



One-step controlled synthesis of hierarchical hollow Ni₃S₂/NiS@Ni₃S₄ core/shell submicrospheres for high-performance supercapacitors

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ABSTRACT

Composition and microstructure are two main factors for enhancing the specific capacity, rate capability, and cycling life of electrode materials in electrochemical energy storage devices. Here, size-tunable hierarchical hollow core/shell submicrospheres based on nickel sulfide are for the first time rationally designed and synthesized through a one-step hydrothermal route, in which Ni₃S₂/NiS hollow submicrosphere works as a core and Ni₃S₄ nanoflakes as shells. The diameter of the hierarchical sphere can be controlled by cetyltrimethyl ammonium bromide. The formation mechanism of this unique structure is systematically investigated, which can be attributed to the combined action of cage effect, Kirkendall effects and Ostwald ripening mechanism. Due to the synergistic effects of various phase nickel sulfide, such hybrids exhibit superior electrochemical performance. When served as electrodes for supercapacitors, the hybrids show a high specific capacity of 1031.3 C g⁻¹ at a current density of 2 A g⁻¹. Even as the current density increases to 40 A g⁻¹, the hierarchical core-shell nanosphere still reserves 614.4 C g⁻¹, exhibiting an excellent rate capacity and a good capacitance retention of 90.3% after 3000 cycles at 10 A g⁻¹. Furthermore, asymmetric supercapacitor based on the Ni₃S₂/NiS@Ni₃S₄ hybrid and reduced graphene oxide shows high power density, high energy density and long cycling lifespan.

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1. Introduction

Driven by the rapidly growing demand needs for sustainable and renewable green power sources, many research communities have been engaged in developing new energy conversion and storage devices [1–4]. Recently, supercapacitors have attracted much attention for its high energy density, high power output, fast recharge capability and excellent cycle stability [5–8]. Supercapacitor successfully fills the gap of power density and energy density between batteries and traditional capacitors [9–11]. Since the performance of a supercapacitor mainly depends on composition and micro-morphology of the electrode materials. Many efforts have been dedicated to exploring high-capacity materials and designing optimal electrode architecture.

Pseudocapacitors, an important type of supercapacitor, which store electrical energy through fast Faradaic reactions instead of

double layer ion-adsorption, can provide much higher specific capacitance than electrical double layer capacitors (EDLC) [12,13]. For the above advantages, pseudocapacitors have attracted intense interests. Transition metal sulfides with promising electrochemical performance have been considered as a potential pseudocapacitor electrode materials [14–17]. The family of nickel sulfides (such as NiS, NiS₂, Ni₂S₃, Ni₃S₄, Ni₇S₆ and Ni₉S₈) have been widely investigated for their excellent redox reversibility, low cost and safety [18]. Among these different phase of nickel sulfides, Ni₃S₂ is an especially potential candidate for pseudocapacitors because of its good metallic conductivity ($1.8 \times 10^{-5} \Omega \text{ cm}^{-1}$ at room temperature), leading to facilitate the transportation of ions and electrons [19]. Ni₃S₄, another phase of nickel sulfide, which exists in nature (polydymite) has aroused great interest to researchers recently [20,21]. When combined with amorphous MoS₂, the Ni₃S₄/MoS₂ composite exhibits high specific capacitance of 1440.9 F g⁻¹ at 2 A g⁻¹ and a good capacitance retention of 90.7% after 3000 cycles at 10 A g⁻¹ [10]. The Ni₃S₄/MoS₂ heterojunction which synthesized via an ionic liquid-assisted method also exhibits a good pseudocapacitor performance. The specific capacity of the Ni₃S₄/MoS₂ heterojunction is 985.21 F g⁻¹ at 1 A g⁻¹, and it can retain 573 F g⁻¹ after 20,000

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cycles at a current density of 10 A g^{-1} [22]. Recent studies have revealed that the pseudocapacitor performances of nickel sulfides can be further improved by formation of various phase nickel sulfides composites, which can offer more active crystal interfaces and rich redox reactions that enable multiple oxidation states of Ni ions [23].

Besides the composition, a desirable morphology and microstructure also plays a crucial role in enhancing the electrochemical performances of electrode materials. Usually, three-dimensional (3D) hollow nanostructures and two-dimensional (2D) nanoflake structures are considered as promising architectures for supercapacitor electrodes. 3D hollow nanostructures can provide rich electroactive sites and short diffusion paths for charge carriers, which benefits to the transfer of both electron and ions [24–27]. 2D nanoflake structures can enhance the effective interaction between the electrode materials and electrolytes [28]. Recently, aiming to taking full advantage of various architectures, many hierarchical hollow structures have been developed, which were composed of both 3D and 2D structures aiming at taking full advantage of these architectures. However, the reported fabrication methods of hierarchical hollow structures cannot avoid fussy multiple steps. There are seldom works for using simple and high-efficiency methods to synthesize hierarchical hollow structure nanomaterials.

