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Enhanced reversible lithium ion storage in stable 1T@2H WS_2 nanosheet arrays anchored on carbon fiber

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ABSTRACT

Recent years, as a competitive anode material for lithium ion batteries (LIBs), tungsten disulfide (WS_2) has attracted significant attention for its high theoretical capacity, abundant resources and low cost, but how to improve the cycle stability and reversible capacity is still an important research subject. In this work, stable metallic WS_2 anchored on carbon fiber cloth was fabricated as flexible anode for LIBs. The transversal displacement of S atoms in WS_2 was induced by incorporation of N atoms, and the stability of metallic phase WS_2 was ensured by the formation of N-W covalent bonds. The results of electrochemical measurement and dynamics analysis demonstrate that the incorporation of metallic phase could not only reduce the initial discharge capacity loss, but also improve the reversible capacity than traditional semi-conducting phase WS_2.

1. Introduction

As prospective graphene-like two-dimensional (2D) materials, transitional metal sulfides (TMDs) have attracted substantial interest and investigation due to the unique morphology structure and excellent performance in a range of fields [1–6]. Among these 2D TMDs, tungsten disulfide (WS_2) has achieved increasing attention due to its excellent thermal, mechanical, optical and electric performances [7–10]. Laminar WS_2 is composed of sandwich construction stacked through the weak van der Waals interaction, while strong covalent bonds in-plane between S atoms and W atoms, which is beneficial for lithium ion storage (theoretical capacity = 433 mAh g^{-1}) [11]. But the low electrical conductivity and unreliable stability during long cycles of WS_2 in nature limits its potential application in LIBs [12–14]. To improve the electrochemical properties, two methods are commonly employed. One is combined with carbon-based materials, which were reported widely in the previous literature [15–17], another effective method is realizing the phase-transformation of WS_2 from semi-conducting phase to metallic phase.

The metallic (1T) phase WS_2 (octahedral coordination) exhibits inequable performances and microstructure compared with semiconducting (2H) phase WS_2 (trigonal prismatic coordination), and can be obtained by the transversal displacement of one of S atomic layer. However, relatively few literature have been reported in the fabrication and application of 1T WS_2. Similar to MoS_2 [18,19], the synthesis path and method for 1T WS_2 mainly include rare metal doping [20], alkali metal and butyllithium intercalation [21–23], ammonia ions intercalation [24], pulsed laser deposition [25]. Liu [24]et al. synthesized 1T-WS_2 nanoribbon by the intercalation of ammonia ions and 0.75 electrons per NH_4^+ are transferred to WS_2. Similarly, Re, Tc, and Mn acting as electron donors can induce the phase transformation of WS_2, and the formation of covalent bonds increases the stability of metallic WS_2 greatly [20]. However, some shortcomings limit the application of these methods, such as complex preparation process, risk of safety or not suitable for large-scale preparation. Therefore to find a simple and efficient method obtaining 1T phase WS_2 is the key to improve its electrochemical performances.

In this study, we propose a novel and universal method for the fabrication of stable 1T phase WS_2 via covalent bond between nitrogen and WS_2. The introduction of nitrogen induces the phase transformation from 2H to 1T and the strong N-W bonds improve the stability of 1T phase. In particularly, 1T@2H WS_2 anchored on the interlinked carbon fiber cloth (CFC) was used as flexible anode without any binder and current collector for lithium ion batteries (LIBs). The electrochemical measurement show that 1T phase

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WS_2@CFC (1T@2H WS_2@CFC) possess a smaller initial discharge capacity loss and a higher reversible capacity than pure 2H phase WS_2@CFC (2H WS_2@CFC), which is critical to the improvement of electrochemical performances.

2. Experimental section

2.1. Preparation of the carbon fiber cloth

The hollow carbon fiber cloth was fabricated by the carbonization of degreasing cotton according to reference [14]. The detailed process is as follows: degreasing cotton was rinsed with ethanol for several times and fully dried before using. A level and smooth degreasing cotton was placed onto an aluminium oxide panel, meanwhile another aluminium oxide panel was placed on the cotton to exert a pressure on it. Then the degreasing cotton was transferred into a tubular furnace and heated to 1000 °C for 2 h under an argon flow with a heating rate of 10 °C min^{-1}, and the sample was cooled down to room temperature naturally after carbonization. The black, thinner and denser CFC with good flexibility was obtained.

2.2. Synthesis of 1T@2H WS_2 nanosheets@CFC

The WS_2 nanosheets were synthesized by a solvothermal method. 1.4 g sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, AR) and 1.50 g thiourea ($CS(NH_2)_2$, AR) were weighed and dissolved in 35 mL deionized (DI) water under vigorous stirring to form a homogeneous solution. Then the solution was carefully transferred into a 50 mL PPL-lined stainless-steel autoclave, maintained at 265 °C for 24 h, and naturally cooled down to room temperature. The obtained black product was washed several times by DI water and dried at 80 °C for the characterization of structure and performance. The WS_2 nanosheets@CFC was obtained through a similar process except the denser CFC being placed in the PPL-lined. Then the composite was put into the tubular furnace for 2 h under argon or ammonia flow at 800 °C and cooled down slowly, the final product was named 2H WS_2 nanosheets@CFC (2H WS_2@CFC) and 1T@2H WS_2 nanosheets@CFC (1T@2H WS_2@CFC) respectively.

