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2 dimensional WS_2 tailored nitrogen-doped carbon nanofiber as a highly pseudocapacitive anode material for lithium-ion battery

Xu Yu, Chengang Pei, Wushuang Chen, Ligang Feng*

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002, China

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ABSTRACT

To efficiently improve the attractive properties of electrode material for lithium ion batteries (LIBs), the uniform hybridization of 2 Dimensional WS_2 nanosheets of nitrogen doped carbon nanofiber (WN-CNF) as a novel anode electrode is synthesized via a facile electrospinning strategy. The well-aligned structure, roughness of surface morphology and chemical composition are characterized by microscopic and spectroscopic analysis. Nitrogen-containing groups and 1 T phase of WS_2 in WN-CNF are demonstrated as the electro-active sites to enhance the capacitive performance. Meanwhile, WN-CNF exhibits a highly reversible specific capacity of 814 mAh g^{-1} at the current density of 100 mA g^{-1}, excellent rate capability of 52% from 100 to 1000 mA g^{-1} and cyclic stability of 87% after 120 charge/discharge cycles. The high performance can be attributed to the synergistic effects of rough surface, heteroatom N incorporation and hybridization with pseudocapacitive 2D WS_2.

1. Introduction

Rechargeable lithium ion batteries (LIBs) as a new generation of energy system have been dominantly and effectively applied in the practical fields due to its high energy density and super-long cycle lives [1–3]. However, limited by the low theoretical capacity of graphite (372 mAh g^{-1}), exploring alternative negative electrodes becomes essential to achieving high capacity [4–7]. To date, one dimensional (1D) carbon nanofibers or nanocomposites fabricated by electrospinning technique have been proposed as alternatives due to their unique structure and chemical composition [8–10]. The hybridization of metal oxide and carbon nanofibers as anode materials has significant enhancements in the specific capacity, but further practical application is restricted by their poor cyclic stability.

Recently, transition metal dichalcogenides (TMDCs) like MoS_2 and WS_2 have attracted extensive attention owing to their high theoretical capacity (670 mAh g^{-1} of MoS_2 and 433 mAh g^{-1} of WS_2) as anode materials, and larger interlayer spacing of TMDCs is favorable to accumulate more lithium ions leading to a superior property [11–13]. The transition metal atoms sandwiched between chalcogen atoms can be classified into trigonal prismatic coordination (2H phase) or octahedral coordination (1 T phase) [14]. Bulk WS_2 with weak van der Waals force between interlayers can be exfoliated to single or few layers using mechanical and solution-exfoliated methods [15]. The 1 T phase of 2 Dimensional WS_2 has been demonstrated as the dominant electrochemical active sites for lithium ion battery, but a fast decay of specific capacity and rate stability from the large volume expansion and poor electrical conductivity still inhibited its wide applications [16,17]. To solve this issue, TMDCs/carbon nanomaterials have been fabricated to modify the chemical structure of electrode to attain the enhancement of electrochemical performance of LIBs. For instance, Wu et al. synthesized WS_2-carbon nanofiber with a discharge specific capacity of 545 mA h g^{-1} at 500 mA g^{-1} [18]; Wang et al. reported the synthesis of WS_2/CNT-RGO, which can deliver a specific capacity of 749 mAh g^{-1} at a current of 100 mA g^{-1} [19] and Kong et al. successfully designed WS_2@graphitic carbon nanotubes with the presence of a reversible capacity of 570 mAh g^{-1} at 200 mA g^{-1} [20]. Heteroatoms incorporated into carbon materials have also been considered as a potential way to modify the anode materials for LIBs by forming different heteroatom-containing groups as electro-active sites [21–23]. According to the different atom size and electronegativity of carbon, heteroatoms can be doped into the carbon lattice to tune the surface chemistry to achieve the enhancement of battery performance. For example, Liu et al. demonstrated a new procedure for the synthesis of N-carbon/rGO [24] and Wang et al. reported an N-doped holey-graphene

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* Corresponding author.
E-mail addresses: ligang.feng@yzu.edu.cn, fenglg11@gmail.com (L. Feng).

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monolith (NHGM) with a dense microstructure [25]. Both N-carbon/rGO and NHGM showed excellent performances in LIBs. However, individual component of TMDCs and heteroatom doped carbon material can not offer its intrinsic advantages like high specific capacity, large surface area and good electrical conductivity. Thus, the combination of TMDCs and heteroatom doped carbon material would be a good pseudocapacitive electrode for LIBs.

Herein, a novel WS_2 decorated nitrogen doped carbon nanofiber (WN-CNF) composite as anode material for LIBs was proposed by a simple and facile electrospinning and thermal activation approach. WN-CNF with a uniform loading of 2D WS_2 on the surface or internal of carbon nanofibers exhibited a superior pseudocapacitive behavior. It can provide a highly reversible specific capacity of 814 mAh g^{-1} at a current density of 100 mA g^{-1} and good rate capability of 52% and excellent cyclic stability of 87% when used as working electrode for LIBs. These features were determined by the synergistic effect of the unique well-aligned structure for fast ion diffusion, modification of surface chemistry by heteroatom incorporation and hybridization of pseudocapacitive material.

2. Experimental

2.1. Synthesis of 2D WS_2

The single or few layers 2D WS_2 was prepared as followings. 400 mg bulk WS_2 was transferred to a 70 mL glass vial by adding 50 mL DMF as the solvent. The mixture was treated by a tip-sonicator instrument with controlling the distance between the tip and glass bottom and exfoliated for 4 h with 20% of power. The as-exfoliated solution was subsequently centrifuged for 3 times at 4000 rpm min^{-1}. The final solution was kept with a concentration of 0.25–0.3 mg mL^{-1}.

