Supporting information:

A Facile Vapor-Phase Hydrothermal Method for Direct Growth of Titanate Nanotubes on a Titanium Substrate via a Distinctive Nanosheet Roll-up Mechanism

Porun Liu,[†] Haimin Zhang,[†] Hongwei Liu, [†] Yun Wang,[†] Xiangdong Yao,[‡] Guangshan Zhu,[‡] Shanqing Zhang,[†] and Huijun Zhao[*,†]

[†]Centre for Clean Environment and Energy and Griffith School of Environment, Griffith University, Gold Coast Campus, QLD 4222, Australia

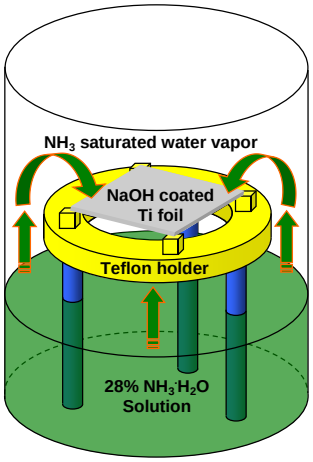
[‡]QLD Micro- and Nanotechnology Centre, Griffith University, Nathan Campus, QLD 4111, Australia

Experimental Section

Synthesis. Prior to the synthesis, Ti metal foils (15 × 20 × 0.25 mm, 99.7%) were orderly washed in acetone, water (Millipore Corp., 18MΩcm) under ultrasonic and then dried in nitrogen flow at room temperature. A NaOH solid layer was coated onto the Ti foils by vertical withdrawing the Ti foils from freshly made NaOH/ethanol solutions (0.5 M) at the speed of 2 mm s^{-1} and dried at 60 °C in an oven for 30 min. A Teflon holder was used to horizontally hold the Ti foil with both sides being exposed above a 10 mL ammonium hydroxide aqueous solution (28% wt) in a Teflon lining. The distance between Ti foil and the solution surface was ~3 cm. The Teflon lining was sealed in a stainless autoclave and kept at 150°C for 1 – 72 h in an oven. After the synthesis, the Ti foils were rinsed in deionised water for three times and finally dried under vacuum at room temperature. Nanotubes can be grown on both sides of the Ti foils. Titanate nanotubes with ~10 nm in diameter were also fabricated on a Ti foil substrate by hydrothermally treating the Ti foil in a 10 mL 10 M NaOH solution at 150ºC for 5 hours.

Characterizations. The morphological properties of samples were investigated by a JSM-6300 scanning electron microscope. The microstructures were examined by field emission TEM Tecnai 20 (F20)

with an accelerating voltage of 200kV. The Ti metal foil samples were cut into small pieces and dispersed in ethanol under ultrasonic. The samples in this suspended liquid were transferred onto TEM copper grids by a drop of the solution. XRD patterns were analysed with a Bruker X-ray diffractometer equipped with graphite monochromatic copper radiation (Cu Ka) operated at 40 kV and 30 mA. Raman spectra were collected with a Renishaw 100 system Raman spectrometer using 632.8 nm He-Ne laser. The scattered light was detected with a Peltier-cooled CCD detector with a spectral resolution of 2 cm^{-1}. The grating was calibrated using the 520 cm^{-1} silicon band. The X–ray photoelectron spectroscopy (XPS) data was acquired using a Kratos Analytical Axis Ultra X–ray photoelectron spectrometer equipped with a monochromatic Al X–ray source (Al Kα, 1.487 keV). The C 1s was used as the charge reference with a binding energy of 284.8 eV. Energy-dispersive X-ray spectroscopy (EDXS) results were acquired with a XL30 SEM.



Scheme S1. VPH experimental set-up.

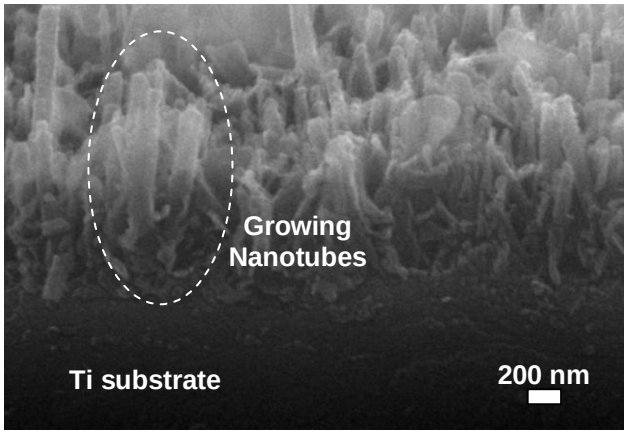


Figure S1. Cross-sectional SEM image of the titanate nanotubes on a Ti foil substrate after 24 hour of VPH reaction.