2.3. Materials characterizations

X-ray diffraction (XRD) was conducted using a Bruker D8 Advance X-ray diffraction with Cu Kα radiation (λ = 0.154178 nm). Raman spectra were acquired on a LabRam HR system from Horiba Jobin Yvon with 532 nm excitation. Scanning electron microscopy (SEM) images were recorded by Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 5.0 kV and energy-dispersive spectrometer (EDS) at 15.0 kV. High-resolution transmission electron microscopy (HRTEM) images were performed using a JEM-2100F high-resolution transmission electron microscope at an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) measurement were carried out using a monochromatized XPS spectrometer (a ThermoFisher ESCALAB 250) with Al (Kα) radiation as the probe. The specific surface area were studied using Brurauer-Emmerr-Teller (BET) Procedure and pore distributions were analyzed.

2.4. Electrochemical measurements

The electrochemical behaviors of the product were measured by CR2032-type coin cells, which were assembled in an argon-filled glove box. The 3D 1T@2H WS_2@CFC was used as working electrode directly without any extra conductive additives and binder, meanwhile lithium foil was used as counter electrode and reference electrode, and the electrolyte was 1 mol L^{-1} $LiPF_6$ dissolved in a mixture of ethylene carbonate/diethyl carbonate/dimethyl carbonate (1:1:1 vol%). The separator was a polypropylene film (Celgard 2320). Electrochemical measurements were conducted by galvanostatic charge-discharge testing between 0.001 V and 3.0 V on a battery testing system BTS (Newarel Electronic Co., Ltd., China) at ambient temperature. The A.C. impedance spectra were tested on a CHI660D electrochemical workstation in the frequency range from 0.01 to 100 kHz and the cyclic voltammetry (CV) curves were performed between 0.001 V and 3.0 V (vs. Li^+/Li).

3. Results and discussion

Fig. 1 illustrates the fabrication process of 1T@2H WS_2@CFC. Flexible CFC was fabricated by the carbonization of degreasing cotton [14], and 2H WS_2 nanosheets@CFC was obtained by a mild hydrothermal method, and then the composite was heated to 800 °C for 2 h under an ammonia flow. The black product was then washed with distilled water and ethanol and then dried under vacuum at room temperature.

Fig. 2a shows the X-ray diffraction patterns of WS_2 nanosheets, as-prepared 2H WS_2@CFC and 1T@2H WS_2@CFC. It was observed that both WS_2 nanosheets and 2H WS_2@CFC show similar peaks [26], this means the WS_2 nanostructure was maintained after being incorporated with CFC. However, the (002) peak of 1T@2H WS_2@CFC was shifted left compared with 2H WS_2@CFC, the difference was ascribed to the reaction of NH_3 and WS_2, which could expand the interlayer distance [27–29]. To further understand the structure of the 1T@2H WS_2@CFC, Raman scattering was performed to investigate the transformation before and after the ammoniation process. As shown in Fig. 2b, there are two apparent peaks at 350 and 416 cm^{-1} in 2H WS_2@CFC, which are attributed to the in-plane E^1_{2g} mode and out of plane A_{1g} mode of the 2H phase WS_2, respectively [30]. After being ammoniated, three additional Raman peaks emerge at low frequency region (130, 260 and 293 cm^{-1}), which are associated with the 2H WS_2 contained 1T phase [31,32]. N dopant, as the donor atom, could induce the phase transition of $MoSe_2$ by means of thermal treatment in NH_3 atmosphere [33]. Enyashin [20] has pointed that the covalently bound lattice of the 1T-phase was more stable compared with the lattice of the alkali intercalated compound. This was because of the additional electrons from a donor atom could occupy the Mo $4d_{xy}$, Mo $4d_{yz}$, Mo $4d_{xz}$ orbitals and increase the stability of the 1T-phase. The specific surface area was measured to investigate the porosity of composite as shown in Fig. 2c and d, the nitrogen adsorption-desorption isotherm is shown in Fig. 2c, and the BET surface is calculated to be as high as 212.5 m^2 g^{-1} (BET surface of 2H WS_2@CFC is 196.4 m^2 g^{-1} (Fig. S1)), which is advantageous to promote the speedy delivery of lithium ion and electron between electrode and electrolyte [34–36].

Fig. 3a shows the SEM image of carbon fiber cloth, carbon fiber with a uniform diameter (ca. 5 μm) can be clearly observed, and the length is beyond several hundred micrometers. The evenly distributed carbon fibers are closely interwoven, which could not only serve as the carbon matrix but also benefit the speedy delivery of lithium ion during the process of charge/discharge. The SEM images of 2H WS_2@CFC are shown in Fig. 3b and c, WS_2 nanosheets are uniformly distributed on CFC, the transverse size of nanosheet is 200 nm and the thickness is about 10 nm. After being ammoniated, the morphology and structure of WS_2 nanosheets remain stable (Fig. 3d), and the digital photo (inset in Fig. 3d) indicates that the composite remains good toughness. The elementary composition of 1T@2H WS_2@CFC is confirmed by energy dispersive X-ray spectroscopy (EDS) in Fig. 3e–f. The SEM image and corresponding elemental mappings reveal that nitrogen atoms in the WS_2