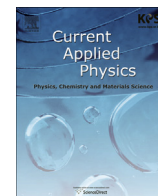




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Nickel cobalt sulfide anchored in crumpled and porous graphene framework for electrochemical energy storage

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ABSTRACT

Energy storage is becoming highly important as renewable generation sources are added to the mix in electrical power generation and distribution systems. Supercapacitors and batteries could allow renewables to overcome intermittency difficulties by regulating the voltage, frequency, and phase angle of the power. Transition-metal oxide, hydroxide, and sulfide forms, carbonaceous materials, and conducting polymers can be used as electrodes for supercapacitors. Graphene is considered to be a promising material for supercapacitors because of its high surface area and theoretical gravimetric capacitance. However, aggregation of graphene sheets severely decreases the accessible surface area and theoretical gravimetric capacitance. Here we report a unique synthesis route of a hybrid nickel cobalt sulfide anchored in a crumpled and porous graphene framework to address the aforementioned problem. The hybrid sample, a nickel cobalt sulfide/crumpled-porous graphene framework, delivered higher specific capacitance and better electronic conductivity than the porous graphene framework when used as a supercapacitor electrode.

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1. Introduction

Energy consumption in the world continues to shift. As reported in world energy outlook, decarbonization of the energy system is one of several energy-related policy priorities being pursued by governments around the world. The electric utility industry is under tremendous pressure to reduce emissions and control costs while maintaining reliable service to customers. There are many alternatives to get energy apart from conventional fossil fuels in order to cope with the stringent regulations on emission reduction. Some of the typical green energy sources are wind energy, solar light, and hydropower. However, adapting these intermittent resources causes irregular loads on the grid. Energy storage systems, such as supercapacitors and batteries, could resolve intermittency problems by regulating voltage, frequencies, and phase angles of

the power [1]. Consequently, energy storage is becoming increasingly important as renewable generation sources are added to the mix in electrical power generation and distribution systems.

Graphene is considered a promising supercapacitor material for high power and energy density because of its high surface area and conductivity. However, strong π - π interaction between graphene sheets leads to the formation of graphite-like powders or films that can severely decrease the accessible surface area (about $2630 \text{ m}^2 \text{ g}^{-1}$) and theoretical gravimetric capacitance (about 550 F g^{-1}). The aggregation arises from the strong van der Waals attraction between parallel sheets, which increases with the overlapping area (S) and the fourth power of the inverse of the separation distance between sheets ($1/d^4$) [2]. In two-dimensional (2D) morphology, graphene-based sheets conform to and contact with a surface or each other, increasing S and decreasing d , thus resulting in strong attraction [2]. Numerous methods have been developed to overcome the attraction problem. Recently, there has been tremendous interest in the synthesis and applications of graphene-based highly porous materials consisting of a three-dimensional (3D) graphene network [3,4]. The porosity and conductive network of a 3D graphene framework can allow the graphene to retain its outstanding properties and be used in energy storage applications, since the 3D

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graphene framework possesses continuously interconnected macroporous structures with a large surface area, low mass density, and high electrical conductivity [3].

Transition-metal-based materials, conversely, can provide higher energy density than is delivered by electrical double-layer capacitors with carbon-based active materials as electrodes. These transition-metal sulfides, hydroxides, and oxides have special physical and chemical properties [5–7]. Among the various transition-metal sulfides, nickel sulfides have drawn much attention, given their advantages of high electrical conductivity, high redox activity, low cost, and ease of fabrication [8,9] and have shown excellent applications in supercapacitors, lithium-ion batteries, and solar energy storage [10–12]. If other transition metals are included in nickel sulfides, higher capacitance can be expected because of the richer oxidation states of the binary metal sulfides. Limited by poor conductivity for supporting fast electron transport, however, the specific capacitances of metal sulfides are relatively low, especially at high current rates; consequently, their cycling stabilities are poor. In order to overcome these inadequacies, it is important to couple the electrodes based on metal sulfides with materials that have good electronic conductivity and stability, such as with porous graphene frameworks (PGFs).

Here, we synthesized a hybrid structure that combined nickel cobalt sulfide (NiCoS) and PGF. Our specific synthesis route by introducing P123 during the metal sulfides loading resulted in changes in morphology, from a simple porous to a crumpled-porous graphene structure. When used as an electrode material, the NiCoS/PGF hybrid structure exhibited a specific capacitance of about 405 F g^{-1} which was better than that of either NiCoS or PGF alone. The PGF supports fast electron transport and showed a nearly rectangular I-V curve, which is nearly ideal capacitive behavior, while the NiCoS acts as a pseudocapacitor. In addition, the NiCoS/PGF hybrid structure showed less charge transfer resistance than PGF.

