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Graphene nanoscroll/nanosheet aerogels with confined SnS_2 nanosheets: simultaneous wrapping and bridging for high-performance lithium-ion battery anodes

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ABSTRACT

In this paper, we report graphene nanoscrolls bridged by crumpled graphene nanosheets as an effective conductive framework for confining SnS_2 nanosheets for lithium-ion battery (LIB) applications. The nanoscroll/nanosheet hybrid aerogels (GNAs) with confined SnS_2 nanosheets are facilely prepared via fast quenching, freeze-drying and thermal annealing. During quenching, wrapping SnS_2 nanosheets in the nanoscrolls and bridging the one-dimensional nanoscrolls by the two-dimensional nanosheets occur simultaneously, and the ratio of nanoscrolls/nanosheets can be controlled by simply adjusting quenching conditions. The optimized SnS_2/GNA is highly porous with a large specific surface area of 127.1 $m^2 g^{-1}$ and multi-scale pore structure, which can effectively prevent SnS_2 aggregation to provide abundant lithiation/delithiation sites, and buffer volumetric change and pulverization of SnS_2 nanosheets. Moreover, the three-dimensional conductive network formed in the hybrid aerogels can remarkably improve its electrical conductivity while providing sufficient channels for the transportation of lithium ions and charges. As a result, the optimized SnS_2/GNA nanocomposite exhibits enhanced electrochemical performance with a high initial reversible capacity (1514.8 mAh g^{-1} at 0.1 A g^{-1}), excellent rate capacity (665.4 mAh g^{-1} at 5 A g^{-1}) and good cyclic stability (1050 mA h g^{-1} at the 50th cycle). This may provide an efficient generic approach for encapsulation of transition metal dichalcogenide materials in conductive nano/micro confined spaces for fabrication of high-performance LIB anodes.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) with high specific capacity, large power density, and long cyclic life are promising power sources for electric vehicles [1–3]. As an alternative to commercial graphite carbon [4], which exhibits relatively low theoretical capacity (372 mAh g^{-1}), transition metal dichalcogenide (TMD) layered materials [5], such as MoS_2 [6–10], $MoSe_2$ [11,12], WS_2 [13,14], WSe_2 [15], VS_2 [16,17], FeS_2 [18], SnS_2 [19–23] are widely considered as potential candidates for LIB anode materials because of their unique sandwiched structures and high theoretical capacity. Many types of TMD nanosheets exhibit, however, relatively low electrical conductivity, and poor structural stability during a long period of fast lithiation/delithiation, hampering their practical application as anode materials. Moreover, the nanosheets fabricated in the form of agglomerates usually suffer from limited specific surface area, which affect the accessibility of lithium ions, also resulting in poor electrochemical performance of the anodes.

To address the aforementioned issues, many approaches have been investigated, including optimization of micro/nano-structures of two-dimensional (2D) TMD nanosheets, fabrication of three-dimensional (3D) flower-like microspheres, and confinement of TMD nanosheets in conductive carbonaceous and polymer matrices with large specific surface areas [24–28]. Of the various approaches, the combination of TMD nanosheets with conductive substrates has attracted much attention because of the potential of this approach to improve electrical conductivity, provide large specific surface area and good accessibility to electrolyte and lithium ions, and stabilize the nanocomposite structures to accommodate the volumetric expansion/shrinkage. Research

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results have shown that graphene is an ideal conductive substrate to disperse and confine active materials because of its excellent conductivity, large specific surface area, robust mechanical strength and remarkable stability. Nevertheless, owing to their open structure, 2D graphene nanosheets could not confine active anode materials very effectively [29]. Hence, another form of graphene, graphene nanoscrolls, has recently attracted significant attention. Graphene nanoscrolls are composed of several rolled-up graphene nanosheets. They exhibit open-ended tubular hollow structure and hence are considered as a much better conductive substrate to confine active materials, while tubular cavities can also provide the channels for ion transport. Piao et al. wrapped sulfur particles in one-dimensional (1D) reduced graphene oxide nanoscroll (GNSC) by freezing the plastic tubes encapsulated with high-temperature precursor suspensions followed by freeze-drying for several days [30]. The prepared sulfur/GNSC nanocomposites showed the effective confinement effect of GNSC for active materials in lithium-sulfur batteries. In a similar way, Xu et al. prepared graphene nanoscroll-wrapped Fe_3O_4 nanoparticles (Fe_3O_4@GNSC) for LIBs [31]. Despite offering significant confinement effect, graphene nanoscrolls are 1D nanomaterials and thus they have a common drawback of 1D nanomaterials, i.e., they are more difficult to form effective conductive networks for electron transport than 2D nanomaterials.

