Full Length Article

Supercapacitive behavior of laminar-structured carbon cloth with alternating graphene and hybrid nanofibers: A synergistic effect of graphene-coating and post-oxidization

Qinxing Xie [a,*], Shuwen Zhou [a], Shihua Wu [b], Yufeng Zhang [a], Peng Zhao [b]

[a] Tianjin Key Laboratory of Advanced Fibers and Energy Storage, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China
[b] Department of Chemistry, Nankai University, Tianjin 300017, China

ABSTRACT

Laminar-structured flexible carbon cloth composed of alternating graphene and nitrogen-enriched carbon/graphene hybrid nanofibers was prepared via alternated electrospinning and graphene oxide coating, followed by stabilization, carbonization and post-thermal oxidization process. The multilayered graphene-coating and post-thermal treatment can exert great influence on microstructure of the as-prepared composite cloth, synergistically resulting in the increased conductivity and specific surface area, optimized pore structure and improved surface contents of nitrogen and oxygen species. Hence, the composite exhibits significantly enhanced supercapacitive performance, such as a high specific capacitance of 241 $F\,g^{-1}$ (294 $F\,cm^{-3}$) at 0.2 $A\,g^{-1}$, a high retention rate of ca. 64% at a current density of up to 50 $A\,g^{-1}$. Additionally, the resulted composite shows no significant capacitance degradation after 2000 charge/discharge cycles at 5 $A\,g^{-1}$, indicating its superior cycling stability for energy storage application.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Flexible supercapacitors have drawn intensive attentions for their potential applications in portable and flexible electronics including electronic papers, bendable cell phone and displays, as well as wearable devices [1–5]. Carbon nanofibers (CNFs) are promising electrodes for flexible supercapacitors because of their extremely high length-to-diameter ratio, nanosized diameter, high surface area and adequate porosity [6–9]. In recent years, more and more research efforts have been devoted to fabricate CNFs by electrospinning using a variety of polymers as precursors in which nitrogen-containing polyacrylonitrile (PAN) has been frequently investigated [6,7,10–14]. It is well known that the doped nitrogen species in carbons is able to improve their conductivity and surface wettability, moreover, provide extra pseudocapacitance [15–18].

It has to be pointed out that the conventional activation methods using KOH or $ZnCl_2$ are not very adoptable for CNFs. The harsh activation can result in decreased mechanical strength, and almost all nitrogen functionalities can be removed during the process [19]. Therefore, more advanced techniques and milder activation

methods have to be developed to achieve increased surface area and more adequate porosity. One strategy is to electrospin a solution of PAN containing one or more sacrificial polymers such as cellulose acetate (CA), Nafion and PMMA or inorganic components such as soluble salts or metal oxides [7,20–24]. Therefore, highly porous CNFs can be then achieved by partially burning off the sacrificial polymers during the carbonization process, or removing the inorganic components via chemical or physical routes. For example, Tran et al. reported the fabrication of porous CNFs by electrospinning a PAN solution containing Nafion in a mass ratio of 80/20, followed by high-temperature carbonization [20]. The decomposed Nafion during carbonization resulted in abundant intra-fiber pores, and the as-prepared porous CNFs exhibited a specific capacitance of 210 $F\,g^{-1}$ at a current density of 1 $A\,g^{-1}$. Béguin and his coworkers also made efforts to prepare porous CNFs by one-step carbonization/activation of PAN nanofibers at temperatures from 700 to 1000 °C in CO_2 atmosphere [6]. The CO_2-assisted activation generally results in more homogeneous porosity within the carbon fibers [25]. The research indicated that the CNFs obtained at 900 and 1000 °C have moderate specific surface area and improved supercapacitive performance in both aqueous and organic electrolytes.

According to our previous investigation, the doped graphene in carbon structure is beneficial for achieving improved energy storage capability due to enhanced conductivity and optimized

microstructure [26,27]. In this work, we fabricated a new kind of laminar-structured flexible carbon composite cloth that is composed of alternating graphene layers and nitrogen-enriched carbon/graphene hybrid nanofibers via alternated electrospinning and surface GO-coating process, followed by stabilization and carbonization. It is expected that the enhanced mechanical strength can be achieved for the as-prepared composite cloth because of the coated-graphene [28]. Hereby, the influence of the multilayered graphene-coating and post-thermal treatment on microstructure and supercapacitive performance of the resulted multilayered carbon/graphene nanofibers@graphene composite cloth (CNF/Gr@Gr) was investigated and reported in detail.

2. Experimental

2.1. Materials preparation

Graphite oxide was prepared by a modified Hummers method [29,30]. An aqueous solution of graphene oxide (GO) with a concentration of 0.1 wt.% was prepared by ultrasonically dispersing 0.1 g of graphite oxide in 100 mL of distilled water for 30 min.

