Hierarchical unidirectional graphene aerogel/polyaniline composite for high performance supercapacitors

Xiaotian Wu[a], Lisheng Tang[a], Shaodi Zheng[a], Yanhao Huang[a], Jie Yang[a], Zhengying Liu[a,*], Wei Yang[a,b], Mingbo Yang[a,b]

[a] College of Polymer Science and Engineering, Sichuan University, Chengdu, 610065, China
[b] State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, China

HIGHLIGHTS

- Polyaniline nanowire arrays were deposited on highly aligned graphene network.
- Graphene network with oriented channels promote ion diffusion and electron transfer.
- The composites with hierarchical ion channel exhibit excellent electrochemical properties.

ARTICLE INFO

ABSTRACT

A free-standing unidirectional graphene aerogel/polyaniline (UGA/PANI) composite possessing the oriented PANI nanowire arrays on highly aligned and interconnected graphene network is obtained, through a facile in-situ polymerization of PANI on a unidirectional graphene aerogel scaffold. The resulted novel hierarchical structure can reduce the internal resistance and facilitate ion diffusion, which allows this electrode material to exhibit better electrochemistry performances. The UGA/PANI composite subsequently displays an enhanced specific capacitance of 538 F g^{-1} at 1.0 A g^{-1} with appreciable rate capability (keeps 73% even at 10 A g^{-1}) as well as fine cycle stability (remains 74% of its initial specific capacitance after 1000 cycles at 3 A g^{-1}). Besides, the electrochemical performances of UAG/PANI composite reported far excel that of conventional graphene aerogel/polyaniline (GA/PANI) composite with random graphene network and tortuous pores (345 F g^{-1} at 1.0 A g^{-1}, 39% retention at 10 A g^{-1}), demonstrating that proper construction of oriented structure is beneficial for achieving potential of PANI.

1. Introduction

Supercapacitors with high-performance are highly desirable for electronic devices, hybrid electric vehicles, and energy stores system [1,2], due to their higher power density, more excellent cycle performance and better operational safety than that of rechargeable batteries and their higher energy density than that of conventional electrical double-layer capacitors [3–5]. According to energy storage mechanisms, supercapacitor can be classified into two categories: one is the electrical double-layer capacitors (EDLCs), in which the capacitance drives from an electrostatic double-layer effect between carbon based materials with high specific surface area and electrolyte [6], such as activated carbons, carbon nanotubes, and porous carbons; another is the pseudocapacitors, in which the charge storage comes from reversible and fast Faradic redox reaction taking place at the

pseudocapacitive materials, such as transition metal oxides [7] or conducting polymers [8].

As is well-known, polyaniline (PANI), one of the most promising conducting polymers, has been fully developed as high-performance electrode materials for supercapacitors because of its ease of synthesis, low cost, good environmental stability and high theoretical specific capacitance [9–11]. However, the periodically volume swelling/shrinkage of PANI during the continuous charging and discharging process would induce the inferior cycling stability [12]. Besides, PANI also suffer from the poor rate performance due to its kinetically slow charge transfer reaction [13]. These deficiencies severely prevented PANI from commercial application in supercapacitors. Considerable efforts to address these issues have been focused on fabricating a composite electrode of PANI and carbon based materials. A mesoporous PANI film on graphene sheets via in situ polymerization was

synthesized by Fan et al., and the composites presented a maximum specific capacitance of 749 F g^{-1} at 0.5 A g^{-1}, and 88% retained capacitance after 1000 cycles at 100 mV s^{-1} [14]. Xie et al. prepared covalently-grafted polyaniline/graphene oxide nanocomposites, which possessed specific capacitance value of 422 F g^{-1} at 1 A g^{-1} and retention ratio of 83% over 2000 cycles at a current density of 2 A g^{-1} [15]. However, it is still a big challenge to utilize graphene sheet completely as free-standing conductive scaffold and support for PANI. The supercapacitor electrodes are usually achieved by blending nanostructured PANI composites with insulating binders (such as polyfluortetraethylene and polyvinylidenefluoride) or conductive additives [16–18]. Addition of binders and additives not only complicates fabrication process, but also reduces the electrochemically active surface area and introduces extra inner resistance [19]. Therefore, a facile route for preparing self-supporting PANI composites is highly significant [20].

Unidirectional graphene aerogel (UGA) is fabricated using a unidirectional freeze casting method [21]. The interconnected structure with the majority graphene preferentially aligned alone the ice growth direction is achieved by the large temperature gradient generated during freeze casting. On the one hand, the formation of graphene aerogels not only markedly inhibits the restacking of individual graphene sheets, but also contributes to a 3D framework with high porosity, large specific surface area and excellent electrical conductivities. One the other hand, UGA possesses long-range ordered and highly aligned graphene networks, which accelerates ion diffusion process in the electrolyte. Therefore, UGA is a fascinating scaffold material for PANI supercapacitor. Based on the above understanding, we developed a facile approach to prepare free-standing porous UGA/PANI composites through in situ polymerization. The as-obtained composite exhibits a high specific capacitance, considerable rate performance as well as long cycling life, which endows it with a promising potential in future energy storage application.