2.2. Preparation of WN-CNF

To obtain the WN-CNF, a facile electrospinning technique was applied. 1 g of PAN powder was mixed with 9 mL WS_2 dispersion with slow magnetic stirring for 3 h to prepare the homogeneous PAN/WS_2 dispersion, and the final concentration of PAN was well controlled at 10%. Subsequently, the mixture was transferred to 20 mL syringe which connected with the applied power. For the electrospinning process, the applied power was controlled at 12 kV, the flow rate of the polymer solution was fixed at 1 mL h^{-1} by a syringe pump, and the distance between the nozzle and collector was 12 cm. The as-obtained PAN/WS_2 nanofiber mat was placed in the center of the tube furnace and thermal-activated at two steps: the PAN/WS_2 nanofibers were initially stabilized at 280 °C for 2 h at air condition, and then carbonized at 800 °C for 10 h at Ar atmosphere to finally obtain the WN-CNF. During the thermal activation process, the generation of ammonia gas from the decomposition of PAN polymer will be further applied as the nitrogen precursor for heteroatom doping. The temperature was increased from room temperature to 800 °C at the heating rate of 5 °C min^{-1}. By comparison, the nitrogen doped carbon nanofiber (N-CNF) without loading of 2D WS_2 was also prepared by electrospinning with the same condition and noted as the control sample. The N-CNF with the mass loading of WS_2 of 3 mL and 6 mL (noted as WN-CNF-3 and WN-CNF-6) was also compared.

2.3. Electrochemical measurement

To verify the electrochemical performance of WN-CNF, the CR 2016 type coin cell was fabricated in the glove box at Ar atmosphere. The working electrode was prepared by mixing active material, activated carbon and Poly (vinylidene fluoride) (PVDF) with a weight ratio of 8:1:1, and the mixture was ground in an agate mortar with few drops NMP as the solvent for 30 min to make a homogeneous slurry. The black slurry was pasted on clean Cu foil and dried in vacuum oven at 80 °C for overnight. And the mass loading of the working electrode was controlled with 2 mg cm^{-2}. The lithium foil was applied as the counter electrode and Celegard 2400 as the separator. 1 M $LiPF_6$ solution (EC/DEC = 1:1) was employed as the electrolyte. The cyclic voltammetry (CV) was measured by CHI 760 workstation with the potential window of 0.01–3 V at the scan rate of 5 mV s^{-1}. Galvanostatic charge-discharge (GCD) and rate-capability performances were measured in a LAND (Wuhan Rambo Testing Equipment Co. Ltd, China) between 0.01 and 3.0 V at current density from 100 to 1000 mA g^{-1}. The electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 10^5 to 10^{-2} Hz with an AC voltage amplitude of 5 mV.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder X-ray diffractometer using a Cu Kα (λ = 1.5405 Å) radiation source operating at 40 kV and 40 mA at a scanning rate of 5° min^{-1}. The morphology and microstructure of product was analyzed by scanning electron microscopy (FESEM, Hitachi, S-4800 II, Japan) and transmission electron microscopy (TEM, Philips, TECNAI 12, Holland). High-resolution transmission electron microscopy (HRTEM) were performed on an FEI Tecnai G2 F30 STWIN (USA) operating at 300 kV. Surface analysis of sample was studied by X-ray photoelectron spectroscopy (XPS, Thermo Science, ESCALAB 250Xi, USA).

3. Result and discussion

The synthetic procedure of WN-CNF was illustrated by electrospinning and thermal activation as shown in Scheme 1. In brief, the homogeneous PAN/WS_2 solution was prepared by mixing PAN powder and WS_2 dispersion under magnetic stirring, which was crucial to obtain the well-defined nanofibers. The applied power was 12 kV, which was high enough to overcome the surface repulsion of the polymer solution. Furthermore, the stability of Tayler cone in the nozzle was an important factor to guarantee the formation of PAN/WS_2 nanofiber without beads and aggregations, and the PAN/WS_2 nanofibers with uniform diameter were collected on the substrate during the electrospinning process. Subsequently, the polymer nanofibers were stabilized at 280 °C with initial evaporation of the solvent and residues, and the carbon nanofibers were finally obtained during the carbonization procedures at 800 °C by thermal annealing.

The surface morphology and structure of WN-CNF were characterized by scanning electron microscopy (FE-SEM). As shown in Fig. 1a and d, pristine PAN and PAN/WS_2 nanofibers were both randomly aligned without any beads and aggregations. From the middle magnification of FE-SEM images (Fig. 1b–e), the diameter of PAN/WS_2 nanofibers was slightly larger than pristine PAN nanofibers. Meanwhile, PAN/WS_2 nanofiber exhibited a rough surface morphology, which was completely different from the smooth surface of pristine PAN nanofiber as shown in Fig. 1c–f. The average diameter of PAN/WS_2 nanofiber was approach to 350–450 nm, which was a little higher than that of pristine PAN nanofiber (300–400 nm) due to the uniform loading of 2D WS_2 on the surface or internal of polymer nanofibers. 2D WS_2 with a thickness of ~4 nm was confirmed by AFM result, indicating that the layer number was less than 5 layers (Fig. S1). After stabilization and carbonization at high temperature, the distribution of WN-CNF was still uniform with an average diameter of 350–450 nm and partially