Synthesis and growth studies of barium titanates: 0–D and 1–D nanostructures using hydrogen titanate precursor

Prateek^{1||}, Mohini Mishra^{1||}, Raju Kumar Gupta^{1*, 2}

¹Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur-208016, UP, India ²Center for Nanosciences and Center for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Kanpur-208016, UP, India

*Corresponding author: Tel: +91-5122596972; Fax: +91-5122590104; E-mail: guptark@iitk.ac.in Contributed equally

Received: 08 November 2016, Revised: 29 November 2016 and Accepted: 13 December 2016

DOI: 10.5185/amlett.2017.1566 www.vbripress.com/aml

Abstract

The present work demonstrates a simple and efficient route to synthesize a variety of barium titanate (BaTiO₃) nanostructures including nanowires, nanoswords, nanostars, nanocubes, and nanoparticles by a facile hydrothermal approach. The experiments showed that different morphologies can easily be tuned by varying the concentration of precursors, i.e., hydrogen titanate (H₂Ti₃O₇) and barium hydroxide octahydrate (Ba(OH)₂.8H₂O), while keeping the molar ratio, reaction temperature and time fixed. The structure and morphology of BaTiO₃ were characterized by field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The results indicate that BaTiO₃ nanowires are in cubic phase with an average diameter of 80-100 nm. The shape of BaTiO₃ changes from nanowires to nanoparticles with an increase in Ba(OH)₂.8H₂O concentration from 0.08 M to 0.51 M. Two possible mechanisms, in-situ topotactic transformation reaction and dissolution-deposition reaction have been suggested for different morphologies of BaTiO₃. The synthesized 0-D and 1-D BaTiO₃ nanostructures are promising materials for many applications because of their excellent dielectric, ferroelectric and piezoelectric properties. The present work will open a new route to single reaction parameter dependent synthesis of 0- and 1-D BaTiO₃ nanostructures which can find a range of applications including electronics, catalysis, energy harvesting, etc. Copyright © 2017 VBRI Press.

Keywords: Nanowires, ceramics, dielectrics, ferroelectrics, nanocrystalline materials.

Introduction

BaTiO₃ nanostructures (0- and 1-D) have emerged as one of the most widely used perovskite titanates because of ease in synthesis, high dielectric constant, spontaneous electric polarization, piezoelectric and ferroelectric response. These find applications in numerous fields, namely, electronics, photonics, sensors, catalysts, energy harvesting, information storage, and mechanical strength enhancement, etc. **[1-4]**. BaTiO₃ of different morphologies such as nanoparticles, nanowires, nanorods, etc. have attracted extensive attention because of their novel-size dependent properties. Among different morphologies, 1-D nanostructures have been expected to improve the electronic performances. So, it is essential to develop a protocol for the stable, repeatable and large scale synthesis of 1-D BaTiO₃ **[1]**.

So far, 1-D BaTiO₃ nanostructures (nanorods, nanowires, nanofibers, etc.) have been synthesized by various routes. The most commonly applied methods include hydrothermal, molten-salt synthesis and

Copyright © 2017 VBRI Press

electrospinning approach [5-12]. Among the various approaches, hydrothermal process is the most widely used technique due to its low cost, scalable, easy synthesis and environmental friendly. Different parameters including reaction temperature and time, nature and concentration of reactants, pH, etc. play a crucial role in deciding the morphology of the BaTiO₃ [9, 13, 14]. One-step hydrothermal approach for BaTiO₃ nanowires with large aspect ratio (>1300) has been conducted by Yang et al. [5]. Tang et al. studied the effect of temperature on the aspect ratios of the BaTiO₃ nanowires by a two-step hydrothermal approach [15]. The aspect ratio of BaTiO₃ nanowires increased from 9.3 to 45.8 with an increase in temperature of second hydrothermal reaction from 150 to 240°C. Similar studies were reported by Wang et al. and Choi et al. [13, 16]. The in-situ stirring during the hydrothermal reaction also controls the nanowires dimension. Recently, Jiang and co-workers reported a novel protocol for synthesizing elongated BaTiO₃ nanowires by a two-step stirring hydrothermal method. The aspect ratio of the nanowires increased with an

