

Supporting Information

Nanotube-based hierarchical titanate microspheres: an improved anode structure for Li-ion battery

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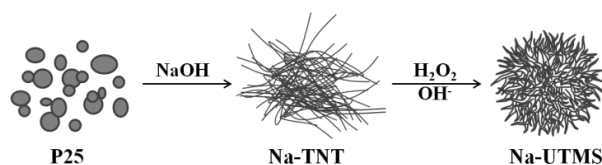
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Experimental Section

Fabrication routes:



Scheme 1. Schematic drawings of the fabrication routes for urchin-like Na-titanate microspheres (Na-UTMS).

Synthesis of Na-titanate nanotubes (Na-TNT): Na-TNT was prepared by hydrothermal reaction of P25 in NaOH solution. Typically, 2 g P25 was put into 40 mL of 10 M NaOH aqueous solution, after ultrasonic with agitation for 5 min, the solution transferred to a 50 mL Teflon-lined stainless steel autoclave, and sealed. The autoclave was put into an oven, heated at 120 °C for 24 h, and cooled naturally in air, producing Na-TNT precipitates. These precipitates were isolated from solution by centrifugation and subsequently washed with deionized water several times to removing excess NaOH, and then dried at 60 °C in vacuum. The H-TNT was prepared by proton-exchange of Na-TNT in 0.05 M HNO₃ solution with agitating for several hours, and then isolated by centrifugation. This step was repeated for 2 times, and then washed again with deionized water until pH ~7 was reached. The obtained H-TNT product was dried at 60 °C in vacuum.

Synthesis of urchin-like Na-titanate microspheres (Na-UTMS): Na-UTMS was prepared by hydrothermal reaction of Na-TNT with H₂O₂ in NaOH solution. Typically, 0.2 g Na-TNT and 1.5 mL H₂O₂ (30%) were put into 40 mL of 1 M NaOH aqueous solution, after ultrasonic with agitation for 5 min, the solution transferred to a 50 mL Teflon-lined stainless steel autoclave, and sealed. The autoclave was put into an oven, heated at 150 °C for 12 h, and cooled naturally in air, producing Na-UTMS precipitates. These precipitates were isolated from solution by centrifugation and subsequently washed with deionized water several times to removing excess NaOH, and then dried at 60 °C in vacuum. The H-UTMS was prepared by proton-exchange of Na-UTMS in 0.05 M HNO₃ solution with agitating for several hours, and then

isolated by centrifugation. This step was repeated for 2 times, and then washed again with deionized water until pH ~ 7 was reached. The obtained H-UTMS product was dried at 60°C in vacuum.

Materials Characterization: The morphologies and the structures of the samples were characterized by scanning electron microscopy (SEM, Hitachi S4800), Energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, FEI Tecnai F30, 300 kV), X-ray powder diffraction (XRD, Rigaku D/max-2500 diffractometer with CuK α radiation, $\lambda=0.1542$, 40 kV, 100 mA), and BET (Micrometrics ASAP 2010).

Electrochemical measurement: Before fabricating electrode, both titanates were heated at 200 °C for 15 min to removing the gaseous adsorbates. Lithium sheet was used as counter electrodes, composite materials comprising active mass (73 wt.%), carbonaceous additive (acetylene black, 15 wt.%) and poly(vinylidene difluoride) (PVDF, 12 wt.%) binder were used as the working electrode, and 1M LiPF₆ solution in a 1:1 (volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte. The galvanostatic cycling was measured on a LAND cell test (Land-CT 2001C) system at a constant at the designed current density in the voltage range from 1.0 V to 3.0 V versus Li/Li⁺.

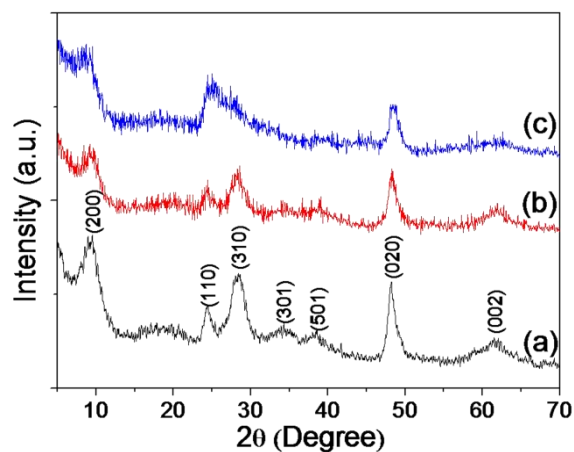


Fig. S1 XRD patterns of (a) Na-TNT, (b) Na-UTMS and (c) H-UTMS.

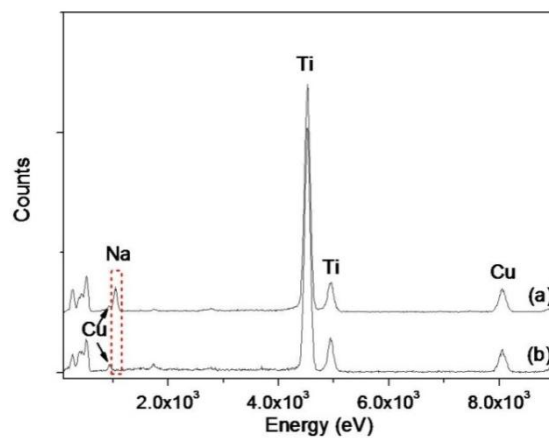


Fig. S2 Energy dispersive X-ray spectroscopy (EDX) of (a) Na-UTMS and (b) H-UTMS. Red dash rectangular indicates the energy position of sodium.