Electronic Supplementary Information

Hierarchical tubular structures constructed from ultrathin TiO_2(B) nanosheets for highly reversible lithium storage

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Experimental Section

Synthesis of Cu nanowires. In a typical synthesis, $CuCl_2\ 2H_2O$ (52 mg), glucose (90 mg) and hexadecylamine (460 mg) were vigorously stirred in 20 mL of deionized water for 6 h to give a light blue emulsion. Then the emulsion was transferred into a Teflon-lined stainless steel autoclave of 50 mL capacity and heated at 120 ^oC for 6 h before cooling down to room temperature naturally. The precipitate was collected by centrifugation and washed by deionized water, ethanol, and cyclohexane repeatedly. Then, the Cu nanowires were dried in a vacuum oven at room temperature overnight.

Preparation of TiO_2(B) hierarchical tubes (HTs). $TiCl_3$ solution (1 mL) and deionized water (1 mL) were added into 30 mL of ethylene glycol under stirring to produce a light purple solution. Then, 8 mg of Cu nanowires was fully immersed into this solution and sealed in an 80 mL Teflon-lined stainless steel autoclave, which was then solvothermally treated at 150 ^oC for 24 h. The as-obtained products were washed with ethanol several times before vacuum drying at room temperature overnight. The TiO_2(B) HTs were then annealed at 350 ^oC for 2 h with a ramping rate of 2 $^oC\ min^{-1}$ to remove the surface-adsorbed organic molecules. The TiO_2(B) nanospheres (NSs) were synthesized under the identical conditions except for the addition of Cu nanowires.

Materials characterizations. XRD patterns of all the products were recorded on a powder X-ray diffractometer (Bruker, D8-Advance XRD, Cu Kα, λ = 1.5406 Å). Morphologies of the samples were examined by field-emission scanning electron microscope (FESEM; JEOL, JEM-6700F, 5 kV) and transmission electron microscope (TEM; JEOL, JEM-1400, 100 kV/JEM-2010, 200 kV). Energy-dispersive X-ray spectroscope (EDX) attached to the FESEM was utilized to analyze the composition. X-ray photoelectron spectroscopy (XPS) measurement was carried out on a VG

Escalab 250 spectrometer equipped with an Al anode (Al Kα = 1846.6 eV). Raman spectrum was recorded on a Renishaw inVia micro-Raman system equipped with a 785 nm excitation laser. Thermogravimetric analysis was performed on a thermal analyzer (PerkinElmer, Diamond TG/DTA) under flowing air with a temperature ramp of 10 ℃ min^{-1}. The specific surface area and porosity of the TiO_2(B) HTs were analyzed with a Quantachrome Autosorb AS-6B system.

Electrochemical measurements. The working electrode slurry was prepared by mixing active materials, carbon black (Super P-Li) and sodium carboxymethyl cellulose binder in deionized water with a mass ratio of 70: 20: 10. The slurry was then spread on copper foil and dried in a vacuum oven at 100 ^{o}C overnight prior to Swagelok-type cell assembly. The active material loading is around 1~1.4 mg cm^{-2} for each electrode. Lithium foil was used as the counter and reference electrode, and 1.0 M $LiPF_6$ in ethyl carbonate/dimethyl carbonate (1:1 v/v ratio) was used as the electrolyte. Cyclic voltammetry (CV; 1.0-3.0 V, 1 mV s^{-1}) measurements were performed on a CHI660C electrochemical workstation. Impedance measurements were performed using a CHI660E electrochemical workstation by applying an ac amplitude of 5 mV over the frequency range from 0.1 to 10^5 Hz. Galvanostatic charging/discharging tests were conducted on a battery tester (NEWAER).

