Supporting Data

Experimental

Preparation of anatase titania nanotubes. Anatase titania nanotube powder was synthesized by the potentiostatic anodization of a titanium foil (0.25mm thickness, Aldrich) which was performed at 20 V in 0.1M perchloric acid aqueous solution using a platinum foil as a cathode. After several minutes, the anodized titania nanotubes were detached from the titanium foil and were precipitated as a powder at the bottom of the reactor. The synthesized titania nanotube powder was washed 4~5 times using a centrifuge in DI water, and then dried at 80°C in an oven, followed by an annealing process at 400 °C for 3hours.

Synthesis of the skein shape TiO₂-B nanotube cluster powder. TiO₂-B nanotube clusters were synthesized as follows. 0.45 g of the anatase TiO₂ nanotube powder was added to a 40 ml of 10M NaOH aqueous solution.¹⁴ After sonication for 30 minutes, the suspension solution was transferred to a Teflon-lined autoclave (60 ml) and hydrothermal reaction was performed at 150 °C for 72hours. The product was washed with DI water, followed by acid treatment, which involved stirring the sample in 0.1M HCl solution for 1hour. The product was then washed by filtration with DI water, dried at 80 °C overnight and sintered at 450 °C for 5hours.

Preparation of electrodes. Composite electrodes were prepared by mixing the TiO_2 -B powder sample, carbon black and poly(vinylidene fluoride) (PVdF) dissolved in N-methyl-2-pyrrolidone (NMP) in the 80:10:10 weight ratio. Carbon black was used as a conductive additive, and PVdF was added as a binder. The mixed active material was deposited on aluminium foil as a current collector, followed by vacuum drying at 120 °C for 12hours. The electrolyte for the cell was LiPF₆ (1 M) with ethylene carbonate (EC)/diethylene carbonate (EMC) (1:1:1 (v/v/v)), Techno SEMICHEM Co., Ltd., Korea). All cells were constructed and handled in an Ar filled glovebox.

Characterization and electrochemical measurement. The morphology of the synthesized TiO₂-B nanotube clusters was examined by field emission scanning tunneling electron microscopy (FE-STEM, S-5500, Hitachi). X-Ray diffraction (XRD) measurements were carried out to observe the crystalline phase with a Siemens diffractometer D500/5000 in Bragg-Bretano geometry under Cu Ka radiation. Cells were galvanostatically charged down to 1.0 V and then discharged up to 2.5 V using a battery tester (Toscat-3000U, Toyo). Rest time between charge and discharge was 10 minutes. For evaluating the rate performance, various C-rates ranging from 0.1 C to 10 C were applied to the discharge process while the current applied to the charge process was kept at 0.1C ($1C = 240 \text{ mA g}^{-1}$). Moreover, high rate charge/discharge tests were also conducted using same C-rates for charge and discharge steps.

¹⁴ A. R. Armstrong, G. Armstrong, J. Canales and P. G. Bruce, J. Power Sources, 2005, **146**, 501.



Figure S1. SEM image of the synthesized TiO_2 nanotube array powder from the anodizing method.



Figure S2. Raman spectra of Na-titanate from two different starting materials; (a) TiO_2 nanotube powder, (b) TiO_2 nanoparticles.



Figure S3. X-ray diffraction patterns of the skein shape TiO2-B nanotube cluster powder prepared from TiO2 nanotubes (upper red line) and TiO2-B nanowires synthesized from TiO2 nanoparticles (lower black line). For comparison, inorganic crystal structure database (ICSD) reference data of TiO2-B (No. 01-074-1940) is displayed at the bottom.



Figure S4. SEM images of the skein shape TiO_2 -B nanotube cluster powder. The synthesized TiO_2 -B is composed of many micron sized particles with various sizes larger than 1 μ m.

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Starting Material: P25	P-25 (anatase)	TiO ₂ -B
Surface area (m ² /g)	50.0	24.5
Pore volume (cm ³ /g)	0.25	0.10
Pore size (nm)	17.5	21.9
Starting Material: TNT	TNT (anatase)	TiO ₂ -B
Surface area	73.9	257.2
Pore volume	0.29	0.64
Pore size	12.3	7.4

Table S1. Surface area, pore volume and pore size of various TiO₂ materials.



Figure S5. (A, B, C) Scanning mode STEM images of TiO_2 -B nanowires from P-25 as the starting material, (D) Corresponding tunneling mode image of C image.



Figure S6. A difference in aggregation density between the skein shape TiO_2 -B nanotube cluster particle and nanowires. (A) scanning and (B) tunneling mode STEM images of TiO_2 -B nanotube particle; (C) scanning and (D) tunneling mode STEM images of TiO_2 -B from P-25 as the starting material. Figure S6 (B) shows the dense particle like morphology of TiO_2 -B nanotube particle, while the loosely gathered TiO_2 -B nanowires are found in Figure S6 (D).



Figure S7. Schematic illustration for the formation of skein shape of Na-titanate.



Figure S8. (A, B) Separate drawings of Figure 3(A); (C) Corresponding differential capacity plots (dQ/dV) of TiO₂-B nanotube powder and nanowires.



Figure S9. Charge/discharge curves of the TiO_2 -B nanowires at various C-rates.



Figure S10. (A) Charge/discharge rate performance of the skein shape TiO₂-B nanotube particle and nanowires. (B) Rated charge/discharge curves at various C-rates. Both high charge and discharge rates are applied. The charge/discharge rate performance applying both high charge and discharge rates is given in Figure S8. Although the discharge capacities under the application of high charge rates are slightly lower at same discharge rates (137 mAh g⁻¹ at 30C, 110 mAh g⁻¹ at 60 C, 86 mAh g⁻¹ at 100 C), the capacities based on electrode weight (80 wt% active material loading) are higher than those (70 wt % active material loading) in the previous study on mesoporous TiO₂-B microspheres.²