The carbon/graphene hybrid nanofiber cloth (CNF/Gr) and CNF/Gr@Gr composite cloth were prepared by electrospinning. In a typical process, 0.5 wt.% GO relative to PAN was first ultrasonically dispersed in DMF, then PAN powder was dissolved into the dispersion under stirring. The resulted viscous mixture was then electrospun into nanofibers by applying a 20 kV bias between syringe needle and a rotating aluminum collector. After spinning for 0.5 h, the nanofiber paper on aluminum foil was coated with GO solution by a simple spraying method, and then dried at 110 °C. The electrospinning process was performed for 30 min again using the GO coated PAN/GO fiber paper (PAN/GO@GO) as collector. The spinning-coating procedure was repeated for ten times in total. The final multilayer PAN/GO@GO paper was thermally stabilized at 280 °C in air for 2 h, then carbonized at 800 °C for 1 h in argon atmosphere. The resulted composite cloth was designated as CNF/Gr@Gr1. A portion of CNF/Gr@Gr1 was heated up to 350 °C at a heating rate of 5 °C min^{-1} and oxidized for 1 h in air, and the product was designated as CNF/Gr@Gr2. For comparison, PAN/GO nanofiber paper was prepared as well but without GO-coating during electrospinning process, the spinning time is 5 h in total to achieve the same thickness. The PAN/GO paper was stabilized and carbonized using the same procedure as mentioned above, and the product was designated as CNF/Gr1. A portion of CNF/Gr1 was thermally oxidized in air and designated as CNF/Gr2 correspondingly.

2.2. Materials characterization

The morphologies and microstructures of the as-prepared composite cloth were analyzed by field-emission scanning electron microscopy (FESEM, Hitachi S-4800), Raman spectroscopy (DXR Raman microscope with a laser excitation of 532 nm, Thermo Scientific). The surface elemental composition was determined by X-ray photoelectron spectroscopy (XPS) measurements which performed on a K-Alpha spectrometer with an Al Kα anode (Thermo scientific). The deconvolution of C1s and N1s XPS spectra were performed based on a Shirley background subtraction and Gaussian-shaped components, and the quantitative analyses of the carbon and nitrogen species were performed according to the peak area ratio of XPS. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) method, and the nitrogen sorption isotherms were collected using a V-Sorb 2800P sorptometer (Gold APP, China). The mesopore size distributions were analyzed with the BJH (Barrett–Joyner–Halenda) method, and the micropore size distributions with the HK (Horvath-Kawazoe) method using nitrogen adsorption data. The total pore volume was determined according to the adsorbed nitrogen amount at a relative pressure (P/P_0) of 0.99.

2.3. Electrochemical measurements

Electrochemical measurements including the cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) profiles and electrochemical impedance spectroscopy (EIS) were all performed using a CHI 660E electrochemical workstation (Shanghai CH Instrument, China) at room temperature. A three-electrode cell was used for the measurements with SCE as reference electrode and Pt foil as counter electrode, and 6 M KOH aqueous solution as the electrolyte. To fabricate the working electrodes, the as-prepared flexible composite paper was cut into small pieces with a size of 1×1 cm^2, and sandwiched between two nickel foams without addition of any binders. Each electrode contains about 3.0 mg cm^{-2} of active material. The CV and GCD measurements were carried out in a potential window ranged from -1.0 V to 0 V. EIS were recorded in a frequency range from 10^5 Hz to 10^{-2} Hz with an amplitude of 5 mV at open circuit potential.

The following equations were used to calculate the gravimetric specific capacitance (C_m) and volumetric specific capacitance of the materials [27,31]: $C_m = I \times \Delta t/(m \times \Delta V)$ and $C_v = \rho \times C_m$, in which I is the discharge current, Δt is the discharge time, ΔV is the potential range, m is the mass of active material, and ρ is the particle density that can be calculated according to the following equation [27,32]:

$$\rho = \frac{1}{V_t + (1/\rho_T)}$$

where V_t is the total pore volume of the materials, and ρ_T is the true density of carbon, 2 g cm^{-3}.

3. Results and discussion

3.1. Materials characterization

Fig. 1 shows the preparation scheme of CNF/Gr@Gr composite. The mixed solution of PAN/GO in DMF was first electrospun for 0.5 h, the collected thin nanofiber paper was then spraying coated with GO aqueous solution. The dried GO-coated nanofiber paper was used as collector so that another layer of nanofibers was electrospun on top of the GO-coating surface. By alternatively performing the spinning and coating process, the multilayered PAN/GO-NFs@GO composite paper was achieved (refer to the cross-section SEM image in Fig. 1). Because of the intertangled nanofiber network, the deep impregnation of GO was inhibited resulting in a multilayered structure with alternating GO layer and PAN/GO hybrid nanofibers. The composite paper was then stabilized and carbonized to obtain a piece of large-sized flexible multilayered CNF/Gr@Gr composite cloth. For comparison, the composites without alternated graphene-coating, i.e. CNF/Gr@Gr(0) were fabricated as well via intermittent spraying of water during the electrospinning process (ref. to Supporting Info). On the contrary, CNF/Gr@Gr(0) composites are more fragile, hence only small-size specimens can be obtained (Fig. S1). This observation indicates that the graphene-coating is able to enhance the flexibility and strength of the composites.

It can be seen from Fig. 2a that the PAN/GO composite paper consists of randomly aligned and loose-packed nanofibers with diameters of ca. 200 nm. The carbonized nanofibers become thinner and 3D-interconnected because of the sticking effect of melted PAN fibers during carbonization process, as shown in Fig. 2b. The SEM image for the surface of CNF/Gr@Gr composite cloth clearly