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MoS_2/nitrogen-doped carbon hybrid nanorods with expanded interlayer spacing as an advanced anode material for lithium ion batteries

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ABSTRACT

MoS_2/nitrogen-doped carbon hybrid nanorods have been successfully synthesized by a facile simultaneous vapor sulfidization and carbonization method using MoO_x/aniline nanorods as the precursor. The obtained hybrid nanorods are composed of MoS_2 with expanded interlayer spacing of 1.02 nm and nitrogen-doped carbon, which exhibit outstanding electrochemical performances as anode materials for lithium-ion batteries including excellent high-rate capability of 667.3 mA h g^{-1} at 10 A g^{-1} and outstanding cyclic stability of 1110 mA h g^{-1} at 1 A g^{-1} after the charge-discharge process at various current densities. The outstanding lithium storage performances of the MoS_2/nitrogen-doped carbon hybrid nanorods can be attributed to the synergistic effects of nitrogen-doped carbon and MoS_2 with expanded interlayer spacing. Importantly, the abundant voids caused by the enlarged interlayer spacing of MoS_2 are in favor of the diffusion of lithium ions, and can buffer the volume changes during the charge-discharge process and create additional active sites for lithium ion storage. Moreover, the hybridization of MoS_2 with nitrogen-doped carbon can facilitate the electron transfer and improve the electronic conductivity.

1. Introduction

In recent years, advanced rechargeable lithium-ion battery (LIB) electrode materials with high energy and power density, fast rate capability, and long cycle life have attracted substantial attention due to their applications in cell phones, laptop computers, and digital cameras [1–4]. Particularly, two-dimensional (2D) transition-metal-dichalcogenide (TMD) compounds have been widely used in the field of renewable energy owing to their 2D morphology and ultrathin thickness with sizable bandgap. As a representative widely used transition metal sulfide for LIB, molybdenum disulfide (MoS_2) has shown fascinating and unprecedented electrical properties for its unique structures: the covalent bonded S − Mo − S layers are weakly stacked together through van der Waals forces, which can facilitate the intercalation of foreign ions and organic polymers as host materials [5–8]. Furthermore, the 4-electron transfer reaction during the insertion and extraction process of lithium ions enables MoS_2 materials to possess high theoretical capacity around 670 mA h g^{-1} higher than the commercial graphite anode counterpart (372 mA h g^{-1}) [9–11]. However, MoS_2 suffers from sluggish kinetics resulting from its poor ionic and electronic conductivity (indirect bandgap of ~1 eV) and limited high-rate performances due to its severe structure collapse during the repetitive charge-discharge process [2,12]. Worse still, the shuttle effects resulting from the dissolving of polysulfide intermediates can cause the loss of electrochemical-active material and capacity decay [13,14].

To solve the problems, numerous efforts have been made including incorporating with stable carbonaceous materials to improve the electrical conductivity and stability or designing nanostructured materials to shorten the electron and ion transport paths [15–20]. Besides, it is reported that nitrogen-doped carbon can greatly ameliorate the electronic conductivity of composites, which is beneficial for the improvement of electrochemical performances [9,21,22]. Xu *et al.* [23] reported a facile method to obtain hierarchical MoS_2/carbon nanosheets by sintering the $(NH_4)_2MoS_4$-polydopamine composite with high specific capacity, high initial Coulombic efficiency, and good rate performances. Qian *et al.* [24] synthesized MoS_2@C nanotube composites through hydrothermal method with the MoS_2 nanotubes and amorphous carbon synchronically generated, manifesting outstanding lithium and sodium storage. Lou et al., [25] prepared one-dimensional MoS_2-C composite nanorods and nanotubes through calcining MoO_x/aniline hybrid in H_2S flow. Recently, a promising approach to improve the capacity and stability is to expand the interlayer distances of MoS_2,

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which can buffer the strain, lower the barrier for lithium ion intercalation, and ameliorate the electron and ion transport [3,26]. Chhowalla *et al.* [27] reported that chemically exfoliated MoS_2 nanosheets can electrochemically intercalate ions such as H^+, Li^+, Na^+, and K^+ to form restacked MoS_2 nanosheets with increased interlayer spacing. Lu *et al.* [13] fabricated nitrogen-doped graphene/MoS_2 nanocomposites with excellent lithium storage performances, which were synthesized by firstly compositing exfoliated MoS_2 monolayers and dopamine through electrostatic interaction, then *in-situ* conversion of dopamine to conductive nitrogen-doped graphene in the interlayer space of MoS_2 at high temperature to form the alternated graphene/MoS_2 structures. Eremenko *et al.* [28] assemblied exfoliated MoS_2 layers with naphthalene derivatives through Coulombic force, which possessed distinct interlayer distances changing with organic cation content. However, a complicated exfoliating process is essential to fabricate the MoS_2 nanocomposites with expanded interlayer spacing, which is time-wasting and cumbersome. Herein, we report a facile simultaneous vapor sulfidization and *in-situ* carbonization method to synthesize MoS_2/nitrogen-doped carbon hybrid nanorods (MCNs) with expanded interlayer spacing by the reaction between MoO_x/aniline nanorods and sublimed sulfur, which manifest excellent high-rate capabilities and cycling stability.

