



Full Length Article

Growth of polyaniline thorns on hybrid electrospun CNFs with nickel nanoparticles and graphene nanosheets as binder-free electrodes for high-performance supercapacitors



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ABSTRACT

Improving the conductivity and active surface area of electrospun carbon nanofibers is beneficial to develop binder-free supercapacitor electrodes for practical application prospects in energy storage field. Herein, we propose a facile and low-cost synthesis of hybrid electrospun carbon nanofibers composites (Ni-G-CNFs) coated with polyaniline thorns (Ni-G-CNFs@PANI) via a combination of electrospinning and followed by carbonization and in situ polymerization processes. The prepared Ni-G-CNFs@PANI as a novel binder-free electrode exhibits a high specific capacitance of 318.0 F g^{-1} at a current density of 0.5 A g^{-1} and an acceptable capacitance retention of 62.1% when the current density increased from 0.5 A g^{-1} to 10 A g^{-1} in three-electrode system. Furthermore, a symmetric all solid-state supercapacitor was assembled by two binder-free electrodes, and the maximum energy density of 14.4 Wh kg^{-1} and maximum power density of 3750.2 W kg^{-1} were achieved in a potential window of 1.5 V. Capacitance retention remained 85.8% after 1000 cycles of charge-discharge process even at a high current density of 10 A g^{-1} . This strategy for growing PANI on electrospun hybrid CNFs paves a new avenue for construction of high-performance binder-free energy storage devices.

1. Introduction

Considering the sustainable use of global energy and the demand for friendly environment, energy storage and conversion devices such as solar cells, fuel cells, supercapacitors and lithium ion batteries have attracted a huge attention in recent years [1–3]. Among the many forms of energy storage and conversion systems, supercapacitors show the advantages of rapid charge/discharge rate, high power density and long cycling stability, while their energy density needs to be improved [4–6]. The electrode material is the most important part of a typical supercapacitor, which has a great influence on their capacitance performance. Generally, in term of charge storage mechanism, supercapacitor can be divided into two categories, e.g. electrical double layer capacitor (EDLC) and pseudocapacitor. Carbon materials are the typical EDLC electrode materials, displaying brilliant cycle stability and rate property, which stem from fast physical adsorption/desorption process of ions. On the other hand, transition metal oxides (hydroxides) and conducting polymers are classed as pseudocapacitor electrode materials, providing admirable capacitance and energy densities through the fast reversible redox reactions [7–10].

Among various types of conducting polymers, polyaniline (PANI) is an ideal candidate as pseudocapacitor electrode material owing to its high theoretical capacitance (2000 F g^{-1}), good electrical conductivity, low cost and easy preparation [11–13]. However, the electrochemical performance based on the PANI electrode is still limited by its poor cycling stability. It is a good idea to combine PANI with carbon materials to improve the specific capacitance and cycling stability. For example, Cheng and co-workers reported the preparation of PANI modified graphene and carbon nanotube composite, which exhibited a high specific capacitance of 270 F g^{-1} and an enhanced capacitance retention of 82% after 1000 cycles [14]. Liang and co-worker demonstrated the synthesis of polyaniline/multi-walled carbon nanotube with high specific capacitance of 180 F g^{-1} at 0.5 A g^{-1} , good energy density of 25 Wh kg^{-1} and good cycle stability (retaining 89% after 1500 charge/discharge cycle) [15].

During the traditional fabrication process of supercapacitor based on the electrode materials in powder form, it is widely acceptable to add polymer binder to increase the adhesion between the electrode materials and the collector. However, the addition of polymer binder always leads to a large contact resistance and “dead volume”, which

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reduces the capacitance performance [7]. Therefore, the fabrication of freestanding binder-free supercapacitor electrodes becomes a popular trend to achieve an exceptional capacitance performance for practical application prospects. As a promising carbon material for binder-free electrodes, electrospun carbon nanofibers (ECNFs) have been widely studied due to their acceptable conductivity, large surface areas and controllable structures [11,16]. Meanwhile, the introduction of metal, metal oxides and other carbon materials with ECNFs as supercapacitor electrodes might lead to a deeper graphitization degree, a higher electrical conductivity and more active sites, thus resulting in an enhanced electrochemical performance [17–20]. Therefore, it is a meaningful strategy to combine pseudocapacitor electrode materials with freestanding ECNFs to construct high-performance binder-free electrodes for supercapacitor applications. Our group has demonstrated a facile hydrothermal reaction for the direct growth of Ni-Mn oxide nanosheets on the surface of freestanding ECNFs as binder-free electrodes for supercapacitors. The supercapacitor showed a good specific capacitance (368.6 F g^{-1}) and excellent rate properties (88.6% retention at 20 times initial current density) in a three-electrode system [21]. Recently, PANI decorated freestanding ECNFs have also been widely studied as binder-free electrodes for supercapacitors [22–25]. The introduction of PANI onto freestanding ECNFs will not only provide a binder-free electrode, but also improve its electrochemical performance due to a synergistic effect. However, it is still a challenge to construct ECNFs/PANI based binder-free electrodes with enhanced electrochemical performance by introducing other types of functional materials.