In this work, considering the synergistic effects of various phase nickel sulfide, we designed a novel $\text{Ni}_3\text{S}_2/\text{NiS}@\text{Ni}_3\text{S}_4$ hierarchical hollow core/shell submicrospheres (NHS). In this structure, the $\text{Ni}_3\text{S}_2/\text{NiS}$ hollow sphere with high work function works as core, as well as the ultrathin Ni_3S_4 nanoflakes with lower work function homogeneously coat on the surface of the hollow sphere as shell. The interfacial electric field in NHS can be generated by the difference of work functions between core and shell, which promote electron transfer during electrochemical process. Due to the high capacitances of Ni_3S_4 and excellent conductivity of Ni_3S_2 , the NHS shows excellent electrochemical performance, including high specific capacity, excellent rate capability, and long cycling lifespan. Additionally, this hierarchical hollow core/shell submicrospheres can be obtained just by a facile solvothermal route. Furthermore, through changing the additive amount of CTAB, the size of submicrospheres can be controlled easily. Our work opens a new avenue for rational designing well-controllable core/shell transition metal nanostructures and applying them in energy storage devices.

2. Experimental Section

2.1. Materials and chemicals

Cetyltrimethyl ammonium bromide (CTAB, Sigma-Aldrich), carbamide ($\text{CO}(\text{NH}_2)_2$, Sigma-Aldrich), acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Sigma-Aldrich) and L-Cysteine ($\text{C}_3\text{H}_7\text{NO}_2\text{S}$, Sigma-Aldrich) were of analytical grade and used without further purification. Deionized water ($18.2 \text{ M}\Omega \text{ cm}$, 25°C) was used throughout the experiment.

2.2. Preparation of $\text{Ni}_3\text{S}_2/\text{NiS}@\text{Ni}_3\text{S}_4$ hollow submicrospheres

In a typical optimized synthesis, 1.880 g of CTAB and 120 mg carbamide were dissolved in 80 mL deionized water at 40°C . Then 3.4 mM nickel acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and 3.4 mM L-Cysteine ($\text{C}_3\text{H}_7\text{NO}_2\text{S}$) were added in sequence into the CTAB/carbamide solution, followed by ultrasonication for 1 h. The homogeneous light brown blend solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. Subsequently, the autoclave was sealed and heated to 220°C for 24 h. The final products were obtained through centrifuging at 10,000 rpm for

15 min and rinsing with acetone and deionized water for several times. After drying at -55°C for 24 h under vacuum, the hollow $\text{Ni}_3\text{S}_2/\text{NiS}@\text{Ni}_3\text{S}_4$ core/shell submicrospheres were prepared and labeled as NHS-3.

For comparison, different amounts (0 g, 0.627 g and 1.253 g) of CTAB were used in the synthesis process, keeping other conditions same. The prepared products were labeled as NHS-0, NHS-1, and NHS-2, respectively.

2.3. Preparation of Ni_3S_2 hollow submicrospheres and Ni_3S_4 nanosheets

The Ni_3S_2 hollow submicrospheres ($\text{Ni}_3\text{S}_2\text{-HS}$) were synthesized through annealing NHS-3 under 500°C for 2 h in nitrogen condition with a heating rate of 2°C min^{-1} . The Ni_3S_4 nanosheets were synthesized according to reference 29 [29].

2.4. Preparation of negative electrode material

In our work, reduced graphene oxide (rGO) was used as negative electrode materials. Through a facile hydrothermal reaction in aqueous solution at 180°C for 12 h, GO was reduced to rGO.

2.5. Material characterizations

The crystal structures were characterized by XRD (Rigaku D/Max-2500) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5604 \text{ \AA}$) over a 2θ range of $5^\circ\text{--}80^\circ$, operating at 40 kV and 30 mA. XPS measurements were performed with a Theta Probe electron spectrometer (ESCALAB 250XI, Thermo Scientific). The binding energies were calibrated using C 1s peak at 284.5 eV as the reference. The microstructure analysis of the obtained NHS was studied by field-emission gun scanning electron microscope (JEOL JSM-7610F, 10 kV). TEM images were taken by JEM 200CX or FEI Tecnai F20. High resolution transmission electron microscope (HRTEM) images, and corresponding EDX were collected by FEI Tecnai F20 equipped with an EDAX SUTW (super ultrathin window) energy-dispersive X-ray spectrometer (EDAX).

2.6. Electrochemical measurement

The working electrode was prepared by mixing active materials, acetylene black (Timcal), and polytetrafluoroethylene (PTFE, J&K) as the binder with a ratio of 80:10:10 in isopropanol to form homogenous electrode slurry. The slurry was pasted on a pre-cleaned nickel foam (nickel foam was immersed in a 3 M HCl solution in an ultrasound bath for 30 min to remove the possible surface oxide layer, then rinsed with deionized water and absolute ethanol several times) as a current collector, which was followed by drying at 60°C in a vacuum oven overnight. The mass of the materials on the electrode was determined by a microbalance using the mass difference before and after materials loading. The area of the electrode is ca. 0.785 cm^2 and mass loading is about 3 mg cm^{-2} .

To construct an asymmetric supercapacitor, the NHS-3 was applied to the positive electrode, the rGO served as the negative electrode, and 6 M KOH was used as electrolyte. The rGO electrode was composed of 90 wt% rGO and 10 wt% PTFE.

The electrochemical characterizations were carried out on electrochemical workstation (CHI660D, CH Instruments Inc. Shanghai) in 6 M KOH aqueous electrolyte with Hg/HgO electrode as a reference electrode, and a platinum electrode as the counter electrode with a typical three-electrode system. Electrochemical Impedance Spectroscopy (EIS) measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz.

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