Applied Surface Science 428 (2018) 348–355

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Three-dimensional N-doped graphene/polyaniline composite foam for high performance supercapacitors

Jun Zhu[a], Lirong Kong[a], Xiaoping Shen[a,*], Quanrun Chen[a], Zhenyuan Ji[a], Jiheng Wang[b], Keqiang Xu[a], Guoxing Zhu[a]

[a] *School of Material Science and Engineering, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China*
[b] *School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, People's Republic of China*

ARTICLE INFO

Article history:
Received 19 May 2017
Received in revised form 26 August 2017
Accepted 18 September 2017

Keywords:
Nitrogen-doped
Graphene
Polyaniline
Three-dimensional structure
Supercapacitor

ABSTRACT

Three-dimensional (3D) graphene aerogel and its composite with interconnected pores have aroused continuous interests in energy storage field owning to its large surface area and hierarchical pore structure. Herein, we reported the preparation of 3D nitrogen-doped graphene/polyaniline (N-GE/PANI) composite foam for supercapacitive material with greatly improved electrochemical performance. The 3D porous structure can allow the penetration and diffusion of electrolyte, the incorporation of nitrogen doping can enhance the wettability of the active material and the number of active sites with electrolyte, and both the N-GE and PANI can ensure the high electrical conductivity of total electrode. Moreover, the synergistic effect between N-GE and PANI materials also play an important role on the electrochemical performance of electrode. Therefore, the as-prepared composite foam could deliver a high specific capacitance of 528 F g^{-1} at 0.1 A g^{-1} and a high cyclic stability with 95.9% capacitance retention after 5000 charge-discharge cycles. This study provides a new idea on improving the energy storage capacity of supercapacitors by using 3D graphene-based psedocapacitive electrode materials.

1. Introduction

With higher power density than batteries and higher energy density than traditional dielectric capacitors, supercapacitors have been regarded as one of the most promising energy storage devices for next-generation vehicles and mobile electronics [1–4]. The energy storage properties of supercapacitors are mainly dependent on the structure and composition of the electrode materials [5]. In general, electrode materials with large surface area and high electrical conductivity usually exhibit high electronic double-layer capacitance (EDLC), while electrode materials with high electrochemical redox activity favor the increase of psedocapacitance. Compared to EDLC, psedocapacitive materials, such as transitional metal oxides and conducting polymers, usually exhibit higher specific capacitance and energy density, and thus may provide more opportunities to satisfy the needs of high-performance supercapacitors [6–13].

As a typical conducting polymer, polyaniline (PANI) has become one of the most promising electrode materials for supercapacitors due to its high environmental stability, high specific capacitance, low cost and synthetic easiness [14]. For example, Wang et al. reported the preparation of PANI nanowires with a specific capacitance of 215 F g^{-1} at the current density of 0.1 A g^{-1} in 1.0 M H_2SO_4 solution [15]. Cao et al. prepared PANI submicrospheres with a specific capacitance of 275 F g^{-1} at the current density of 0.5 A g^{-1} in 1.0 M H_2SO_4 [16]. Although PANI has a high psedocapcitance, it usually suffers from a low conductivity and therefore poor cycle life. The poor cycling stability is caused by the swelling and shrinkage of the polymer network during its doping/de-doping process, which leads to the mechanical degradation of the electrode material and fading of its electrochemical performance [17,18]. In order to overcome the shortcomings above mentioned, researchers usually incorporate PANI into highly conductive carbon matrix to enhance the conductivity and prevent PANI from being attacked, and thus improve its electrochemical stability. Moreover, confining PANI nanostructures in carbon matrix could effectively restricts its swelling and shrinkage, and thus prevents it from being degraded. Among a variety of carbon materials, two dimensional (2D) graphene with sp^2-hybridized carbon nanophase [19] is a good candidate for electrode materials for its high theoretical surface area and excellent electrical conductivity. Recently, by preparing PANI nanofibers on the surface of graphene nanosheets, Dai et al.

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* Corresponding author.
E-mail address: xiaopingshen@163.com (X. Shen).

http://dx.doi.org/10.1016/j.apsusc.2017.09.148
0169-4332/

obtained the nanocomposite with a high specific capacitance of 250 F g^{-1} in 1 M H_2SO_4 [20]. However, the specific capacitance of the reported graphene/PANI products is far lower than the theoretical values due to the serious restacking of graphene sheets caused by the strong π-π interaction between them [21,22].

Since three-dimensional (3D) graphene and nitrogen-doped graphene (N-GE) could exhibit a much larger surface area and possess more porous structure than pristine 2D graphene [23–27], which facilitate the immigration and storage of the electrolyte ions, supercapacitors with 3D graphene or N-GE based electrodes usually exhibit higher specific capacitance and energy density as compared with pristine 2D graphene. For instance, Rao's group synthesized N-GE/PANI composites by in-situ growth of PANI nanoparticles on N-GE nanosheets. The composites exhibited excellent capacitance performance [26]. Liu et al. prepared 3D N-GE/PANI composites by in-situ polymerization and using polystyrene as the sacrificial template to build 3D frameworks. The capacitance performance of the 3D N-GE/PANI was largely enhanced [17]. Encouraged by these works, in this paper, we report a new N-GE/PANI foam prepared by encapsulating PANI submicrospheres into 3D nitrogen-doped graphene monolith. It is found that the N-GE/PANI exhibits a high specific capacitance of 528 F g^{-1} at the current density of 0.1 A g^{-1} and a high cyclic stability with 95.9% capacitance retention after 5000 charge-discharge cycles. The high electrochemical energy storage performance of the N-GE/PANI foam can be ascribed to the 3D hierarchical porous structure of N-GE aerogel, the high psedocapacitance of PANI submicrospheres, and the synergistic effect between them.

