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Original Research Paper

Tailoring synthesis of Ni_3S_2 nanosheets with high electrochemical performance by electrodeposition

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ABSTRACT

Nickel sulfide nanosheets with high electrochemical performance were successfully synthesized by an electrochemical deposition method. It is interesting to notice that the size, thickness and surface area were simply tailored by adjusting the initial potential during synthesis without changing other reaction conditions. The highest electrochemical performance was achieved on the nickel sulfide sample prepared at initial potential of −0.9 V. This sample not only presented high specific capacitance at low current density (1958.0F g^{-1} at 3.3 A g^{-1}), but also exhibited excellent high rate performance (672.8F g^{-1} at 98.7 A g^{-1}). To the best of our knowledge, these values are in the highest level as compared with other works. The high electrochemical performance of nickel sulfide sample originates from its thin thickness.

1. Introduction

Supercapacitors have significant features such as high-power density and long lifecycle as compared with batteries. There are two types of supercapacitors (electrical double-layer capacitors and pseudocapacitors). The energy storage of the former-type supercapacitors depends on the electrostatic charge separation at the interface between carbon-based electrode materials and electrolyte [1–4]. For the latter-type supercapacitors, three electrochemical mechanisms are involved including underpotential deposition, redox capacitance and intercalation capacitance [5]. The redox-type supercapacitors following the redox capacitance mechanism is considered as an important and promising candidate for energy storage system, since its can provide a higher instantaneous power density output and shorter charging time than batteries, and also higher energy density than conventional dielectric capacitors [6–8]. Traditional inorganic electrode materials for redox supercapacitor include several transitional metal oxide and metal hydroxide (RuO_2, MnO_2, NiO, Co_3O_4, $Ni(OH)_2$, $Co(OH)_2$ etc.) [8–12]. These materials have their respective advantages and disadvantages in the application of supercapacitors. However, potential for the further development of these materials is gradually depleted although extensive effort has been devoted including building hierarchical nanostructures, controlling dimension, compositing with highly conductive materials and so on [13–15]. As a result, new electrode materials for redox supercapacitor are emerging, trying to open a new pathway. Transitional metal sulfides are one category of the most promising new materials due to their presented advantages of unique physical and chemical properties, as well as appropriate capacitance [16–18].

Various metal sulfides as electrode materials were developed such as iron sulfide, copper sulfide, cobalt sulfide, nickel sulfide, manganese sulfide etc. [18–24]. Among these materials, nickel sulfide is one intensively investigated sulfide because of its excellent thermostability and appropriate electrochemical properties [18]. It is known that the family of nickel sulfide consists of compounds with disparate combinations of Ni to S ratios including $Ni_{3+x}S_2$, Ni_3S_2, Ni_6S_5, Ni_7S_6, Ni_9S_8, NiS, Ni_3S_4, and NiS_2 [17,18]. They have wide range of applications in dye-sensitized solar cells, catalysis, hydrogen and electrodes of LIBs and SCs [25–28]. In the application of redox supercapacitors, building various nanostructures such as thin film, nanocubes, nanowires, nanoflowers etc. [29–36] is the most frequently used strategy to achieve nickel sulfide with high electrochemical performance. In a typical work [37], Ni_3S_2-NiS nanowires presented redox reactivity with a specific capacitance of 1077.3F g^{-1} at current density of 5.0 A g^{-1}. In another work [38], hierarchical NiS microflowers were synthesized using $Ni(OH)_2$ as precursors through sulfuration process, presenting a specific capacitance of 1127.0F g^{-1} at current density of 1.0 A g^{-1}. Unfortunately, to the best of our knowledge, the specific capacitance of nickel sulfide in most works is still less than 1200F g^{-1} [23–25,28–33,38–45], which is much inferior to transitional metal oxides/hydroxides [9,10].

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In this work, we successfully tailored the formation of Ni_3S_2 nanosheets using an electrochemical deposition method. We controlled the size and thickness of nickel sulfide products by adjusting the initial potential of electrodeposition. Characterization results indicated that the nickel sulfide sample prepared at initial potential of −0.9 V had the smallest size/thickness and largest specific surface area. Consequently, this sample presented the highest specific capacitance (1978.0F g^{-1} at low current density 3.3 A g^{-1} and 672.8F g^{-1} at high current density of 98.7 A g^{-1}), which is much higher than other works.

2. Experimental

2.1. Materials

Nickel chloride ($NiCl_2{\cdot}6H_2O$, ≥99.0%) and thioacetamide (C_2H_5NS, ≥99.0%) were purchased from Aladdin and used as-received.

2.2. Chronoamperometry deposition of Ni_3S_2 nanosheets

0.01 mol $NiCl_2{\cdot}6H_2O$ and 0.1 mol CH_3CSNH_2 were dissolved in 100 mL distilled water under ultrasonification, forming a transparent solution. The solution was used as electrolyte solution for carrying out the chronoamperometry deposition of nickel sulfide sample by a IVIUMSTAT electrochemical workstation in three-electrode configuration. In this configuration, two surface-cleaned nickel foams with the size of 1.0 × 2.0 × 0.15 cm were used respectively as working electrode and counter electrode, and Ag/AgCl was used as reference electrode.

The electrodeposition of nickel sulfide was performed respectively at initial potentials of −0.7 V, −0.9 V, −1.1 V, −1.3 V, −1.5 V and −1.7 V for 1 h. During the deposition process, black substance was gradually detached from the working electrode. After the electrodeposition operation, the black substance was collected and rinsed with deionized water and ethanol. Subsequently, the substance was dried in vacuum at 60 °C for 12 h.

2.3. Characterization

The crystalline phase of the samples was measured with a Rigaku SmartLab III diffractometer using Cu Kα radiation (λ = 1.5406 Å). The morphology of samples was observed using a JEOL JEM-1400 transmission electron microscope (TEM). The TEM sample was prepared by dispersing a little amount of powder sample in ethanol under ultrasonification, followed by drying one drop of suspension on a 400 mesh carbon-coated copper grid. The N_2 adsorption/desorption isotherms of samples were measured by an ASAP-2010 surface area analyzer. The electrochemical measurements were carried out using an IVIUMSTAT electrochemical workstation in a three-electrode cell equipped with a working electrode, a platinum plate counter electrode and an Hg/HgO reference electrode.

2.4. Preparation of working electrodes and electrochemical measurement

The working electrode was prepared by inserting a paste which was formed by adding a few drops of ethanol to a mixture of 80.0 wt% nickel sulfide and 20.0 wt% acetylene black into a nickel foam substrate. After a brief evaporation of ethanol, the paste was pressed at 10 MPa to the nickel foam with a nickel wire for electrical connection. Each electrode contained ~3.0 mg electroactive materials and had a geometric surface area of 1 cm^2. The electrode was activated by 100 cycles of cyclic voltammetry from 0.0 to 0.55 V versus Hg/HgO at 100 mV s^{-1} in 3 M KOH aqueous solution and used as a working electrode in the electrochemical measurements. The electrochemical tests on working electrodes including cyclic voltammetry (CV), Galvanostatic charge–discharge and electrochemical impedance spectroscopy were performed in 3 M KOH aqueous solution. Typical CV curves were respectively measured between the potential window of 0–0.55 V at scan rates of 5, 10, 20, 50, and 100 mV s^{-1}. Galvanostatic charge–discharge tests were performed between the potential windows of 0.0–0.55 V. The calculation of specific capacitance was based on the description in literature [46].

3. Results and discussions

The nickel sulfide samples were prepared by electrodeposition under the exact same conditions except for the initial potential. In order to explore the influence of initial potential on the phase of products, XRD measurements were carried out on the samples prepared at different initial potential between −0.7 and −1.7 V. As shown in XRD patterns (Fig. 1), the three typical samples respectively prepared at initial potential of −0.7 V, −0.9 V and −1.7 V present the characteristic structure of Ni_3S_2 (JCPDS 44-14180). This result indicates that the initial potential does not influence the phase of materials.

The morphology of three Ni_3S_2 samples respectively prepared at initial potential of −0.7, −0.9 and −1.7 V was observed by transmission electron microscopy. As shown in the obtained images (Fig. 2a–f), all samples present stacked fractional nanosheets-like morphology with different lateral size and thickness. It seems that the Ni_3S_2 sample prepared at −0.9 V is composed of nanosheets with the smallest lateral size and thinnest thickness as compared with other two samples. A preliminary conclusion could be inferred from these TEM images: the initial potential during synthesis does influence the morphology and size of final products. The following electrochemical measurements would prove that the initial potential also influences the electrochemical performance of Ni_3S_2 samples.

We carried out electrochemical measurements on Ni_3S_2 samples, trying to determine the optimum initial potential. The cyclic voltammograms (CV) of Ni_3S_2 samples prepared at different initial potentials were measured within a potential window of 0–0.55 V at various scan rates ranging from 5 to 100 mV s^{-1}. The results in Fig. S1 shows that the CV curves of all these samples at different

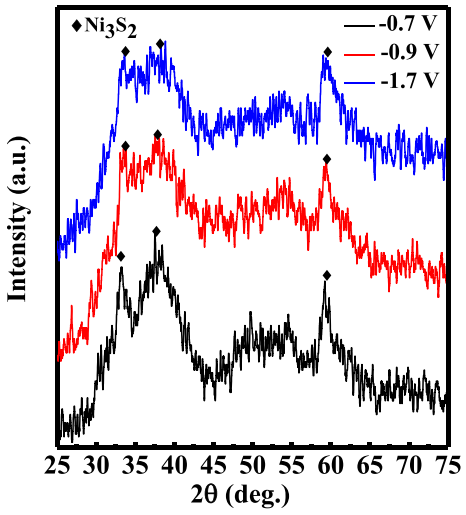

Fig. 1. XRD patterns of nickel sulfide samples prepared at initial potential of −0.7 V, −0.9 V and −1.7 V.

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