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Rapid self-assembly of porous square rod-like nickel persulfide *via* a facile solution method for high-performance supercapacitors

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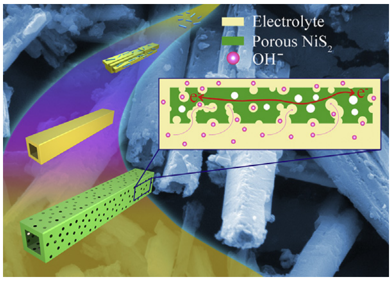
HIGHLIGHTS

- The porous rod-like NiS_2 precursor is synthesized by a facile solution method.
- The NiS_2 delivers a high specific capacitance and excellent cycling stability.
- The NiS_2//rGO supercapacitor exhibits a high energy and power densities.

GRAPHICAL ABSTRACT



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ABSTRACT

The square rod-like NiS_2 with open ends is synthesized by a general solution method without substrate followed by a post annealing treatment. This method involves a rapid self-assembly and a spontaneous aging process controlled by the time of the solution reaction. And the one-step solution-controlled reaction benefits for the convenient fabrication of metal sulfide precursors. The NiS_2 with the length varying from 3 to 8 μm and the width of 2 μm has both open ends, and the BET surface area and average pore diameter of the NiS_2 are 59.2 $m^2\ g^{-1}$ and 24.4 nm, respectively. The porous NiS_2 square rods show a high specific capacitance (1020.2 F g^{-1} at 1 A g^{-1} and 534.9 F g^{-1} at 10 A g^{-1}) as well as excellent cycle life (93.4% of the initial specific capacitance remains after 1000 cycles). Furthermore, an asymmetric supercapacitor device fabricated by using the NiS_2 as the cathode and reduced graphene oxide as the anode delivers an energy density of 32.76 Wh kg^{-1} at a power density of 954 W kg^{-1}. Therefore, the porous square rod-like NiS_2 synthesized by an effective route exhibits outstanding electrochemical performance as a promising cathode material for supercapacitors.

1. Introduction

For the past decades, numerous research efforts have focused on the development of energy storage systems [1–3]. Supercapacitors, as a kind of ideal energy storage devices, have attracted intense interests owing to their high power density, fast charging/discharging process and long cycle life [4–6]. Moreover, according to the energy storage mechanism, supercapacitors can be divided into

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electrical double layer capacitors (EDLC), where the capacitance originates from the pure electrostatic charges adsorbed on electrode/electrolyte interface, and pseudocapacitors, in which fast electrochemical reactions occur at the presence of electrochemically active materials [7]. Despite of the difference of energy storage mechanisms, the capacitor performance is mainly determined by the electrode materials [8]. Therefore, the development of the electrode materials synthesized by a facile method with good capacitive and long cycle span remains a challenge.

Transition metal sulfides, such as Co_8S_9 [9], NiS [10], CuS [11], MoS_2 [12], have been widely considered as a new type of promising pseudocapacitor electrode materials, due to both their specific capacitance and cost effectiveness. As an important branch of transition metal chalcogenides, nickel sulfides with various micro/nanostructures such as hollow spheres [13], nanotubes [14], nanowires [15], layer-rolled structures [16] were synthesized for applications as ceramic tougheners [17], hydrogenation catalysts [18], lithium-ion batteries [19] and photocatalytic H_2 production [20]. For instance, Yang et al. [21] utilized solvothermal method to synthesize hierarchical flower-like β-NiS with high specific capacitance of 857.76 F g^{-1} at 2 A g^{-1}. Zhu et al. [10] investigated hierarchical nickel hollow spheres synthesized by an efficient template-engaged conversion method. However, to improve the electrochemical performance of nickel sulfide materials is still a severe challenge for supercapacitor applications.

Among the abundant micro/nanostructures, one-dimensional materials, such as nanowires and nanorods, have been extensively employed as electrode materials due to their large surface area and fast electrical pathway for electron transport [22,23]. Zhou et al. [24] synthesized Ni_3S_2 nanorod@$Ni(OH)_2$ nanosheet core−-shell nanostructures by a one-step hydrothermal method, which delivers a specific capacitance of 1037.5 F g^{-1} at 5.1 A g^{-1}. Wang et al. [25] reported Ni_3S_2@MoS_2 core/shell nanorod arrays on Ni foam with a specific capacitance of 848 F g^{-1} at 5 A g^{-1}. However, these metal sulfides synthesized by conventional methods usually demand complicated equipment, toxic organic solvents, substrates and high reaction temperature. It remains much room for improvement of preparation of one-dimensional nickel sulfides with high electrochemical performance.

Herein, we develop a facile solution route to synthesize square rod-like NiS_2 precursor with open ends. In contrast to conventional hydrothermal synthesis for particular structural materials with many conditional limitations, this method can be easily carried out in a mild experimental environment and expand to fabricate other metal sulfide precursors. The possible mechanism for the self-assembly process of the square rod-like NiS_2 precursor was investigated depended on the solution reaction time. Moreover, the porous NiS_2 square rods obtained by an annealing treatment exhibit a high specific capacitance of 1020.2 F g^{-1} at 1 A g^{-1} and an excellent cycle life. And an asymmetric supercapacitor was fabricated using the porous NiS_2 as a positive electrode and reduced graphene oxide as a negative electrode in safe aqueous KOH electrolyte.

2. Experimental sections

2.1. Synthesis of square rod-like nickel persulfide

All chemicals were analytical grade and used as received without further purification. In a typical synthesis, the alkali solution was prepared by dissolving 0.2 mol NaOH in 30 mL deionized (DI) water in an open reactor and heated in water bath at 60 °C. Then 7 mL ethylenediamine (EDA), 40 μL 85% hydrazine monohydrate, 4 mmol sulfur and 0.1 mmol cetyltrimethyl ammonium bromide (CTAB) were added into the alkali solution. After sulfur was completely dissolved, the prepared nickel chloride solution (2 mmol nickel chloride in 10 mL DI water) was added into the mixture. The reactor was exposed in the air and maintained at 60 °C for 6 h. Then the precipitate (nickel persulfide precursor) was collected, rinsed with water and ethanol for several times and dried in an electric oven at 60 °C for 24 h. Finally, the as-prepared product was heat treated at 300 °C for 2 h in argon gas.

2.2. Synthesis of reduced graphene oxide (rGO)

Graphene oxide was synthesized from natural graphite by a modified Hummers method [26,27]. 100 mg graphene oxide powder was dispersed in 200 mL DI water with ultrasonication to obtain homogeneous graphene oxide dispersion. The resulting 200 mL homogeneous dispersion was mixed with 2 mL hydrazine in a 250 mL round-bottom flask, and then refluxed at 80 °C for 3 h. Finally, the graphene dispersion was filtered and washed several times with distilled water and alcohol, dried at 60 °C for 12 h in a vacuum oven.

2.3. Characterization

The phase of the samples were characterized by X-ray diffraction (XRD) (Philips X'Pert PRO; Cu Kα, $\lambda = 0.1542$ nm) and X-ray photoelectron spectroscopy (XPS; Kratos AXIS-ULTRA DLD-600W). The morphology and size of the rod-like NiS_2 were observed by FEI Quanta 200 scanning electron microscope (SEM) and a field emission scanning electron microscopy (FESEM; Sirion 200, Philips-FEI Co., Holland). The structure of porous rod-like NiS_2 was investigated by means of transmission electron microscopy (TEM, Philips, TecnaiG 20). Brunauer–Emmett–Teller (BET) surface areas and pore volumes were measured on a Micromeritics ASAP 2020 sorptometer using nitrogen adsorption at 77 K.

2.4. Electrochemical measurements

The working electrodes were prepared by mixing 80 wt% active material, 10 wt% acetylene black (AB), and 10 wt% Poly tetrafluoro ethylene (PTFE). Then the mixture was pressed onto a nickel foam (10 MPa) served as a current collector. The geometric area of electrodes was 1.13 cm^2 with single electrode mass loading of about 4–5 mg cm^{-2} for NiS_2 and about 10–12 mg cm^{-2} for rGO. Then electrodes were dried in an electric oven at 60 °C for 12 h. Electrochemical performance of the as-prepared electrodes was evaluated by cyclic voltammetry and galvanostatic current charge–discharge *via* a CHI660E electrochemical working station. Electrochemical measurements were carried out in a three-electrode cell with Pt foil as the counter electrode and Hg/HgO electrode as the reference electrode in 6 M KOH aqueous electrolyte.

3. Results and discussion

3.1. Growth process and structural characterization

The process of the morphology evolution is schematically illustrated in Fig. 1a. (1) In the beginning, the sulfur was dissolved by ethylenediamine and hydrazine to form S_2^{2-} polyanions in high concentrate NaOH solution [28–30]. Then nickel chloride solution was added into the mixed solution, Ni^{2+} was chelated by EDA to form Ni–EDA metal complex [30,31]. Because this reactions were carried out in an opened reactor, the metal complex could catalyze the dioxygen reactions to form Ni–EDA–dioxygen complex [31]. In such strong alkaline solution, the complex was short-lived and quickly reacted with sulfur polyanions to form $Ni(EDA)_xS_y$ complex