



Reduced CoNi₂S₄ nanosheets with enhanced conductivity for high-performance supercapacitors

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ABSTRACT

Defect engineering on transition metal dichalcogenides has been regarded as an effective method to improve electrochemical properties in terms of generating active sites and enhancing the intrinsic conductivity. This study reports a new high-performance electrochemical supercapacitor made of reduced CoNi₂S₄ (r-CoNi₂S₄) nanosheets, which are synthesized via a facile moderate-reduction process. The sulfur-deficient r-CoNi₂S₄ nanosheets exhibit significantly enhanced conductivity which is induced by abundant sulfur vacancies formed in the reduction reaction. Compared with the pristine CoNi₂S₄ nanosheets, the r-CoNi₂S₄ nanosheets are characterized with a higher specific capacity (1117C g⁻¹ at current density of 2 A g⁻¹) as well as excellent rate capability and stable cycling performance. First-principle analysis confirms that the sulfur vacancies originating from the reduction lead to improve hybridization between the Ni and Co d states and the S p states close to the fermi level, and consequently enhance conductivity with the CoNi₂S₄ nanostructure. Moreover, an ultrahigh energy density of 55.4 Wh kg⁻¹ at the power density of 8 kW kg⁻¹ is obtained in an asymmetric supercapacitor configuration, and 80% capacitance of the supercapacitor remains even after 10000 cycles.

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1. Introduction

Nickel cobalt sulfide (Ni-Co-S), a unique ternary sulfide of metallic nature, is well known for its high conductivity, favorable corrosion stability, and excellent redox activity [1–4]. Its low-cost and simple fabrication make it promising for electrochemical energy storage and conversion, especially for realizing practical lithium-ion batteries, fuel cells, supercapacitors, electrochemical water splitting/oxygen reduction reactions, etc. [5–14]. Since the Ni-Co-S microstructure is a main factor determining its electrochemical performance, a variety of Ni-Co-S nanostructures with different morphologies have been investigated. The typical structures include urchin-like [15] and cauliflower-like [16] structures, as well as spheres [17,18], which can facilitate charge transfer and thus enhance the performance of supercapacitors. In addition, in order to reduce contact resistance and enhance electrochemical

performance, direct growth of Ni-Co-S onto conductive substrates such as nickel foam, carbon cloth and graphene has also been considered [19–24]. Furthermore, to promote charge transfer in supercapacitors, the improvement of the intrinsic conductivity of Ni-Co-S compounds is also an effective but challenging strategy. It has been reported that defect engineering on transition metal oxides can be an effective method for generating active sites and enhancing the intrinsic conductivity [25–29]. If the defects, such as sulfur vacancies [30,31], can be introduced into the metallic Ni-Co-S compounds, more active sites and higher conductivity are expected to be obtained and the electrochemical performance of the Ni-Co-S system can be further improved.

To generate surface sulfur vacancies in transition metal sulfide materials, such as MoS₂ [32,33] and Zn-Cd-S [34], a variety of methods have been explored, including annealing in the reducing atmosphere, and argon or hydrogen plasma exposure. However, the annealing method requires relatively high temperature and vast quantities of hydrogen, while plasma sputtering demands expensive inductively coupled plasma systems and vacuum conditions. These peculiarities are not capable of energy saving and restrict the

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general utility of these approaches. Recently, a moderate solution process was developed, by employing NaBH₄ solution, to reduce Fe₁Co₁-O nanosheets [35] and Co₃O₄ nanowires [36], which generated surface oxygen vacancies and thus improved the electrical conductivity and electrochemical performance of these materials. Because of its safety, convenience, as well as low-cost and low-energy features, this solution method is attractive for producing metal sulfides with surface defects. To the best of our knowledge, there is still no research work reported on metallic Ni-Co-S nanosheets synthesized via the reducing treatment, and the electrical conductivity and electrochemical properties have not been explored yet.

Herein, we report the reduction of CoNi₂S₄ nanosheets with NaBH₄ solution treatment and the superior supercapacitor performance obtained with the reduced products. The ultrathin structural nature of the CoNi₂S₄ nanosheets allows efficient reduction treatment and charge carrier transport at the surface. Compared with the pristine CoNi₂S₄ nanosheets, the reduced CoNi₂S₄ (r-CoNi₂S₄) nanosheets exhibit a much higher capacity of 1117C g⁻¹ at 2 A g⁻¹, along with excellent rate capability and cycling performance. First-principle analysis reveals that the introduction of sulfur vacancies can effectively enhance the orbit hybridization between the Ni and Co d states, and the S p states near the Fermi level, leading to enhancement of the conductivity of CoNi₂S₄. In addition, an asymmetric supercapacitor device, with r-CoNi₂S₄ nanosheets as anode and activated carbon (AC) as cathode, exhibits ultrahigh energy density of 55.4 Wh kg⁻¹ at a power density of 8 kW kg⁻¹, as well as excellent electrochemical stability. Our results suggest that the r-CoNi₂S₄ nanosheets are a type of excellent electrode material for supercapacitor applications.

