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Decoration of carbon nanofibers with $NiCo_2S_4$ nanoparticles for flexible asymmetric supercapacitors

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ABSTRACT

Flexible supercapacitors with both high energy and high power densities are critical for flexible electronics. In this paper, hybrid flexible carbon nanofibers decorated with $NiCo_2S_4$ nanoparticles are successfully prepared by combination of electrospinning, carbonization and hydrothermal treatments. The obtained hybrid carbon nanofibers display remarkable specific capacitance (527.8 F g^{-1} at the current density of 0.2 A g^{-1} and 622.5 F g^{-1} at 2 mV s^{-1}), good rate capability (310.5 F g^{-1} at 4.0 A g^{-1}) and excellent cycle stability (retaining 90.0% after 3000 cycles). The flexible asymmetric supercapacitors based on carbon nanofibers decorated with $NiCo_2S_4$ and porous carbon nanofibers coated with activated charcoal are fabricated. The combined unique properties of each of these components enable highly flexible and mechanically strong films that can serve as electrodes directly without using any current collectors or binders. The fabricated device shows an energy density of 32.1 Wh kg^{-1} at power density of 67.6 W kg^{-1} and cycle stability retaining 88.5% after 1500 cycles at 1.0 A g^{-1}. Therefore, the novel flexible asymmetric device with perfect flexibility and stability can be applied as one of the most promising power supplies.

1. Introduction

With the rapid development of flexible electronics in recent years, it requires energy storage devices must be flexible, and have excellent electrochemical performance [1,2]. Therefore, it is critical to design storage devices with high specific capacitance, high cycle stability and high flexibility. Due to their high power density and long cycle life, the supercapacitors (SCs) have attracted great attention [3]. SCs have been applied in electric vehicle as high power output device and widely regarded as a kind of important new energy storage devices [4]. However, the shortage of the energy density and insufficient flexibility have limited the development of flexible supercapacitors (FSCs). Therefore, further research for FSCs will focus on: (1) maintaining the power density and cycle life of FSCs, while rapidly improve its energy density; (2) FSCs need to be lightweight, thin, flexible, and even can be folded [5]. Flexible electrodes, as one of the key components of FSCs, affect capacitance performance, flexibility and stability.

Nanofiber materials obtained by electrostatic spinning technology are suitable used as flexible electrode due to their excellent flexibility [6]. For example, the bamboo-like nanofibers were fabricated for all-solid-state supercapacitors and the supercapacitors exhibited flexible, foldable, and twistable properties [7]. The flexible porous carbon nanofibers as electrodes materials were prepared for high-performance all-carbon supercapacitors [8]. The flexible symmetrical supercapacitors were fabricated by growth of MnO_2 nanoparticles on hybrid carbon nanofibers with maximum specific energy power density of 20.1 Wh $kg^{-1}$and power density of 230.4 W kg^{-1} [9]. However, carbon-based materials intrinsically lower specific capacitance and energy density have held them back from outperforming commercial batteries and limited them further applications. Transition metals oxides as a kind of pseudocapacitors (PCs) exhibit much higher specific capacitance due to the reversible faradaic redox reactions. Ternary transition metals oxides, such as

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MCo_2O_4 (M = Ni [10], Mn [11] and Zn [12], etc), are generally used as electrode materials for high performance PCs. Combining carbon materials with transition metals oxides provide an effective method to improve energy density of the whole materials. For example, the asymmetric supercapacitor of $MnCo_2O_4$ nanofibers and N-doped reduced graphene oxide aerogel displayed energy density and power density at 54 Wh kg^{-1} and 9851 W kg^{-1}, respectively [13]. The flexible hybrid membranes of $NiCo_2O_4$-doped carbon nanofiber@MnO_2 exhibited a good specific capacitance of 918 F g^{-1} at a scan rate of 2 mV s^{-1} [14]. In our previous work, electrospun carbon nanofibers coated with urchin like $ZnCo_2O_4$ nanosheets could be used as a flexible electrode material with specific capacity of 459.48 mAh g^{-1} at 20 mV s^{-1} [15], electrospun carbon nanofiberic coated with ambutan-like $NiCo_2O_4$ microspheres exhibited a specific capacity of 160 mAh g^{-1} at 1 mA cm^{-2} in 2 M KOH aqueous solution [16].

More recently, inspired by the excellent electrochemical performance of ternary transition metals oxides, ternary transition metal sulfides, such as MCo_2S_4 (M = Ni [17], Cu [18], and Fe [19]), have been proved to be the novel SCs materials [20]. Due to its high electric conductivity and excellent pseudocapacitive performance, $NiCo_2S_4$ has been regarded as the most potential electrode materials during these ternary transition metals sulfides [21,22]. In addition, ternary metal sulfides can offer higher electrochemical activity and capacity than dual metal sulfides [23].