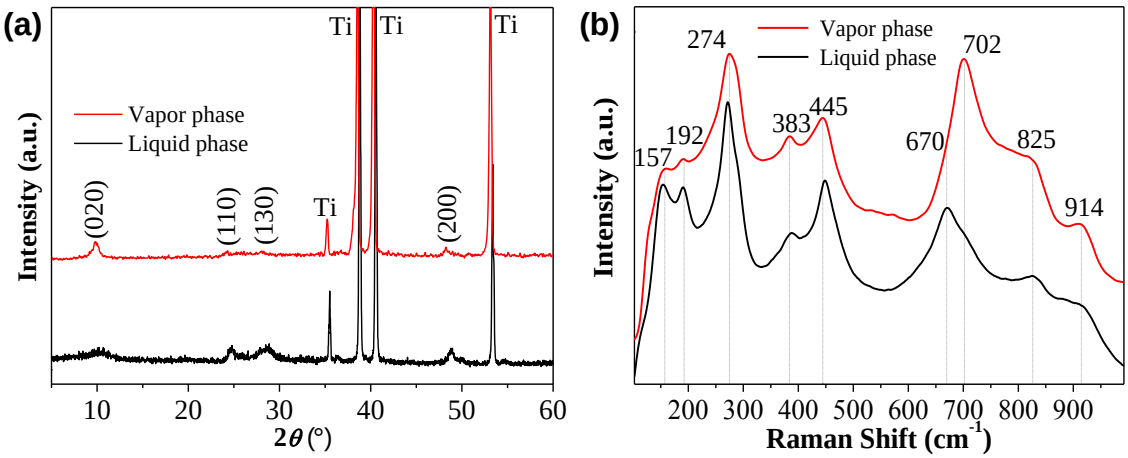


Figure S2. (a) XRD data and (b) Raman spectra of the titanate nanotubes prepared by VPH and LPH methods, respectively.

Table S1. Diffraction data of the titanate nanotubes prepared by VPH method.

d value measured in XRD	d value measured in SAED	$H_{0.7}Ti_{1.825}\square_{0.175}O_4 \cdot H_2O$[a]				
		d	2θ(°)	h	k	l
9.04	8.98	9.37	9.44	0	2	0
3.66	3.65	3.71	24.09	1	1	0
3.18	-	3.26	27.84	1	3	0
-	3.02	3.12	29.65	0	6	0
-	2.30	2.33	39.09	0	5	1
1.89	1.88	1.89	48.10	2	0	0
1.85	-	1.85	49.19	2	2	0
-	1.51	1.51	62.26	2	4	1
-	1.16	1.17	83.24	3	6	0

[a] Calculated from the body-centred orthorhombic (*Immm*) titanate $H_{0.7}Ti_{1.825}\square_{0.175}O_4 \cdot H_2O$, with cell parameters of a = 0.3783 nm, b = 1.8735 nm and c = 0.2978 nm. Refer $(Cs_{0.48}H_{0.22}(Ti_{1.825}O_4)(H_2O)_{0.5}$ (ICDD/PDF number: 83-0702, ICSD code: 79799) for further information of the lepidocrocite-type titanate structure.

