Supporting Information for

Mesoporous TiO₂-B Microflowers Composed of $(1 \overline{1} 0)$ Facet Exposed Nanosheets for Fast Reversible Lithium-Ion Storage

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Experimental Section

Material Synthesis

TiO₂-B microflowers were synthesized by a hydrothermal method. In a typical synthesis, 1 cm² Ti-foil (99.9 %, MTI) was submerged into 16 mL of 1 M NaOH solution with 0.58 mL of 30 wt. % H₂O₂ (*CAUTION: extremely caustic*). This mixture was heated to 150 °C for 5 h in a 23 mL Teflon-lined stainless steel autoclave (Parr instruments); heating and cooling rates were 10 °C/min. *CAUTION: Due to the formation of highly reactive hydrogen peroxide anion* (HO_2^-), extreme care should be taken while handling the basic solution of H_2O_2 ($H_2O_2 + NaOH$). After cooling, unreacted Ti-foil was physically removed, and the white product of the hydrothermal reaction was washed several times with deionized water, and dried overnight in a vacuum oven at 80 °C to give 20 mg of white powder (0.056 mmol, 10 % based on starting Ti) of the sodium titanate intermediate (Na₂Ti₂O₅•H₂O). This intermediate was immersed in 200 mL of a 0.05 M HNO₃ solution for 10 hours, and then isolated by centrifugation. This step was repeated two additional times, and the product was washed with deionized water several times with near quantitative conversion to hydrogen titanate (H₂Ti₂O₅•H₂O). The bronze-phase product was obtained after heating the hydrogen titanate intermediate at 300 °C for 1 h in an MTI compact muffle furnace. For comparison,

TiO₂-B bulk, nanotubes and nanoparticles were prepared by following their previously reported synthesis methods.

Material Characterization

X-ray diffraction (XRD) patterns (2 θ range 10 – 70°) were collected on a Bruker D8 advance diffractometer equipped with a Lynx-Eye detector and parallel beam optics using Cu-K α radiation ($\lambda = 0.154184$ nm). Raman spectra of TiO₂-B microflowers were recorded with a Renishaw inVia Reflex micro-Raman system equipped with a 647 nm Ar⁺ ion laser. An Inspect FEI Nova-200 Nanolab microscope equipped with an EDX spectrometer was employed for the scanning electron microscopy (SEM) studies. A JEOL JEM-3011 and JEOL JEM-2100F microscopes working at an accelerating voltage of 300 kV was used for transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) respectively. The nitrogen adsorption and desorption isotherms were collected using a Quantachrome 2000e surface area analyzer. FTIR spectra were recorded using a Nicolet Magna 560 spectrometer.

Electrochemical Evaluation

Working electrodes were fabricated by a conventional coating technique. A slurry of TiO₂-B (70 wt %), Super-P carbon black (20 wt %) and polyvinylidene fluoride (PVDF, 10 wt %) in *N*-methyl-2-pyrrolidone (NMP) was coated onto a copper foil using the doctor blade instrument. Then, the foil was dried in the vacuum oven overnight at 80 °C, and then pressed under a pressure of 0.5 metric ton to provide compaction. The active material loading was $1 - 2 \text{ mg/cm}^2$. These electrodes were assembled into Swajelock-type cells using a glass fiber separator, 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC, 2:1 vol %) electrolyte solution and Li-foil counter electrode. The electrochemical cells were assembled in a glovebox (Vacuum Atmospheres.) filled with high-purity argon (99.9995%). The glovebox was equipped with O₂ and H₂O absorbers and detectors in order to bring the oxygen and

moisture contents in the atmosphere to below the parts per million level. A Vencon UBA5 battery analyzer was used for the galvanostatic charge-discharge cycling of the two electrode cells in the potential range of 1.0 - 3.0 V vs. Li^{+/0}. Galvanostatic cycling experiments at various C rates (0.5–20) (current densities of 0.021–8.4 mA/cm² respectively) were repeated at least three times, and the results were within the 5 % error limit.



Figure S1. X-ray diffraction patterns of (a) Bulk TiO_2 , (b) TiO_2 -B nanoparticles, and (c) TiO_2 -B nanotubes



Figure S2. EDX spectra of (a) Na₂Ti₂O₅•H₂O and (b) TiO₂-B microflowers.



Figure S3. HRTEM images of TiO₂-B microflowers

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Figure S4. (a) N₂ adsorption-desorption isotherm, and (b) pore size distribution of TiO₂-B microflowers.



Figure S5. TGA trace for TiO₂-B microflowers



Figure S6. FTIR spectra of (a) hydrothermally synthesized H₂Ti₂O₅·H₂O intermediate treated with D₂O; (b) TiO₂ microflowers formed after annealing the D₂O-treated intermediate to 300°C; (c) Untreated TiO₂-B microflowers for comparison.

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Figure S7. TGA trace comparison among TiO₂-B microflowers, bulk, nanoparticles, and nanotubes.



Figure S8. Electrochemical rate performance of (a) bare TiO₂-B nanosheets and (b) TiO₂-B microflowers composed of nanosheets



Figure S9. Coulombic efficiency of TiO₂-B microflower electrodes at various charge/discharge rates.



Figure S10. SEM image of TiO₂-B microflowers after 1000 charge/discharge cycles

Table S1. Water content in TiO₂-B by mass as determined by weight loss after 300 °C.

Sample	H ₂ O (wt %)
Bulk TiO ₂ -B	0.28
TiO ₂ -B Microflowers	3.55
TiO ₂ -B Nanoparticles	2.42
TiO ₂ -B Nanotubes	1.12