



Novel surfactant-stabilized graphene-polyaniline composite nanofiber for supercapacitor applications



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ABSTRACT

In this work, we present a new synthesis method for surfactant stabilized graphene (SSG) combined with polyaniline nanofiber (PANI-Nf) and apply the composite material as supercapacitor (SC) electrodes by screen-printing technique. Surfactant stabilized graphene polyaniline nanofiber composite (PANI-SSG) was synthesized by electrolytic exfoliation of graphite and subsequent interfacial polymerization. Firstly, graphite was electrolytically exfoliated in an electrolyte containing anionic surfactant. Next, ammonium peroxydisulfate initiator and hydrochloric acid were added to the graphene dispersion to form the aqueous phase for interfacial polymerization of polyaniline nanofiber. This dispersion was then added to the water-insoluble solvent phase containing aniline monomer. The polymerization only occurred at the interface of the two immiscible phases leading to polyaniline nanofiber decorated graphene structures. Characterizations by scanning electron microscopy, transmission electron microscopy, atomic force microscopy and Raman spectroscopy suggested nanocomposite formation with intermolecular π - π bonding of graphene with polyaniline nanofibers. Pastes of the materials were screen printed on stainless steel current collectors and tested for SC performance by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements with 2 M H₂SO₄ electrolyte using a home-built two-electrode test-cell. CV results showed redox peaks of polyaniline with wide cyclic loop, indicating large pseudocapacitance of the nanocomposite. From GCD measurement, a high specific capacitance of 690 Fg⁻¹ at 1 Ag⁻¹ was achieved. Therefore, PANI-SSG nano-composite prepared by electrolytic exfoliation and interfacial polymerization is a promising candidate for SC applications.

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1. Introduction

Supercapacitors (SCs), electrochemical energy storage devices which take an intermediary position between batteries and conventional capacitors, are of great interest for a vast range of modern electronic applications such as portable systems, hybrid electric vehicles, memory protection in CMOS logic circuits, home-electronics, PCs, UPS in security alarm systems, remote sensing, smoke detectors and so on due to their high power density, long life time and high reliability (maintenance free) [1]. In addition, SCs provide an extremely high energy density compared to conventional dielectric capacitors. SCs can operate based on two distinct

mechanisms, electrical double layer capacitance and pseudocapacitance. Carbon based SCs work primarily based on the former mechanism, in which energy is stored and released by ion adsorption and desorption at the interface between electrode and electrolyte [2]. The specific capacitance of this type of SC is determined by the relative proportion between the pore size of the active electrode material and the size of ions in the electrolyte, i.e. the electrochemically effective surface area. In the latter mechanism, which occurs in some electroactive materials including conductive polymers such as polyaniline (PANI) and metal oxides such as MnO₂, charge storage is caused by faradic processes (redox reactions) or by the progressive occupation of surface sites on an electrode by chemical species through underpotential-deposition [3]. The pseudocapacity of PANI is due to the polymer's redox reactions with in/out-flux counter-ions. In acidic aqueous electrolytes, which are the most commonly used for PANI based SCs, the

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polymer can be charged by oxidation or doping with H^+ ions. This allows electron delocalization along the polymer chains causing high conductivity. Upon discharging, the polymer is reduced or dedoped and H^+ ions are released back to the electrolyte [4]. The combination of both mechanisms offers considerably higher capacitance value than that of SCs operated only with electric double layer. However, pseudocapacitive materials tend to suffer from low conductivity, which causes series resistance and limited specific capacitance. Moreover, many conducting polymers exhibit low cycling stability [5]. The combination of highly conductive carbon-based and pseudocapacitive materials is a potential solution to these problems. Therefore, SCs based on carbon/polymer/metal oxide hybrids have recently been widely investigated [6–9].

The performances, particularly specific capacitance, of hybrid SCs can be optimized by enlarging the surface area and electrical conductivity of the electrode material. For this purpose graphene, an atomically thin two-dimensional sheet of sp^2 -hybridized carbon atoms arranged in a honeycomb crystal lattice, is a very promising candidate as the carbon component in the hybrid due to its high carrier mobility, large electrical conductivity and high specific surface area [10–13]. It has been demonstrated that graphene's high specific surface area leads to a large theoretic double layer capacitance of up to $21 \mu F cm^{-2}$ [14]. However, agglomeration of graphene due to strong attractive forces among sheets is a challenging obstacle in the way of large scale production of high quality graphene hybrids for SC applications. To overcome this problem, various methods of graphene surface modification has been developed to allow molecular dispersion of individual (or at least a few layer) graphene sheets while retaining its desirable intrinsic properties. For instance, covalent functionalization of graphene with oxygen-containing groups ('graphene oxide') has been shown to significantly improve their dispersability [15,16]. However, this leads to inferior physical and electronic properties due to lattice defects. Non-covalent methods through supramolecular interactions such as π - π stacking, electrostatic interaction and hydrogen bonding are better alternatives because the unique electronic properties of graphene can be preserved without serious damage. Since graphene sheets consist of two-dimensional sp^2 -bonded carbon, the p_z -orbitals perpendicular to the plane are unaffected resulting in a large π electronic surface available for non-covalent π - π stacking. With this method, graphene can be combined with planar aromatic molecules such as aniline/polyaniline. In the case of PANI, graphene sheets can be decorated with aniline molecules, which are subsequently polymerized into PANI forming graphene-PANI network. The non-covalent functionalization of graphene with these substances allows the possibility to synergistically combine their advantageous properties [17–22].