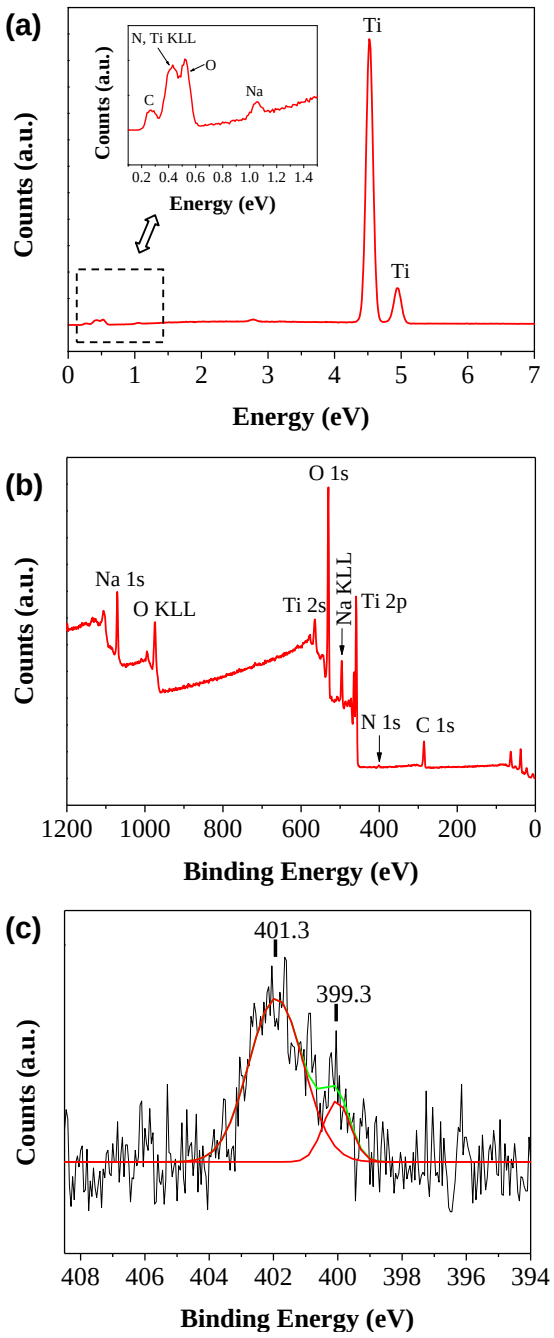


Figure S3. (a) EDXS, (b) survey XPS and (c) N 1s XPS spectra of the titanate nanotubes.

EDXS and XPS analyses were conducted to analyze the cation content. The EDXS results show the presence of small amount of sodium. The N peak is not well defined due to its overlapping with Ti KLL peak. Also, the XPS data indicate the presence of small amount of nitrogen species, which may be attributed to the chemically absorbed nitrogen species (*Science* **2001**, *293*, 269). However, we are not able

to eliminate the possibility of trace amount of ammonium ions (binding energy centered at ~401 eV). In fact, it is very likely that the ammonium ions (generated by the ionization of ammonium hydroxide molecules) intercalate into the multilayered nanosheet/nanotube under the ammonia-abundant reaction conditions. We therefore believe that $H_{0.7-x-y}Na_x(NH_4)_yTi_{1.825}\square_{0.175}O_4 \cdot H_2O$ (where □ = vacancy) would be the best formula to represent the actual chemical composition of the nanotubes. The subscription x and y are dependent on the extent of cation exchange during the washing process.

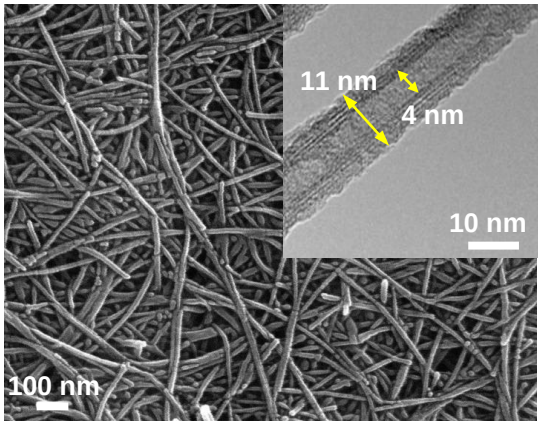


Figure S4. SEM and TEM images (inset) of titanate nanotubes fabricated by LPH method.

