



L-Cysteine-assisted hydrothermal synthesis of nickel disulfide/graphene composite with enhanced electrochemical performance for reversible lithium storage



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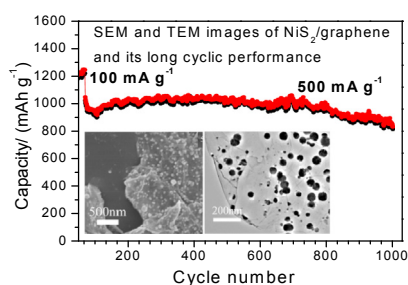
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HIGHLIGHTS

- L-Cysteine-assisted hydrothermal route for facile synthesis of NiS₂/graphene composite.
- NiS₂ sphere-like nanoparticles are well dispersed on the corrugated graphene.
- The composite delivers a reversible capacity as high as 1200 mAh g⁻¹.
- The NiS₂/graphene exhibits the excellent cyclic stability and enhanced rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

NiS₂/graphene composite is synthesized by a facile hydrothermal reaction between NiCl₂ and L-cysteine in the presence of graphene oxide sheets. L-Cysteine serves as both the sulfur source for NiS₂ and reductant for reduction of graphene oxide sheets. The reduced graphene oxides can be used as a platform for growth of NiS₂ particles and restrain NiS₂ from agglomerating during hydrothermal process. The results of characterizations show that the sphere-like NiS₂ particles exhibit smaller sizes and are well dispersed on the surface of reduced graphene sheets. The electrochemical measurements demonstrate that the NiS₂/graphene composite delivers a reversible capacity as high as 1200 mAh g⁻¹ at a current density of 100 mA g⁻¹ and enhanced high-rate capability of 740 mAh g⁻¹ at a high current density of 1000 mA g⁻¹. After 1000 cycles, the NiS₂/graphene still preserves the reversible capacity about 810 mAh g⁻¹ at a current density of 500 mA g⁻¹, indicating its excellent cyclic stability.

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1. Introduction

Lithium ion batteries (LIBs) with high energy density, no memory effect and long service life have become dominant power sources for portable electronic devices and electric vehicles. The physical and chemical property of electrode materials wherein is a

determining factor for the energy density and performance of LIBs. Even if graphite has been ubiquitously used as a commercialized anode material for LIBs due to its excellent cycling performance, its poor rate-capability and relatively low specific capacity (theoretical capacity of 372 mAh g⁻¹) are limiting the development of next-generation LIBs [1]. It's necessary to devote some efforts to study alternative anode materials with higher specific capacity, desirable rate capability and long cycle life to meet the ever-increasing performance demands. Transition metal sulfides such as copper

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sulfides [2,3], ferric sulfides [4,5], cobalt sulfides [6–8] and nickel sulfides [9–13] have been actively investigated as possible candidates for anode materials due to their high capacity, low cost and eco-friendliness. Among the family of transition metal sulfides, nickel sulfides have caused a special attention due to their interesting electronic, magnetic, optical properties [14,15] and their multiple potential applications including LIBs [9–13], supercapacitors [16–18] and catalysts [19,20]. It was reported that the various phases of nickel sulfides such as NiS [9], Ni₃S₂ [10,11], Ni₃S₄ [12], Ni₇S₆ [13] exhibited higher specific capacity as anode materials of LIBs compared to graphite anode material. The electrochemical lithium storage of the nickel sulfides is based on the conversion reaction ($\text{NiS}_x + 2x\text{Li} = \text{Ni} + x\text{Li}_2\text{S}$). According to this conversion reaction, cubic pyrite NiS₂ should deliver a theoretical capacity of 870 mAh g⁻¹, which is higher than that of NiS (591 mAh g⁻¹), Ni₃S₂ (447 mAh g⁻¹), Ni₃S₄ (705 mAh g⁻¹) and Ni₇S₆ (530 mAh g⁻¹). However, to our best knowledge, there are few literatures about the synthesis of NiS₂, especially as the anode material of LIB. Even if it has been demonstrated that these nickel sulfides exhibited higher capacity than graphite anode, they go through a rapid deterioration and have low retention of capacity due to volume change during lithium ions insertion/extraction process, which leads to electrode pulverization and the loss of the electrical contact. In addition, the low electronic conductivity of the nickel sulfides would lead to their poor rate capability. To resolve these drawbacks, one of the effective methods is to fabricate composite with carbon nanomaterials (such as carbon nanotubes and graphene sheets). In particular, graphene, a two-dimensional single atomic sheet of sp² carbon atoms, has attracted intensive attention due to its extraordinary properties, including high electrical conductivity, giant charge mobility, large theoretical specific surface area (2600 m² g⁻¹), excellent flexibility and chemical stability [21,22]. These novel properties make graphene become an ideal substrate for the growth of other nanomaterials to construct heterostructural composites for LIBs application. When nickel sulfides/graphene composites are used as the anode materials for LIB, the graphene can not only provide an elastic space to buffer the volume change of the electrode materials during the repetitive charge/discharge process, but also facilitate the faster electron transport, resulting in an enhanced electrochemical performance. It has been demonstrated that the solvothermal synthesized NiS/graphene composite and Ni₃S₂/N-doped graphene composite exhibited the enhanced electrochemical performances as LIB anodes in comparison with the NiS and Ni₃S₂ [9,11].

