A self-standing nanocomposite foam of polyaniline@reduced graphene oxide for flexible super-capacitors

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A B S T R A C T

Self-standing three-dimensional nanocomposite foam of polyaniline (PANI) and reduced graphene oxide (rGO) has been fabricated by a convenient template-directed preparation of rGO and subsequent *in situ* polymerization of aniline on pre-formed rGO foam, which can be directly used as electrodes for flexible supercapacitors. The nanocomposite foam of PANI@rGO possesses the advantages of self-standing, foam-like high porosity, low density ($\sim$8.3 mg cm^{-3}), good flexibility and improved durability, which collaboratively lead to superior electrochemical performance, as a result of enhanced charge-transfer and mechanical support afforded by the rGO skeleton. The nanocomposite-based supercapacitor not only displays a high specific capacitance of 701 F g^{-1} at the current density of 1 A g^{-1}, but also demonstrates improved cycling stability, retaining 92% of its starting capacitance after 1000 charge–discharge cycles. Moreover, the bended symmetric pseudocapacitor based on the flexible nanocomposite foam of PANI@rGO exhibits a high specific capacitance of 285 F g^{-1} at 1 A g^{-1}, indicating excellent potential for real energy storage in flexible supercapacitors. The approach presented here shows great promise for the development of flexible low-density electrode materials with good potential for applications in portable electronic devices.

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1. Introduction

Supercapacitors, also known as electrochemical capacitors, have attracted tremendous attention in recent years due to their high power density, fast charge–discharge process, and long cycling life in general [1–11]. Electric double layer capacitors (EDLCs) and pseudocapacitors are two major types of supercapacitors. EDLCs are often made of carbon materials and possess better cycling stability and mechanical strength, whereas pseudocapacitors, which are based on Faradaic mechanism, normally demonstrate higher capacitance but limited durability [12,13]. Thus it has been envisioned that the combination of pseudocapacitive material with carbon material would deliver a pseudocapacitive composite with both superior energy density and excellent electrochemical stability [9,14,15].

Polyaniline (PANI) is one of the commonly investigated pseudocapacitive materials, owing to its easy synthesis, good conductivity, low cost, environmental friendliness and high specific pseudocapacitance conferred by multiple redox states [16,17]. However, the practical application of PANI in supercapacitors is still hindered by two challenges. First, the mechanical degradation caused by swelling and shrinkage during doping and dedoping process leads to limited cycling life of PANI-based supercapacitors [18]. Second, the charge transfer of PANI during the charging–discharging reactions is kinetically slow and thus results in poor rate capability.

Recently, graphene, a two-dimensional carbon material with outstanding electrical properties, good chemical stability, high mechanical strength and large surface area, has been utilized to form synergistic hybrid material with PANI to overcome its constraints [5,12,19–26]. The resultant composite materials, such as PANI nanowire arrays on graphene oxide (GO) and PANI nanorod on graphene nanoribbons, have demonstrated enhanced rate capability and cyclability [27,32–35]. Unfortunately, these nanocomposites were prepared as powders via a non-template-directed approach and the nanocomposite electrodes were usually prepared by the protocol of mixing the powder with binders and pasting the mixture onto collector electrodes [35,36], which not only limits the control over microstructure, but also reduces the electrical and electrochemical properties of the resultant

electrodes. In recent years, nanocomposite films of graphene and PANI have been fabricated to achieve better control over the microscopic structure, and have demonstrated improved pseudo-capacitive performance, including PANI-embedded graphene hydrogel film [16], three-dimensional (3D) porous graphene-PANI film [37], etc [38,39]. Although these porous nanocomposite films are self-standing and can be applied as binder-free electrodes, most of them exhibit poor flexibility and are easy to crack and collapse when bended without supporter, due to the hollow internal structure and sparse skeleton.

The growing demand for portable and wearable energy storage system has driven rapid development of flexible supercapacitors over the past decade [7,40–42]. Thus it is desirable to develop a flexible nanocomposite of PANI and graphene, particularly for flexible supercapacitors. Recently, good mechanical flexibility has been shown for graphene-PANI papers or films [43–45], and high-performance flexible supercapacitors have been constructed based on these nanocomposite electrode. Yet, an effective way to prepare a nanocomposite material of PANI and graphene, which not only has highly porous structure and excellent pseudocapacitance, but also possesses good flexibility, remains to be explored.

Herein, a nickel (Ni) template-directed approach has been developed to fabricate flexible self-standing nanocomposite foam of PANI and reduced graphene oxide (rGO), which can be directly applied as a working electrode without any binders, avoiding the unwanted conductivity impairment and energy loss caused by the resistance of binders. The PANI@rGO nanocomposite foam was prepared by deposition of GO on Ni foam (NF), followed by reduction, removal of NF, and a facile in situ polymerization of aniline. The obtained 3D foam-like PANI@rGO nanocomposite shows interconnected porous structure, which enables electrolyte to access the internal surface and thus ensures high specific capacitance ($701\,F\,g^{-1}$ at the current density of $1\,A\,g^{-1}$). Good cycling durability has also been observed with 92% of the starting capacitance retained after 1000 charge–discharge cycles. More-over, the PANI@rGO nanocomposite achieved exhibits good flexibility and is able to deliver a high specific capacitance of $285\,F\,g^{-1}$ at $1\,A\,g^{-1}$ in a bended symmetric system, indicating excellent potential for real energy storage in flexible super-capacitors.

