



Three-dimensional tungsten nitride nanowires as high performance anode material for lithium ion batteries



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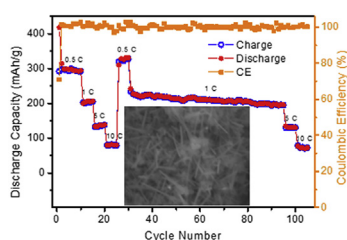
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HIGHLIGHTS

- WN nanowires were synthesized on carbon cloth by a facile hydrothermal process.
- The WNNW electrode could deliver a high capacity of 400 mAh g⁻¹ at 200 mA g⁻¹.
- The WNNW electrode also show a good rate and cyclic performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructure materials often achieve low capacity when the active material mass loading is high. In this communication, high mass-loading tungsten nitride nanowires (WNNWs) were fabricated on a flexible carbon cloth by hydrothermal method and post annealing. The prepared electrode exhibited remarkable cyclic stability and attractive rate capability for lithium storage. It delivers at a current density of 200 mA g⁻¹, a high capacity of 418 mAh g⁻¹, which is higher than that of conventional graphite. This research opens more opportunity for the fabrication of three-dimensional metal nitrides as negative electrode material for flexible lithium ion batteries.

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1. Introduction

In the last two decades, lithium-ion batteries (LIBs) have been widely used in portable electronic devices and explored as power sources for electric or hybrid electric vehicles [1–5]. To achieve suitable LIBs for practical usage, new electrode materials with high performance such as high capacity, excellent stability and high rate

capability call for attention [6–8]. In this vein, transition metal nitrides with high electronic and thermal conductivity when compared to the matured transition metal oxides and sulfides [9–13] have also been used for different purposes such as in semiconductor industries, as electrocatalyst [14], energy storage [15–17] and coating material [18] and so on. Among these metal nitrides, tungsten nitrides (WN) hold great promise as anode for LIBs because they possesses significant advantages of moderately high capacity and good electrical conductivity [19,20]. However, WN is less frequently reported as LIB anode material due to the fact that it has high atomic weight, which could lead to low capacity

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[19]. Thus, it is necessary to fabricate WN with high capacity.

Nanostructured materials have drawn intense attention when developing highly efficient electrochemical energy devices because of their high surface area, more active sites for the accommodation of ions, significantly enhanced kinetics, decreased huge volume changes and provide short diffusion pathways for ion insertion and extraction [21–26]. Among various nanostructures, three-dimensional (3D) nanostructures have recently attracted intensive research interests because they have much higher surface area than low dimensional materials and supply enough absorption sites for all involved species in a small space [27–29]. Moreover, such 3D materials with high porosity could lead to better transportation of ions and electrons [25]. However, tungsten nitride 3D nanostructures are rarely reported. Furthermore, the most common problem of nanomaterials is the inability to achieve high specific capacity when the mass of the active materials is too high. High mass loading electrode materials are necessary for industrial applications in order to attain satisfactory capacity required to power a device. Hence, high mass loading electrodes call for urgent attention.

Herein, we synthesized high mass loading tungsten nitride nanowires (WNNWs) with 8.0 mg/cm^2 through hydrothermal process and post-annealing of tungsten oxide (WO_3). When used as anode material for LIBs, they exhibited a high initial capacity of 418 mAh g^{-1} at a current density of 200 mA g^{-1} , which is higher than that of conventional graphite (372 mAh g^{-1}). When the current density was increased to 4000 mA g^{-1} , the WNNWs could retain a capacity of 110 mAh g^{-1} after 110 cycles. The lithium storage performance can be attributed to the synergistic effects of the nanowire nanostructure and robust 3D carbon cloth substrate. Even at a higher current density equivalent to 10 C, a capacity of about 100 mAh g^{-1} can be recovered, which suggest its use as high performance anode for lithium ion batteries. Additionally, the growth of the WNNW on 3D flexible substrates also creates opportunity for the utilization of high mass loading electrode as flexible anode for lithium ion batteries.