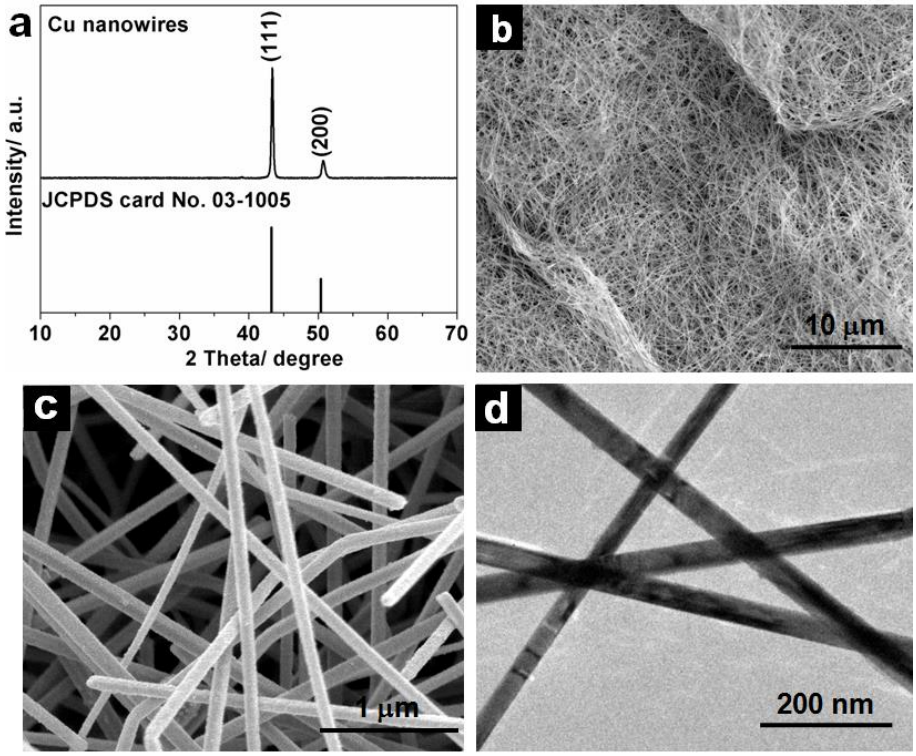

Fig. S1 (a) XRD pattern, (b, c) FESEM images, and (d) TEM image of Cu nanowires.

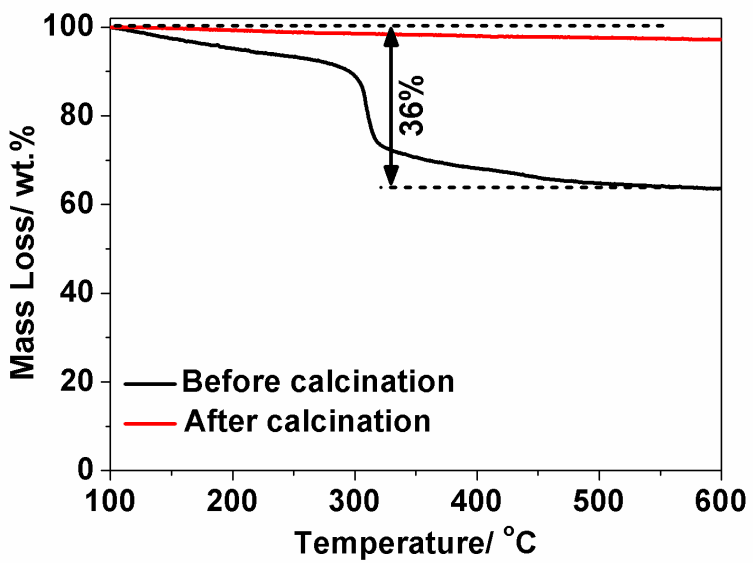

Fig. S2 TGA profiles of TiO_2(B) HTs before and after calcination.

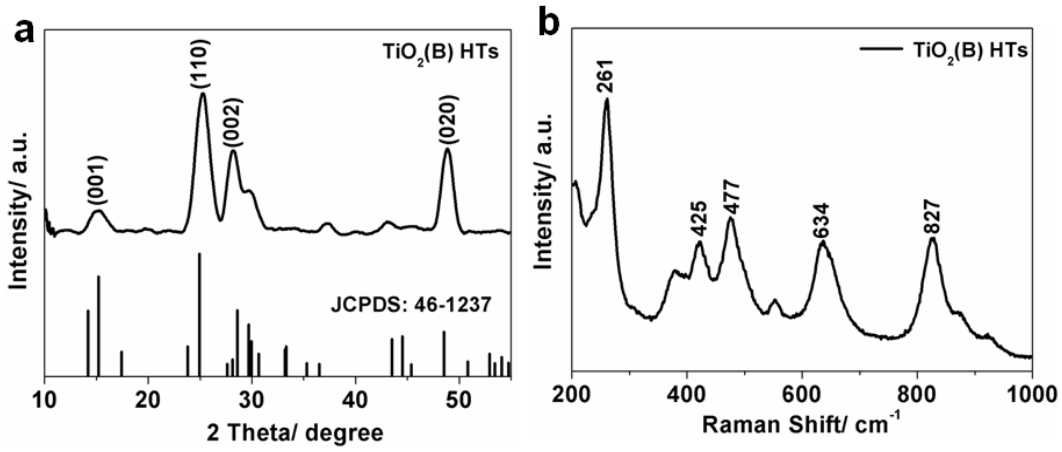

Fig. S3 (a) XRD pattern and (b) Raman spectrum of TiO_2(B) HTs before annealing.

