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Layer-by-layered SnS_2/graphene hybrid nanosheets via ball-milling as promising anode materials for lithium ion batteries

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ABSTRACT

Layer-by-layered SnS_2/graphene (LL-SnS_2/G) hybrid nanosheets are fabricated via a simple ball-milling of SnS_2 nanoplates obtained through hydrothermal treatment and commercial graphene. When assessed as anode materials for LIBs, LL-SnS_2/G shows a high initial reversible capacity of 696.27 mAh g^{-1} with a high initial coulombic efficiency (74.16%) at 200 mA g^{-1}, and negligible capacity fading over 180 cycles. Moreover, LL-SnS_2/G also has an excellent rate capability, which delivers a high capacity of 567.78 mAh g^{-1} at 2000 mA g^{-1}. Benefits from synergism between SnS_2 nanoplates with high specific capacity and graphene, the graphene increases the conductivity of SnS_2, buffers the volume change during lithiation/de-lithiation processes, and provides an effective physical barrier between the active materials and the electrolyte to suppress the shuttle effect of polysulfides formed during de-lithiation processes. LL-SnS_2/G shows excellent electrochemical performance and is a promising anode material candidate for lithium ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used to multifarious renewable electric power storage (REPS) devices such as portable electronics products, electrical vehicles and others high energy storage applications on account of their high energy density and long-term cycling life span [1–4]. Towards achieving the goals of higher energy density , more stable cycle performance and safer batteries for REPS, stepped-up research efforts have been focused on the exploitation of novel electrode materials for LIBs [5,6].

Transition-metal sulfides (TMS) have attracted significant research interest as anode materials for LIBs owing to their much higher theoretical capacities compared to traditional intercalation graphite electrodes [7–13]. For instance, tin disulfide (SnS_2) exhibits a maximum theoretical capacity of 1231 mAh g^{-1} [14], which is exceed triple that of intercalation graphite anodes (372 mAh g^{-1}). However, the conversion reactions of the metal sulfide to metal and Li_2S, which accompanies multiple electron transfers, is largely irreversible [15]. To top it off, the fatal volume changes happen in lithiation/de-lithiation processes due to the alloy/de-alloy reaction could lead to the pulverization and exfoliation of active material [16]. Thus, like almost all TMS, SnS_2 shows terrible cyclability, which is the main bottleneck of its application for LIBs.

To break through this bottleneck, lots of efforts have been made. Such as Wang et al. reported the performance of two-dimensional SnS_2@PANI nanoplates in LIBs, and they found its reversible capacity could be improved to 730.8 mAh g^{-1} after 80 cycles at 100 mA g^{-1} [17]. Carbon-coated SnS_2 investigated by Kim et al. showed reversible capacity of 668 mAh g^{-1} after 50 cycles at 50 mA g^{-1} [18]. Many other researches were devoted to compositing with graphene via hydrothermal reactions, solvothermal reaction and others wet-chemical methods [19–26], owing to the graphene can act as “buffer medium” to endure volume expansion/shrinkage of SnS_2 during Li^+ insertion/extraction process. Nevertheless, these wet-chemical methods are difficult to achieve mass-produced in industry.

Herein, we report layer-by-layered SnS_2/graphene (LL-SnS_2/G) hybrid nanosheets via simple ball-milling process of SnS_2 nanoplates obtained through hydrothermal treatment and commercial

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graphene. The cycling performance of such composite is greatly improved owing to the synergistic effects of SnS_2 with graphene. Not just that, LL-SnS_2/G displays large initial reversible capacity, high initial coulombic efficiency and excellent rate capability, which makes it promising be employed as a superior anode material for high-performance LIBs.

2. Experimental section

2.1. Synthesis of SnS_2 nanoplates

SnS_2 nanoplates were prepared by a hydrothermal method. First , 1 mmol Tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) (Aladdin Industrial Corporation, China) and 4 mmol L-Cysteine (Aladdin Industrial Corporation, China) were dissolved in 30 mL deionized water, respectively. Then, the latter solution was dropwise added into the former solution under continuous magnetically stirring at room temperature for 1 h. The resulting mixture was loaded into a sealed 80 mL Telfon-lined stainless-steel autoclave and maintained at 180 °C for 18 h. And then the autoclave was cooled to room temperature naturally, the dark green precipitates were centrifuged, and washed with deionized water and anhydrous ethanol for several times. The final products were dried in vacuum oven at 80 °C overnight to obtain pristine SnS_2 nanoplates, which were denoted as P-SnS_2.