To enhance both the confinement effect and electron transport, in this work, for the first time we fabricated 3D nanoaerogels composed of graphene nanoscrolls bridged by curved graphene nanosheets, and used these nanoscroll/nanosheet hybrid nanoaerogels to confine SnS_2 nanosheets for high-performance LIB anodes. As a typical type of TMD nanomaterials, SnS_2 is low-cost, non-toxic, easy to be prepared, and exhibits relatively good chemical stability and high theoretical capacity. Typical SnS_2 nanosheets exhibit layered CdI_2-type structure composed of tin atoms sandwiched between double layers of close-packed sulfur atoms, which is suitable for fast intercalation/de-intercalation of lithium ions. So far although many SnS_2-based nanocomposite systems, such as SnS_2/graphene [20,32,33], SnS_2/CNT [34], SnS_2/graphene/CNT [35], SnS_2/vanadium nitride [36], SnS_2/conductive polymers [7,37], SnS_2/SnO_x [21,22,38] have been developed, approaches that can simultaneously promote the confinement effect and conductive network formation for enhancing both structural stability and electron transport has not been demonstrated. In this work, SnS_2 nanosheets were used as a model TMD material to investigate the possibility of simultaneously confining TMD active materials in nanoscrolls and promoting conductive network formation via bridging the nanoscrolls by graphene nanosheets. The motivation was to provide an efficient generic approach for simultaneous enhancing structural stability and electron transport of various TMD nanomaterials for fabrication of advanced electrode materials for lithium-ion batteries. Our highly porous SnS_2-encapsulated graphene nanoscroll/nanosheet nanoaerogel (SnS_2/GNA) contains controllable amounts of hollow tubular graphene nanoscrolls and curved graphene nanosheets. The inter-connected tubular graphene nanoscrolls and curved graphene nanosheets form 3D networks, which not only offer abundant conductive channels for the transport of lithium ions and charges, but also provide spacious inter-space to buffer SnS_2 nanosheet volumetric expansion/shrinkage and pulverization during the repeated lithiation/delithiation in cycling tests. As a result, the optimized SnS_2/GNA nanocomposite exhibits a high initial reversible capacity (1514.8 mAh g^{-1} at 0.1 A g^{-1}), excellent rate capacity (665.4 mAh g^{-1} at a high current density of 5 A g^{-1}), and good cyclic stability. The superior electrochemical performance with high reversible capacity, high coulombic efficiency, good cycling and rate capability makes SnS_2/GNA as a promising anode material for LIBs.

2. Experimental section

2.1. Materials

Natural graphite powder with the size of 325 mesh was obtained from Alfa-Aesar. 98% H_2SO_4, 30% H_2O_2, $KMnO_4$, 37% HCl, KOH, tin (IV) chloride pentahydrate, and thioacetamide were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized (DI) water was used as the solvent throughout the experiments.

2.2. Preparation of SnS_2 nanosheets, SnS_2/GNAs, and GNA

Neat SnS_2 nanosheets were synthesized by adopting a reported hydrothermal method [35]. Graphene oxide (GO) powder was prepared from natural graphite powder using Hummer's chemical oxidation method [39]. The well exfoliated GO suspension with 0.5 mg mL^{-1} was prepared by continuous ultrasonicating GO powder in DI water for 3 h. The SnS_2/GNAs with different amount of SnS_2 nanosheets were fabricated by the processes of cold quenching, freeze-drying, and thermal annealing as schematically shown in Scheme 1. Typically, pure SnS_2 nanosheets were dispersed in the as-prepared GO suspension by continuous ultrasonicating, and the weight ratios of pure SnS_2 nanosheets and GO nanosheets are 1:2, 1:1 and 2:1. Then, the mixed dispersion was dropped into liquid nitrogen to fabricate 3D GO nanoscroll/nanosheet wrapped and encapsulated SnS_2 networks. After that, the obtained frozen globules were quickly dried in a lyophilizer to obtain SnS_2/GO nanoscroll/nanosheet nanoaerogels (SnS_2/GONAs), and donated as SnS_2/GONA-0.5, SnS_2/GONA-1, and SnS_2/GONA-2, respectively. In order to reduce GO to graphene and perfect crystalline structure of SnS_2, the as-prepared SnS_2/GONAs was calcined at 350 °C for 2 h under argon atmosphere. The SnS_2/GNAs with GO to SnS_2 weight ratio of 1/2, 1/1 and 2/1 are labelled as SnS_2/GNA-0.5, SnS_2/GNA-1, and SnS_2/GNA-2, respectively. Moreover, pure GNA was prepared by the aforementioned process with any SnS_2 nanosheets.

2.3. Characterization

The structures and morphologies of the as-prepared samples were investigated by a field emission scanning electron microscopy (FESEM, JEOL JSM 7600) at an acceleration voltage of 5 kV and a transmission electron microscope (TEM, JEOL 2100) at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Bruker GADDS X-ray diffractometer with CuKα radiation ($\lambda = 0.1542$ nm) from $2\theta = 5°-80°$ at the voltage of 40 kV and current of 40 mA. TEM and XRD studies were also carried out to examine the structure and morphology of SnS_2/GNA-1 after 50 cycles of charge/discharge. Before the examination, the electrodes were washed with aceton for several times to eliminate the electrolyte and residues. X-ray photoelectron spectroscopy (XPS) measurements were collected on a device of Kratos Analytical AXIS with a monochromatized Al Ka X-ray source (1486.6 eV phoyons). All XPS spectra were corrected using C 1s line at 284.5 eV. Thermogravimetric analysis (TGA, TA Q500) was conducted under air flow from 100 to 800 °C at a heating rate of 20 °C min^{-1}. The specific surface area and pore size distribution were characterized by a surface area and porosity test instrument (Micromeritics, Tristar II 3020) by N_2 physisorption at 77 K.

2.4. Electrochemical measurements

The as-prepared electrode materials (pure SnS_2 nanosheets, SnS_2/GNAs, and pure GNA) were assembled into standard CR2032 coin cells in an argon filled glovebox. In these coin cell electrodes, Celgard 2400 film was used as separator, lithium foils were applied