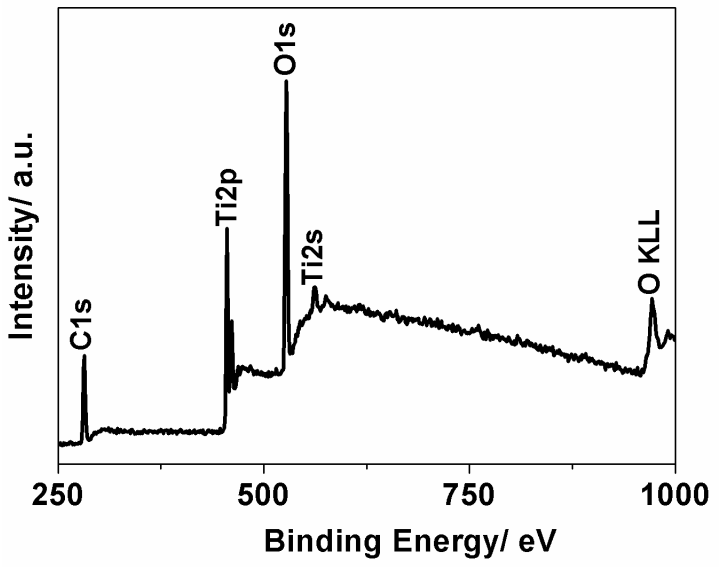

Fig. S4 XPS spectrum of TiO_2(B) HTs obtained after solvothermal reaction for 24 h.

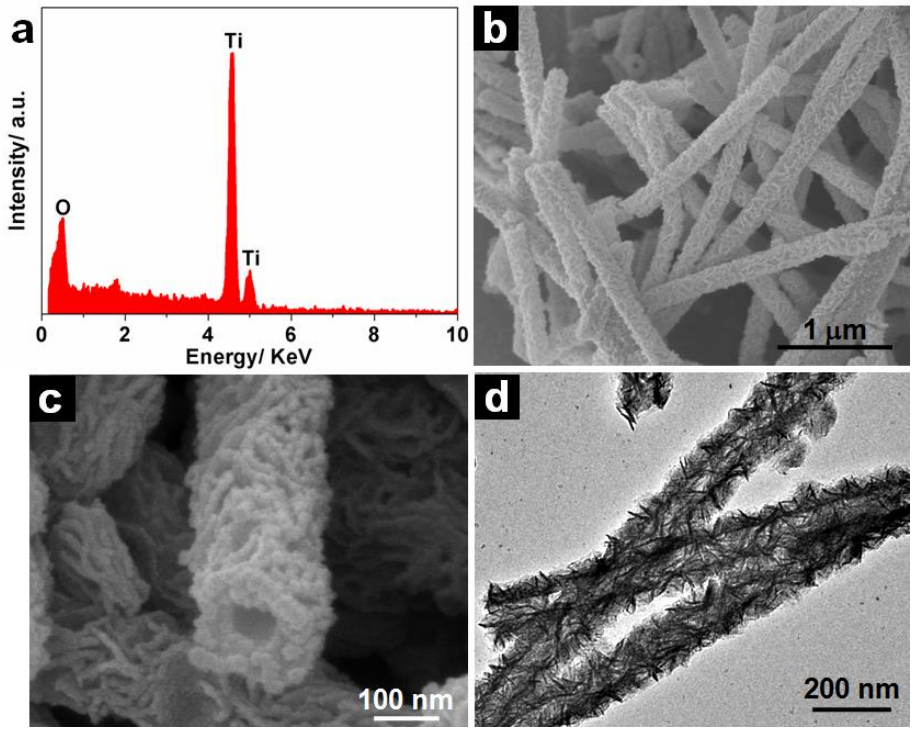

Fig. S5 EDX spectrum (a), FESEM images (b, c) and TEM image (d) of TiO_2(B) HTs after calcination.

