Three-dimensional nitrogen-doped graphene frameworks anchored with bamboo-like tungsten oxide nanorods as high performance anode materials for lithium ion batteries

Xinyuan Gu [a], Feilong Wu [a], Bingbing Lei [a], Jing Wang [a], Ziliang Chen [a], Kai Xie [a], Yun Song [a], Dalin Sun [a], Lixian Sun [b], Huaiying Zhou [b], Fang Fang [a, *]

[a] Department of Materials Science, Fudan University, Shanghai 200433, China
[b] School of Materials Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China

HIGHLIGHTS

- Nanocrystallization and N-doped 3D graphene are realized by a hydrothermal method.
- Bamboo-like WO_3 nanorods are anchored on the surface of fungus-like 3DNGF.
- r-WO_3/3DNGF exhibits great cycle stability and excellent rate performance.

GRAPHICAL ABSTRACT
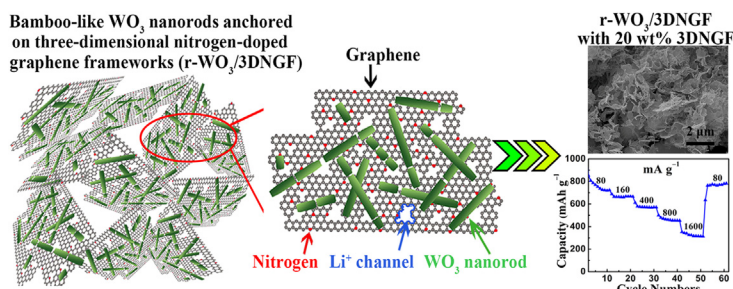
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ABSTRACT

Bamboo-like WO_3 nanorods were anchored on three-dimensional nitrogen-doped graphene frameworks (r-WO_3/3DNGF) by a facile one-step hydrothermal synthesis plus heating processes. There is a strong dependence of the obtained r-WO_3/3DNGF nanostructures on the content of 3DNGF. The composite with 20 wt% 3DNGF content shows the most favorable structure where bamboo-like WO_3 nanorods lie flat on the surface of fungus-like 3DNGF, and exhibits a high discharge capacity of 828 mAh g^{-1} over 100 cycles at 80 mA g^{-1} with the largest capacity retention of 73.9% for WO_3 and excellent rate capacities of 719, 665, 573, 453 and 313 mAh g^{-1} at 80, 160, 400, 800 and 1600 mA g^{-1}, respectively. The electrochemical performance is better than most of reported WO_3-based carbonaceous composites, which can be attributed to the synergistic effects of the following actions: i) WO_3 nanorods effectively shorten the diffusion path of Li^+; ii) mechanically strong 3DNGF alleviates the huge volume change of WO_3 upon Li^+ intercalation/extraction; and iii) nitrogen-doping in 3D graphene frameworks improves electronic conductivity and provides large numbers of lithium ion diffusion channels.

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1. Introduction

Lithium ion batteries (LIBs) have been considered as key devices for energy storage and power supply in portable applications, such as cellular phones and laptop computers, as well as in electric

* Corresponding author.
  E-mail address: f_fang@fudan.edu.cn (F. Fang).

vehicles (EVs) [1–3]. However, graphite, as the current commercial anode material for LIBs, cannot entirely fulfill the requirements for EVs because of its limited theoretical specific capacity (372 mAh g^{-1}) and poor rate capability [4–6]. Therefore, great efforts have been undertaken to seek alternative anode materials with high theoretical capacities [7–10].

WO_3, as a transition metal oxide (TMO), is a promising potential anode material due to its high theoretical capacity (693 mAh g^{-1}), low cost and environmental friendliness [11–15]. But its practical application is constricted due to the following two reasons: (i) the huge volume change of WO_3 upon Li^+ intercalation/extraction easily leads to the electrode pulverization and capacity loss during cycling [16–17]; (ii) the low intrinsic electronic conductivity and the poor lithium ion diffusion of bulk WO_3 result in the inferior rate capability of WO_3 electrode. For instance, after 50 cycles, dense WO_3 particles retained less than 10% of their initial discharge capacity of 713 mAh g^{-1} at a current density of 200 mA g^{-1} and showed a significant decreasing in rate capability to 48 mAh g^{-1} when the current density was increased to 1000 mA g^{-1} [18].