2.2. Synthesis of layer-by-layered SnS_2/graphene (LL-SnS_2/G) hybrid nanosheets

As shown in Fig. 1, layer-by-layered SnS_2/graphene (LL-SnS_2/G) hybrid nanosheets were prepared by mixing the as-prepared SnS_2 nanoplates with commercial graphene (CG) (The Sixth Element Materials Technology co., Ltd, China) via a wet ball-milling method. Typically , 1.0 g of as-prepared SnS_2, 0.2 g CG and 20 mL anhydrous ethanol were mixed to ball-milling for 6 h in a planetary mill at a steady speed of about 500 revolutions per minute. And then the obtained composites were dried in vacuum oven at 60 °C for 4 h.

2.3. Structure and morphology characterization

The crystalline structures of the samples were characterized by powder X-ray diffraction (XRD, Burker AXS D8 ADVANCE diffractometer with Cu-Kα radiation) at a scanning rate of 5° min^{-1}. Raman spectra of the samples were measured using a confocal Raman microspectrometer (Renishaw InVia, Derbyshire, England) with 514 nm laser source. The morphologies were observed by Scanning electron microscope (SEM, JEOL JSM-6610). The distribution of element for the sample was determined by using energy-dispersive X-ray spectrometry (EDS) with SEM. Transmission electron microscopy (TEM, JEOL JEM-2100F TEM) was employed to record the internal microstructure and interplanar distance. Thermogravimetric (TG) measurement was carried out on a TGA/DSC1/1600HT analyzer (METTLER TOLEDO Instruments). An atomic force microscopy (AFM) instrument (MUITIMODEPICOFOREE) was used to observe the thickness of samples. BET surface area and pore volume were tested using Micromeritics Instrument Corporation TriStar II 3020.

2.4. Electrochemical tests

The slurry for electrode casting was prepared by mixing the active materials, acetylene black (AB), and carboxymethyl cellulose Na salt (CMC) with the weight ratio of 6:2:2 in deionized water through magnetic stirring. The Cu foil loaded slurry was dried at 80 °C in vacuum, then punched into disks with diameter of 1 centimeter to form working electrodes. The electrochemical performance of the electrodes was assessed within CR2032 coin cells with celgard 2300 film as separator and lithium metal as the counter/reference electrode. The coin cells were assembled in an argon-filled glove box in which O_2 and H_2O level below 1 ppm. The electrolyte was composed of 1 M $LiPF_6$ in EC (ethylene carbonate)/DMC (dimethyl carbonate) with 1:1 volumetric ratio. Charge/discharge performance was assessed by BT3008W battery test system (Neware, Shenzhen, China) under galvanostatic condition at different current densities between 0.01 and 3.0 V. CHI604E electrochemical workstation (Chenhua, Shanghai, China) is used to execute the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests. The CV tests were accomplished at a scan rate of 0.1 mV s^{-1} on the potential interval 0.01–3.0 V. And the EIS measurements implemented a sine wave with a frequency range from 0.01 Hz to 100 KHz in an AC amplitude of 5 mV.

3. Results and discussion

XRD analysis (Fig. 2(a)) suggests that the diffraction patterns of LL-SnS_2/G composite are similar to that of the P-SnS_2. The diffraction patterns of P-SnS_2 and LL-SnS_2/G have several uniform intensive peaks at 15.0°, 28.2°, 32.1°, 41.9°, 50.0° and 52.5°, corresponding to (001), (100), (101), (102), (110) and (111) reflection peaks of trigonal SnS_2 with P-3m1 space group (JCPDS Card No. 23-0677), respectively. There are no impurity peaks are observed, suggesting the obtained samples have high purity. There is no

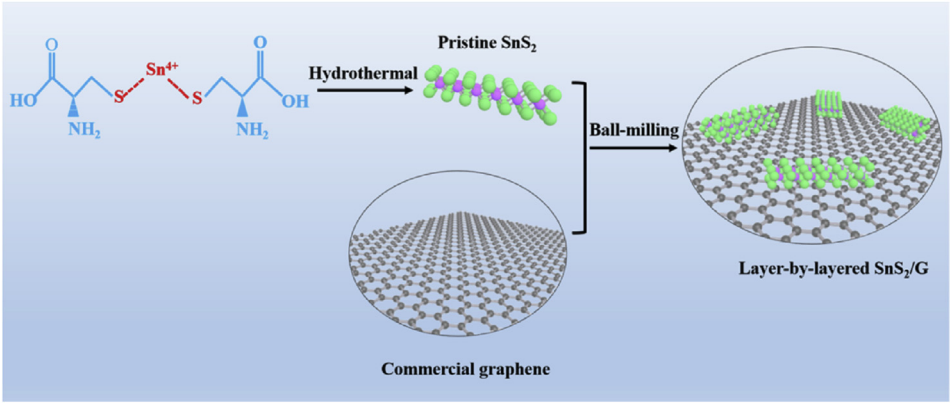

Fig. 1. Schematic illustration of the formation of LL-SnS_2/G hybrid nanosheets.