increase in stirring speed. The critical stirring process helps in maintaining homogeneous reaction condition by intimate mixing and improves the diffusion and chemical reaction rates [14, 17]. Thus, hydrothermal reactions can be optimized to get desired products. Few researchers have synthesized different BaTiO₃ morphologies through controlled hydrothermal reactions. Lee et al. studied the effect of solvents (ethanol/water mixed solvent systems) for the synthesis of 0-D-1-D BaTiO₃ nanostructures [18]. Bao et al. have systematically grown BaTiO₃ of different morphologies, including nanosheets, nanocubes, starfish, sword and coral-like nanostructures, by controlling various experimental parameters like precursor concentrations, temperature, etc. [19]. Maxim et al. investigated the detailed kinetics of BaTiO₃ growth and synthesized dendritic particles with "wild" and "seaweed" morphologies [20]. Table 1 summarizes the recent works of 1-D BaTiO₃ synthesis. Till date, many attempts have been carried out to prepare BaTiO₃ of different morphologies. However, a simple route to synthesize one parameter dependent BaTiO₃ nanostructures of different morphologies through hydrothermal reaction, keeping other reaction parameters fixed, has not been reported yet. In the present work, different BaTiO₃ nanostructures are prepared by varying only the concentrations of H₂Ti₃O₇ nanowires w.r.t. Ba(OH)₂.8H₂O, while keeping all other parameters including molar ratio, temperature and time of the reaction, constant. We have successfully synthesized different 0-D and 1-D BaTiO₃ nanostructures including nanowires, sword, star, cubic, spherical shapes.

Experimental

Materials

Titanium (IV) dioxide (TiO₂) (≥99%, reagent plus) and barium hydroxide octahydrate (Ba(OH)₂.8H₂O) (≥98%)

were purchased from Sigma Aldrich. Sodium hydroxide (NaOH) pellets and hydrochloric acid (HCl) (37%, w/w) were purchased from Merck. All the chemicals were used as received.

Material synthesis

Synthesis of different BaTiO₃ nanostructures

Experimental details are summarized in Fig. 1 [13, 15, 21]. The BaTiO₃ nanostructures were synthesized using three-step reactions. In the first step, sodium titanate (Na₂Ti₃O₇) nanowires were synthesized by hydrothermal treatment. First, 0.4338 g TiO₂ was homogeneously dispersed in 11 M NaOH solution (21 mL) by stirring and sonicating for 30 min and 5 min, respectively. The reaction was carried out at 200°C for 24 h in a 25 mL hydrothermal reactor (reaction 1) [15, 21]. After that, the reactor was removed from the oven and cooled down to room temperature by natural cooling. The product (Na₂Ti₃O₇ nanowires) was washed with deionized water (DI) water using centrifuge at 9500 rpm for 15 min for three times and dried at 60°C for 24 h. In the second step, H₂Ti₃O₇ nanowires were synthesized by soaking Na₂Ti₃O₇ nanowires into 0.2 M HCl solution for 4 h (reaction 2) [15, 21]. H₂Ti₃O₇ nanowires were washed with DI water using centrifuge at 10000 rpm for 7 min for three times and dried at 60°C for 15 h.

In the third step, Ba(OH)₂.8H₂O concentration was varied from 0.03 M to 0.51 M, while fixing the molar ratio of Ba(OH)₂.8H₂O to H₂Ti₃O₇ at 6:1. H₂Ti₃O₇ nanowires were mixed with Ba(OH)₂.8H₂O aqueous solution by sonicating and stirring for 5 min and 1 h, respectively under nitrogen (N₂) environment to avoid formation of barium carbonate (BaCO₃) [**22**]. The reaction was carried out at 210 °C for 1.5 h in a 25-mL hydrothermal reactor.



Fig. 1. Schematic diagram for the synthesis mechanism of BaTiO₃ nanostructures with different morphologies.

Table 1. List of the synthesis of 1-D $BaTiO_3$ nanostructures.