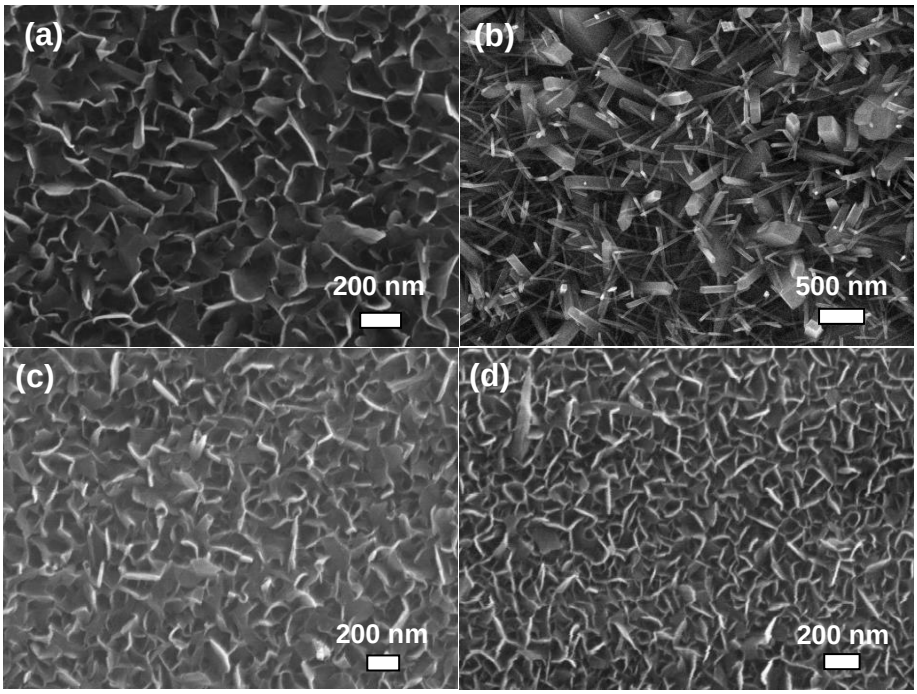


Figure S5. SEM images of the samples prepared by VPH reaction at 150°C for 24 h: (a) with NaOH coating only in water atmosphere; (b) without NaOH coating in HCl atmosphere supplied by 4 % HCl solution; (c) with NaOH, NH_4Cl coatings in water atmosphere; (d) with NaOH, NH_4NO_3 coatings in water atmosphere.

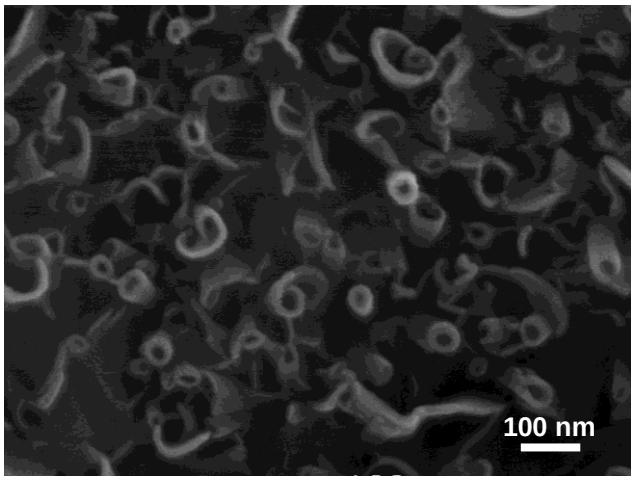
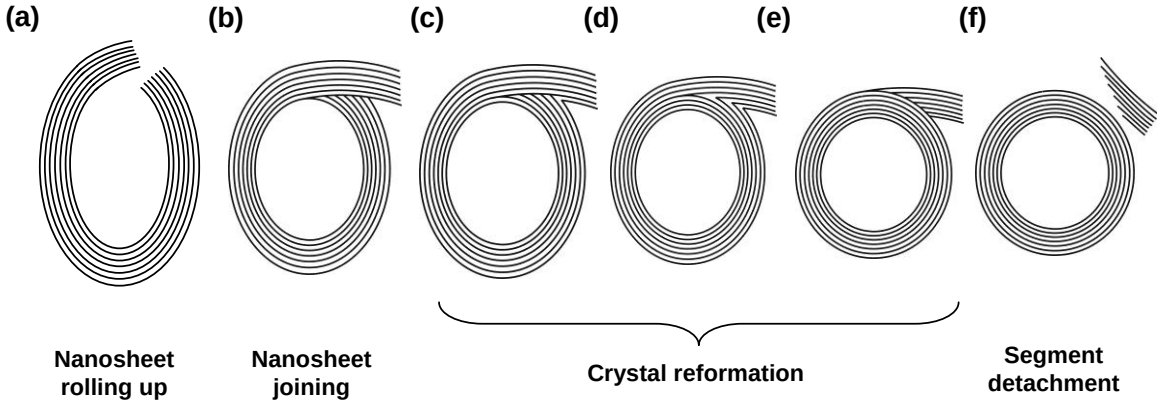


Figure S6. SEM images of the sample prepared by VPH reaction at 150°C for 18 h.



Scheme S2. Schematic illustration of the roll-up and crystal reformation process of the nanotube viewed from the tubular axis.