We wonder if electrochemical performance and flexibility of the composites could be improved by combining nanofibers (CNFs) with $NiCo_2S_4$. In this work, the hybrid flexible CNFs decorated with $NiCo_2S_4$ nanoparticles ($NiCo_2S_4$@CNFs), serving as positive electrode, were successfully prepared. The as-fabricated $NiCo_2S_4$@CNFs exhibited good electrochemical performance with high mass capacitance, good rate capability and cycle stability. The porous carbon nanofibers (pCNFs) coated with activated charcoal (AC) were fabricated (AC@pCNFs) and used as negative electrode. The asymmetric flexible supercapacitors (AFSCs) were assembled and their electrochemical performances were investigated as well.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, M_w = 150,000) power, N, N′-dimethylformamide (DMF, AR), cerium (III) nitrate hexahydrate ($Ce(NO_3)_3\cdot 6H_2O$, AR), nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$, AR), cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$, AR), thioacetamide (CH_3CSNH_2, AR), ammonium fluoride (NH_4F, CP), terephthalic acid (PTA), Hexamethylenetetramine ($C_6H_{12}N_4$), potassium hydroxide (KOH, AR) and activated charcoal (AC) were purchased from Aladdin Co. Ltd. (China) and used as received without further purification.

2.2. Preparation of CNFs and pCNFs

Typically, the electrospinning solution was prepared by dissolving 1.0 g PAN and 0.05 g PTA in 10 mL DMF. Then, the mixture was mild stirring for several hours to obtain a homogeneous transparent solution. Subsequently, about 6 mL of the solution was placed in a 10 mL syringe. The syringe was placed in a syringe pump that maintained a solution feeding rate of 0.6 mL h^{-1}. A grounded metallic rotating roller covered with a piece of aluminum foil was used as collector, which rotated at 500 rpm. The distance between the needle tip and collector was 18 cm, and the voltage was set at 18 kV. The preoxidation and carbonization of composite nanofibers were performed in an electric heat-treating furnace. The dried nanofibers membranes were preoxidized in an air atmosphere under 200–250 °C for 1 h with a heating rate of 3 °C min^{-1}. Then, the hybrids were heated up to 1000 °C at a rate of 3 °C min^{-1} and carbonized for 30 min under N_2 atmosphere to obtain CNFs.

The pCNFs were prepared by similar process described above. The precursor solution was prepared by dissolving 1.0 g PAN and 0.02 g $Ce(NO_3)_3\cdot 6H_2O$ in 10 mL DMF under mild stirring for several hours. Then, the composite nanofibers were further treated by preoxidation and carbonization to obtain CeO_2 loaded CNFs [24]. Finally, the pCNFs were obtained after etching CeO_2 in 10 wt % HF aqueous solution.

2.3. Decoration of the $NiCo_2S_4$ on CNFs

The $NiCo_2S_4$@CNFs were prepared by a facile hydrothermal reaction. Typically, $Ni(NO_3)_2\cdot 6H_2O$ (0.25 mM), $Co(NO_3)_2\cdot 6H_2O$ (0.5 mM), thioacetamide (8 mM) and NH_4F (4 mM) were dissolved in 50 mL deionized water. The as-prepared CNFs (2 × 3 cm) was put into the mixed solution. Subsequently, the mixed solution was transferred into a 90 mL Teflon-lined stainless steel autoclave under 120 °C for 12 h. Finally, the product was dried at 60 °C for 6 h to obtain $NiCo_2S_4$@CNFs.

2.4. Preparation of AC@pCNFs

Briefly, AC and polyvinylidene fluoride (PVDF) in N-Methyl pyrrolidone (NMP) were mixed with weight ratio at 90:10. Then, the uniformly mixed slurry was brush-coated on pCNFs and dried at 70 °C for 5 h.

2.5. Assembly of asymmetric flexible supercapacitors

NKK films (MPF30AC-100, Japan) were used as separator between $NiCo_2S_4$@CNFs and AC@pCNFs of 15 × 15 mm rectangular using 3 M KOH as the electrolyte. Then, they were covered in plastic wrap as package and sealed by heating under weak sealing machine (FS-200, Bake Easy).

2.6. Electrochemical measurements

All the electrochemical experiments of samples were tested by using CHI660D (Shanghai) electrochemical workstation, and cycle stability was studied using a LAND battery system (CT2001A, Wuhan). For three-electrode electrochemical measurements, the prepared pCNFs, AC@pCNFs and $NiCo_2S_4$@CNFs (1 × 1 cm^2) were acted as the working electrode, Hg/HgO as reference electrode, a platinum net acted as the counter electrode with an electrolyte of 3 M KOH. The cyclic voltammetry (CV) tests were performed at the scan rate of 1, 2, 5, 10, 20, and 50 mV s^{-1}. The galvanostatic charge-discharge (GCD) tests were conducted at various current densities. Electrochemical impedance spectroscopy (EIS) tests were collected using a frequency ranging from 100 kHz to 0.01 Hz at open circuit potential. The cyclic stability of the result samples was tested with repeated charge-discharge processes. The specific capacitance of electrodes can be calculated from the CV curves using the following equation [25]:

$$C = \frac{1}{m \times s \times \Delta V}\int IdV \quad (1)$$

where I is the current, m is the mass of the electrode material, s is the scan rate and ΔV is the potential window. The mass specific capacitances of the samples were calculated from the GCD curves using the following equation [26]: