



One-step synthesis of nickel sulfide/N-doped graphene composite as anode materials for lithium ion batteries



Hua-Chao Tao, Xue-Lin Yang*, Lu-Lu Zhang, Shi-Bing Ni

College of Materials and Chemical Engineering, China Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China
Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, China Three Gorges University, China

ARTICLE INFO

Article history:

Received 29 August 2014

Received in revised form 20 October 2014

Accepted 28 October 2014

Available online 12 December 2014

Keywords:

Lithium ion batteries

Anode

Nickel sulfide

N-doped graphene

One-step

ABSTRACT

Nickel sulfide/N-doped graphene composite as high performance anode materials has been synthesized through a simultaneous hydrothermal method. The morphology, structure and electrochemical performance of nickel sulfide/N-doped graphene composite were investigated by field emission scanning electron microscopy, transmission electron microscope, X-ray diffraction, Raman spectra, Fourier transform infrared spectra, X-ray photoelectron spectroscopy and electrochemical measurements. The nickel sulfide with a length of about 500 nm and diameter of 100 nm clung to the N-doped graphene matrix. The nickel sulfide/N-doped graphene composite exhibits a relatively high reversible capacity and good cycling stability as anode materials for lithium ion batteries. The good electrochemical performance can be attributed to N-doped graphene, which improves the electronic conductivity of composite and suppresses the volume effect as elastic matrix. The one-dimensional structure of nickel sulfide facilitates the diffusion of lithium ions and electrons.

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1. Introduction

As a widely used anode material for commercial lithium ion batteries, graphite (theoretical capacity 372 mA h g^{-1}) cannot meet the demand of electric vehicles and large energy storage devices with high energy density. In this context, various anode materials with high capacity were investigated, such as silicon (4200 mA h g^{-1}) [1], tin (994 mA h g^{-1}) [2] and their composites [3–8]. Nanomaterials of metal sulfur, such as SnS [9], Bi_2S_3 [10], FeS [11], MoS_2 [12], CoS_2 [13] have been intensively studied as anode materials for lithium ion batteries to achieve higher specific capacities than graphite. However, the practical use of these materials is greatly hindered by their large volume changes during Li insertion/extraction and low electronic conductivity. Among these metal sulfides, nickel sulfides (NiS , NiS_2 , Ni_3S_2 , Ni_3S_4 , Ni_6S_5 , Ni_7S_6 , Ni_9S_8 and Ni_xS) have been studied due to their high theoretical capacities and low cost, and NiS has been widely investigated in these nickel sulfides [14–17].

To overcome the fast capacity fading problem, combining these high-capacity materials with carbonaceous materials is an effective way. For the nanostructured high-capacity materials

dispersed in a carbon matrix, the carbon serves as a buffer to alleviate the strain caused by the volume change of the electrochemically active particle during the discharge–charge process. Graphene with large surface area, excellent electronic conductivity and high mechanical strength has been regarded as an ideal carbon matrix which can be used to design high performance composites for lithium ion batteries. Up to now, various graphene-based composite such as NiO/graphene [18], SnO_2 /graphene [19], Si/graphene [20], TiO_2 /graphene [21], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene [22], Fe_3O_4 /graphene [23] have been prepared to obtain enhanced electrochemical performance. Recently, NiS nanosheets/graphene composite has also been synthesized to exhibit the improved electrochemical performance by hydrothermal method using the additional surfactant [24].

In addition, lots of chemical methods have been investigated for reducing graphene oxide to graphene. A large number of reducing agents have been applied in reducing graphene oxide, such as NaBH_4 [25], LiAlH_4 [26], thiourea [27], NaHSO_3 [28], hydrazine [29], HI [30], HBr [31]. Furthermore, doping is a common strategy in tuning the properties of carbon materials. Experimental studies have shown that hetero-atom doping in graphene can tailor the physical and chemical properties of graphene. Lots of studies showed that the nitrogen doping in graphene can enhance the electrochemical properties and the charge capacity for lithium ion batteries [32]. To produce the N-doped graphene, some methods such as chemical vapor deposition (CVD) in NH_3 [33],

* Corresponding author at: College of Materials and Chemical Engineering, China Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China. Fax: +86 717 6397505.

E-mail address: xyang@cgtu.edu.cn (X.-L. Yang).

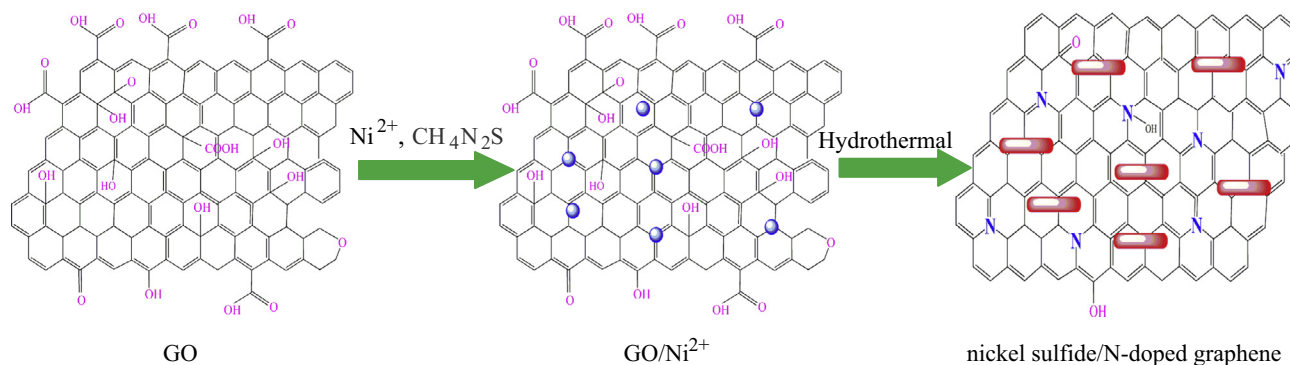


Fig. 1. Schematic illustration for the fabrication process of nickel sulfide/N-doped graphene composite.

arc charge method [34], have been developed. But quick, easy and mass-producing method for N-doped graphene is still a challenge.