Synthesis route	Average diameter (nm)	Average length (µm)	Shape of BaTiO ₃ nanostructure	Titanium/barium precursors	Reaction condition for BaTiO ₃ synthesis	References
hydrothermal	60-300, 50- 200, <100 at 250, 500, 1000 rpm, respectively	3-9, 10, 20 at 250, 500, 1000 rpm, respectively	nanowires	Na2Ti3O7 nanowires, Ba(OH)2·8H2O	85°C, 20 h	[14]
surfactant assisted sonochemical method followed by quenching post- calcination	Thickness: (i) 20-60 , (ii) 20- 30	(i) 0.3–0.8 , (ii) ~1	nanorods	titanium tetrachloride (TiCl4), barium chloride dehydrate (BaCl2.2H2O)	800 °C for 2 h with (i) cooled slowly (cooling rate 1 °C/min), (ii) rapidly quenched to room temperature.	[8]
hydrothermal	240	4.4	nanowires	H2Ti3O7 nanowires, Ba(OH)2·8H2O	200 °C, 24 h	[16]
hydrothermal	70 at 1000 rpm	tens of micrometers at 1000 rpm	nanowires	Na2Ti3O7 nanowires, Ba(OH)2·8H2O	85 °C for 20 h	[17]
hydrothermal	300	-	nanowires	potassium tetratitanate (K ₂ Ti ₄ O ₉) nanowires, barium hydroxide (Ba(OH) ₂)	100–180 °C for 12 h	[37]
molten salt route	100-1000	20-80	nanowires	TiO_2 , barium oxalate (Ba ₂ C ₂ O ₄)	950 °C for 5 h	[38]
hydrothermal	40	1	nanowires	tetrabutyl titanate (TBOT), Ba(OH) ₂ ·8H ₂ O	200 °C for 12 h	[39]
hydrothermal	35	1.3	nanowires	TBOT, Ba(OH)₂·8H₂O	200°C for 12 h	[40]
hydrothermal	147	0.441	nanorods	titanium isopropoxide (Ti(C3H7O)4), barium acetate (Ba(CH3COO)2)	135 °C for 24 h	[10]
hydrothermal	~90	~1	nanowires	TiO ₂ nanowires	150–240°C for 4 to 8 h	[41]
hydrothermal	630	40	nanowires	Na2Ti3O7 nanowires, Ba(OH)2·8H2O	150–250°C	[42]
hydrothermal	270, 420, 450, 500 at 150, 180, 200, 240°C	2.5, 6.8, 14.4, 23.0 at 150, 180, 200, 240°C	nanowires	H ₂ Ti ₃ O ₇ nanowires, Ba(OH) ₂ ·8H ₂ O	1.42 h	[15]
molten salt route	30–100	several micrometers	nanowires	TiO2, barium nitrate (Ba(NO3)2)	850°C for 4 h	[43]
hydrothermal	~156	~4	nanowires	Na ₂ Ti ₃ O ₇ nanowires, Ba(OH) ₂	100°C for 24 h	[44]
hydrothermal	~6	several tens of micrometers	nanowires	TBOT, Ba(OH)2·8H2O	200°C, 12 h	[5]
hydrothermal	90	~1	nanowires	TiO ₂ nanowires, Ba(OH) ₂ ·8H ₂ O	210 °C for 8 h	[45]
hydrothermal	80-100	-	nanowires	H2Ti3O7 nanowires, Ba(OH)2·8H2O	210°C for 1.5 h	present work

The reactor was removed from the oven, cooled down to room temperature and washed using centrifuge with 0.1 M HCl solution, DI water and ethanol, respectively, at 10000 rpm for 7 min for three times. The product was dried at 60° C for 15 h [13, 15, 21].

$$2NaOH + 3TiO_2 \xrightarrow{200^{\circ}C/24 \text{ h}} Na_2Ti_3O_7 + H_2O$$
(1)

$$Na_{2}Ti_{3}O_{7} + 2HCl \longrightarrow H_{2}Ti_{3}O_{7} + 2NaCl$$
(2)

$$H_2Ti_3O_7 + 3Ba(OH)_2.8H_2O$$
 3BaTiO₃ + 28H₂O (3)

 $210^{\circ}C/1.5$ h

Characterizations

The morphologies of nanostructures were characterized by field emission scanning electron microscope (FESEM; TESCAN–MIRA3). The FESEM images were analyzed with ImageJ software. The X-ray diffraction (XRD) patterns were determined by an X-ray diffractometer (PANalytical, X'Pert Powder) with Cu K_a as the X-ray source ($\lambda = 1.5406$ Å). The chemical formula and the phase were analyzed by XRD pattern using X'Pert HighScore Plus software.

