchange treatment followed by heat-treatment, the precursor material becomes pure anatase with a little influence on the arrayed nanowire structure. The overall reactions (without the lattice water) can be expressed as:
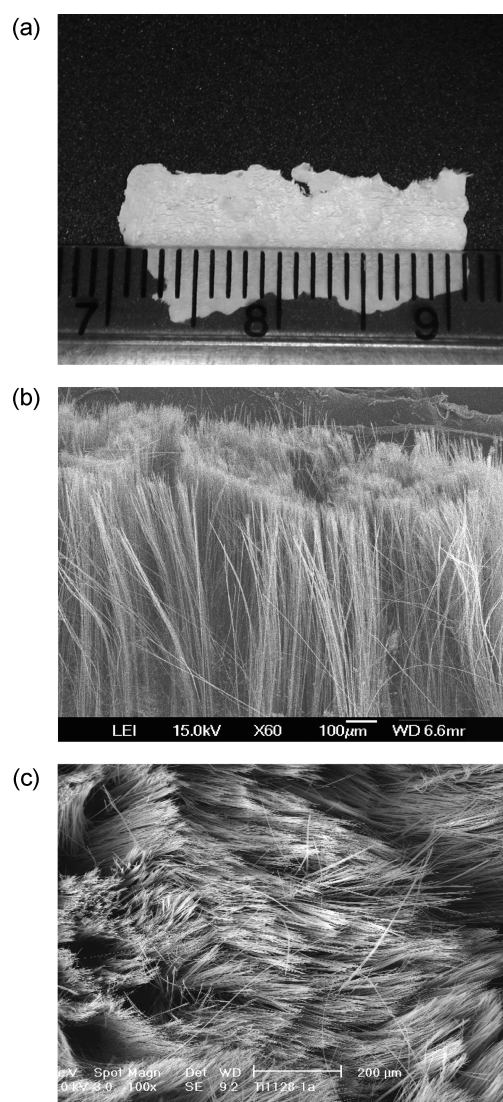


(a)

(b)

(c)

**Figure 1**. Large scale optical (a), side-view SEM (b), and top-view SEM images (c) of $Na_2Ti_6O_{13} \cdot xH_2O$ (x~4.2) nanowire arrays. The smallest scale in (a) is 1 mm.

$$6Ti + 12H_2O_2 + 2NaOH \rightarrow Na_2Ti_6O_{13} \cdot xH_2O + 13H_2O \quad (1)$$

$$Na_2Ti_6O_{13} \cdot xH_2O + 2H^+ \rightarrow H_2Ti_6O_{13} \cdot x'H_2O \quad (2)$$
(proton exchange)

$$H_2Ti_6O_{13} \cdot x'H_2O \rightarrow 6TiO_2 + (1 + x')H_2O \quad (3)$$
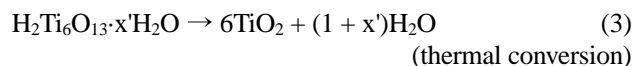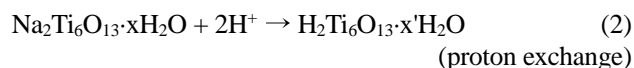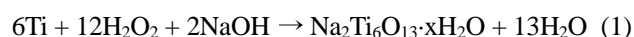(thermal conversion)

Figure 3a shows the XRD pattern of the $TiO_2$ nanowire arrays obtained by calcination of the acid treated precursor. The diffraction peaks are in good agreement with the tetragonal anatase phase with lattice constants a = 3.785 Å and c = 9.513 Å (space group *I4₁/amd*; JCPDS Card 21-1272) with no impurity peaks. EDX analysis on individual nanowires showed only Ti and O peaks with the O:Ti atomic ratio of 2. The Raman spectrum (Figure 3b) shows all the five characteristic peaks of anatase with no peaks corre-sponding to other titania phases indicating that our sample is a pure anatase phase. The peak positions (143 $cm^{-1}$ ($E_g$), 195
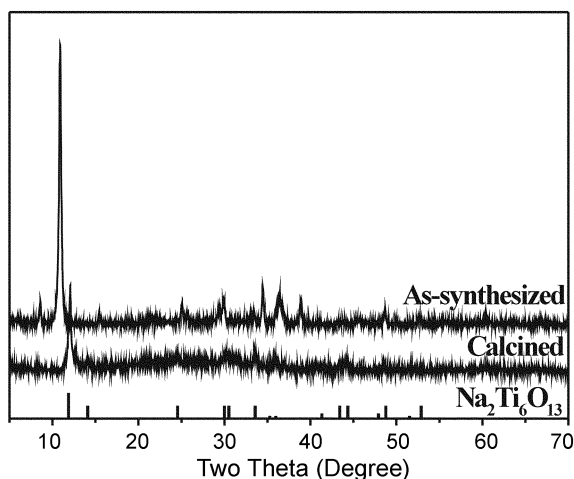
**Figure 2**. XRD patterns of $Na_2Ti_6O_{13}\cdot xH_2O$ (x~4.2) as-synthesized and heat treated, and the JCPDS pattern of $Na_2Ti_6O_{13}$.