2. Experimental methods

2.1. Preparation of PGF and NiCoS/PGF

First, a modified Hummers method was used to prepare graphite oxide. Then 80 mg of graphite oxide was sonicated in 40 ml deionized (DI) water for 1 h to get graphene oxide (GO). The GO dispersion was then treated with H_2O_2 at 100°C . Next, 0.352 g of L-ascorbic acid was added to the as-obtained porous graphene dispersion under stirring; it was then transferred to a Teflon-lined stainless steel autoclave and was kept at 180°C for 12 h. The as-obtained PGF was taken out of the autoclave and soaked in DI water to further clean the PGF.

Nickel nitrate and cobalt nitrate in a molar ratio of 1:2, 0.8 g of Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol), and 2 mmol of hexamethylenetetramine were added in a 40 ml ethylene glycol-ethanol solution. Then the cleaned PGF, after removal of residues from the hydrothermal process, was immersed in the prepared solution containing metal precursors and a block copolymer (P123) for 24 h and was then transferred into an autoclave and maintained at 170°C for 2 h. The intermediate, which contained precipitated nickel cobalt hydroxide in PGF, was soaked in DI water and finally sealed in an autoclave containing 10 mmol $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and held at 160°C for 6 h to finally get the NiCoS/PGF composite, which was steeped in DI water several times to remove any impurities. NiCoS was prepared in the same way as NiCoS/PGF, except that no PGF was used.

2.2. Structural characterization

The crystalline structures of the as-synthesized samples were observed by means of x-ray diffraction (PDR-XRD, Bruker D8 FOCUS) with $\text{CuK}\alpha$ radiation. Raman spectra were obtained by using a Witec Alpha300 M+ with a 532 nm excitation laser. Fourier transform infrared spectroscopy (FT-IR) was also recorded using (Bruker IFS-66/S) FT-IR spectrometer. A field-emission scanning electron microscope (FESEM, JEOL 7500F) was used to assess the surface morphology. A transmission electron microscope (TEM) and High-Resolution TEM (HRTEM, 200 kV) were used to analyze the microstructures of the hybrid NiCoS/PGF. Energy-dispersive x-ray spectroscopy (EDS) and EDS elemental mapping were employed to study the composition of the NiCoS/PGF.

2.3. Electrochemical measurements

The electrochemical measurements were carried out in a three-electrode system. A thin piece from the as-prepared PGF or NiCoS/PGF was directly pressed on Ni foam ($1 \text{ cm} \times 1 \text{ cm}$) at 10 MPa, without adding a binder or conducting agent, to get a working electrode. We prepared a NiCoS-based working electrode by mixing NiCoS, carbon black, and polytetrafluoroethylene (PTFE) in a ratio of 85:10:5. A Pt wire and Ag/AgCl were used as a counter and reference electrode, respectively. Cyclic voltammetry (CV) (-0.8 to 0 V) and electrochemical impedance spectroscopy (EIS) tests in 1 M Na_2SO_4 were conducted to study the electrochemical properties. The mass loading of each electrode was $\sim 1 \text{ mg cm}^{-2}$.

3. Results and discussion

The synthesis procedure to prepare the NiCoS/PGF is described in Fig. 1. The PGF was prepared by a two-step process with low-temperature etching using H_2O_2 to get pores in the graphene sheets and self-assembly of porous graphene sheets into a 3D network (PGF) during the hydrothermal process. Then, metal salts were dispersed in an ethanol and ethylene glycol solution containing PGF in the presence of P123. Successive solvothermal-hydrothermal treatments first produced the nickel cobalt hydroxide intermediate and finally NiCoS nanoparticles firmly attached in the PGF.

The morphology, size, and microstructure of the as-synthesized products were investigated by FESEM, TEM, and HRTEM. The FESEM image in Fig. 2a shows the as-prepared flower-like NiCoS particles, whose average particle size was more than $5 \mu\text{m}$. It appears that the NiCoS flower-like 3D hierarchical structure was obtained because the 2D NiCoS sheets tend to self-assemble. The sheets can initially be formed with the help of the inverse lamellar micelles of the P123 surfactant with ethylene glycol in ethanol [13]. Fig. 2b shows the 3D and porous nature of the PGF with continuously interconnected macroporous structures that can contribute to large surface area and high electrical conductivity. In addition, the pores on the PGF serve as ion-transport pathways between adjacent layers of graphene to significantly promote facile ion transport through the PGF. NiCoS nanoparticles trapped and distributed throughout the PGF are shown in Fig. 2c. It is clear that, after NiCoS/PGF formation, the morphology of the PGF was changed from a simple porous structure (Fig. 2b) to a crumpled-porous one (Fig. 2c and inset in Fig. 2c). These two features of the PGF, in both the bare PGF and the NiCoS/PGF composite, arise from the unique synthesis route we followed. In bare PGF, only porous networks can be seen because of the low-temperature etching of the graphene sheets using H_2O_2 and self-assembly. On the other hand, the NiCoS/PGF composite exhibited a porous structure from the H_2O_2 etching and was crumpled by successive solvothermal and hydrothermal

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