Results and discussion

Fig. 2(a) shows FESEM image of $Na_2Ti_3O_7$ nanowires. $H_2Ti_3O_7$ nanowires having average diameter of 60-80 nm (**Fig. S1(a-b**)) are shown in **Fig. 2(b**).

The XRD patterns of Na₂Ti₃O₇ (JCPDS: 01-072-0148) and H₂Ti₃O₇ (JCPDS: 00-047-0561) nanowires confirm the pure phase, as shown in Fig. 3(a) and (b), respectively. The complete conversion of Na₂Ti₃O₇ to H₂Ti₃O₇ nanowires was confirmed by shifting of the main diffraction peak from 10.5° in Na₂Ti₃O₇ to 10.9° in H₂Ti₃O₇ [13, 23]. The conversion of Na₂Ti₃O₇ into $H_2Ti_3O_7$ is because of layered $H_2Ti_3O_7$ which is a very good precursor for soft chemical reaction exhibiting good ion exchange properties [15, 24]. Pure BaTiO₃ nanowires were obtained at 0.08 M Ba(OH)₂.8H₂O, as shown in Fig. 2(e), with average diameter of 80-100 nm (Fig. S1(c-d)). The XRD pattern of BaTiO₃ (JCPDS: 01-081-2202) nanowires (Fig. 3 (c)) confirms the absence of any byproducts, viz., BaCO₃ and TiO₂. However, two diffraction peaks at 8.36° and 10.6° show the presence of minimal amount of H₂Ti₃O₇ in pure BaTiO₃ nanowires [13, 23].

Many mechanisms have been proposed earlier for the synthesis of nanotubular structures using $H_2Ti_3O_7$ as precursor. Some suggest that tubular layered structures were due to the rolling or curling of planes around the crystal axis. The rolling of the $H_2Ti_3O_7$ is associated with the surface tension because of the imbalance of hydrogen ions (H⁺) ions on the surface layers. The dimension of the nanotube is controlled by the surface tension along with interlayer coupling energy and Coulombic force **[25-30]**. Suggestive mechanism for the current work is that Na₂Ti₃O₇ nanowires are arranged in a layered titanate

nanosheets formed by sharing of three edges of TiO_6 octahedrons in a zigzag pattern, while sodium ions (Na⁺) are attached through electrostatic interaction in space among the layers as shown in **Fig. 1** [13, 31]. The high concentration of NaOH helps in the formation and stabilization of monoclinic layered structure of Na₂Ti₃O₇ [32].



Fig. 2. FESEM images of (a) $Na_2Ti_3O_7$ nanowires, (b) $H_2Ti_3O_7$ nanowires, and intermediate products at $Ba(OH)_2.8H_2O$ concentration (c) 0.03 M, (d) 0.05 M, and $BaTiO_3$ nanostructures at (e) 0.08 M, (f) 0.1 M, (g) 0.15 M, (h) 0.2 M, (i) 0.3 M, (j) 0.4 M, (k) 0.51 M.

The acid treatment converts $Na_2Ti_3O_7$ into $H_2Ti_3O_7$ nanowires because of ion exchange reaction between hydronium (H_3O^+) **[13, 19, 24]**. The conversion of $Na_2Ti_3O_7$ into $H_2Ti_3O_7$ nanowires can be explained as follows **[26]**. The H⁺ ions are highly reactive because of very small size of only about 1/64,000th of the hydrogen atom. Furthermore, Na⁺ ions have weak bonding with negatively charged $Ti_3O_7^{2-}$ layers. Thus, H⁺ ions can react and exchange easily with Na⁺, the rate being controlled by the diffusion of the ions in and out of the exchanger structure. This exchange reaction is irreversible, as the H– O bond length in $H_2Ti_3O_7$ (1 Å) is less than Na–O bond length (2Å) in $Na_2Ti_3O_7$. Therefore, the conversion of $Na_2Ti_3O_7$ into $H_2Ti_3O_7$ is supposed to occur through following reactions (**reaction 4-7**).