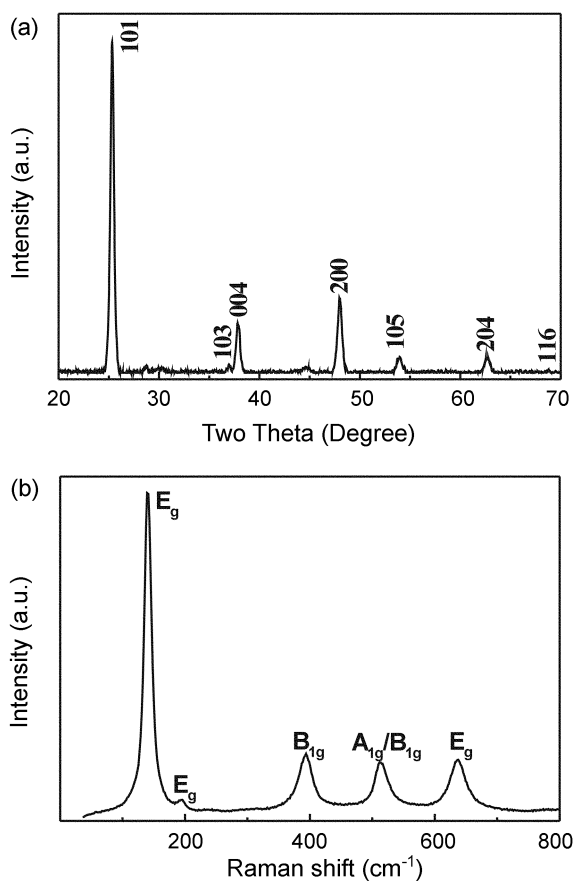**Figure 3**. (a) XRD pattern and (b) Raman spectrum of anatase nanowire arrays obtained by ion-exchange and heat-treatments of $Na_2Ti_6O_{13}\cdot xH_2O$ (x~4.2).
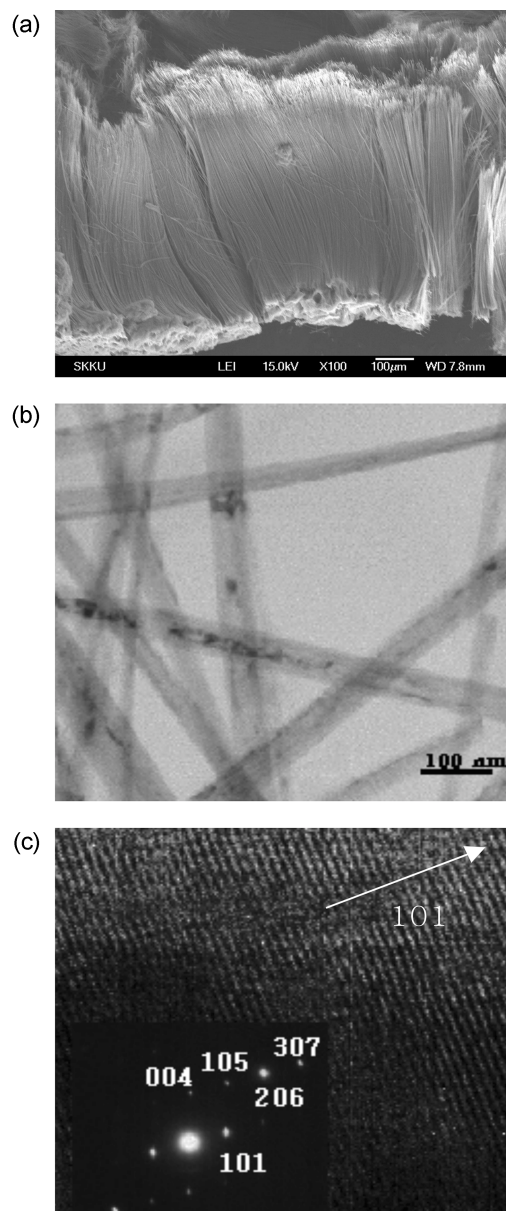


**Figure 4**. (a) SEM (b) TEM, and (c) HRTEM images of anatase nanowire arrays. The inset in (c) is a SAED pattern in the same orientation as the HRTEM image.

