

Supporting Information for

Hierarchical Protonated Titanate Nanostructures for Lithium-ion Batteries†

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1. Experimental Section

1.1 Synthesis of hierarchical NaTNFs and PTNFs

The Ti foil (99.7%, Aldrich Corporation) was subjected to galvanostatic anodization current (0.5 A cm^{-2}) in a two-electrode electrochemical cell connected to a DC power supply. A platinum foil was served as the counter electrode. The experiments were conducted in 10 M NaOH aqueous solutions starting at room temperature (about $25 \text{ }^{\circ}\text{C}$) without any heating or stirring outside during the whole anodization process. After anodization, the grey white precipitate collected from the solution was centrifuged and then washed with distilled water, yielding NaTNFs. The PTNFs were obtained by washing NaTNFs with HCl solution (0.1 M) and distilled water in order until the pH value reached 7, and then dried in air. The morphologies of the titanate flowers formed under different current densities (0.25 A cm^{-2} , 0.5 A cm^{-2} , 0.75 A cm^{-2} and 1.00 A cm^{-2}) are quite similar, thus we focus on one of them (0.5 A cm^{-2}) in all subsequent studies.

1.2 Preparation of 1D PTNTs and PTNWs by hydrothermal method

The 1D PTNTs and PTNWs can be synthesized by hydrothermal method in alkaline conditions at different temperatures. In a typical process, the commercial anatase titania powder (~2 g) and an aqueous solution of NaOH (10 M, 75 mL) were placed into a Teflon-lined autoclave. The mixture was stirred to form a milk-like suspension, sealed and hydrothermally treated at 130 °C (PTNTs)/170 °C (PTNWs) for 48 h. Then the precipitate was separated by filtration and washed with deionized water until a pH value near 8 was reached. The proton-exchange was conducted in 0.1 M HCl acid solution for 3 times yielding the PTNTs and PTNWs.

1.3 Preparation of PTBMs by solid state method

In the typical process, the trititanate ($\text{Na}_2\text{Ti}_3\text{O}_7$) can be synthesized by heating mixtures of Na_2CO_3 and TiO_2 (molar ratio=2.9) at 900 °C for 24 h. The pure phase of the trititanate ($\text{Na}_2\text{Ti}_3\text{O}_7$, JCPDS-031-1329) possesses a monoclinic unit cell of $a=0.913$ nm, $b=0.381$ nm, $c=0.857$ nm, and $\beta=101.45^\circ$). The hydrogen-exchange of $\text{Na}_2\text{Ti}_3\text{O}_7$ (~1 g) was performed in 100 mL of 1 M HCl acid solution for 3 times. The acid solution should be changed every day in order to remove Na^+ completely from the compounds. Then products were washed with distilled water and dried in air at 80 °C.

2. Analytical methods

The morphology of the as-synthesized samples were investigated by using field emission scanning electronic micrograph (FESEM; JEOL, JSM-6340F) and transmission electron micrograph (TEM; JEOL, JEM-2010). A Shimadzu 6000 X-ray diffractometer with a Cu K_α source was used for phase identification. Nitrogen adsorption/desorption isotherms were measured at 77 K using ASAP2000 adsorption apparatus from

Micromeritics. The samples were degassed under vacuum before analysis.

3. Electrochemical measurements

The electrochemical performance was investigated using coin-type cells (CR 2032) with lithium metal as the counter and reference electrodes. To make the working electrode, each of the active materials (PTNFs, NaTNFs, PTNTs, PTNWs and PTBMs) was mixed with acetylene black and polyvinylidene fluoride (PVDF) binder with a typical weight ratio of 80:15:5. The electrolyte was 1 M LiPF_6 in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. The cells were assembled in a glove box with the oxygen and water contents below 1.0 and 0.5 ppm, respectively. Charge-discharge cycles of titanate materials/Li half-cell were tested between 1.00 and 3.00 V vs Li^+/Li at a constant current density of 50 mA g^{-1} with a NEWARE battery tester. Cyclic voltammetric (CV) tests were conducted from 3.00 to 1.00 V using an electrochemical analyzer (Gamry Instruments. Inc).

4. Supplementary results

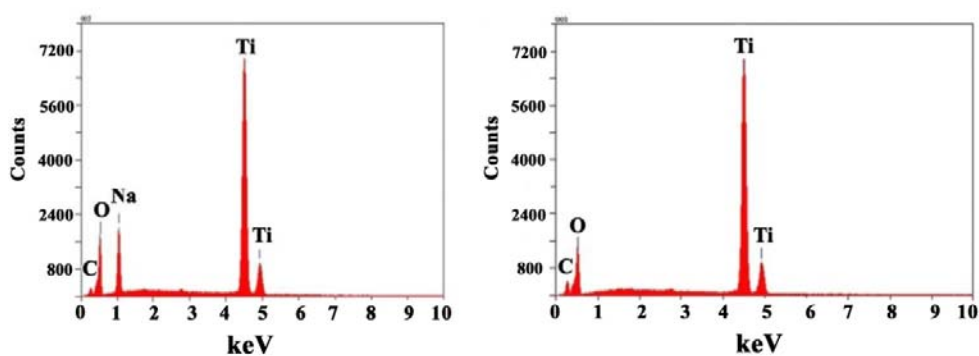


Fig. S1. EDS data of as prepared powers of (a) NaTNFs and (b) PTNFs.