Dissolution-crystallisation reaction:

 $Na_2Ti_3O_7 \longrightarrow 2Na^+ + 2Ti_3O_7^{2-}$ (4)

Ion exchange reaction: $2Na^{+} + Ti_{3}O_{7}^{2^{-}} + H^{+} + Cl^{-} \longrightarrow H^{+} + Ti_{3}O_{7}^{2^{-}} + 2Na^{+} + Cl^{-}$ (5)

Crystallisation reaction for salt formation:

 $Na^+ + Cl^- \longrightarrow NaCl (dissolved in aqueous solution)$ (6)

Crystallisation reaction for titanate formation:

(7)

$$2H^+ + Ti_3O_7^2 \longrightarrow H_2Ti_3O_7$$

In another study, An *et al.* experimentally deduced that ion exchange reaction between $Na_2Ti_3O_7$ and $H_2Ti_3O_7$ is thermodynamically favourable at low pH [**33**]. The SEM image confirms that the morphology of $H_2Ti_3O_7$ (**Fig. 2(b**)) is similar to that of $Na_2Ti_3O_7$ (**Fig. 2(a**)).

Further, the reaction of H₂Ti₃O₇ nanowires with Ba(OH)₂.8H₂O at high temperature causes exchange reaction of H₃O⁺ or H⁺ ions of H₂Ti₃O₇ layered structure with barium (Ba²⁺) ions. Different intermediates were obtained by varying the Ba(OH)₂.8H₂O concentration (0.03 M-0.51 M) (Fig. 1 and Fig. 2(c-k)). The nanowires morphology were retained at $Ba(OH)_2.8H_2O$ concentrations of 0.03, 0.05 and 0.08 M (Fig. 2(c-e)). At Ba(OH)₂.8H₂O concentration of 0.03 M, pure H₂Ti₃O₇ nanowires (JCPDS: 00-047-0561; Fig. S2(a)) were obtained, while an intermediate product was formed at 0.05 M, which could not be identified properly (Fig. S2(b)). However, the formation of BaTiO₃ nanowires were started at 0.08 M Ba(OH)₂.8H₂O having little amount of $H_2Ti_3O_7$ (reaction 3; Fig. 3(c)).



Fig. 3. XRD spectra of (a) $Na_2Ti_3O_7$ nanowires, (b) $H_2Ti_3O_7$ nanowires, and (c) $BaTiO_3$ nanowires at 0.08 M $Ba(OH)_2.8H_2O$ (* represents peaks of $H_2Ti_3O_7$ nanowires).

Further increase in concentration of Ba(OH)₂.8H₂O from 0.1 M to 0.51 M led to morphological changes from sword (0.1 M & 0.15 M), stars (0.2 M), cubes (0.3 M & 0.4 M) and finally into spherical particles (0.51 M) as shown Fig. 2(f-k). For all these cases, pure BaTiO₃ was obtained as confirmed from XRD analysis (JCPDS: 01-081-2202; Fig. S2(c), here XRD data is shown only for 0.1 M Ba(OH)₂.8H₂O). Two different mechanisms have been suggested for different morphologies of BaTiO₃. Starting with $H_2Ti_3O_7$, the nanowires morphology of BaTiO₃ is retained under mild Ba(OH)₂.8H₂O concentration. The possible mechanism is associated with in situ topotactic transformation reaction in which BaTiO₃ remains in layered structure due to the

formation of intermediate sub-lattices and transforms into perovskite form on hydrothermal treatment by continuous shifting of intermediate sub-lattices at sub-nanometer scale [13, 24, 34, 35]. However, when the Ba(OH)₂.8H₂O concentration is increased, the dissolution-deposition reaction occurs, in which crystal-axis orientation property diminishes and further leads to synthesis of BaTiO₃ of different morphologies, viz. sword, star, cubic, sphere [19, 20, 36].

Conclusion

In summary, we have successfully synthesized different BaTiO₃ nanostructures using hydrothermal approach. The synthesis process provides a facile, environment friendly, low cost and highly efficient way to prepare a range of morphologies including nanowires, nanoswords, nanostars, nanocubes and nanoparticles. To the best of our knowledge, this is the first protocol to synthesize different morphologies by only varying the concentration of the precursors, keeping molar ratio, reaction temperature and time fixed. We conclude that concentration of precursors is a key parameter for achieving pure product with desired morphologies. BaTiO₃ nanowires with an average diameter of 80-100 nm were obtained at 0.08 M Ba(OH)₂.8H₂O, while further increase in concentration led to other morphologies i.e. sword, star, cubic, sphere. This study can potentially be used to synthesize a range of BaTiO₃ nanostructures with different aspect ratios and is best suitable for many applications such as in capacitors, detectors, sensors, etc.