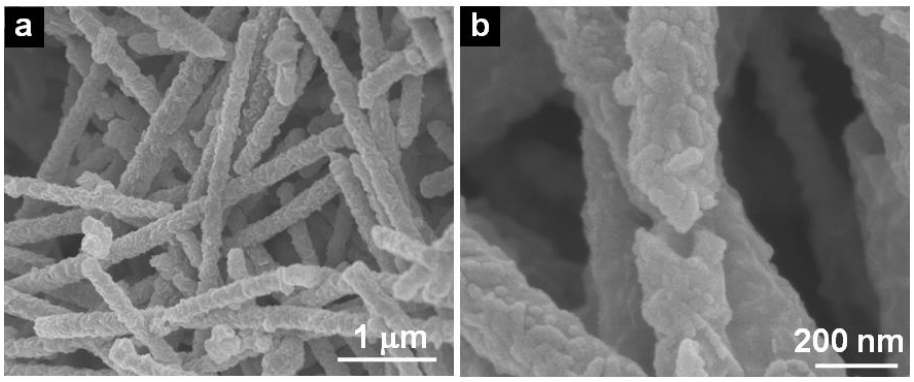

Fig. S6 FESEM images of Cu@TiO_2(B) core-shell structures after reaction for 6 h.

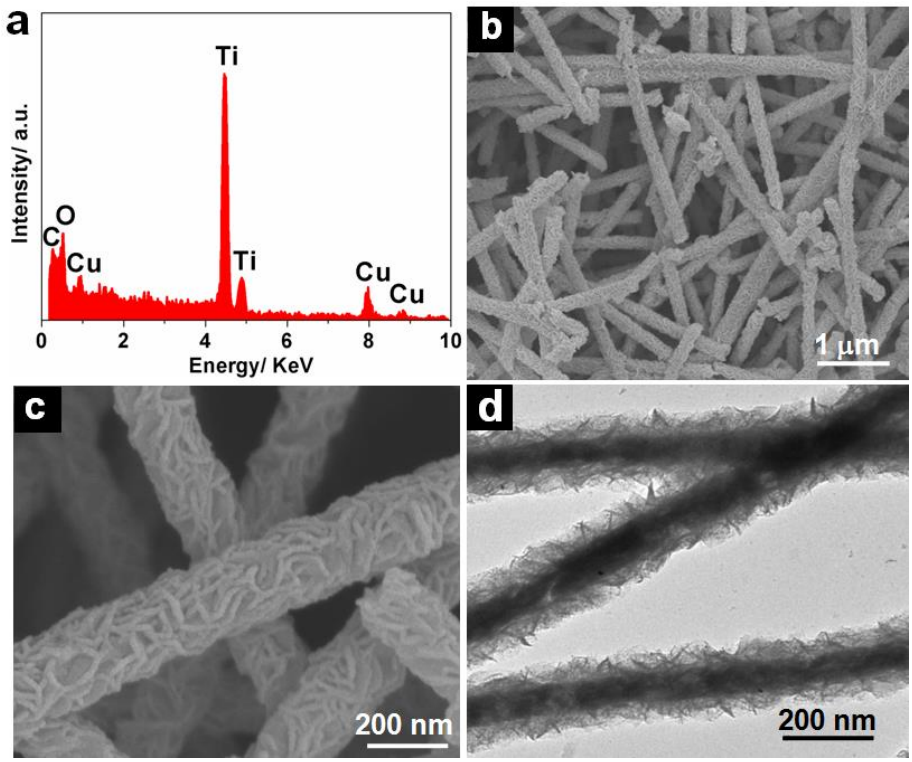

Fig. S7 EDX spectrum (a), FESEM images (b, c) and TEM image (d) of Cu@TiO_2(B) core-shell structures after reaction for 9 h.

