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Binary Ni-Al sulfide/nickel foam electrodes with hierarchical hyacinth-like structure for supercapacitance performance

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ABSTRACT

The binary Ni-Al sulfide with hyacinth-like structure was grown directly on Ni foams via a facile two-step hydrothermal process as supercapacitor electrode materials. The structure and surface morphology were characterized by X-ray diffraction analysis, field emission scanning electron microscopy (FESEM), respectively. The amorphous porous Ni-Al binary sulfuration achieved outstanding electrochemical performances with high specific capacitance of 2030 F/g under current density of 1A g^{-1}, excellent cycle stability in 500 continuous cycles (only 8.5% decay after 500 cycles at 1A g^{-1}), and good rate capability. The brilliant property of Ni-Al binary sulfide can be owed to the macroporous structure with high conductivity and transport rate for electrolyte ions and electrons, rich redox reactions and large surface area. The results demonstrate that the Ni-Al sulfides are the promising electrode materials in supercapacitor applications.

1. Introduction

With the time passing by, development of high-performance electrochemical energy storage devices has been one of the focus issues and has caused a great impact on the improvement of human life [1,2]. Among various energy storage devices, electrochemical supercapacitors (SC), are considered typically as one of the most promising energy storage and conversion devices owing to their rapid charge-discharge rates, environmental friendliness and long cycle life [3,4]. However, the relatively lower energy density of supercapacitors compared with the lithium-ion batteries seriously restricts the applications of electrical systems [5]. Therefore, all research efforts are attempted to improve on the energy density of supercapacitors without consuming their high power density and high circulation capacity. In terms of energy storage mechanisms, supercapacitors are divided into two categories: electrical double layer capacitors (EDLCs), where capacitance derivers from the separation of charge at the electrode/electrolyte interface; fast Faradaic redox reactions (pseudocapacitance), where capacitance comes from reversible Faradaic reactions occurring at the electrode/electrolyte interface [6]. Pseudocapacitance such as transition metal oxides, hydroxides, and conducting polymer has higher specific capacitance and larger energy density than EDLC. Therefore, a variety of pseudocapacitance electrode materials with excellent properties were synthesized by different methods [7].

So far some transition metal or metal (Co, Ni, Ru, Mn, Al etc) oxides, hydroxides, sulfides are the most notable candidates in pseudocapacitors. Significant work has been bended to using the binary composites to substitute individual metal oxides/hydroxides as the electrode materials of supercapacitors or lithium-ions batteries, such as Ni-Co [8], Co-Mn [9], Ni-Al [10], Ni-Mn [11], etc. Wang et al. prepared Ni-Al layered double hydroxide by step-by-step in situ growth method, which displayed a large specific capacitance of 795 F g^{-1} at 0.5A g^{-1} and a long cycle life after 1000 cycles [12]. Among these composites, metal sulfides have attracted tremendous attention by virtue of their outstanding performances, and they have been widely applied in the field of solar energy, batteries and catalysis. Moreover, metal sulfides exhibit richer redox reaction and higher electronic conductivity compared to metal oxides. The reason is that the substitution of sulfur could form a more flexible structure because the electronegativity of sulfur is lower than that of oxygen [13,14]. Xia and co-authors reported NiS, CoS, and CoS/NiS as electrode materials have higher conductivity than Ni-Co oxide for energy storage [15] Li et al. synthesized $NiCo_2S_4$@$Co(OH)_2$ composites with high area

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capacitance of 9.6 F cm^{-2} at 2 mA cm^{-2} [16]. Zhu et al. have fabricated $FeCo_2S_4$-$NiCo_2S_4$ composite nanotube as high-performance wearable supercapacitors to achieve remarkable cycling stability [17]. The similar binary Ni-Al sulfide is extremely expected that it should be also excellent electrode material. In addition, there have not any reports focused on binary Ni-Al sulfide. Because of intercomponent synergy, the combination with other materials can further improve electrochemical property [18]. Therefore, it is very important to prepare different kinds of binary sulfide with outstanding electrochemical performance by some simple methods.

In accordance with the above considerations, a simple two-step method is used to synthesize Ni-Al binary sulfide to gain a high capacitance for supercapacitor application. In this work, Ni-Al binary sulfides grown directly on nickel foams are firstly prepared by a simple hydrothermal method with different Ni/Al molar ratios. Hence, we firstly report hierarchical porous structure Ni_4AlS_2 grown on Ni foam for supercapacitor applications. Obviously, this fabricated electrode possesses high specific capacitance and good rate capability with excellent cycling stability. It is expected that the binary Ni-Al sulfide electrode material grown on Ni foam can act as high performance energy storage systems for supercapacitor applications.

2. Experimental

2.1. Materials synthesis

2.1.1. Preparation of Ni-Al precursor

First of all, the Ni foam (1 cm^2 dimensions) was sonicated in a 2 M HCl solution for 15min to remove the surface oxide layer, followed washing in ethanol and deionized water for 15 min, respectively. The Ni foam was dried in vacuum at 60 °C and weighted before use. All other chemicals were of analytical grade and used directly without further purification.