$cm^{-1}$ ($E_g$), 395 $cm^{-1}$ ($B_{1g}$), 514 $cm^{-1}$ ($A_{1g}$ and $B_{1g}$), 638 $cm^{-1}$ ($E_g$)) match well with those of an anatase single crystal.[45-48] Especially, it is known that the lowest-frequency $E_g$ mode is affected by the structure:[45-49] Oxygen stoichiometry and phonon confinement effects were reported to contribute significantly to the frequency of the $E_g$ mode. Increasing the ratio of oxygen to titanium blueshifts its frequency, reaching 143 $cm^{-1}$ when the ratio is 2.[49] As the size of $TiO_2$ nanocrystal decreases, the contribution from off-center phonons increases, which broadens and redshifts the $E_g$ peak.[47] Our observed strong intensity of the $E_g$ peak and its frequency, 143 $cm^{-1}$, indicate that the nanowires adopt well-ordered structure to the long-range with a negligible oxygen deficiency. Also, the well-resolved higher frequency Raman lines with substantial intensities point out that the nanowires are highly crystalline with few defects.

The SEM (Figure 4a) image of our anatase sample shows that the array structure of the precursor is maintained and that the nanowires are as long as 0.5 mm. The TEM image (Figure 4b) shows titania nanowires with thickness in the

(a)



(b)



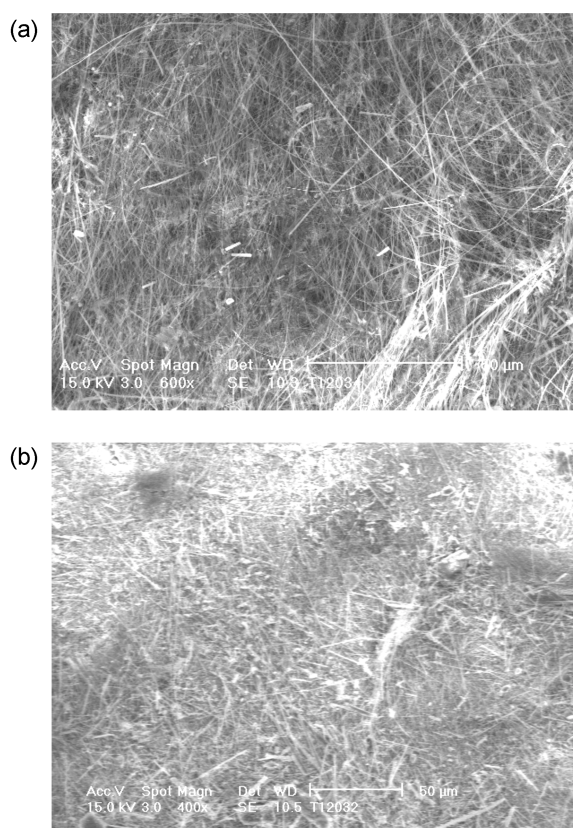**Figure 5**. SEM images of $Na_2Ti_6O_{13} \cdot xH_2O$ (x~4.2) nanowires synthesized using different Ti sources: (a) Ti foil and (b) Ti wire.