Herein, a facile and simple one-step hydrothermal route has been used to synthesize the nickel sulfide/N-doped graphene composite using thiourea as sulfur source and reducing agent. Nickel sulfide particles grow on the N-doped graphene sheets. As conductive, electrochemical active and elastically strong substrate, graphene can enhance the electrochemical performance of composite as anode materials for lithium ion batteries.

2. Experimental

2.1. Synthesis of nickel sulfide/N-doped graphene composite

Graphite oxide was synthesized from natural graphite using the modified Hummers method [35]. Graphite oxide was exfoliated through ultrasonication to form graphene oxide (GO) suspension. In a typical synthesis, GO (100 mg) was diluted with 40 mL of deionized water. A certain amount of nickelous acetate (4 mmol) and thiourea (4 mmol) was added into the solution under stirring for 1 h at room temperature. Then this mixture was transferred to 50 mL Teflon-lined autoclave and the reaction occurred in oven at 180 °C for 24 h. After the completion of reaction, the solid product was collected by centrifugation and washed with water and ethanol repeatedly for several times. The final product was dried in vacuum oven at 80 °C for 24 h. Nickel sulfide was prepared under the same condition without adding the GO suspension.

2.2. Structural characterizations

The structure of the nickel sulfide/N-doped graphene composite was determined by X-ray diffraction (XRD, Rigaku D/max) using Cu K α . The morphology and microstructure of nickel sulfide/N-doped graphene were characterized by field emission scanning electron microscopy (FESEM, JSM-7500F), transmission electron microscope (TEM, JEM-2100F) and high-resolution TEM (HRTEM). Raman spectra measurements were recorded on a Jobin-Yvon Labor Raman HR-800 Raman system using 514.5 nm Ar-ion laser. The chemical states of composite were analyzed using X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600 W). Fourier transform infrared (FTIR) spectra were collected with on a NEXUS FTIR spectrometer ranging from 500 to 4000 cm⁻¹. Thermogravimetric analysis and differential scanning calorimetric (TGA/DSC, STA449C) were carried out in air atmosphere from 50 to 1000 °C.

2.3. Electrochemical measurements

The working electrodes were prepared by coating slurries consisting of active materials (nickel sulfide and nickel sulfide/N-

doped graphene composite) with acetylene black and poly (vinylidene fluoride) with a weight ratio of 70:20:10 in N-methyl-2-pyrrolidinone solvent. Then the resultant slurry was uniformly pasted on a copper foil. The paste was dried at 120 °C for 24 h under vacuum to remove the moisture or solvent contents present in active materials. The electrolyte was 1 M LiPF₆ solution in ethylene carbonate (EC)/dimethyl carbonate (DMC) with a volume ratio of 1:1. Lithium foil acted as counter electrodes and a Celgard 2300 membrane was used as separator to separate cathode from anode electrode. The cells were assembled in an argon-filled glove box with moisture and oxygen contents below 1 ppm. Galvanostatic discharge/charge measurements were performed over a potential range of 0.01–3 V vs. Li/Li⁺. Cyclic voltammetry (CV) curves of electrode were carried out on a CHI660C Electrochemical Workstation (Shanghai Chenhua) between 0.01 and 3 V under a scan rate of 0.2 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was collected in the range of 100 kHz–0.1 Hz with an alternating voltage amplitude of 5 mV using CHI660C Electrochemical Workstation (Shanghai Chenhua). All the performances were performed at room temperature.

3. Results and discussion

The formation process of the nickel sulfide/N-doped graphene composite may be divided into three steps, as shown in Fig. 1. Firstly, GO has abundant oxygenate groups on its surface, and these functional groups are assumed to be uniformly distributed on the

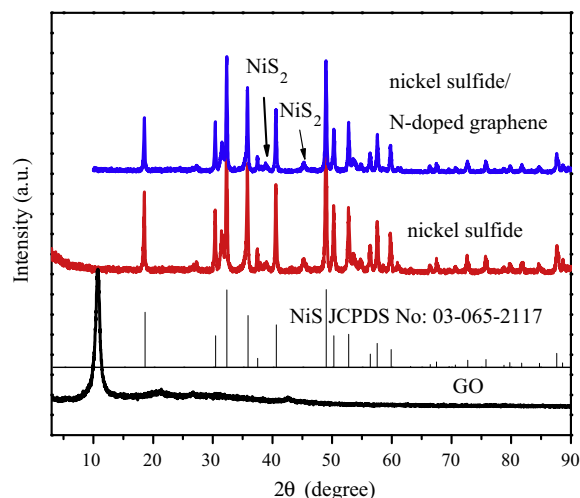


Fig. 2. X-ray diffraction patterns for graphite oxide, nickel sulfide and nickel sulfide/N-doped graphene composite.

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