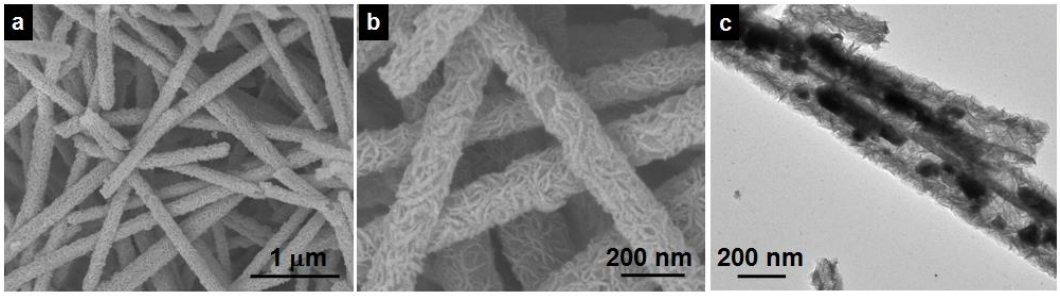

Fig. S8 FESEM images (a, b) and TEM image (c) of the product after reaction for 12 h.

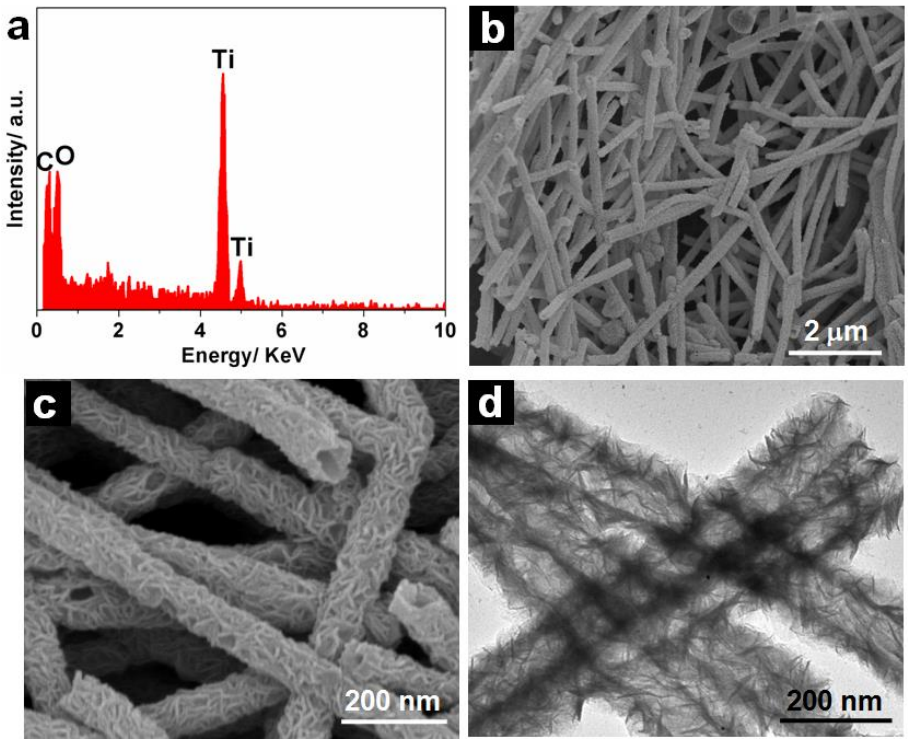

Fig. S9 EDX spectrum (a), FESEM images (b, c) and TEM image (d) of TiO_2(B) HTs after reaction for 24 h.

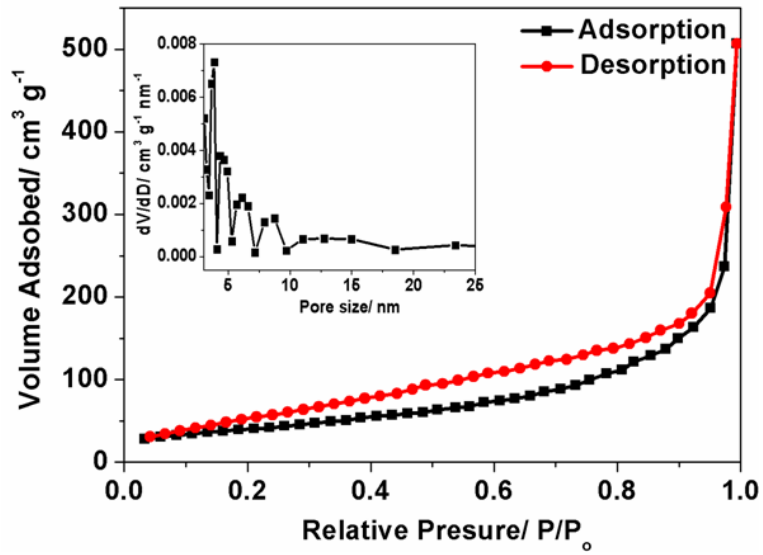

Fig. S10 N_2 adsorption/desorption isotherm of the TiO_2 (B) HTs after calcination. The inset shows the pore size distributions calculated using the BJH method.