2. Experimental

2.1. Materials

Natural graphite flakes was purchased from Shenghua Research Institute (Beijing, China). Aniline was obtained from Adamas Reagent Co. Ltd (Shanghai, China). Ammonium peroxydisulfate was purchased from Tianjin Bodi Chemical Reagent Company (Tianjin, China). Concentrated sulfuric acid (98 wt %) and hydrochloric acid were bought from Xilong Scientific Company (Chengdu, China). All the chemicals were directly used without further treatment.

2.2. Fabrication of UGA and graphene aerogel

The graphene oxide (GO) was synthesized by a modified Hummers method [22] and through unidirectional freeze casting of GO dispersions, UGA was fabricated [23,24]. Typically, GO dispersion at a mass-volume concentration of 10 mg/mL was poured into rectangular corundum crucible and then the crucible was placed on Al platform in liquid nitrogen. The GO dispersion in crucible was unidirectionally frozen from the bottom to the top with the temperature gradient, thus causing oriented graphene networks. The frozen GO dispersion was subsequently freeze-dried (FD-1A-50, Beijing Boyikang, China) for 24 h, and then was thermally reduced to form UGA at 1100 °C for 1 h in a flowing argon atmosphere in a tube furnace (GSL-1700X, Hefei Kejing, China) with the heating rate of 10 °C/min below 500 °C and 4 °C/min over 500 °C. Finally, the unidirectional graphene aerogel (UGA) with high conductivity was obtained. For comparison, GO dispersion was frozen in a normal refrigerator and then freeze-dried and thermally reduced by the same conditions to obtain conventional graphene aerogel (GA).

2.3. Fabrication of UGA/PANI composites and GA/PANI composites

The UGA was cut to the square about 1.2 cm on a side followed by immersion in 10 ml of 1.0 M HCl aqueous solution containing 0.3 ml of aniline in a vacuum vessel for several minutes, which would be helpful for complete immersion of solution. The mixture was subsequently put in ice bath for 2 h 10 ml of 1.0 M HCl aqueous solution containing 0.18 g ammonium peroxydisulfate was pre-cooled in ice bath before it was poured into the above mixture. Then the mixture continued to be left in ice bath for another 1 h, 2 h, 4 h and 6 h, respectively, and the resulted composites were denoted as UGA/PANI-1, UGA/PANI-2, UGA/PANI-4 and UGA/PANI-6 (the approximate mass ratios of polyaniline of UGA/PANI composites were listed in Table S1), orderly. The obtained composites were washed by HCl aqueous solution, ethanol, and deionized water subsequently. Finally, the as-prepared composites were freeze-dried for 24 h. For comparison, we also fabricated GA/PANI composites with the same procedure with the polymerization time of 4 h. And pristine PANI was also synthesized based on the above method without the addition of UGA. (The UGA/PANI in the paper referred to polymerization time of 4 h unless noted otherwise).

2.4. Characterization

SEM images of the samples were taken on a field-emission scanning electron microscope. X-ray diffraction (XRD) patterns were performed on a DX-1000 diffractometer using Cu K α radiation (λ = 0.154 nm) at an operating voltage of 40 kV and current of 30 mA. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrometer (Nicolet Instrument Company, USA) using KBr pellets in the wavenumber range of 4000–400 cm^{-1}. Raman spectra were conducted on A DXRxi Raman Microscope (Thermal Scientific, USA) at a laser excitation wavelength of 532 nm. X-ray photoelectron (XPS) spectra were collected on a XSAM800 (Kratos Company, UK) instrument using Al K α radiation (hυ = 1486.6 eV).

2.5. Electrochemical measurements

All the electrochemical measurements were performed using a three electrode setup in 1 M H$_2$SO$_4$ aqueous electrolyte. The working electrode was prepared by implanting UGA/PANI composite (also other electrode materials) square (about 1*1 cm^2) into graphite electrode with a square hole (1*1 cm^2). The mass loading of electrode was ~2 mg. The digital photographs in Fig. S1 illustrate the freestanding feature of UGA/PANI. Saturated calomel electrode (SCE) and platinum sheet were used as reference electrode and the counter electrode, respectively. All electrochemical performances were tested on an electrochemical workstation (CHI 660E, Shanghai Chenhua). Cyclic voltammetry (CV) tests were done from −0.2–0.8 V (vs. SCE). Galvanostatic charge/discharge (GCD) was measured in the potential range of 0–0.8 V (vs. SCE) at different current densities from 1 to 10 A g^{-1}. The electrochemical impedance spectroscopy (EIS) data were collected in the frequency range from 0.1 Hz to 100 kHz.

3. Results and discussion

3.1. Microstructure characterizations

The morphology and microstructure of the as-prepared UGA scaffold and UGA/PANI composites are shown in Fig. 1. The UGA exhibits a highly anisotropic graphene network. During the vertical growth of ice crystals from the bottom up, the two-dimensional graphene oxide sheets are excluded by the ice front and assemble between the ice crystals (Scheme 1), causing oriented and straight pores after ice sublimation [25]. The top view of UGA (Fig. 1a) shows tightly arranged anisotropic pores and the side view (Fig. 1b) indicates well-aligned graphene sheets structure. After in situ polymerization of PANI on UGA