



High-performance porous electrodes for pseudosupercapacitors based on graphene-beaded carbon nanofibers surface-coated with nanostructured conducting polymers



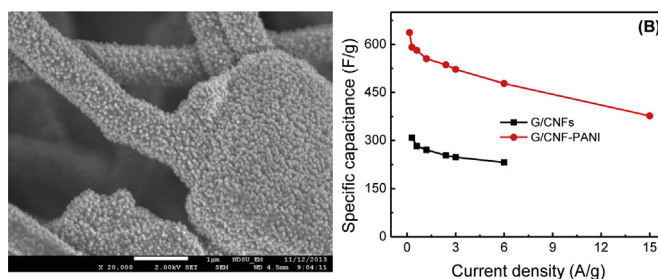
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HIGHLIGHTS

- Graphene-beaded carbon nanofibers coated with polyaniline were synthesized.
- Pseudosupercapacitor electrodes based on novel nanofibrous electrodes were fabricated.
- Microstructures and electrochemical properties of the electrodes were tested.
- Improved electrochemical performance of the new nanofibrous electrodes was observed.
- Mechanisms responsible for the improved performance were explored.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 December 2013
 Received in revised form
 18 March 2014
 Accepted 20 March 2014
 Available online 27 March 2014

Keywords:

Pseudosupercapacitor
 Carbon nanofibers
 Conducting polymer
 Electrospinning
 Electrode materials

ABSTRACT

This paper reports the fabrication and electrochemical properties of novel high-performance pseudosupercapacitor electrodes made of graphene-beaded carbon nanofibers (G/CNFs) surface-coated with nanostructured conducting polymers. The G/CNFs were produced by electrospinning the precursor graphene-beaded polymer nanofibers, followed by controlled pyrolysis. *In situ* polymerization in aqueous solution was utilized to coat an ultrathin layer of thorn-like polyaniline (PANI) nanorods onto the G/CNFs to form ternary PANI-coated G/CNFs (PANI-G/CNFs). The highly porous network morphology of PANI-G/CNFs exhibited a very large specific surface area, low internal resistance, and fast redox rate. Electrochemical characterization indicated that the PANI-G/CNF based pseudosupercapacitors carried a high value of specific capacitance up to 637 F g^{-1} at a current density of 0.15 A g^{-1} and still maintained the high value of specific capacitance of 478 F g^{-1} (only 25% decrease) even at a high current density of 6 A g^{-1} . The pseudosupercapacitor showed a very good cycling stability of 87% after 1000 charge/discharge cycles at a very high current density of 15 A g^{-1} . The experimental results indicated that the novel hierarchical, porous PANI-G/CNFs are a promising electrode material for use in high-performance energy storage devices.

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1. Introduction

Graphene consists of two-dimensional (2D) monolayers of sp^2 -bonded carbon atoms and has attracted extensive attention in the last decade [1–6]. Graphene exhibits unique physical and chemical

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properties including excellent electrical conductivity ($\sim 2 \times 10^3 \text{ S cm}^{-1}$) [7], very large specific surface area ($\sim 3100 \text{ m}^2 \text{ g}^{-1}$) [8], and amazing intrinsic electron mobility ($\sim 200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [9]. These unique features make graphene a promising nanostructured material for broad applications in microelectronics, energy storage devices, fuel cells, sensors, and gas sorbents, among others [10–12]. In particular, graphene-based materials can be used as high-performance electrodes for electrochemical double-layer capacitors (EDLCs) and pseudocapacitors, which have demonstrated higher values of specific capacitance than other carbonaceous materials, e.g., carbon nanotubes (CNTs), carbon nanofibers (CNFs), and activated carbon [10–13]. Graphene can also be conveniently manufactured in large quantity at low cost from graphite by means of chemical exfoliation [14]. Furthermore, recent intensive investigations have pointed out that metal oxides (e.g., RuO_2 , MnO_2 , etc.) or conducting polymers (e.g., polyaniline (PANI), polythiophene, polypyrrole, etc.) doped onto the surface of graphene nanosheets can noticeably enhance the electrochemical performance of the resulting supercapacitors with graphene as electrodes [15–18]. Among a variety of conducting polymers, PANI has been under intensive investigation due to its high specific capacitance (up to 750 F g^{-1}), low cost, easy synthesis, and favorable environmental stability [15]. However, several outstanding issues (e.g., the redox switching, low electrical conductivity and poor cyclability) influence the pseudocapacitive performance of PANI when structured as electrode material of supercapacitors [16]. These issues need to be resolved in rendering PANI as a highly effective electrode material to meet the practical requirements of supercapacitors.

