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Flexible free-standing SnS_2/carbon nanofibers anode for high performance sodium-ion batteries

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ABSTRACT

To solve the problems of insufficient conductivity and volume expansion of SnS_2 during cycling when applied as anode for sodium-ion batteries (SIBs), we designed flexible and self-standing SnS_2/carbon nanofibers (SnS_2/CNFs) film by electrospinning technology and post sulfuration, in which the ultrafine SnS_2 nanoparticles (~5 nm) are preganated in the carbon nanofibers. The three-dimensional carbon nanofibers serve as flexible scaffold with high electrical conductivity to buffer the aggregation and pulverization of SnS_2 particles. The obtained flexible SnS_2/CNFs film can be directly used as anode for SIBs without adding binder and carbon additive, and exhibits excellent electrochemical performance. The SnS_2/CNFs delivers a high capacity of 570.8 mAh g^{-1} at 0.2 A g^{-1}. Even at a high rate of 5 A g^{-1} a high capacity of 247.1 mAh g^{-1} is still achieved. It also maintains 378.9 mAh g^{-1} after 100 cycles at 0.5 A g^{-1}.

1. Introduction

With increased demand of high energy density and long cycling life for mobile electrical equipment, limiting lithium sources leads to high cost, which restricts the application of lithium ion batteries (LIBs) in energy storage equipment [1,2]. To meet the progressive requirement of low-cost and large-scale energy storage applications, many researchers show renewed interest in SIBs due to the abundant sodium resources. It's pivotal to develop high performance electrode materials and stimulate the commercial development of high-efficiency and low-price devices during sodium-ion batteries system [2–5].

Metal sulfides (e.g. SnS_2 [6–9], SnS [10], FeS_2 [11], FeS [12], etc.) have attracted much attention used as anode for SIBs due to high energy-density and high-rate performance [13,14]. Among metal sulfides, SnS_2 is a promising anode for SIBs owing to high theoretical capacity (1137 mAh g^{-1}) and better reversibility than SnO_2 due to weaker M–S ionic bonds [15]. However, the insufficient conductivity and the serious volume change (420%) during cycling lead to the poor electrochemical performance [16]. In order to improve the electronic conductivity and buffer the volume change of the SnS_2, carbon materials are used to integrate with the nanostructured SnS_2 [7–9]. Jiang et al. developed ultrasmall SnS_2 nanocrystals grown on the nitrogen-doped graphene sheets (SnS_2–NGS), exhibiting excellent electrochemical properties due to the synergistic function between NGSs and SnS_2 [7]; Zhang et al. synthesized SnS_2 particles fixed on a small number of layered reduced graphene oxides (SnS_2/rGO). The dispersing and conducting effects of rGO greatly increased the capacity of the SnS_2/rGO [9]. Besides the performance of the electrode material itself, energy density is also very vital for whole battery systems. To construct SIBs with high energy density, another effective way is to fabricate a self-supproting electrode without using heavy metal substrate, binder and carbon additive [17,18]. Wang et al. synthesized free-standing flexible nitrogen-doped carbon nanofibers (N-CNFs), which had good rate performance and cycle stability [19]. Balogun et al. synthesized carbon quantum dot-coated VO_2 nanowires (CQDs) grown on carbon fibers which showed good sodium storage performance [20]. Thus, it is desirable to design self-supporting SnS_2 electrode with high electrochemical performance for high performance SIBs.

In this work, we first design SnS_2 nanoparticles impregnated in the carbon nanofibers (SnS_2/CNFs) through electrospinning and post sulfuration to take advantages of high capacity of SnS_2 nanoparticles and the self-standing electrode. The carbon nanofibers network provides a conductive host and inhibits the aggregation and the volume expansion of SnS_2, thereby maintaining the structural stability of the electrode. The as-prepared free-standing SnS_2/CNFs with good flexibility can be directly used as anode for SIBs and shows excellent electrochemical performance.

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2. Experimental section

2.1. Preparation of SnS_2/CNFs

0.25 g of anhydrous $SnCl_2$ (99%, Aladdin Industrial Inc.) was dissolved in 5 g of *N*,*N*-dimethylformamide (DMF; Aladdin Co. Ltd.) and 0.4 g of PAN (PAN, Mw = 150,000, Sigma Aldrich) was added. The mixture was stirred at 40 °C for 6 h. The mixture was loaded into a 5 mL syringe for electrospinning at a push-up rate of 0.375 mL h^{-1} with a voltage of 10.6 kV. The as-spun nanofibers were preheated at 250 °C in Ar for 2 h and then carbonized at 700 °C for 1 h to obtain Sn/C nanofibers. The Sn/C nanofibers and sulfur were placed at two separate crucible boat with sulfur at the upstream side of the furnace, and calcined at 400 °C for 2 h in Ar. To remove residual sulfur, the material was treated at 250 °C for 5 h in Ar, and then immersed in CS_2 for 5 h.

2.2. Materials characterization

The crystal structure was characterized by X-ray diffraction (XRD; Bruker D8 Advance, Cu-Kα radiation). The morphology was collected via scanning electron microscopy (SEM; Hitachi SU8200) and transmission electron microscopy (TEM; FEI Tecnai G2 F30). Thermogravimetric analysis (TGA; NETZSCH TG209F1) was measured from 30 to 800 °C at a heating rate of 10 °C/min in air.