Secondly, nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) and aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$) mixtures according to the mole ratio of (2: 1, 4: 1 and 1: 3) were put into three beakers with 75 mL deionized water to form homogeneous solution. Then 0.016M hexamethylenetetramine was added into the above solution, each mixture was stirred by magnetic for 30 min. The pretreated Ni foam was transferred into the 100 ml Tefln-lined stainless autoclave containing the above solution, followed by heating the autoclave to 90 °C for 8 h. When the autoclave cooled in room temperature, the Ni-Al precursor was taken out by cleaning with ethanol and deionized water and drying at 60 °C for 5 h.

2.1.2. Preparation of Ni-Al sulfide

The Ni-Al precursor on Ni foam was shifted into stainless steel autoclave containing 0.28M Na_2S solution. After heating to 110 °C for 8 h and then cooling down to room temperature. The as-gained Ni-Al sulfide grown on Ni foam was washed with ethanol and deionized water and dried at 60° C for 5 h.

2.1.3. Preparation of Ni-Al oxide

In order to compare the electrochemical properties of Ni-Al sulfide and oxide, the Ni-Al oxide was prepared by annealing as-prepared precursors at 300°C in air for 2 h, the heating rate was 1°Cmin $^{-1}$.

2.2. Electrochemical measurements

All electrochemical experiments were carried out in three-electrode mode by CHI660E electrochemical analyzer. The working electrode was the Ni-Al precursor, oxide and sulfide on Ni foam, a platinum sheet and a saturated calomel (SCE) electrode were used as the counter electrode and reference electrode, respectively.

2.3. Characterization

The powders peeled off the Ni foam substrate were gathered and the structures and morphologies were characterized by the X-ray diffraction (XRD, Cu Kα radiation, $\lambda = 0.15406$ nm), X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA), field emission electron microscopy (JSM-6701F, Japan), respectively.

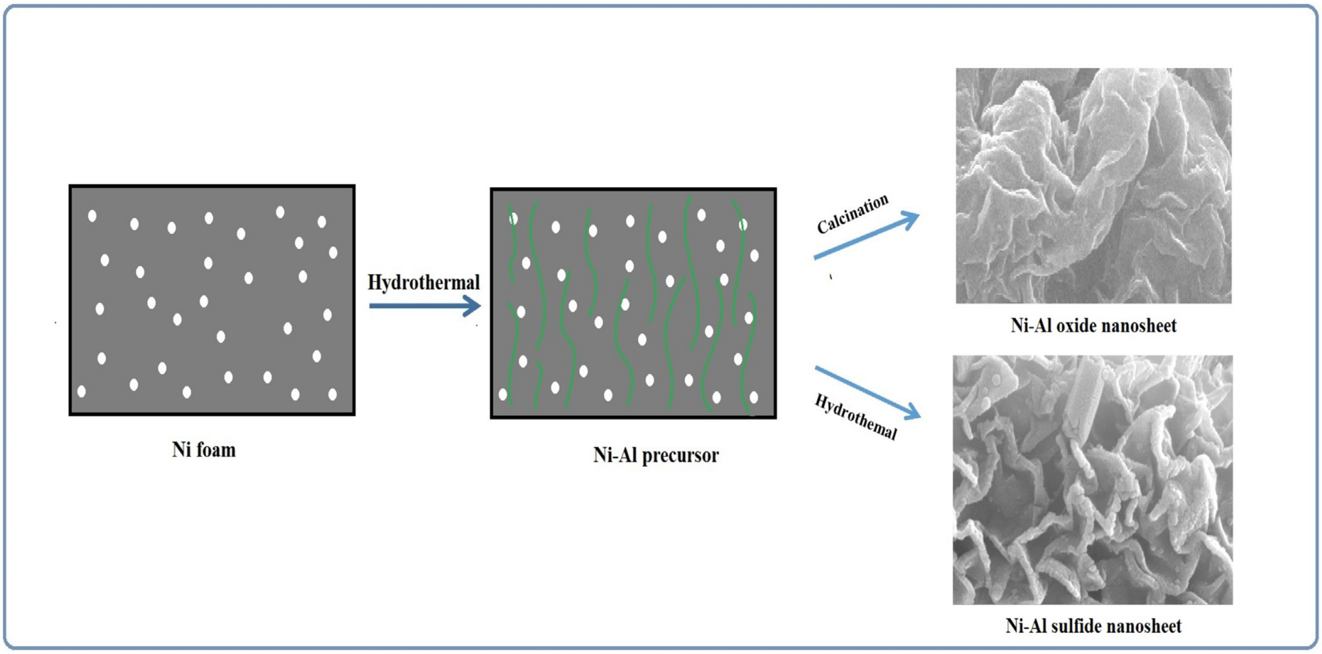

Fig. 1. Schematic illustration of the preparation process for the Ni-Al precursor, oxide and sulfide nanosheet.