



# Synthesis of cobalt nanofibers @ nickel sulfide nanosheets hierarchical core-shell composites for anode materials of lithium ion batteries



Xuefang Chen <sup>a, b</sup>, Ying Huang <sup>a, b, \*</sup>, Xiaopeng Han <sup>a, b</sup>, Kaichuang Zhang <sup>c</sup>

<sup>a</sup> Department of Applied Chemistry and The Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China

<sup>b</sup> MOE Key Laboratory of Material Physics and Chemistry Under Extraordinary Conditions, School of Natural and Applied Science, Northwestern Polytechnical University, Xi'an 710072, PR China

<sup>c</sup> Shijiazhuang Mechanical Engineering College, Shi Jia Zhuang 050003, PR China

## ARTICLE INFO

### Article history:

Received 28 February 2018

Received in revised form

12 June 2018

Accepted 24 July 2018

Available online 29 July 2018

### Keywords:

Cobalt nanofibers

Ni<sub>3</sub>S<sub>2</sub> nanosheets

Anode materials

Electrochemical properties

## ABSTRACT

Cobalt nanofibers @ Ni<sub>3</sub>S<sub>2</sub> nanosheets (Co@Ni<sub>3</sub>S<sub>2</sub>) composites with high surface area (241.67 m<sup>2</sup>/g) were successfully synthesized via a chemical conversion route. The special nanostructure afforded sufficient space for the volume change, ensured efficient electrolyte penetration, increased contact area between electrolyte and active material during discharge–charge process. Moreover, the existence of the cobalt nanofibers with high conductivity provided a possibility for the rapid transportation of the electrons and lithium ions. The composite electrodes presented a reversible discharge capacity of 531 mAh/g with a good cyclic stability. This research perhaps inspired the designing of high performance electrode materials with a novel structure for high performance energy storage devices.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

The ever-increasing demands for power sources in the field of hybrid electric vehicles and portable electronic devices have stimulated extensive research beyond lithium ion battery technologies [1,2]. Anode material as one key part of the lithium ion batteries plays an important role in determining the performance of the batteries [3,4]. At present, the most commonly-used anode material is graphite-based materials [5]. However, the low special capacity and poor safety are still significant obstacles, which perhaps limit the application of high performance batteries in future [6,7]. Exploiting novel electrode materials with high specific capacity, superior cycle stability and remarkable rate capability is of great urgency [8,9].

Recently, transition metal sulfides compounds (such as SnS<sub>2</sub>, MoS<sub>2</sub>, CoS<sub>2</sub>, CuS, WS<sub>2</sub>, NiS, etc) have been considered as promising candidates because of their properties of high energy density, low

cost as well as easy preparation [8,10–16]. Nickel sulfides (Ni<sub>x</sub>S<sub>y</sub>) were considered as one kind promising anode material owing to the advantages of competitive cost and high specific capacities [17,18]. Unfortunately, poor electronic conductivity and severe volume changes in the repeated charging/discharging process were key problems, which resulted in severe deterioration of electrode structure and poor electrode reaction kinetics and leading to a rapid capacities loss [19]. Designing specific morphology and dimensionality of the electrode materials was one efficient method to improve the properties of lithium storage. For example, one-dimensional (1D) structure with high surface-to-volume ratio can remarkably shorten diffusion length of Li<sup>+</sup> and fasten electrode reaction kinetics [20]. Two-dimensional (2D) nanosheet structure can offer massive contact area for the volume effects during the repeated charging/discharging process [21]. In addition, compositing Ni<sub>x</sub>S<sub>y</sub> with conductive materials to prepare composite structures was also proved an effective way to improve cyclic stability of electrodes, which can offer significant electrical conductivity and low ion diffusion resistance [22].

Herein, we design Co@Ni<sub>3</sub>S<sub>2</sub> composites via a well-known Stöber process and three hydrothermal methods. A simple schematic illustration of the formation process of the Co@Ni<sub>3</sub>S<sub>2</sub> was shown in Fig. 1. Firstly, cobalt nanofibers were synthesized by a

\* Corresponding author. Department of Applied Chemistry and The Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China.

E-mail addresses: [1021633952@qq.com](mailto:1021633952@qq.com) (X. Chen), [yingh@nwpu.edu.cn](mailto:yingh@nwpu.edu.cn) (Y. Huang).

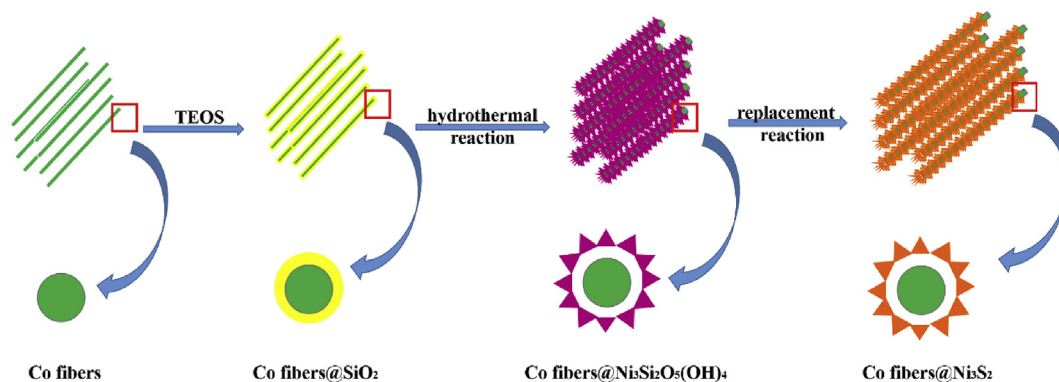


Fig. 1. Formation mechanism of the Co@Ni<sub>3</sub>S<sub>2</sub> composites.