2. Experimental section

2.1. Sample preparation

All the reagents used were of analytical grade and were used directly without any purification. Free-standing WNNWs were grown on carbon cloth by a two-step process. WO_3 nanowires were firstly synthesized on carbon cloth via a seed-assisted hydrothermal method. Carbon fabric cloth ($2 \text{ cm} \times 3 \text{ cm}$) was cleaned with ethanol and distilled water, followed by being immersed in a solution containing 0.695 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 10 mL of 3 M HCl , and 2 mL of H_2O_2 (30 vol% aqueous solution) for 5 min and blow-dried with compressed air. The dried carbon cloth was further heated on a hotplate in air at $300 \text{ }^\circ\text{C}$ for 5 min, forming WO_3 nanoparticles on the carbon fabric cloth. 1.33 g of H_2WO_4 was dissolved in a mixed solution of 22 mL of distilled water and 6 mL of H_2O_2 (30 vol% aqueous solution), then 16 mL of ethanol and 0.04 g of NH_4Cl were added into 4 mL of the previous solution and stirred into a clear solution. 20 mL of this clear solution mixture together with the carbon fabric cloth coated with WO_3 nanoparticles were transferred to a Teflon-lined stainless-steel autoclave (25 mL volume). The sealed autoclave was heated in an electric oven at $180 \text{ }^\circ\text{C}$ for 12 h, and then allowed to cool down slowly at room temperature. A light-blue WO_3 film was uniformly coated on the carbon fabric cloth surface. The sample was thoroughly washed with deionized (DI) water and dried. Finally, the WO_3 nanowires were converted to WN nanowires by annealing in N_2 up to $600 \text{ }^\circ\text{C}$ and then NH_3 for 30 min.

2.2. Material characterization

Structure and morphology of the as-prepared samples were characterized by X-ray diffraction spectrometry (XRD, D8 ADVANCE) with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), Raman spectrometry (Renishaw inVia) at room temperature with Ar^+ laser of 514.5 nm excitation, field-emission scanning electron microscopy (FESEM) (FESEM, JSM-6330 F), and transmission electron microscopy (TEM) (JEM2010-HR, 200 KV).

2.3. Electrochemical test

The electrochemical tests were carried out with CR2032 coin type cells. The samples grown on carbon textile were first cut into many smaller square pieces with 1.0 cm^2 area. Both the carbon textile with loading samples and bare carbon textile were weighed in a high-precision analytical balance (Sartorius, max. weight 5100 mg , $d = 0.001 \text{ mg}$). The reading difference was the exact mass of the coating on carbon textile. The reading difference was taken from the same carbon textile before and after the hydrothermal and annealing process of the WNNWs. The loading density of the active materials is 8.0 mg/cm^2 . The samples grown on carbon textile were used as the working electrodes. Coin cells were assembled in an argon-filled glove box [Mikrouna (China) Co., Ltd.] with the WNNWs sample used as the working electrode, Celgard 2400 as the separator, lithium foil as counter and reference electrode with an electrolyte consisting of 1 M LiPF_6 in 1:1 by volume of ethylene carbonate (EC)/dimethyl carbonate (DMC). Charge and discharge measurements were carried out on a Neware battery tester (CT-3008-164, Shenzhen, China) at a voltage range of $0.01\text{--}3 \text{ V}$ (vs. Li^+/Li). Cyclic voltammetry (CV) at a scan rate of 0.1 mV/s and cell impedances measurements for the two-electrode arrangement were conducted on an electrochemical work station (CHI 760d, Chenhua, Shanghai) in a frequency range of $10^{-1} \text{ Hz}\text{--}10^5 \text{ Hz}$.

2.4. Assembling of the flexible LIBs

Flexible LIB was assembled by using the flexible WNNW as the anode ($2 \text{ cm} \times 3 \text{ cm}$), an Al foil coated with LiCoO_2 as the cathode ($2.5 \text{ cm} \times 3 \text{ cm}$) and Celgard 2400 as the separator. The Cu foil was joined to the edge of the flexible WNNW anode and sticks to the carbon cloth with a conductive tape, and sealed by a sealing machine. The Cu foil joined to the edge of the flexible WNNW anode was used as the current conductor to enhanced easy sealing because the carbon textile 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 glove box.

3. Results and discussion

Free-standing WNNWs were fabricated on a flexible carbon cloth in two steps. WO_3 nanowires were first grown on the flexible carbon cloth as discussed in the experimental section. Images from the field-emission scanning electron microscope (FESEM) shows that the carbon cloth was uniformly coated with WO_3 nanowires (Fig. 1a). The nanowires of the diameters ranged $50\text{--}80 \text{ nm}$ (Fig. 1b). These nanowires were then subjected to annealing in N_2 to $600 \text{ }^\circ\text{C}$ at a ramping rate of $5 \text{ }^\circ\text{C}$ per minute. At $600 \text{ }^\circ\text{C}$, the flowing gas was changed to NH_3 gas for 30 min. After cooling, the product obtained was WNNWs. As observed in Fig. 1c and d, the nanowire morphology was maintained after annealing.

Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were carried out to reveal detailed morphology of the WNNWs. TEM image confirms that the WN are nanowire-like in nature with rough surface (Fig. 2a). The bright and

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