2. Materials and methods

2.1. Materials

Potassium persulfate ($K_2S_2O_8$, A.R., Xilong Chemical Co., LTD.), ammonium persulfate (($NH_4)_2S_2O_8$, A.R., Xilong Chemical Co., LTD.), phosphorus pentoxide (P_2O_5, Tianjin Fuchen Chemical Factory), ammonia ($NH_3 \cdot H_2O$, A.R., Beijing Chemical Factory), graphite (45 μm, A.R., Sigma,), aniline ($C_6H_5NH_2$, A.R., Xilong Chemical Co., LTD.), ethanol (C_2H_5OH, A.R., Beijing Chemical Factory), hydrochloric acid (HCl, A.R., Beijing Chemical Factory), ferric chloride ($FeCl_3 \cdot 6H_2O$, A.R., Beijing Chemical Factory), hydrazine hydrate ($H_2NNH_2 \cdot H_2O$, Tianjin Fuchen Chemical Factory), and concentrated sulfuric acid (H_2SO_4, A.R., Beijing Chemical Factory) were used as received. Nickel foams (1.5 mm thick, 110 ppi, 99.8% purity) were purchased from Tianyuan Lizhiyuan Technology Co. All solutions were prepared with ultrapure water (resistance >18 MΩ cm^{-1}).

2.2. Preparation of rGO foam

Graphene oxide (GO) was prepared from graphite powder via a modified Hummers method as previously described [46,47]. Nickel foam (NF) was used as the template for the fabrication of GO foam. Briefly, NF was sequentially washed with acetone, water, 1:10 HCl,

water and alcohol under sonication for 15 min each, and dried under vacuum for 4 h before use. Then, 0.9 mL GO suspension (CGO = 3.75 mg mL^{-1}) was dropped onto NF (a square of 1.5×1.5 cm) and the NF filled with GO suspension was subse-quently dried under room temperature to deposit GO sheets on the NF surface (GO@NF). Next, GO@NF was transferred into an autoclave with 10 μL hydrazine monohydrate and heated at 90 °C for 16 h to obtain rGO@NF. The removal of NF from rGO@NF was achieved by immersing rGO@NF in a solution containing hydrochloric acid (2.0 M) and FeCl$_3$ (0.8 M) overnight at room temperature. The resultant rGO foam was rinsed with deionized water several times to remove residual acid and metal ions.

2.3. In situ polymerization

In-situ polymerization of aniline on the pre-formed rGO foam was carried out by using a protocol adopted from previous reports to obtain the PANI@rGO nanocomposite foam [16,25]. The rGO foam was immersed in 5 mL 1.0 M HCl aqueous solution containing 0.15 mL aniline. The mixture was stored at 4 °C for 1 h. Then, 5 mL 1.0 M HCl aqueous solution containing 0.09 g ammonium persul-fate (pre-cooled to 4 °C) was poured into the above mixture, and the resultant mixture was left at 4 °C for another 0.5 h. The obtained nanocomposite foam was thoroughly rinsed with HCl aqueous solution, ethanol, ammonia and water.

2.4. Electrochemical measurement

Electrochemical measurements were performed at room temperature using a CHI 660E electrochemistry workstation. A conventional three-electrode system was set up to characterize electrochemical properties, including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) cycling and electrochemical impedance spectra (EIS). The PANI@rGO nanocomposite foam was transferred onto Indium-Tin Oxide (ITO) glass to be used as the working electrode. Platinum wire and AgCl/Ag electrode (saturated with KCl) were adopted as the counter electrode and the reference electrode, respectively. 1 M H$_2$SO$_4$ solution was used as the electrolyte in all electrochemical measurements. CV tests were carried out at a scan rate ranging from 5 mV s^{-1} to 1000 mV s^{-1} under the potential between −0.2 V and 0.8 V. The GCD cycling was carried out within the same potential range at current densities ranging from 0.5 A g^{-1} to 10 A g^{-1}. The performance of symmetric pseudocapacitor was measured in a two-electrode system, composed of two identical working electrodes, which were prepared by gluing the PANI@rGO nanocomposite foam onto two slices of ITO-PET (polyethylene terephthalate) in same shape and size with AB glue at four corners. A piece of filter paper soaked with 1 M H$_2$SO$_4$ electrolyte was used as the separator. Rubber bands were used to bend the prepared electrodes, during the performance measurement for flexible symmetric pseudocapaci-tor.

2.5. Material characterization

Scanning electron microscopy (SEM) images were collected on a JEOL JSM-7500F field emission scanning electron microscope. Fourier transform infrared (FT-IR) spectra were collected on an FT-IR spectrometer (SHIMADZU IRAffinity-1) using KBr pellets (32 scans), and the spectra were recorded at a resolution of 4 cm^{-1}. Atomic force microscopy (AFM) under tapping mode was carried out with a commercial instrument (Digital Instrument, Nanoscope III, and Dimension 3000) at room temperature in air. UV–vis absorption spectra were taken in a quartz cell with light path of 1 cm on a SHIMADZU UV-2550 spectrophotometer (200–800 nm).