Herein, the NiS₂/graphene composite was synthesized via a hydrothermal reaction between NiCl₂ and L-cysteine in the presence of graphene oxide sheets. The result composite was characterized by XRD, SEM and TEM. As an anode material of LIB, the as-prepared NiS₂/graphene composite exhibits a high reversible capacity of 1200 mAh g⁻¹ with long cycle life and desirable rate capability. The reversible capacity of more than 800 mAh g⁻¹ can be preserved after 1000 cycles at 500 mA g⁻¹. This work shows that the novel NiS₂/graphene composite can be used as a promising anode material for high-performance LIBs.

2. Experimental

2.1. Synthesis of NiS₂/graphene composite

Graphene oxide sheets were prepared from natural graphite powder (Shanghai Colloid Chemical Plant, China) by the modified Hummers method, the details of which was described elsewhere [23]. In a typical batch, a solution of L-cysteine (L-cys, 7.5 mmol) and NiCl₂·6H₂O (1.5 mmol) in 50 mL deionized water was introduced to 30 mL suspension of graphene oxide sheets (3 mmol) under

vigorous stirring for 2 h. Afterward, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed tightly and heated at 200 °C for 24 h. The autoclave was then cooled to room temperature naturally. The black precipitate was collected by centrifugation, washed with deionized water and ethanol for several times. Finally, NiS₂/graphene composite was dried in a vacuum oven at 80 °C for 12 h. For comparison, the pristine NiS₂ was also prepared by the similar process in the absence of graphene oxide sheets.

2.2. Characterizations

An X-ray powder diffraction (XRD) pattern was recorded by a Bruker D8 Advance diffractometer with Cu-K α radiation ($\lambda = 0.15405$ nm). The structure and morphology of the samples were characterized by field emission scanning electron microscopy (FESEM; Hitachi SU8010) and high resolution transmission electron microscopy (HRTEM; JEM 2100F). The elemental composition of the composite was analyzed by energy dispersive X-ray spectroscopy (EDS; Hitachi SU8010 IXRF Systems). Thermo-gravimetric analysis (TGA) was carried out with a NETZSCH STA 409 PC apparatus in air atmosphere and heated at a rate of 10 °C min⁻¹.

2.3. Electrochemical measurements

The electrochemical measurements were evaluated using two-electrode cells assembled in an argon-glove box where both the moisture and oxygen contents were below 1.0 ppm. Li sheets served as the counter electrode and reference electrode, and a polypropylene film (Celgard-2300) was used as the separator. The electrolyte was 1.0 M LiPF₆ in a mixture of ethylene carbonate and dimethyl carbonate (EC/DMC, 1:1 in volume). The working electrode was prepared by a slurry coating procedure. The slurry consisted of 80 wt% active material (NiS₂ or NiS₂/graphene), 10 wt% acetylene black and 10 wt% polyvinylidene fluorides dispersed in N-methyl-2-pyrrolidinone. The obtained slurry was spread on a copper foil, dried at 120 °C for 12 h under vacuum, and then pressed to form the working electrode. Galvanostatic charging/discharging cycles were carried out on a LAND 2001A Battery Tester with the voltage between 0.005 and 3.00 V at various current densities. Cyclic voltammetry was implemented on an electrochemical workstation (CHI 660B) at a scanning rate of 0.5 mV s⁻¹ over the potential range of 0.005–3.00 V vs. Li⁺/Li. Electrochemical impedance spectroscopy (EIS; PARSTAR 2273) were obtained by applying a sine wave with an amplitude of 5.0 mV over the frequency range from 200 kHz to 0.01 Hz.

3. Results and discussion

3.1. Characterizations of structure and morphology

The structure and morphology of samples were characterized by XRD, SEM and TEM. The XRD patterns of the graphene sheets, pristine NiS₂ and NiS₂/graphene composite are illustrated in Fig. 1. Fig. 1(a) shows a broad diffraction peak at $2\theta = 24.7^\circ$, which is assignable to the (002) plane of graphene nanosheets [24], indicating that the restacking of graphene monolayers occurred in the hydrothermal process. As shown in Fig. 1(b, c), both samples display diffraction peaks at $2\theta = 27.2^\circ, 31.4^\circ, 35.3^\circ, 38.9^\circ, 45.1^\circ, 53.4^\circ, 56.0^\circ, 58.6^\circ$ and 70.0° , which can be readily indexed to the (111), (200), (210), (211), (220), (311), (222), (230) and (321) plane of the cubic pyrite NiS₂ (JCPDS Card No.11-0099). Additionally, the composite does not display the (002) peak of the graphene nanosheets, indicating that the stacking of graphene nanosheets does not occur. It is ascribed to the dispersion of NiS₂ nanoparticles on the surface of

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