Supporting Information

Facile Synthesis of Titanium Nitride Nanowires on Carbon Fabric for Flexible and High-Rate Lithium Ion Batteries

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Experimental Section
Synthesis of Electrode material
a. Materials
Titanium (IV) chloride (TiCl₄, 99%), concentrated hydrochloric acid (HCl, 36.46 wt. %), tetrabutyl titanate [Ti (OCH₂CH₂CH₃CH₃)₄, 98%], ethanol (99.7 %) were purchased from Tianjin Fuchen Chemical Reagents Factory, China and used without further purification and carbon fabric was purchased from Fuel Cell Earth LLC, United States.

b. Synthesis of TiN Nanowires
The carbon fabric substrate with 3 cm x 5 cm surface area was cleaned by sonication sequentially
in deionized (DI) water and ethanol for 30 mins. TiO$_2$ nanowires were grown on a carbon fabric by hydrothermal method according to our previous report. A piece of carbon fabric was cleaned with deionized water and ethanol ultrasonically and then allowed to dry at room temperature. The carbon fabric was then immersed in 0.2 M aqueous titanium (IV) chloride solution for two minutes and then allowed to be dried by blowing in the compressed air. The blow dried carbon fabric was then heated on a hotplate at about 320 °C for few minutes which generates a nanoparticle on the surface of the carbon fabric. This process was repeated about four times to ensure uniformity. 40 mL of concentrated hydrogen chloride acid was diluted in 40 mL deionized water and then mixed with 1.2 mL of tetrabutyl titanate and then stirred on a magnetic stirrer until a clear solution was obtained. The carbon fabric was then immersed in the clear solution and transferred to a 50 mL Teflon-lined stainless steel autoclave. The sealed autoclave was heated in an electric oven at 160 °C for 5.5 hours. The autoclave was then allowed to cool down at room temperature and a white TiO$_2$ nanowire coated uniformly was obtained on the carbon fabric surface. The sample was then washed thoroughly with deionized water and allows to air dry.

The synthesized TiO$_2$ was then calcined in air at 550 °C for 60 minutes followed by further annealing in NH$_3$ gas (at a rate of 200 mL/min) for 60 minutes at temperatures of 800 °C, 900 °C and 1000 °C respectively. The as-prepared products were denoted as TiN-800, TiN-900 and TiN-100 respectively.

**Material Characterization**

The morphology and the microstructure of the products were characterized by field emission scanning electron microscope (FE-SEM, JSM-6330F) and transmission electron microscopy (TEM, JEM2010-HR, 200 KV). The phase and composition of the samples were investigated via X-ray diffraction (XRD, Bruker, D8 ADVANCE) with Cu Kα radiation ($\lambda = 1.5418$ Å), X-ray Photoelectron Spectroscopy (XPS, ESCALab250, Thermo VG) with 200 W Al Kα radiation in twin anode, and the Raman spectroscopy that performed on a FT-IR, Nicolet 330 at room temperature with Ar$^+$ laser of 514.5 nm excitation. For the XPS spectra, the binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference.

**Electrochemical test**

**Fabrication of the coin cell and Flexible battery device**

The electrochemical performance of the as-synthesized TiN NW arrays was investigated by using
carbon fabric as a binder-free anode in LIB in a coin-type half-cell, which was laboratory-assembled by a CR2032 in an argon-filled glove box [Mikrouna (China) Co., Ltd.]. A pure Li foil was used as the counter electrode. A piece of TiN NW arrays with active mass of 2.09 mg was used as the working electrode without any binder such as PVDF or PTFE. Celgard 2400 polymer separators were employed between the two electrodes. The electrolyte was made of LiPF6 (1 M) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio 1:1.

The cell was galvanostatically charged and discharged between 0.001 and 3.0 V versus Li+/Li at room temperature on a Neware battery tester (CT-3008-164, Shenzhen, China) at a voltage range of 0.01 – 3 V (vs Li+/Li) and cyclic voltammetry (CV) were conducted on electrochemical working station (CHI 1040c, Chenhua, Shanghai) at a scan rate of 0.1 mV/s. Electrochemical impedance spectroscopy (EIS) was measured on an AC voltage of 5 mV amplitude in the frequency range from 100 kHz to 0.1 Hz using an electrochemical workstation (CHI660D, Chenhua, Shanghai).

In addition, a flexible lithium ion battery was assembled by using a the carbon fabric coated uniformly with TiN-900 NW arrays the anode, an Al foil with LiCoO2 loading as the cathode, and Celgard 2400 as the separator. Each electrode was cut into a square of 1 cm x 2 cm with a Cu foil and Al foil as the current collector for the anode and cathode respectively. The Cu foil was used as the current conductor. Cu foil was joined to the edge of the flexible TiN-900 anode to enhanced easy sealing because the carbon fabric is too thick to be sealed with the Al bag. The electrolyte was dropped on the electrodes in Al bag and sealed in argon-filled glovebox. The loading density of the active material i.e. TiN-900 was calculated to be 0.8 ~ 1.5 mg cm⁻². The charge/discharge measurements were carried out on a Neware battery tester (CT-3008-164, Shenzhen, China) at a voltage range of 2.0 – 4.0 V (vs Li+/Li).
Supplementary Figures

Figure S1. Structure and Morphology of TiO$_2$ nanowires. (a) Image of TiO$_2$ nanowires grown on a carbon fabric fiber. (b) High magnification SEM image. (c) TEM image. Inset is the SAED pattern. (d) Lattice-resolved TEM image collected at the edge of the nanowires.
Figure S2. SEM images of the TiN nanowires after annealing the TiO$_2$ nanowires at (a, c) 800 °C (b, d) 1000 °C

Figure S3. (a) XPS Survey. (c) core level O 1s XPS spectra of TiO$_2$ and TiN Nanowires.

In the spectra of O 1s core level, TiO$_2$ and TiN nanowires exhibits the peak at 529.9 eV that corresponds to the characteristic peak of Ti–O–Ti $^1$ but a lower intensity in TiN nanowires (Figure S3b). Additional characteristic peak was observed in TiO$_2$ NW at a binding energy of 531.4 eV tracing to be the peak of Ti-OH $^2$ which was very negligible in the TiN nanowires sample due to nitridation.
Figure S4. (a) CV curves of the TiN electrodes. (b) CV curves at the high voltage region.

Figure S5. Charge/discharge curves of TiN-900 at the 1st, 2nd, 3rd and 100th cycles.
Figure S6. Cyclic performance of the LiCoO$_2$/TiN-900 flexible full battery at the normal and bent position.

References