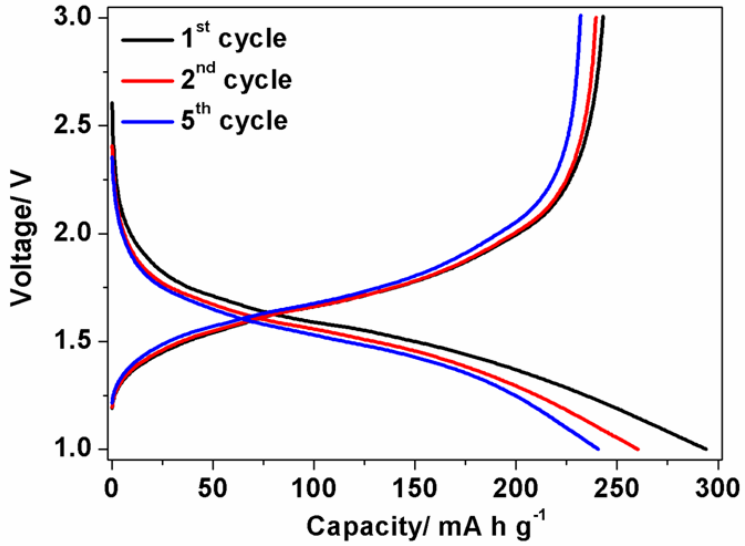

Fig. S11 Discharge-charge voltage curves of the TiO_2(B) HTs for the 1st, 2nd and 5th cycles at a current rate of 1 C.

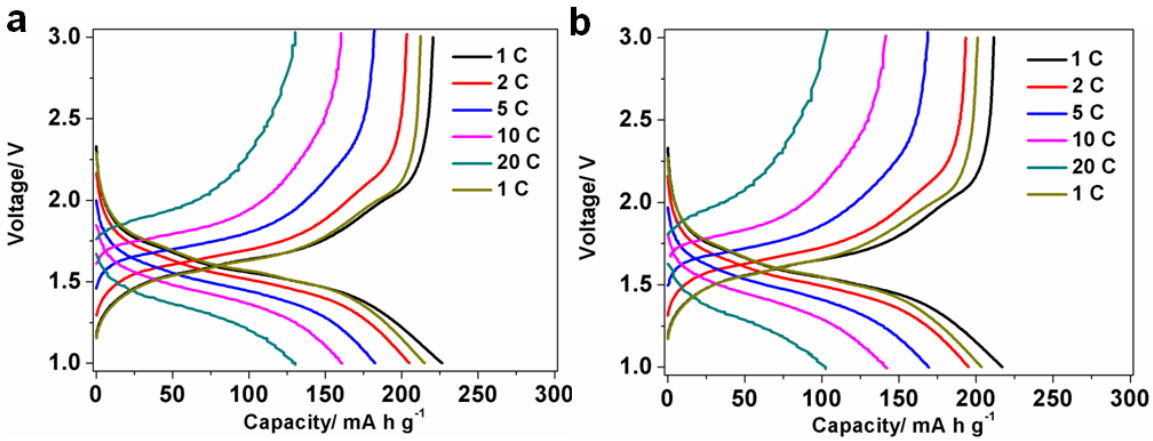

Fig. S12 Discharge-charge voltage curves of the TiO_2(B) HTs (a) and TiO2(B) NSs (b) at different current rates. The profiles were generated from the first stabilized cycles at each current rate of Fig. 4b.

