



A smart architecture of nickel-cobalt sulfide nanotubes assembled nanoclusters for high-performance pseudocapacitor



Mingxia Dong^a, Zhixing Wang^a, Xinhai Li^a, Huajun Guo^a, Jiexi Wang^{a, b, *}

^a School of Metallurgy and Environment, Central South University, Changsha 410083, PR China

^b State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, PR China

ARTICLE INFO

Article history:

Received 8 February 2018

Received in revised form

12 June 2018

Accepted 17 June 2018

Available online 19 June 2018

Keywords:

Ion-exchange

Nickel-cobalt sulfide

Pseudocapacitor

Specific capacitance

Asymmetric supercapacitor

ABSTRACT

To develop a high-performance capacitive material with both superior power density and energy density, it is very important to construct a nanomaterial with a well-controlled structure. In this work, we report the preparation of NiCo₂S₄ nanotubes-assembled nanoclusters with a combination of hydrothermal and ion exchange processes. By optimizing the ion-exchange temperature, the tubular morphology can be both achieved and optimized. By tuning the conditions of the synthesis process, the diameter of the primary 1D structure can be increased, which leads to a compact cluster with decreased surface area. In particular, the sample prepared at 180 °C (NCS2) shows the morphology of nanoclusters assembled nanotubes with a wall thickness of about 7 nm. Such an architecture shows excellent electrochemical performance as a pseudocapacitor. It shows an initial specific capacitance of 1005 F g⁻¹ at the current density of 1 A g⁻¹ and remains 896 F g⁻¹ at a current density of 20 A g⁻¹. Moreover, it displays a favorable capacitance retention of 79.34% after 5000 cycles at a current density of 10 A g⁻¹. Furthermore, the NCS2//AC asymmetric supercapacitor exhibits excellent rate performance (retaining 81% of the initial capacity when the current density increases from 1 A g⁻¹ to 20 A g⁻¹) and a high energy density of 52 Wh kg⁻¹ at a power density of 9288 W kg⁻¹. This work lays the foundation for the design and optimization of NiCo₂S₄ based nanostructured materials for energy storage.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

The burning of fossil fuel causes several severe problems such as environmental pollution, greenhouse effect, and the depletion of natural resources [1–3]. These issues motivate the development and utilization of secondary energy sources such as wind, solar, and tidal energies. However, these renewable energy sources always show discontinuous availability. Therefore, effective energy storage/conversion devices are urgently needed to achieve the practical utilization of these clean energy sources [4–6]. Lithium batteries and supercapacitors are the two main streams in a corresponding device development [7–9]. In particular, supercapacitors have attracted significant attention due to their high power density, super-long life cycle, and fast charge/discharge capabilities [10–12]. However, the unsatisfactory energy density limits the application of supercapacitors [10,13]. Different types of electrode materials show

significant differences in specific capacity and energy density [14]. Until now, several types of materials have been studied, such as carbon materials (carbon nanotube/nanowire [15], graphene [16,17]), metal oxides (MnO₂ [18], NiO [19], Co₃O₄ [20], NiCo₂O₄ [21]), transition metal hydroxides (Co(OH)₂ [22], Ni(OH)₂ [23]), transition metal sulfides (NiS [24], Ni₃S₂ [25], CoS [26], Ni_xCo_{3-x}S₄ [27,28]), and conducting polymers (3,4-ethoxy two thiophene polymer [29]). Among these, bimetallic transition metal sulfides exhibit unique advantages resulting from the synergistic effect originating from the presence of two or more transition metal sulfides [30–33]. This type of material has been reported to demonstrate improved electronic conductivity and high specific capacitance due to the low band gap energy value [34,35]. In several transition metal sulfides, NiCo₂S₄, with low electronegativity and high electrochemical activity, has been widely reported as one of the most promising capacitive materials [36,37]. Since the large specific surface area is vital for achieving high specific capacity of the material, numerous forms of NiCo₂S₄ prepared as nanostructures, such as nanoflakes [38], nanotubes [39], hollow nanocolloids [40], and nanoprisms [28], have been reported to

* Corresponding author. School of Metallurgy and Environment, Central South University, Changsha 410083, PR China.

E-mail address: wangjiexi@csu.edu.cn (J. Wang).

exhibit excellent performance in supercapacitors. However, the reported methods for preparing nanosized NiCo_2S_4 suffer from shortcomings of a lengthy process and lack of controllability. In addition, the effects of structure and morphology on the stability of NiCo_2S_4 still need to be determined. Therefore, it is important to find a simple and controllable method for the preparation of the electrode material, to accordingly optimize the microstructure of the NiCo_2S_4 , and to clarify the impact of the morphology on its electrochemical performance.

In this paper, a novel architecture of NiCo_2S_4 nanotubes-assembled nanoclusters is proposed by combining hydrothermal method and ion exchange process. By changing the ion exchange temperature, the NiCo_2S_4 is transformed from a solid nanoneedle into a hollow nanotube, which can significantly increase the surface area of the material. We expect that this unique nanostructure may exhibit superior electrochemical performance when used in a pseudocapacitor.

2. Experimental

2.1. Synthesis of NiCo_2S_4

All chemicals were of analytical grade purity and were used without further purification. In a typical synthesis process of Ni-Co precursor, 10 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 5 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 mL deionized water. Then, 18 mmol of urea was added under stirring for 15 min to form a homogenous pink solution. After that, the pink solution was placed into a Teflon-lined stainless-steel autoclave (200 mL) and heated at 120 °C for 10 h. After cooling to room temperature, the products were filtered and repeatedly washed with deionized water and anhydrous ethanol. Finally, the resulting wet powders were freeze-dried for 24 h to obtain Ni-Co precursor.