(a)



(b)
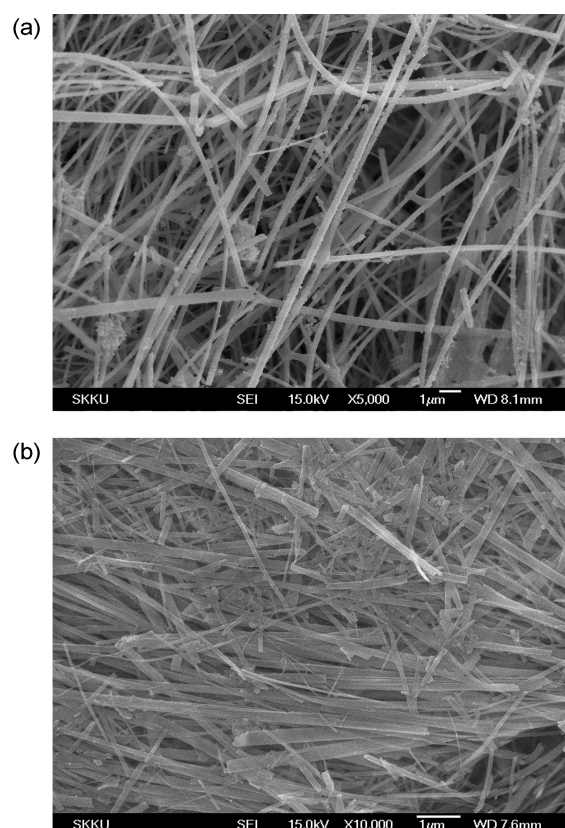


**Figure 6**. SEM images of $Na_2Ti_6O_{13} \cdot xH_2O$ (x~4.2) nanowires synthesized at different temperatures: (a) 180 °C and (b) 240 °C.

range of 25-80 nm. The two nanowires in the upper part of this figure imply that they are, in fact, nanoribbons or nanobelts slightly twisted. Unfortunately, we could not obtain any further information on the true morphology. With the dimensions measured from the SEM and TEM images, the aspect ratios of these nanowires are calculated to be as high as 20,000. The HRTEM image in Figure 4c shows lattice stripes with an interval of 0.35 nm that corresponds to the d-spacing of the (101) planes of anatase. Selected area electron diffraction pattern recorded of the same nanowire, perpendicularly to the long axis (inset of Figure 4c), can be indexed with (101), (004), (202), (105) and (206) diffractions of anatase. All these results of XRD, Raman, SEM, and TEM studies indicate that arrays of anatase nanowires with very high aspect ratio are formed and that the nanowires are single crystals grown along the [101] direction.

To our knowledge, it is the first time for isolating a 1-D nanomaterial arrays under a hydrothermal condition without templates or substrates. It is noteworthy that our nanowires have exceptionally high aspect ratios and are highly crystalline. The key step of our synthesis of titania nanowire arrays is the production of the sodium titanate arrays, and this appears to be governed by the kinetics of crystal growth based on the following observations. While the arrays could be synthesized repeatedly as long as titanium powder was used, the same reactions with titanium foil (thickness 0.127

mm) or wire (diameter 0.25 mm) produced randomly oriented $Na_2Ti_6O_{13} \cdot xH_2O$ nanowires along with unreacted titanium metal (Figure 5). These observations suggest that the high-density of crystallization seeds of the powder case provides a situation where the nanowire crystals grow in a self-supportive way. Similar observations were reported in the hydrothermal synthesis of ZnO nanowire arrays, in which ZnO nanoparticle undercoating was crucial for the self-supportive growth of ZnO nanowires.[22,32] Another evidence of the importance of crystal growth kinetics for the array formation is obtained from reactions with different temperatures. When reactions were performed at higher or lower temperatures than 220 °C, only random orientated sodium titanates nanowires were obtained (Figure 6). The optimal reaction temperature we have found is 220 °C. Apparently, the crystal growth and the reaction (1) must occur in compatible rates in order to form the nanowires into arrays. The subsequent conversion of the sodium titanate precursor into anatase appears to occur topotactically.

It is interesting to note that the same reactions with KOH or RbOH in the place of NaOH produce randomly grown nanowires of $A_2Ti_8O_{17}$ (A=K, Rb) phases. While the nanowire formation can be understood with the anisotropic nature of the crystals and their different kinetics of the crystal growth depending on the crystallographic phases, the lack of the arrayed structure in these cases is an additional, albeit indirect, support for the importance of the control of

reaction rates for the array formation.

In summary, from the combination of the crystal chemistry of alkali titanates and their ion-exchange properties, we have developed a facile chemical method for preparing large-area, freestanding, high aspect ratio anatase nanowire arrays. XRD, Raman, TEM and SAED data indicate that these nanowires are nearly single crystalline. The formation of the arrays appears to be governed by the kinetics of the crystal growth. With the high aspect ratio and large area of alignment, our titania nanowires, either as individual nanowires or arrays, may find applications in the development of nanodevices.

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