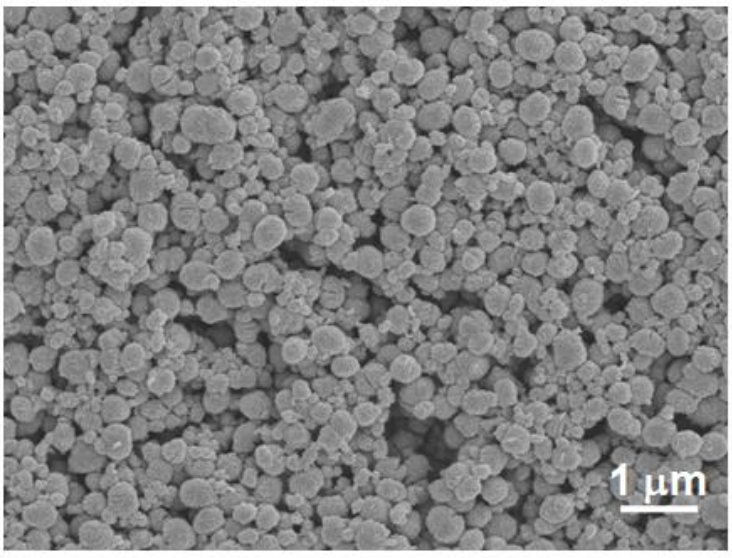

Fig. S13 FESEM image of TiO_2(B) NSs synthesized without Cu nanowires.

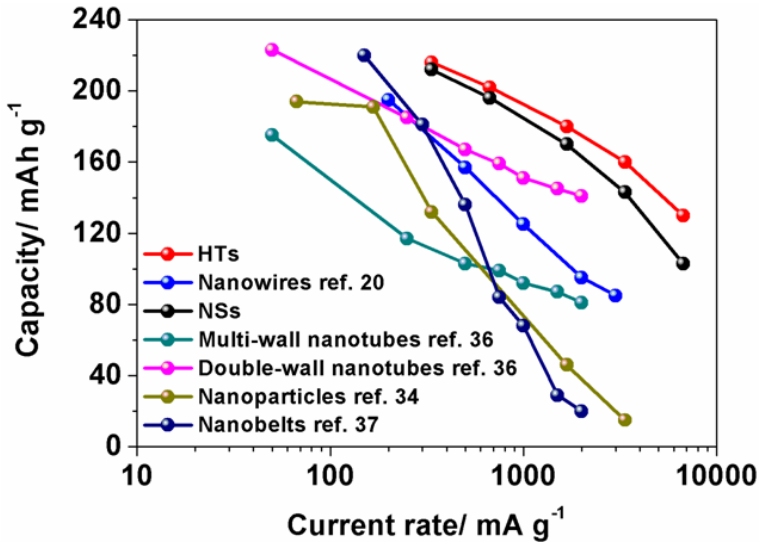

Fig. S14 Comparison of rate performance of different TiO_2(B) nanostructures.

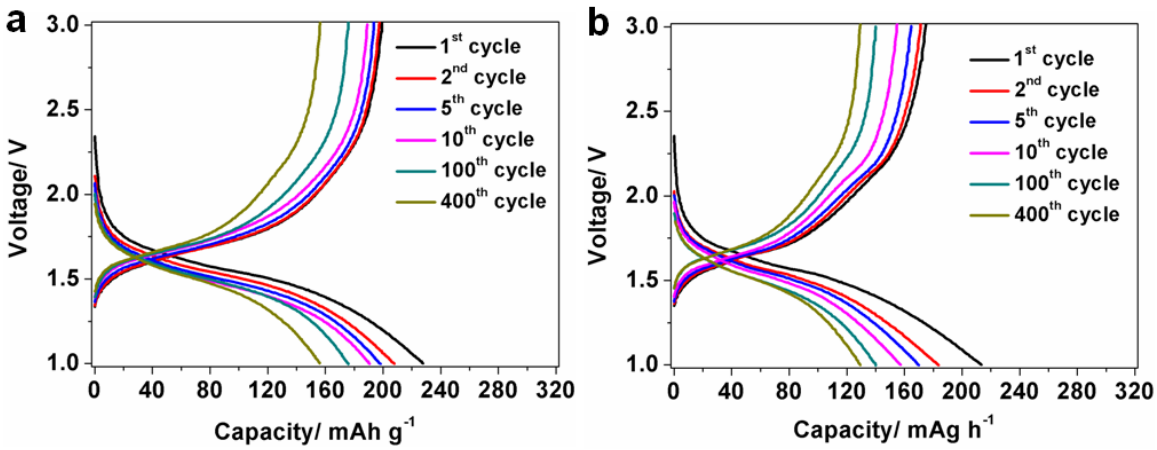

Fig. S15 Discharge-charge voltage curves of the TiO_2(B) HTs (a) and TiO_2(B) NSs (b) of different cycles at a current rate of 5 C.