PANI is a well-known conducting polymer exhibiting good environmental stability, interesting electrochemical activity and unusual doping/dedoping chemistry [23]. PANI occurs in three idealized oxidation states; i) leucoemeraldine; ii) emeraldine; iii) (per)nigraniline. Conductivity of PANI increases from the undoped insulating base form to the fully doped, conducting acid form. The polyemeraldine-salt is the most electrically conductive form with its imine nitrogens protonated. PANI is another important candidate for SC applications due to its relatively high electrical conductivity and high faradic reactivity. PANI based materials have been demonstrated to exhibit high pseudocapacitance [24]. In particular, PANI-graphene hybrids prepared by various methods have recently been reported to yield high specific capacitance ranging from 200 to 900 $F g^{-1}$ [4,9,25,26]. Electrochemical and oxidative polymerizations are among the most widely used processes for PANI synthesis in these hybrids. In this work, we present a novel synthesis method for PANI-SSG composite and apply the composite material as SC electrodes by screen printing technique.

Non-covalent surfactant-functionalized graphene is synthesized by electrolytic exfoliation in a surfactant solution and PANI-SSG composite is then formed by an interfacial polymerization technique. The composite is subsequently screen-printed on stainless-steel current collectors and tested for SC performances in two-electrode configuration.

2. Materials and methods

2.1. Preparation of electrode materials

SSG was prepared by electrolytic exfoliation of graphite rods in an electrolyte containing sodium dodecylbenzenesulfonate (SDBS). High-purity graphite rods were purchased from Electron Microscopy Sciences. SDBS and aniline were purchased from Sigma Aldrich. 0.1 M (~35 mg/ml) SDBS solution was prepared in deionized water and electrolysis was performed with a constant voltage of 10 V at room temperature for 24 h, followed by ultrasonication for 1 h. A major advantage of the electrolytic method is that it, in contrast to other graphene synthesis methods (e.g. graphite oxidation and graphene oxide reduction), does not require any hazardous or environmentally harmful reactants. The resulting graphene dispersion was then washed by mixing with 75% ethanol at a ratio of 1:3 and stirred vigorously for 5 min. After that the dispersion was left standing until a black precipitate settled down and the supernatant was discarded. This washing procedure was repeated 5 times. Next, ethanol was removed by dialysis with regenerated cellulose membranes (MWCO 12–14 kD) in DI water.

Next, graphene/PANI composite material was fabricated by interfacial polymerization. The aqueous phase for interfacial polymerization was prepared by adding ammonium peroxydisulfate (APS) initiator and 1 M hydrochloric acid (HCl) to the graphene dispersion while the solvent phase of aniline monomer was separately produced in chloroform. The weight ratio of graphene, aniline and APS was approximately 1:10:6. The two solutions were then mixed in a reaction vessel and gently stirred. Due to the immiscibility between chloroform and aqueous phase, polymerization only took place at the interface. Moreover, the polymerized aniline migrated into the aqueous phase since PANI in the emeraldine salt form was hydrophilic. The migration prevented secondary growth, resulting in fibrous structures. Also, the produced PANI nanofibers congregated with graphene in the aqueous phase leading to PANI-Nf-decorated graphene structure. After the polymerization was completed, the product was washed with DI water by vacuum filtration with a $0.45 \mu m$ nitrocellulose membrane until the pH of the filtrate became neutral. The solid product was then collected and dried overnight at 80 °C. The weight ratio between surfactant-stabilized graphene and polyaniline in the resulting powder was determined to be approximately 1:10 by precision weighing of dried powders before and after interfacial polymerization. However, the weight composition of SBDS surfactant relative to graphene could not be evaluated because the surfactant was bound together with graphene during electrolytic exfoliation process and partially washed out by subsequent dialysis and filtration. Pure PANI-Nf was also produced for comparison by the analogue procedure with the absence of graphene in the aqueous phase.

2.2. Preparation of SC electrodes and electrochemical measurements

SC electrodes were prepared by screen printing using 100 μm thick polyester masks in a circular area of a 1.5 cm diameter. Printable paste was prepared by mixing graphene, PANI-Nf and PANI-SSG powders in an agate mortar with 15 %wt acetylene black and 5 %wt polytetrafluoroethylene binder (60% dispersion in H_2O)

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