Acknowledgments

RKG acknowledges financial support from Department of Atomic Energy (DAE), BRNS, India for grant 34/14/14/2014–BRNS. DST support is acknowledged to the Center for Nanosciences.

Supplementary information

FESEM images and size distribution of $H_2Ti_3O_7$ and $BaTiO_3$ nanowires, XRD spectra of intermediate products at $Ba(OH)_2.8H_2O$ concentrations of 0.03, 0.05 and 0.1 M.

References

- 1. Rørvik, P. M.; Grande, T.; Einarsrud, M.-A.; *Adv. Mater.*, **2011**, *23*, 4007.
- DOI: <u>10.1002/adma.201004676</u>
- Bao, N.; Shen, L.; Gupta, A.; Tatarenko, A.; Srinivasan, G.; Yanagisawa, K.; *Appl. Phys. Lett.*, **2009**, *94*, 253109.
 DOI: 10.1063/1.3159817
- 3. Prateek; Thakur, V. K.; Gupta, R. K.; Chem. Rev., 2016, 116, 4260.
- **DOI:** <u>10.1021/acs.chemrev.5b00495</u>
 4. Wang, Y.; Xu, G.; Yang, L.; Ren, Z.; Wei, X.; Weng, W.; Du, P.; Shen, G.; Han, G.; *Mater. Lett.*, **2009**, *63*, 239.
- **DOI:** <u>10.1016/j.matlet.2008.09.050</u>
 Yang, J.; Zhang, J.; Liang, C.; Wang, M.; Zhao, P.; Liu, M.; Liu, J.; Che, R.; *ACS Appl. Mater. Interfaces*, **2013**, *5*, 7146. **DOI:** 10.1021/am4014506
- Cheng, L.-Q.; Li, J.-F.; *J. Materiomics*, 2016, 2, 25.
 DOI: <u>10.1016/j.jmat.2016.02.003</u>
- Fu, J.; Hou, Y.; Zheng, M.; Zhu, M.; CrystEngComm, 2017, 19, 1115.
 DOI: 10.1039/C6CE02504H