To overcome these problems, two strategies have been proposed. The first strategy is to fabricate composites consisting of WO_3 and carbon matrix, which can buffer volumetric stress and improve electronic conductivity [19–21]. For example, compared with the rate capabilities of 200, 160 and 48 mAh g^{-1} at current densities of 200, 400 and 1000 mA g^{-1} for dense WO_3 particles, the composite of WO_3/two-dimensional (2D) graphene nanosheets delivered higher capabilities of 564, 469, 307, 192 and 125 mAh g^{-1} at current densities of 80, 160, 400, 800 and 1600 mA g^{-1}, respectively [22]. Following these improvements, the rate capabilities can be further enhanced by fabricating 2D graphene nanosheets into three-dimensional (3D) graphene frameworks. For instance, Zhang et al. reported that WO_3/3D graphene webs showed improved rate capacities of 434, 306 and 200 mAh g^{-1} at current densities of 500, 1000 and 2000 mA g^{-1}, which could be attributed to enhanced electronic conductivity and faster Li-ion transport kinetics provided by continuous 3D graphene frameworks [23]. Recently, nitrogen-doping (N-doping) in graphene has been demonstrated not only to improve the electronic conductivity due to the electron-donating character of nitrogen but also to introduce large quantities of surface defects to form disordered honeycomb carbon structures, which can provide channels for lithium ion diffusion [24–29]. Therefore, introducing nitrogen into WO_3/3D graphene frameworks composite would provide a promising approach for further improving the electronic conductivity and facilitating the lithium ion diffusion of WO_3. The second strategy is nanocrystallization, which can enhance reaction activity and shorten the diffusion path of lithium ion [30–32]. For instance, Yu et al. synthesized WO_3 nanorods with diameters of 50 nm and lengths of 800 nm. These WO_3 nanorods showed a high initial discharge capacity of 1029 mAh g^{-1} at 100 mA g^{-1} and rate capacities of 270, 220 and 165 mAh g^{-1} at current densities of 200, 400 and 800 mA g^{-1}, which are superior to those for dense WO_3 particles. However, these WO_3 nanorods still suffer from poor cycle stability as the capacity fades from 514 mAh g^{-1} after 1 cycle to only 234 mAh g^{-1} after 100 cycles at 100 mA g^{-1}, indicating that huge volume change of WO_3 nanorods is not effectively inhibited upon Li^+ intercalation/extraction [20]. In light of the stabilized capacity of 801 mA g^{-1} over 300 cycles for WO_3/3D graphene webs [23], it can be assumed that the huge volume change could be alleviated by embedding nanocrystallized WO_3 into 3D graphene frameworks. Therefore, it is highly expected that significant improvements of electrochemical performance of WO_3 can be achieved by combining nanocrystallization of WO_3 and N-doping in 3D graphene frameworks together.

In this study, we synthesized a series of WO_3 nanorods/3D N-doped graphene frameworks (r-WO_3/3DNGF) with different contents of 3DNGF using a facile one-step hydrothermal method plus heating processes. Among prepared composites, the optimized r-WO_3/3DNGF with 20 wt% 3DNGF exhibited a high reversible discharge capacity of 828 mAh g^{-1} over 100 cycles at 80 mA g^{-1} and demonstrated excellent rate capacities of 719, 665, 573, 453 and 313 mAh g^{-1} at 80, 160, 400, 800 and 1600 mA g^{-1}, respectively. The excellent electrochemical performance should originate from inhibited volume change, improved electronic conductivity and facilitated lithium ion diffusion, which were provided by 3DNGF and bamboo-like WO_3 nanorods.

2. Experimental section

2.1. Synthesis of samples

Graphene oxides (GOs) were prepared from natural graphite flakes by a modified Hummers method [33]. The r-WO_3/3DNGF composites were synthesized by a hydrothermal method plus heating processes. In a typical experiment, GOs (20, 40, 80 and 120 mg) were dispersed in 80 mL of hydrochloric acid solution (pH = 1.0) with continuous sonication for 90 min at room temperature. With vigorous stirring, 1 g ammonium tungstate ((NH_4)$_{10}H_2(W_2O_7)_6$), 2 g oxalic acid ($H_2C_2O_4$) and 8 g ammonium sulfate ((NH_4)$_2SO_4$) were dissolved into the mixed solution. The resulting dispersion was mixed with 4 mL purified pyrrole as the swelling agent and the nitrogen source. Next, the mixture solution was transferred to a Teflon-lined autoclave container (100 mL), followed by hydrothermal treatment at 180 °C for 24 h. After natural cooling to ambient temperature, the samples were collected by centrifugation, washed by de-ionized water and ethanol for three times, and then dried at 70 °C for 6 h. After that, the products obtained were calcined at 800 °C for 2 h under argon. Lastly, the composites were annealed in a furnace at 450 °C for 2 h in air to remove amorphous carbon and to fully crystallize WO_3. According to the different addition contents of GOs, the weight ratios of 3DNGF to WO_3 were calculated to be 5, 10, 20 and 30 wt%, and the corresponding composites were recorded as r-WO_3/3DNGF-x (x = 5, 10, 20 and 30). For comparison, using the same experiment steps, a WO_3/2D graphene (WO_3/2DG) composite was obtained in the absence of pyrrole, and a pure WO_3 was prepared without GOs and pyrrole.

2.2. Characterizations

The morphology of the as-prepared samples was characterized by field-emission scanning electron microscope (FE-SEM, LEO 1530Gemini) and a field-emission transmission electron microscope (FE-TEM, Tecnai G^2 F20 S-Twin). The phase analysis was carried out on an X-ray diffractometer (XRD, D2 PHASER, Bruker AXS) with Cu Kα (λ = 0.152 nm) radiation at 30 kV and 10 mA in a 2θ range from 20° to 60° at a scan rate of 0.5° min^{-1}. Thermal gravimetric analysis (TGA) curves were obtained by a thermal analyzer (TG, Netzsch STA 409 PC) over the range of 25–800 °C at a heating rate of 10 °C min^{-1} under an air flow of 30 cm^3 min^{-1}. X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra spectrometer (Kratos, UK) with an Al monochromatic source operated at 15 kV.

2.3. Electrode fabrication and electrochemical measurements

The electrochemical performance of r-WO_3/3DNGF as an anode for LIBs was evaluated using coin cells (CR2032) on a battery test instrument (CT2001A, LANHE) with a cutoff voltage of 0.05–3.0 V vs. Li/Li^+. For anode preparation, the active material (r-WO_3/