2. Experimental section

2.1. Synthesis of MCNs

MoO_x/aniline nanorods were synthesized via a facile precipitation method based on the report [29]. In a typical experiment, 1.24 g of ammonium heptamolybdate tetrahydrate was dissolved in 20 mL of distilled water, and 1.67 g of aniline was added. Then 1 M HCl aqueous solution was added dropwise into the mixture with magnetic stirring until a white precipitate emerged (at pH 4–5) at room temperature. After a reaction at 50 °C for 4 h in oil bath with stirring, the products were thoroughly washed with ethanol for three times, and then dried at 60 °C overnight. Then the sample (0.5 g) and sublimed sulfur (1 g) were putted into two separated porcelain boats with sublimed sulfur at the upstream side of the furnace. Afterwards, the samples were heated to 650 °C with a heating rate of 3 °C min^{-1} and kept at 650 °C for 5 h under 95% Ar/H_2 flow, and then naturally cooled to ambient temperature. For comparison, bulk MoS_2 was obtained by replacing the MoO_x/aniline nanorods with ammonium heptamolybdate tetrahydrate with procedures staying the same.

2.2. Characterizations

X-ray diffraction (XRD Rigaku D-max-γA XRD with Cu Kα radiation, $\lambda = 1.54178$ Å) from 5° to 70° was used to precisely determine the crystal phases of carbon/MoS_2 hybrids and bulk MoS_2. The morphologies of the as-made samples were characterized by a field-emission scanning electron microscopy (FE-SEM, JSM 6700F) and a transmission electron microscopy (TEM, JEOL 2100F). Energy dispersive X-ray spectrometry (EDS, Oxford Instruments INCA) was used to analyze the element. The X-ray photoelectron spectroscopy (XPS) analyses were implemented on a Perkin-Elmer PHI 550 spectrometer with Al Kα (1486.6 eV) as the X-ray source. The Brunauer-Emmett-Teller (BET) method was selected to record the specific surface area of the samples. The data of pore diameters were collected from the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. Thermogravimetric (TG) analysis was conducted on a TG instrument (NETZSCH STA449C) in air atmosphere from 20 °C to 800 °C with the ramp of 10 °C min^{-1}.

2.3. Electrochemical measurements

The CR2032-type coin cell was used to implement the electrochemical measurements at room temperature. The working electrodes were prepared by blending the samples, poly(vinyl difluoride) (PVDF), and carbon black (Super-P) at a weight ratio of 70:20:10 and pasting onto the Cu foil. The electrode area is 1.13 cm^2. The loading mass of the active material for the MCNs and bulk MoS_2 are 6.69×10^{-4} gcm^{-2} and 6.07×10^{-4} gcm^{-2}, respectively. Pure lithium foil was selected as the counter electrode and Celgard 2500 membrane separator was used to separate the lithium foil and the working electrode. The electrolyte was constituted of a solution of 1 mol L^{-1} $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1:1 by volume). A glove box filled with high purity argon gas was used to assemble the cells. Cyclic voltammetry (CV) curves were performed on an Autolab PGSTAT302N electrochemical workstation with a scanning rate of 0.1 mV s^{-1}, and electrochemical impedance spectroscopy (EIS) measurements were also performed by this machine by applying a sine wave with the amplitude of 10.0 mV over the frequency range from 100 kHz to 10 mHz. The galvanostatic discharge-charge experiments were implemented over a voltage range from 0.01 V to 3.0 V (vs. Li^+/Li) with different rates using a LAND CT2001A battery tester.

3. Results and discussions

The MCNs were synthesized by the facile vapor sulfidation reaction of the MoO_x/aniline nanorods at 650 °C with sublimed sulfur as S source. Fig. 1a presents typical XRD pattern of the MoO_x/aniline precursor synthesized via the reaction between ammonium heptamolybdate and aniline at 50 °C. The diffraction peaks demonstrate that the white precursor is monoclinic MoO_x/aniline, which is consistent with the previous report [29]. The interplanar spacing of $(10\bar{1})$ is 1.37 nm (corresponding 2 theta ~6.4°). The XRD pattern of bulk MoS2synthesized with ammonium heptamolybdate as precursor is shown in Fig. 1b. All the diffraction peaks of various planes can be well indexed to the hexagonal MoS2 (JCPDS 37–1492) [30], and no obvious diffraction peaks of impurities are detected, indicating that the relatively pure crystalline bulk MoS2 are synthesized by setting the reaction temperature at 650° C. In comparison with bulk MoS2, besides the typical diffraction peaks of MoS2, two new sharp and strong diffraction peaks at 8.8° with an interlayer spacing of 1.01 nm and 17.6° appear in the pattern of MCNs in Fig. 1b. As reported previously [31], oxygen-incorporated MoS2 ultrathin nanosheets with expanded interlayer spacing of 0.95 nm prepared by hydrothermal method show a structural conversion to the thermodynamically stable 2H-MoS2 during the heating process from room temperature to 600° C, so the existence of two diffraction peaks at 8.8° and 17.6° of MCNs indicates the process of structural conversion to the 2H-MoS2 is blocked by carbon during the vapor sulfidization and in-situ carbonization process.

SEM image of the MoO_x/aniline precursor in Fig. S1a (see

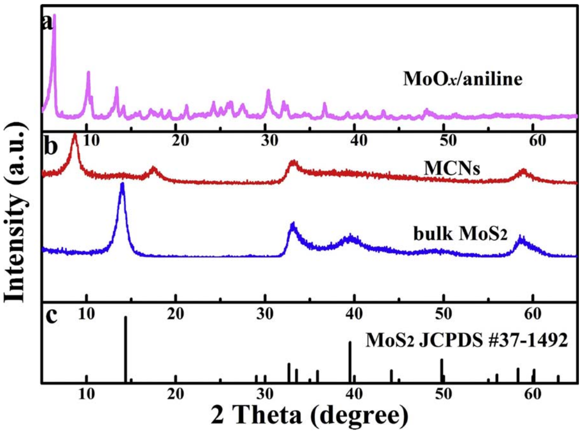

Fig. 1. XRD patterns of the MoO_x/aniline nanorods (a), bulk MoS_2 and MCNs (b); and XRD standard pattern of MoS_2 (JCPDS 37–1492) (c).