Herein, we have prepared PANI throns wrapped ECNFs with Ni nanoparticles and graphene nanosheets (Ni-G-CNFs@PANI) via an electrospinning, carbonization and in situ polymerization processes. When employed as binder-free electrode materials for supercapacitor, a high specific capacitance of 318.0 F g^{-1} at the current density of 0.5 A g^{-1} in a three-electrode system has been achieved. In addition, a symmetric all solid-state supercapacitor was built up to investigate practical applications of the binder-free electrode materials. The Ni-G-CNFs@PANI based all solid-state symmetric supercapacitor displayed a maximum energy density of 14.4 Wh kg^{-1} at a power density of 375.2 W kg^{-1} . In addition, the supercapacitor also exhibited an admirable cycle stability. Owing to the unique electrochemical performance, the Ni-G-CNFs@PANI is expected to be a promising alternative to the electrode materials for high-performance supercapacitors.

2. Experimental sections

2.1. Materials and methods

Polyacrylonitrile (PAN, $M_w = 80\,000$) was obtained from Jilin Chemical Plant. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was purchased from Tianjin Tiantai Fine Chemicals Co., Ltd.. Aniline monomer was achieved from Xilong Chemical Co., Ltd., which was distilled under reduced pressure before use. Graphene nanosheets were obtained from Aladdin Industrial Corporation. *N,N*-dimethylformamide (DMF), concentrated hydrochloric acid (HCl), concentrated sulfuric acid (H_2SO_4), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, APS) were purchased from Beijing Chemical Works.

2.2. Preparation of Ni-G-CNFs composite

Ni-G-CNFs composite was initially synthesized via a conventional electrospinning followed by a calcination process. In a typical procedure, 0.1 g of graphene nanosheets were dispersed in 9.0 g of DMF under sonication for more than 2 h. Then, 1.0 g of PAN was added in the above solution and stirred at 90°C for 4 h. After cooling down to room temperature, 0.1 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added into the solution, which was stirred until a uniform spinning solution was obtained. The electrospinning process was operated at an applied voltage of 19 kV

with a distance of 25 cm between the needle tip and the collector plate. After the electrospinning process, PAN nanofiber membrane with $\text{Ni}(\text{NO}_3)_2$ and graphene nanosheets ($\text{Ni}(\text{NO}_3)_2$ -G-PAN) was achieved. Subsequently, the $\text{Ni}(\text{NO}_3)_2$ -G-PAN membrane was converted to Ni-G-CNFs membrane in a tube furnace via a reported carbonization procedure (240°C in air for 2 h with a heating rate of 1°C min^{-1} , 900°C in Ar for 2 h with a heating rate of 3°C min^{-1}). The CNFs and Ni-CNFs as contrasts were also prepared via similar electrospinning processes and same carbonization procedures.

2.3. Preparation of Ni-G-CNFs@PANI composite

An in situ polymerization approach was applied to prepare Ni-G-CNFs@PANI composite. Firstly, $23 \mu\text{L}$ of aniline and one piece of Ni-G-CNFs membrane (about 5 mg) were added into 20 mL of HCl (1 M). Secondly, 68 mg of APS which was dissolved in 10 mL of HCl (1 M) was transferred into the above solution, and the reaction was kept shaking in an ice-water bath ($0\text{--}5^\circ\text{C}$) for 4 h. Finally, Ni-G-CNFs@PANI membrane (about 10 mg) was cleaned with water and ethanol for several times, and then dried at 50°C for 12 h. CNFs@PANI and Ni-CNFs@PANI were prepared by using CNFs and Ni-CNFs as substitutes for in situ polymerization.

2.4. Electrochemical measurements

Three-electrode and two-electrode systems were carried out to explore the electrochemical performance of these samples. Cyclic voltammetry (CV) measurements, galvanostatic (GV) charge-discharge and electrochemical impedance spectroscopy (EIS) measurements were carried out on CHI 660E electrochemical workstation (Shanghai Chenhua instrument Co., Ltd.). Cycling stability and Coulombic efficiency measurements were examined on a Land Battery workstation (Wuhan Land Instrument Company, China). In detail, the three-electrode system was composed of a counter electrode (platinum foil), a reference electrode (Ag/AgCl) and a working electrode (directly pressing the active material (CNFs@PANI, Ni-CNFs@PANI and Ni-G-CNFs@PANI) on current collector of stainless steel mesh). In particular, for the fabrication of CNFs, Ni-CNFs, Ni-G-CNFs electrodes, acetylene black and polytetrafluoroethylene (PTFE, Aladdin) were added to electrodes because of their poor adhesion between the electrode materials and the steel mesh. 1 M H_2SO_4 solution was selected as electrolyte. In a two-electrode system, two working electrodes were separated by PVA- H_2SO_4 . The PVA- H_2SO_4 was prepared as follows: 1 g of PVA was added into 10 mL of water containing 1 g of H_2SO_4 at 85°C under stirring. After dissolving and cooling down to room temperature, working electrodes were soaked in PVA- H_2SO_4 gel and dried at room temperature for several times until completely solidify.

2.5. Characterization

A field-emission scanning electron microscope (FESEM, FEI Nova NanoSEM) and a transmission electron microscope (TEM, JEOL JEM-2000 EX) were used to investigate the surface morphology of the as-prepared samples, which were operated at 15 and 100 kV, respectively. The crystallographic structures of the samples were characterized using X-ray diffraction (XRD, PANalytical B.V. Empyrean) with Cu K α radiation ($5\text{--}90^\circ$). X-ray photoelectron spectra (XPS, Thermo Scientific ESCALAB250) with the excitation source of Al K α were carried out to analyze the chemical composition of Ni-G-CNFs@PANI product. The chemical structure of the samples was investigated by Fourier-transform infrared spectra (FTIR, Bruker Vector 22 spectrometer) and Raman measurement (Horiba LabRAM HR Evolution apparatus) using a 633 nm laser as the excitation source.

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