2. Experimental section

2.1. Materials

All reagents and solvents were of analytical grade. Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99.5%), Nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98%), Acetic acid sodium salt (CH₃COONa, 99%), Sodium tetrahydroborate (NaBH₄, 98%), Thioacetamide (CH₃CSNH₂, 99%), Ethanol (EtOH, 99.7%), Ethylene glycol (EG, 99%), and Polyethylene glycol 200 (PEG, 99.9%) were purchased from Sinopharm Chemical Reagent Co., Ltd (China), and used as received without further purification.

2.2. Preparation of the nickel cobalt (Ni-Co) precursor

According to the reported method, a modified solvothermal process was developed to synthesize the Ni-Co precursor [38]. Typically, a mixture of Ni(NO₃)₂·6H₂O (5 mmol, 1.454 g), Co(NO₃)₂·6H₂O (5 mmol, 1.455 g) and CH₃COONa (10 mmol, 1.6406 g) was dissolved in 20 mL of polyethylene glycol 200 (PEG-200) and 20 mL of ethylene glycol (EG) under stirring to form a transparent pink solution. The solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave and then placed in an oven at 200 °C for 16 h. The resulting precipitate was collected by centrifugation and washed with water and ethanol for several times, and finally dried at 80 °C for 12 h to have the Ni-Co based precursor.

2.3. Preparation of the CoNi₂S₄ nanosheets

A solution sulfidation process was utilized to convert the nickel cobalt precursors into the CoNi₂S₄ nanosheets. Briefly, 60 mg of the as-synthesized nickel cobalt precursors was dispersed into 40 mL ethanol, followed by the addition of 120 mg thioacetamide (TAA). The mixture was transferred into a Teflon-lined stainless steel

autoclave and heated at 140 °C for 1 h. The product was collected by centrifugation and washed with water and ethanol for several times, and finally dried at 80 °C for 12 h to obtain the CoNi₂S₄ nanosheets.

2.4. Preparation of the r-CoNi₂S₄ nanosheets with sulfur vacancies

The CoNi₂S₄ nanosheets were simply immersed in 0.9 M NaBH₄ solution at room temperature for 1.5 h to yield the reduced CoNi₂S₄ nanosheets. The products were collected by centrifugation, washed with distilled water for several times, and then dried in a vacuum oven at 80 °C for 12 h.

2.5. Characterization

The morphology, microstructure of the products were investigated by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800), transmission electron microscopy (TEM, JEM-2100F) and energy-dispersive X-ray spectroscopy (EDX) attach to the TEM. The crystallinity of the samples was characterized by powder X-ray diffraction (XRD) on a Philips PW3040/60 X-ray diffractometer using Cu-Kα radiation at a scanning rate of 0.06° s⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALab MKII X-ray photoelectron spectrometer with a Mg Kα X-ray radiation.

2.6. Electrochemical measurements

The electrochemical properties of the CoNi₂S₄ and r-CoNi₂S₄ electrode were investigated under a three-electrode configuration in 6.0 M KOH aqueous solution using Pt foil as a counter electrode and Hg/HgO electrode as reference electrode. The working electrodes were prepared by first mixing the as-obtained active materials, carbon black (super P), and polyvinylidene difluoride with a mass ratio of 70:20:10, and the mixture was then pressed onto a foam nickel and dried at 80 °C for 12 h. The mass loading of the activate materials was about 1.5–2.0 mg cm⁻². All the tests including cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) were conducted on a Zennium E (Zahner, Germany) electrochemical workstation. EIS measurements were obtained by employing an AC voltage with 5 mV amplitude in the frequency range of 10 mHz–100 kHz at open circuit potential. The specific capacitances (C_s) were obtained from the galvanostatic discharge curves according to the following formula:

$$C_s = (I \times \Delta t) / (m \times \Delta V) \quad (1)$$

where I is the discharge current, Δt the discharge time, ΔV the voltage range upon discharging, and m the mass of the active material.

The electrochemical performance of the r-CoNi₂S₄ was further evaluated through an asymmetric supercapacitor. The asymmetric supercapacitor was assembled into a cell device by using r-CoNi₂S₄ nanosheets as the positive electrode, active carbon (AC) as the negative electrode, and one piece of cellulose paper as the separator in 6.0 M KOH electrolyte. The negative electrode was prepared by first mixing AC, carbon black, and poly (tetrafluoroethylene) with N-methyl-2-pyrrolidone with a weight ratio of 80:10:10, and the mixture was then casted onto nickel foam. The mass ratio of the r-CoNi₂S₄ to AC was determined to be 0.1 to obtain the charge balance between the two electrodes. The mass loading of AC and r-CoNi₂S₄ is about 12.0 mg and 1.2 mg, respectively. The energy density (E) and power density (P) were obtained based on the total weight of the active materials in the cell device according to the

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