It has been reported that graphene nanosheets surface-coated with nanostructured PANI (e.g., nanotubes, nanorods or nanospheres) have demonstrated improved capacitive performance compared to other carbonaceous counterparts and pure PANI [17–21]. Yet, most graphene/PANI electrode materials reported in the literature are in the powder form. Such generic discrete structure requires conductive additives and binders (e.g., polyvinylidene difluoride (PVDF)) to bind the active material and the electrode to the current collector in the process of supercapacitor fabrication. In addition, the effective electrochemical performance of a supercapacitor is limited by the restacking and aggregation of graphene nanosheets, which typically results in irreversible agglomeration and folding/scrolling [13]. Recently, we reported a unique route to synthesize innovative graphene-beaded CNFs (G/CNFs) for use as porous electrode material, in which the synthesis relies on the top-down electrospinning technique followed by controlled pyrolysis and activation [22]. In such a process, graphene nanosheets were covalently connected to the CNFs. Such unique carbonaceous nanostructures can provide very large specific surface area and high electrical conductivity, which can effectively suppress the restacking and aggregation of graphene nanosheets and meanwhile eliminates the need of conductive binder typically used for electrodes. In addition, porous G/CNF films can be directly utilized as supercapacitor electrodes with high specific capacitance.

In this work, a new technical route is devised to introduce the unique pseudocapacitive effect of G/CNF-based electrode materials via coating an ultrathin layer of thorn-like PANI nanorods onto G/CNFs to form a ternary multifunctional electrode material: PANI-coated G/CNFs (PANI-G/CNFs). Such porous, multifunctional PANI-G/CNF films carry superior intrinsic connectivity and very high specific surface area due to the formation of thorn-like PANI nanorods on the graphene nanosheets and backbone CNFs. Field-emission scanning electron microscopy (FE-SEM) was employed to characterize the unique morphology and microstructure of the G/CNFs and PANI-G/CNFs. The electrochemical behavior of the novel porous electrode materials was characterized in $1 \text{ M H}_2\text{SO}_4$

aqueous solution based on a two-electrode cell that was made of a pair of electrodes of $1.0 \text{ cm}^2 \text{ G/CNF}$ and $1.0 \text{ cm}^2 \text{ PANI-G/CNF}$ films, respectively. Cyclic voltammetry and galvanostatic charging/discharging behavior were studied to evaluate the pseudocapacitive behavior and specific capacitance of the novel hierarchical porous electrodes, respectively. The microstructures and electrochemical performances of the G/CNF and PANI-G/CNF electrodes were discussed and compared. Consequently, the conclusions of the research were made.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, $M_w = 150,000$) powder, *N,N*-dimethylformamide (DMF, 99%), ammonium persulfate (APS), sulfuric acid (H_2SO_4), and aniline monomer were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). Graphene nanosheets were supplied by XG Sciences, Inc. (Lansing, MI, USA). All the chemicals were used as received without further purification or modification.

2.2. Preparation of porous G/CNF and PANI-G/CNF films

The precursor graphene-beaded PAN (G/PAN) nanofibers with the diameter $\sim 300 \text{ nm}$ were prepared by electrospinning. During the process, PAN powder and graphene nanosheets (mass ratio 5:2) were first added into DMF to form an electrospinnable solution. The electrospinning process was performed in a high DC electrical field of 80 kV m^{-1} , which was generated by applying a 20 kV DC voltage to a 25 cm gap between the spinneret and the nanofiber collector. The graphene-beaded carbon nanofibers (G/CNFs) were yielded by consecutive stabilization, carbonization and activation of the electrospun precursor G/PAN nanofibers in a tubular quartz reaction furnace according to our recent synthesis route [22]. Subsequently, the yielded G/CNF films ($\sim 0.38 \text{ g}$) were coated with an ultrathin layer of thorn-like PANI nanorods to form ternary porous PANI-G/CNFs via *in situ* polymerization of aniline monomer in aqueous solution. During the process of polymerization, the as-prepared G/CNF mats had been first immersed into 200 mL aniline (0.03 M)/ H_2SO_4 (1 M) aqueous solution in an ice bath ($\sim 0\text{--}5 \text{ }^\circ\text{C}$) for 6 h . Then, APS dissolved in another 50 mL $1 \text{ M H}_2\text{SO}_4$ aqueous solution was slowly added dropwise into the mixture. The molar ratio of aniline/APS was adjusted to 4:1. The mixture had been continuously stirred for 12 h , and the color of the solution slowly changed into dark green. After polymerization, the resulting precipitates were filtered out and washed sequentially with deionized water and acetone. Finally, the wet product had been dried in a vacuum oven at $80 \text{ }^\circ\text{C}$ for 10 h . The areal mass density (mg cm^{-2}) of PANI-G/CNFs was calculated as ~ 1.5 . The mass fraction of PANI in PANI-G/CNFs was $\sim 52\%$ based on the weight difference of the G/CNFs before and after polymerization.

2.3. Microstructural and electrochemical characterization

The surface morphology of as-prepared G/CNF and PANI-G/CNF mats was analyzed by using a high-resolution FE-SEM (JEOL JSM-7600F). Electrochemical characterization was performed using a two-electrode cell setup. $1 \text{ M H}_2\text{SO}_4$ aqueous solution and stainless steel wire meshes were utilized as the electrolyte and the current collector, respectively. The electrochemical performance of the supercapacitor cells was evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge testing, and electrochemical impedance spectroscopy (EIS). The CV and galvanostatic charge/discharge curves were obtained by using a battery tester BT 2000

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