In the ion-exchange process, 0.2 g of Ni-Co precursor was added to 100 mL of 0.07 M $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solution. After stirring for 30 min, a homogenous suspension was obtained and transferred into a Teflon-lined autoclave (200 mL). After heating at 170–200 °C for 8 h, the black precipitates were obtained, filtered and washed with deionized water and anhydrous ethanol thrice. Finally, the products were freeze-dried for 24 h. The samples obtained at 170, 180, 190, and 200 °C were marked as NCS1, NCS2, NCS3, and NCS4, respectively.

2.2. Characterization of morphology and structure

Scanning electron microscopy (SEM, JEOL, JSM-5600LV) and transmission electron microscopy (TEM, JEM-2100F) were utilized to characterize the microstructure and morphology of as-prepared samples. X-ray diffraction (XRD Rint-2000, Rigaku) with $\text{Cu-}\alpha$ irradiation was used to determine the phase of samples. XRD data were collected in the 2θ range from 10° to 80°.

2.3. Electrochemical characterization

The as-prepared materials and conductive carbon were mixed with ethyl alcohol/deionized water solution (the volume ratio is 3:1), followed by grinding to form a uniform slurry. After that, polytetrafluoroethylene (PTFE) latex (60 wt%) was added into the slurry and stirred to form a sticky-like silly putty. The mass ratio of as-prepared material, conductive carbon, and PTFE was 8:1:1. Then, the mixture was cast on a glass and rolled into a slice. Finally, the slice was cut into 10 × 10 mm and was placed between two cleaned nickel forms, followed by pressing at 30 MPa and vacuum drying for 6 h.

Electrochemical tests were performed in three-electrode

electrochemical cells as well as in asymmetric supercapacitors. In the three-electrode system, a platinum foil was used as counter electrode, a Hg/HgO electrode was used as reference electrode and an aqueous solution containing 6 mol L⁻¹ of KOH was used as electrolyte. Cyclic voltammograms (CV) of the samples were measured on an electrochemical workstation (CHI660E, Chenhua, Shanghai) in a potential range of 0–0.55 V (vs. Hg/HgO) at different scan rates. Galvanostatic charge-discharge (GCD) tests were acquired through the LAND electrochemical test system in a voltage window of 0–0.5 V vs. Hg/HgO. The current densities of GCD tests varied between 1 and 20 A g⁻¹. The cycle performances of the samples were estimated at a current density of 10 A g⁻¹ for 5000 cycles.

The asymmetric supercapacitors were assembled by using NCS2 and active carbon as the positive and negative electrodes, respectively. An aqueous solution containing 6 mol L⁻¹ KOH was used as electrolyte. The electrochemical performance was characterized in the voltage window of 0–1.6 V. The CV and EIS tests of NCS2 samples were performed using an electrochemical workstation (CHI660E, Chenhua, Shanghai). The GCD tests were conducted with the LAND electrochemical testing system with current densities of 1–20 A g⁻¹. The cycle performance was estimated at 10 A g⁻¹ for 5000 cycles.

3. Results and discussion

Fig. 1 shows the XRD patterns of the materials. All patterns contain diffraction peaks at 26.8°, 31.6°, 38.3°, 47.4°, 50.5°, and 55.3°, which can be indexed as (311), (220), (400), (422), (511), and (440) peaks of the cubic NiCo_2S_4 (JCPDS 73-1704), respectively. In addition, the impurity peaks at 29.9° and 52.1° are in accordance with (311) and (440) crystallographic planes of Co_9S_8 (JCPDS 86-2273), respectively. The reason for the impurity peaks is due to the fact that a small amount of Co is replaced by Ni during the preparation of NiCo_2S_4 , which is in accordance with previously reported results [41]. However, the XRD pattern of the NCS2 sample shows that the impurity peaks for Co_9S_8 are weak, indicating high purity of the target phase NiCo_2S_4 .

Fig. 2 shows the morphologies of as-obtained NiCo_2S_4 samples at different ion-exchange temperatures. Fig. 2(a–d) shows that the cluster consisting of nanoneedles inherited from the precursor

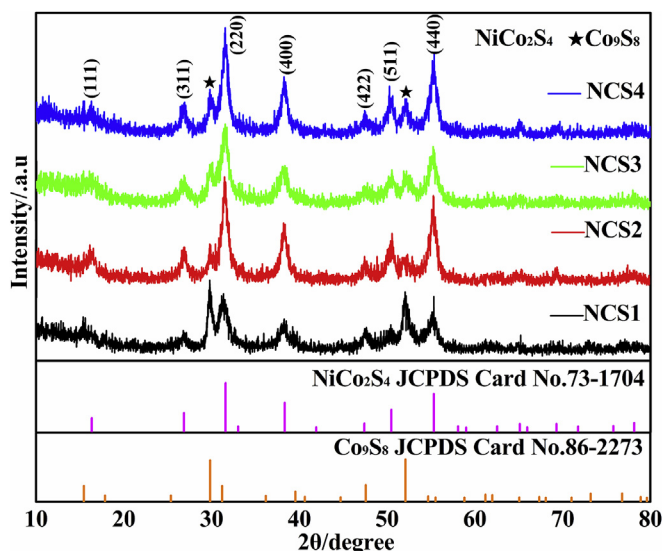


Fig. 1. XRD patterns of samples obtained at different ion-exchange temperatures.

Download English Version:

<https://daneshyari.com/en/article/7990541>

Download Persian Version:

<https://daneshyari.com/article/7990541>

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