2. Experimental

2.1. Materials

Natural flake graphite with a particle size of *ca.* 150 μm (99.9% purity) was purchased from Qingdao Guyu Graphite Co., Ltd. All of the other chemical reagents used in our experiments were obtained from Sinopharm Chemical Reagent Co., LTD, which were of analytical grade and used without further purification. Graphite oxide was prepared from natural flake graphite using a modified Hummers method [28].

2.2. Synthesis

2.2.1. Synthesis of PANI submicrospheres

PANI submicrospheres were synthesized according to the reported method [29]. Briefly, 1 mmol of aniline monomer was dissolved in 40 mL of H_3PO_4 aqueous solution (0.4 M) by vigorous stirring. Then, 0.12 mL of H_2O_2 solution (30%) and 0.02 mL of $FeCl_3$ (0.1 M) aqueous solution were added into the above solution successively. After further stirring for 15 min, the mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 140 °C for 6 h. The resulted product was centrifugated, washed with deionized water and ethanol, respectively, and finally dried in vacuum at 60 °C.

2.2.2. Synthesis of N-GE/PANI composite foam

In a typical synthesis, 100 mg of graphite oxide was dispersed into 30 mL of deionized water by ultrasonication to form a homogeneous graphene oxide (GO) suspension. Subsequently, a certain amount of the as-prepared PANI submicrospheres and 0.9 g of ascorbic acid were added into the above suspension under vigorous stirring. After stirring for 0.5 h, 1 mL of $NH_3 \cdot H_2O$ (28 wt.%) was added in. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave, and then heated at 180 °C for 12 h. After the autoclave was cooled down to room temperature naturally, the resulting cylindrical product was collected, dipped in deionized water and absolute ethanol for several times to remove the residual impurities, and finally frozen in a refrigerator. The frozen product was dried in a freeze-drying machine under reduced pressure overnight to yield the final 3D N-GE/PANI foam. According to the different weight percentages of PANI submicrospheres in N-GE/PANI composites, the obtained products were designated as N-GE, N-GE/PANI-20%, N-GE/PANI-25% and N-GE/PANI-30%, respectively.

2.3. Instrumentation and measurements

The morphology and microstructure of the products were investigated by scanning electron microscopy (SEM, JSM-6010PLUS/LA), and transmission electron microscopy (TEM, JEOL-2100) with an acceleration voltage of 200 KV. The phase structures of the products were characterized by powder X-ray diffraction (XRD, Bruker D8 Advance) with Cu K_α radiation (λ = 1.5406 Å). Fourier transform infrared (FT-IR) spectra were taken on a Nicolet Nexus 470 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. Raman spectra were measured on a JYHR800 Raman spectrometer using a 532 nm laser source. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250XI system with Al K_α X-ray as an excitation source.

2.4. Electrochemical measurements

Electrochemical measurements were carried out on a typical three-electrode system using a CHI 760E electrochemical analyzer (Chen Hua Instruments, Shanghai, China) at room temperature. Hg/Hg_2Cl_2 (Saturated KCl) and Pt foil were used as the reference and counter electrodes, respectively. The working electrodes were fabricated by mixing 80 wt.% of active materials (N-GE/PANI composites, N-GE or PANI), 10 wt.% of acetylene black and 10 wt.% of poly(vinylidene fluoride) (PVDF) binder in *N*-methyl-2-pyrrolidone solvent under vigorous stirring to form a homogeneous slurry. After that, the slurry was pasted onto a graphite paper (surface area 1 cm^2), and then the graphite paper was placed into a vacuum oven at 60 °C to remove the solvent. The electrochemical properties of the obtained products were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The CV and GCD measurements were performed over a voltage range of −0.2–0.8 V. According to the GCD results, the specific capacitances of the supercapacitors were calculated from the equation of $C = I\Delta t/m\Delta V$, where I is the discharge current, Δt is the discharge time, m is the total mass of active materials in the electrode, and ΔV is the voltage drop upon discharge.

3. Results and discussion

3.1. Structural and morphological characterization

The morphology and microstructure of the as-prepared samples were investigated by SEM and TEM images. As shown in Fig. 1a and b, an interconnected framework of thin and wrinkled N-GE nanosheets with a fluffy porous structure could be observed. The pore sizes are in the range from a few hundred nanometers to several micrometers, which could offer more paths for the immigration of the electrolyte ions. Moreover, the 3D structure of N-GE can provide a large accessible surface area by preventing the adjacent graphene nanosheets from aggregating together. When PANI submicrospheres with a size of *ca.* 400 nm (the inset in Fig. 1d) are incorporated into the 3D N-GE framework, the obtained N-GE/PANI composite shows a similar 3D porous structure with N-GE but has a more rough and wrinkled surface (Fig. 1c and d). Moreover, it was found that the PANI submicrospheres cannot be clearly observed