simple hydrothermal method, which were not only served as one mechanical support, but also served as a template to form one-dimensional nanostructures. Secondly, a thin SiO<sub>2</sub> layer was coated on the surface of the cobalt nanofibers under alkaline conditions using TEOS as raw materials. Then, a hydrothermal process was performed in order to form Co@ nickel silicate composites. In this hydrothermal process, the SiO<sub>2</sub> layer on the surface of the cobalt nanofibers was gradually dissolved and reacted with nickel ions to form nickel silicate. Finally, the nickel silicate nanosheets converted into Ni<sub>3</sub>S<sub>2</sub> nanosheets through a chemical conversion route with sodium sulfide as sulfur source [23]. In the composites, the Ni<sub>3</sub>S<sub>2</sub> nanosheets provided the active sites to accommodate lithium ions, and cobalt nanofibers acted as a mechanical support to increase electrical conductivity. In addition, the existence of voids buffered the volume effect during the repeated charging/discharging process. Simultaneously, the voids offered fast channels for the diffusion of lithium ions. All of the above mentioned advantages helped to improve the electrochemical properties.

In addition, it well known that the capacity fade was inevitable in the repeated charging-discharging process due to the decomposition of electrolyte, the formation of SEI film, the dissolution of active material and other side reactions. Here, we researched the structural changes of the anode materials, the possible composition of SEI film and the impedance changes. All these works provided the basis for the optimal design of anode material for lithium-ion batteries.

## 2. Experimental

### 2.1. Sample preparation

Cobalt nanofibers were prepared using a step hydrothermal method based on our previous experiment [24,25]. 0.02 mol CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.01 mol nitrilotriacetic acid were dissolved in a solution of 54 mL distilled water and 18 mL isopropanol. The mixed solution was stirred for 1 h and then heated at 180 °C for 6 h by a hydrothermal method. Clearing the cooled products repeatedly and the then were dried in a vacuum.

Then 200 mg cobalt nanofibers were added in a solution that was composed of ultra-pure water (10 mL), ammonium hydroxide (3 mL, 28 wt %) and ethyl alcohol (80 mL). 0.15 g polyvinylpyrrolidone (PVP) was added to activate the surface of the cobalt nanofibers. Then 0.8 mL tetraethyl orthosilicate (TEOS) was added and the reaction was kept for 10 h form SiO<sub>2</sub> on the surface of the cobalt nanofibers. The products were separated by centrifugation and repeatedly washing using distilled water and ethanol, which were then dried in a vacuum at 60 °C.

In order to prepare Co@ nickel silicate composites, we firstly synthesized Co @ nickel silicate composites. In a typical experiment, 0.12 g prepared Co@SiO<sub>2</sub> nanocomposites were added in 30 mL ultra-pure water. 0.44 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.8 g NH<sub>4</sub>Cl and 1.5 mL NH<sub>3</sub>·H<sub>2</sub>O were decomposed in 45 mL ultra-pure water. Then the later solution was added dropwisely to the former solution. The mixed solution was vigorously stirred for 1 h, and then was transferred into a 100 mL Teflon-lined stainless steel autoclave. The Teflon-lined stainless steel autoclave was then heated at 180 °C for 24 h. When the temperature dropped, the precipitations were washed with ultra-pure water and ethanol repeatedly, and then were dried in a vacuum.

In order to prepare Co@Ni<sub>3</sub>S<sub>2</sub> composites, 20 mg prepared Co@ nickel silicate composites were added in a mixed solution of 60 mL ultra-pure water and 20 mL ethanol by ultrasonic dispersion. 80 mg Na<sub>2</sub>S·9H<sub>2</sub>O were added and then the mixed solution was stirred for 1 h, then was poured into one 100 mL Teflon-lined stainless steel autoclave, which was then heated at 120 °C for 12 h. After the temperature cooled down to room temperature, the products were completely cleared by with ultra-pure water and ethanol, and were dried at 60 °C for 12 h in a vacuum.

### 2.2. Materials characterization

A transmission electron microscope (TEM, USA, model Tecnai F30G2, FEI Co.,) and a scanning electron microscope (SEM, VEGA 3, The Czech Republic, TESCAN) were used to characterized the morphology of the Co@Ni<sub>3</sub>S<sub>2</sub> composites. The elemental distribution was analyzed using an energy dispersive spectroscopy (EDS). The crystal structure of the Co@Ni<sub>3</sub>S<sub>2</sub> composites were measured by X-ray diffraction (XRD) (Rigaku, D/max-2500 system at 100 mA of Cu Ka and 40 kV). Nitrogen adsorption-desorption isotherms and pore size distribution of the Co@Ni<sub>3</sub>S<sub>2</sub> composites were obtained at 77 K by an adsorption instrument. X-ray Photoelectron Spectroscopy (XPS) was measured using a Thermal Scientific K Alpha photoelectron spectrometer.

Co@Ni<sub>3</sub>S<sub>2</sub> composites (70 wt%), PVDF (15 wt%) and acetylene black (15 wt%) were dispersed in 1-methyl-2-pyrrolidinone (NMP). The mixed slurry was painted on a copper foil, which was dried at 100 °C for 12 h. The prepared electrodes were assembled to form CR2016-type coin batteries using lithium foil as the counter electrode, polypropylene (PP) film (Celgard 2400) as the separator in an argon-filled glovebox. The electrolyte was a solution of 1 M LiPF<sub>6</sub>, which was composed of ethylene (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC). The volume ratio was 1:1:1.

The electrochemical properties were measured using Multi-channel current static system Land (LAND CT2001A) at a range of

Download English Version:

<https://daneshyari.com/en/article/6601981>

Download Persian Version:

<https://daneshyari.com/article/6601981>

[Daneshyari.com](https://daneshyari.com)