2.3. Electrochemical characterization

The CR2032 coin-cells were assembled in an argon-filled glovebox using sodium metal as the counter electrode. A glass fiber membrane (Whatman, Grade GF/B) was used as a separator. The electrolyte was 1 M $NaPF_6$ in dimethoxyethane (DME). The capacity is calculated based on the whole SnS_2/CNFs electrode, and the mass loading of the electrode is ~1.5 mg cm^{-2}. Galvanostatic charge/discharge tests were carried out on a NEWARE battery test system in a voltage range of 0.01–3.0 V.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the material before and after sulfuration. All the diffraction peaks of the material before sulfuration can be indicated as a tetragonal crystal Sn. After sulfuration, the Sn has been fully converted to SnS_2. The TGA test was conducted to determine the mass loading of SnS_2 in carbon nanofibers (Fig. 1(b)). From 30 °C to 800 °C, the mass of SnS_2/CNFs decreased

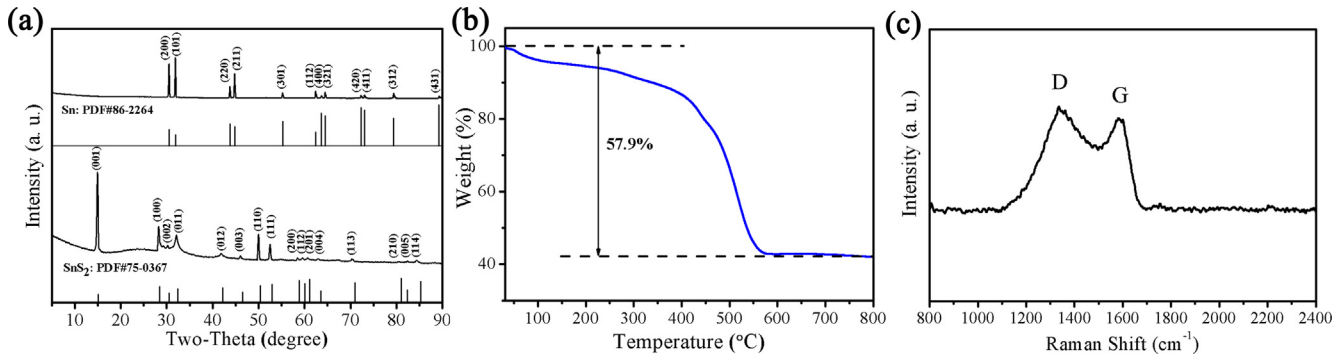

Fig. 1. (a) XRD patterns of the material before and after sulfuration; (b) TGA result, and (c) Raman spectrum of SnS_2/CNFs.

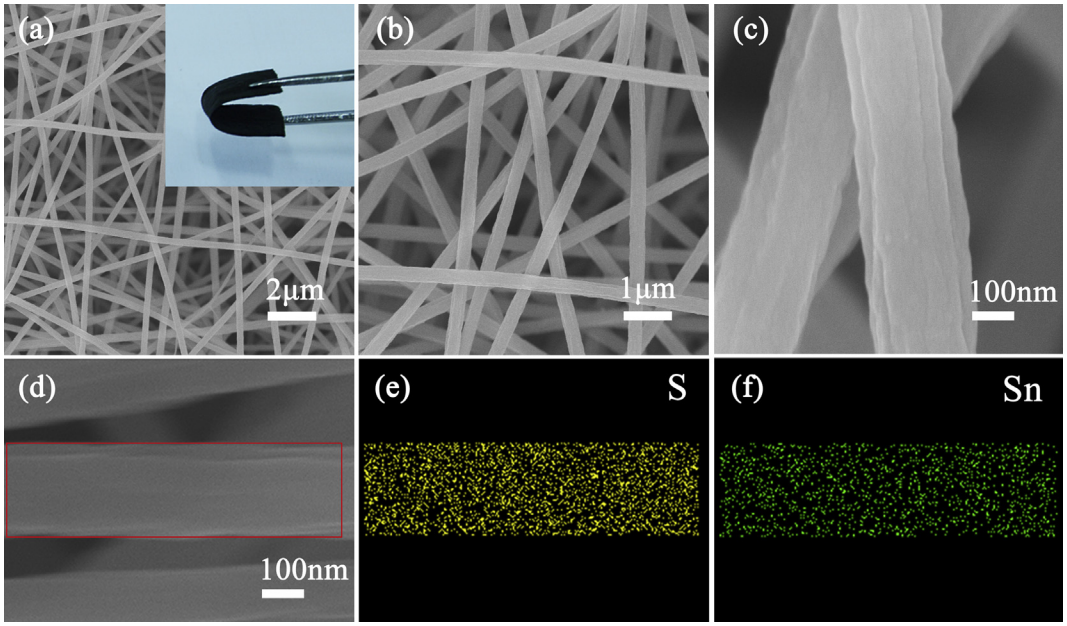

Fig. 2. (a–c) Optical and SEM image of SnS_2/CNFs; (d–f) elemental mapping of SnS_2/CNFs.