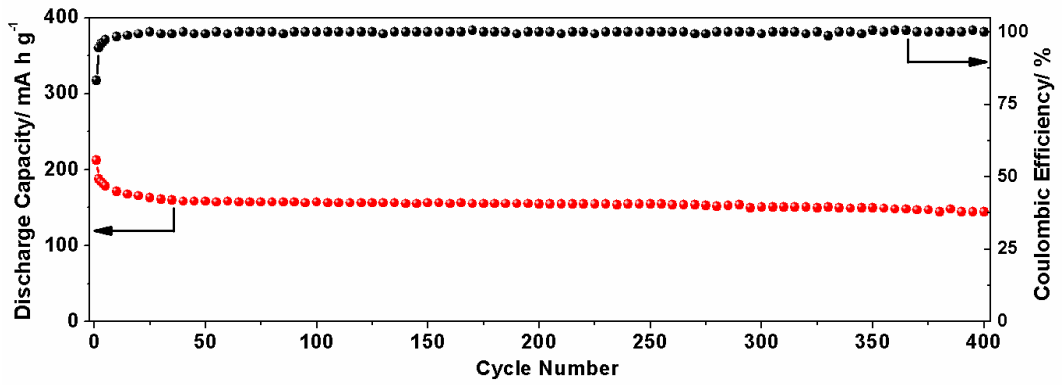

Fig. S16 Cycling performance of TiO_2(B) HTs at a constant current rate of 10 C.

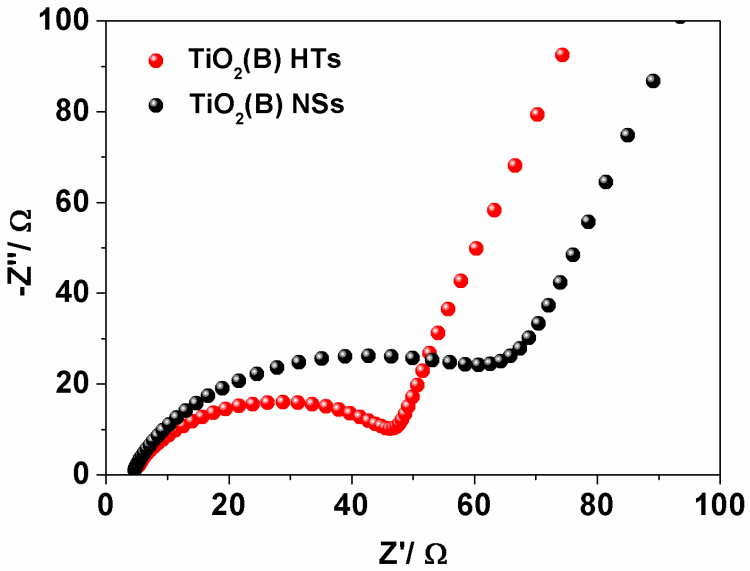

Fig. S17 Nyquist plots of the cells based on electrodes of TiO_2(B) HTs and TiO_2(B) NSs.

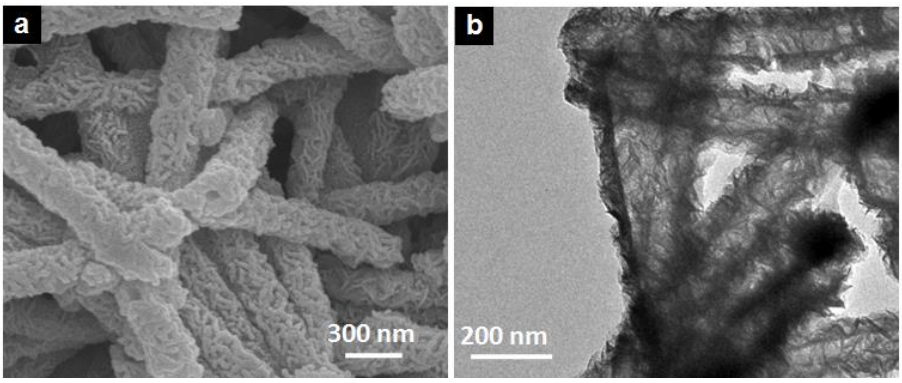

Fig. S18 FESEM image (a) and TEM image (b) of TiO_2(B) HTs after being discharged/charged over 400 cycles at a current density of 5 C.