- Loganathan, A.; Manoharan, D.; Nesamony, V. J.; *Mater. Lett.*, 2017, 186, 305.
 DOI: <u>10.1016/j.matlet.2016.10.048</u>
- Munoz-Tabares, J. A.; Bejtka, K.; Lamberti, A.; Garino, N.; Bianco, S.; Quaglio, M.; Pirri, C. F.; Chiodoni, A.; *Nanoscale*, 2016, *8*, 6866.
 DOI: <u>10.1039/C5NR07283B</u>
- Maxim, F.; Berger, D.; Teodorescu, F.; Hornoiu, C.; Lete, C.; Tanasescu, S.; *J. Nanomater.*, **2015**, 2015, 10 pages. **DOI:** 10.1155/2015/827641
- Hu, P.; Shen, Y.; Guan, Y.; Zhang, X.; Lin, Y.; Zhang, Q.; Nan, C.-W.; Adv. Funct. Mater., 2014, 24, 3172.
 DOI: 10.1002/adfm.201303684
- Pan, Z.; Yao, L.; Zhai, J.; Shen, B.; Liu, S.; Wang, H.; Liu, J.; J. Mater. Chem. A, 2016, 4, 13259.
 DOI: <u>10.1039/C6TA05233A</u>
- 13. Wang, G.; Huang, X.; Jiang, P.; ACS Appl. Mater. Interfaces, 2015, 7, 18017.
- DOI: <u>10.1021/acsami.5b06480</u>
 14. Xie, B.; Zhang, H.; Kan, H.; Liu, S.; Li, M.-Y.; Li, Z.; Zhu, S.; Qiu, S.; Jiang, S.; *Ceram. Int.*, **2017**, *43*, 2969.
- DOI: <u>10.1016/j.ceramint.2016.11.049</u>
 15. Tang, H.; Zhou, Z.; Sodano, H. A.; *ACS Appl. Mater. Interfaces*, 2014, *6*, 5450.
- **DOI:** <u>10.1021/am405038r</u>
- Choi, W.; Choi, K.; Yang, G.; Kim, J. C.; Yu, C.; *Polym. Test.*, 2016, *53*, 143.
 DOI: <u>10.1016/j.polymertesting.2016.05.018</u>
- Xie, B.; Zhang, Q.; Zhang, H.; Zhang, G.; Qiu, S.; Jiang, S.; Ceram. Int., 2016, 42, 19012.
 DOI: <u>10.1016/j.ceramint.2016.09.057</u>
- Lee, D. K.; Cho, I.-S.; Lee, S.; Kim, D. H.; Shim, H.-W.; Kim, D.-W.; Hong, K. S.; *Eur. J. Inorg. Chem.*, **2010**, 2010, 1343.
 DOI: <u>10.1002/ejic.200901230</u>
- Bao, N.; Shen, L.; Srinivasan, G.; Yanagisawa, K.; Gupta, A.; J. Phys. Chem. C, 2008, 112, 8634.
 DOI: 10.1021/jp802055a
- Maxim, F.; Vilarinho, P. M.; Ferreira, P.; Reaney, I. M.; Levin, I.; Cryst. Growth Des., 2011, 11, 3358.
 DOI: 10.1021/cg101466u
- 21. Tang, H.; Lin, Y.; Sodano, H. A.; Adv. Energy Mater., 2013, 3, 451.
- **DOI:** <u>10.1002/aenm.201200808</u>
- Viviani, M.; Lemaitre, J.; Buscaglia, M. T.; Nanni, P.; J. Eur. Ceram. Soc., 2000, 20, 315.
 DOI: <u>10.1016/S0955-2219(99)00150-8</u>
- Lu, H.; Wang, Y.; Wang, Y.; Liang, W.; Yao, J.; *RSC Adv.*, 2015, 5, 89777.
- **DOI:** <u>10.1039/C5RA17692A</u>
 24. Feng, Q.; Hirasawa, M.; Yanagisawa, K.; *Chem. Mater.*, **2001**, *13*, 290.
 - **DOI:** <u>10.1021/cm000411e</u>
- Zhang, S.; Peng, L. M.; Chen, Q.; Du, G. H.; Dawson, G.; Zhou, W. Z.; *Phys. Rev. Lett.*, **2003**, *91*, 256103.
 DOI: <u>10.1103/PhysRevLett.91.256103</u>
- Razali, M. H.; Noor, A.-F. M.; Mohamed, A. R.; Sreekantan, S.; J. Nanomater., 2012, 2012, 10 pages.
 DOI: 10.1155/2012/962073
- Bavykin, D. V.; Friedrich, J. M.; Walsh, F. C.; *Adv. Mater.*, 2006, 18, 2807.
- **DOI:** <u>10.1002/adma.200502696</u> Nakabira A · Kubo T · Numako C ·
- Nakahira, A.; Kubo, T.; Numako, C.; *Inorg. Chem.*, 2010, 49, 5845.
 DOI: 10.1021/ic9025816
- Zhang, Y. X.; Li, G. H.; Jin, Y. X.; Zhang, Y.; Zhang, J.; Zhang, L. D.; Chem. Phys. Lett., 2002, 365, 300.
 DOI: 10.1016/S0009-2614(02)01499-9
- Riss, A.; Berger, T.; Stankic, S.; Bernardi, J.; Knözinger, E.; Diwald, O.; Angew. Chem., Int. Ed., 2008, 47, 1496.
 DOI: 10.1002/anie.200703817
- 31. Zhang, T.; Chen, Q.; Peng, L.-M.; *Adv. Funct. Mater.*, **2008**, *18*, 3018.
- DOI: 10.1002/adfm.200800360
 32. Zhao, B.; Lin, L.; He, D.; *J. Mater. Chem. A*, 2013, *1*, 1659.
 DOI: 10.1039/c2ta00755j