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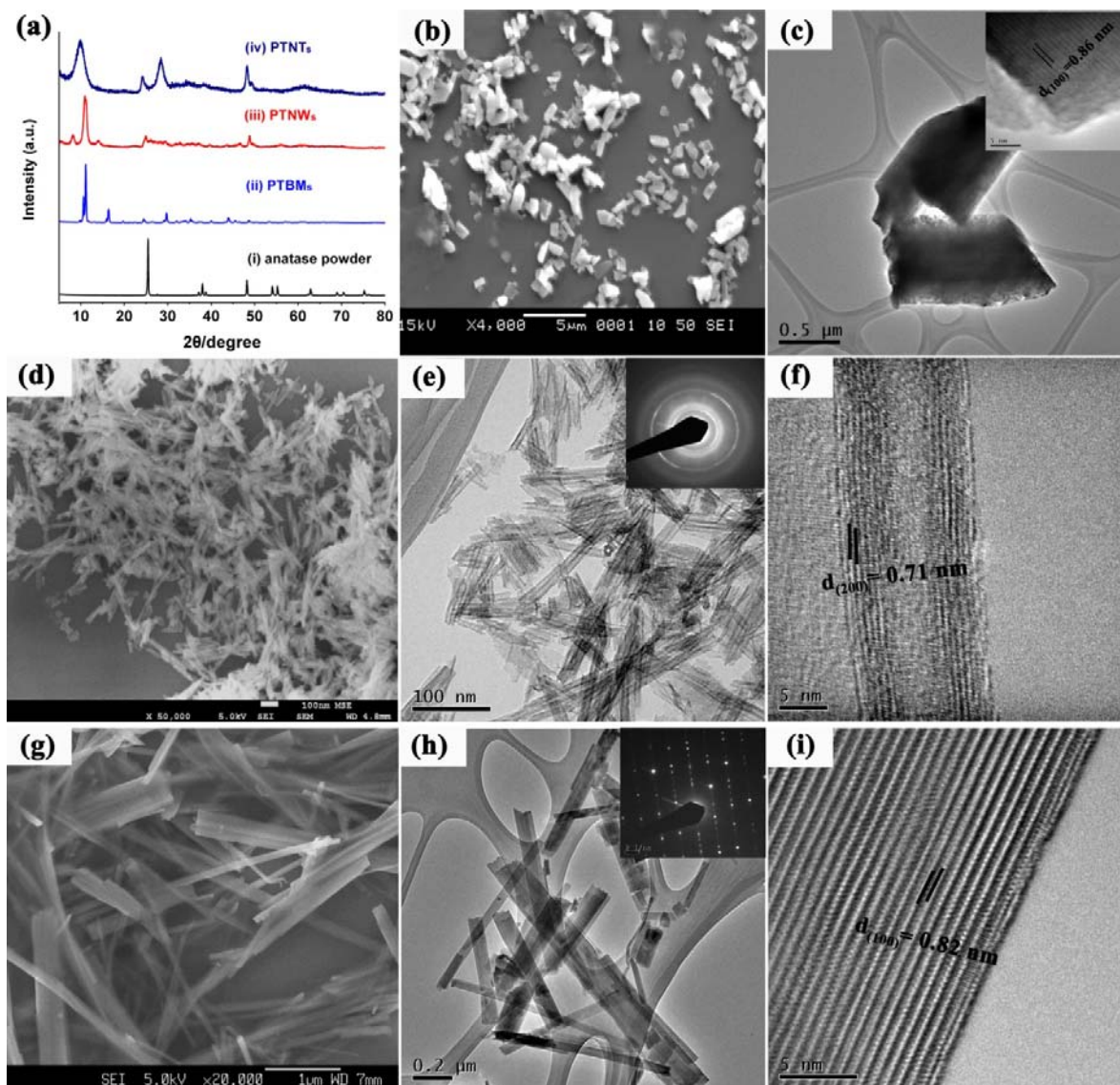


Fig. S2. (a) The XRD patterns of (i) starting material anatase powder, (ii) PTBMs, (iii) PTNWs, (iv) PTNTs; (b) The SEM image and (c) TEM image of PTBMs (H₂Ti₃O₇); (d) The SEM image, (e) TEM image and (f) High resolution TEM image of PTNTs synthesized at 130 °C for 48 h in 10 M NaOH solution; (g) The SEM image, (h) TEM image and (i) High resolution TEM image of PTNWs synthesized at 170 °C for 48 h in 10 M NaOH solution. The insets in (e) and (h) are the diffraction patterns of PTNTs and PTNWs, respectively.

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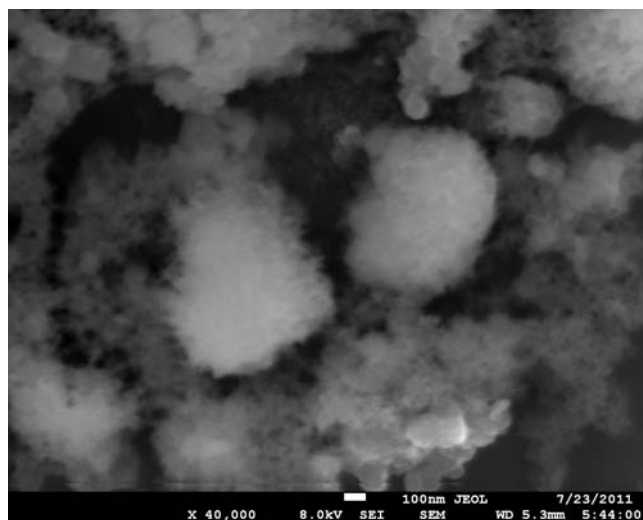


Fig. S3. FESEM image of the PTNFs after charge/discharge for 100 cycles.