- An, Y.; Wang, D.; Wu, C.; *Phys. E*, **2014**, *60*, 210.
 DOI: <u>10.1016/j.physe.2014.03.001</u>
- Kang, S.-O.; Park, B. H.; Kim, Y.-I.; Cryst. Growth Des., 2008, 8, 3180.
 DOI: <u>10.1021/cg700795q</u>
- Wang, F.; Wang, J.; Zhong, X.; Li, B.; Liu, J.; Wu, D.; Mo, D.; Guo, D.; Yuan, S.; Zhang, K.; Zhou, Y.; *CrystEngComm*, **2013**, *15*, 1397.
 DOI: 10.1039/c2ce26330k
- Feng, Q.; Hirasawa, M.; Yanagisawa, K.; *Chem. Mater.*, **2001**, *13*, 290.
- DOI: <u>10.1021/cm000411e</u>
 37. Zhang, M.; Gao, T.; Wang, J.; Liao, J.; Qiu, Y.; Xue, H.; Shi, Z.; Xiong, Z.; Chen, L.; *Nano Energy*, **2015**, *11*, 510.
 DOI: <u>10.1016/j.nanoen.2014.11.028</u>
- Zhao, H.; Yang, G.; Wang, Z.; Cao, X.; Gu, L.; Zhao, N.; J. Exp. Nanosci., 2015, 10, 1126.
 DOI: 10.1080/17458080.2014.980445
- Feng, Y.; Li, W. L.; Hou, Y. F.; Yu, Y.; Cao, W. P.; Zhang, T. D.; Fei, W. D.; *J. Mater. Chem. C*, **2015**, *3*, 1250.
 DOI: 10.1039/c4tc02183e
- Wang, M.; Li, W. L.; Feng, Y.; Hou, Y. F.; Zhang, T. D.; Fei, W. D.; Yin, J. H.; *Ceram. Int.*, **2015**, *41*, 13582.
 DOI: <u>10.1016/j.ceramint.2015.07.153</u>
- 41. Koka, A.; Zhou, Z.; Sodano, H. A.; *Energy Environ. Sci.*, **2014**, *7*, 288.
- DOI: <u>10.1039/c3ee42540a</u>
 Koka, A.; Sodano, H. A.; *Adv. Energy Mater.*, **2014**, *4*, 1301660.
 DOI: <u>10.1002/aenm.201301660</u>
- 43. Li, B.-r.; Shang, W.; Hu, Z.-l.; Zhang, N.-q.; Ceram. Int., 2014, 40, 73.
- **DOI:** <u>10.1016/j.ceramint.2013.05.105</u> 44. Park, K.-I.; Bae, S. B.; Yang, S. H.; Lee, H. I.; Lee, K.; Lee, S. J.;
- Nanoscale, 2014, 6, 8962. DOI: 10.1039/C4NR02246G 45. Zhou, Z.; Tang, H.; Sodano, H. A.; ACS Appl. Mater. Interfaces,
- Zhou, Z.; Tang, H.; Sodano, H. A.; ACS Appl. Mater. Interfaces, 2013, 5, 11894.
 DOI: <u>10.1021/am403587q</u>



Publish your article in this journal

Advanced Materials Letters is an official international journal of International Association of Advanced Materials (IAAM, www.iaamonline.org) published monthly by VBRI Press AB from Sweden. The journal is intended to provide high-quality peer-review articles in the fascinating field of materials science and technology particularly in the area of structure, synthesis and processing, characterisation, advanced-state properties and applications of materials. All published articles are indexed in various databases and are available download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review article, research article, notes, letter to editor and short communications.

Copyright © 2017 VBRI Press AB, Sweden

www.vbripress.com/aml

Copyright © 2017 VBRI Press

Supporting information



Fig. S1. (a-b) FESEM image of $H_2Ti_3O_7$ nanowires and their size distribution and (c-d) FESEM image of $BaTiO_3$ nanowires at 0.08 M $Ba(OH)_2.8H_2O$ and their size distribution.



Fig. S2. XRD spectra of (a) $H_2Ti_3O_7$ nanowires at 0.03 M Ba(OH)₂.8H₂O (* represents peaks of $H_2Ti_3O_7$); (b) intermediate product nanowires at 0.05 M Ba(OH)₂.8H₂O and (c) BaTiO₃ swords at 0.1 M Ba(OH)₂.8H₂O.

Copyright © 2017 VBRI Press