Magnetically enhanced plasma exfoliation of polyaniline-modified graphene for flexible solid-state supercapacitors

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ABSTRACT

Flexible solid-state supercapacitors featuring lightweight and large capacitance have many attractive applications in portable and wearable electronics. Nitrogen-doped graphene is a promising electrodes material due to the extraordinary properties of graphene. This study demonstrates a magnetically enhanced dielectric barrier discharge that has the potential to efficiently exfoliate polyaniline-modified graphene at low input power. The plasma exfoliated N-doped graphene is subsequently used to fabricate flexible solid-state supercapacitors, which exhibit large specific capacitance of $45\,\mathrm{mF/cm^2}$ at $0.2\,\mathrm{A\,cm^{-2}}$ charging rate, ~100% capacitance retention after 1000 charge/discharge cycles at different current densities, and outstanding mechanical flexibility. The magnetically enhanced plasma exfoliation of graphite oxide offers a potentially cost-effective approach to producing high-quality carbon nanomaterials for energy storage.

1. Introduction

Portable and wearable electronics, such as smart watches, bendable displays, wearable sensors, artificial electronic skin, and implantable medical devices, have been explosively increasing in recent years. Flexible batteries and supercapacitors are the essential components in these devices [1–4]. Among the energy storage components, flexible supercapacitors exhibit attractive features, such as fast charge/discharge rates, high power density, and long operation life. Similar to conventional supercapacitors, flexible supercapacitors include symmetric and asymmetric flexible supercapacitors. The symmetrical supercapacitors present more stable performance because they use carbon-based electrode materials that can withstand the harsh electrolytes.

Carbon nanotubes, carbon fibers, and activated carbon have been extensively studied as the electrode materials in symmetric supercapacitors [5–7]. However, only limited capacitances of ~20% of the theoretical values were achieved [8]. Recently, it was found that polypyrrole, polyaniline and polythiophene [7,9,10] could improve the capacitance performance of carbon electrodes *via* a pseudocapacitive effect arose from the nitrogen element contained in these polymers [11–16]. On the other hand, graphene has been considered an excellent energy storage material owing to its outstanding mechanical strength, high electrical conductivity, large specific surface area, giant electron mobility, and high theoretical capacitance [17,18]. So far, a variety of methods have been developed to fabricate graphene,

including mechanical cleaving, epitaxial growth, chemical vapor deposition, tearing of carbon nanotubes, reduction of graphene oxide, and direct exfoliation of graphite [19–22]. Nevertheless, most of the methods involve high-temperature processes under high vacuum and are energy intensive with complex procedures.

Recently, plasma etching technology was reported in the preparation of highly efficient electrocatalysts for oxygen evolution reaction and water oxidation [23–26]. Meanwhile, a recent study indicated that graphite oxide (GO) could be rapidly exfoliated into graphene at room temperature by plasmas and supercapacitors made of CH_4 plasma exfoliated graphene displayed excellent capacitance performance [27]. Based on the optical emission spectroscopy analysis, the efficiency of GO exfoliation depended on the plasma density [27]. This effect could be understood from two aspects: 1) a higher plasma density leads to more negatively charged GO surfaces due to fast electron accumulation; and 2) a higher density plasma contains more reactive species (e.g. H^+ ions) that break the C-O-C bonds. In typical discharges, the plasma densities are proportional to the applied power and the loss of high-energy electrons accounts for an essential reason of limited plasma density. Therefore, reducing the loss of high-energy electrons and achieving high plasma density with low input power are expected to enable energy-efficient exfoliation of GO and subsequent low-cost energy storage devices.

This study aims to develop efficient plasma exfoliation of GO that can be subsequently used for flexible energy storage devices. The research includes a combined effort of the following three aspects: 1)

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establishing a magnetically enhanced dielectric barrier discharge (MEDBD) through modeling to create high-density plasmas; 2) plasma exfoliation of polyaniline-modified GO to obtain N-doped graphene; and 3) fabricating high-performance solid-state flexible supercapacitors using the plasma-exfoliated N-doped graphene.

2. Experimental and theoretical methods

2.1. Preparation of activated carbon

Graphite oxides were prepared by oxidizing of graphite with a modified Hummers' method. Graphite flakes (2.5 g, Fisher Scientific) were mixed with concentrated sulfuric acid (H_2SO_4, 75 ml, Fisher Scientific) under vigorous stirring at 0 °C for 4 h. Then, sodium nitrate ($NaNO_3$, 1.25 g, Fisher Scientific) and potassium permanganate ($KMnO_4$, 7.5 g, Fisher Scientific) were slowly added in sequence. After 12 h of reaction at room temperature, 25 ml deionized water was slowly added into the mixture and the temperature was increased to 98 °C before additional 75 ml deionized water was added. After 4 h, 7.5 ml hydrogen peroxide (H_2O_2, 30 $wt\%$ Fisher Scientific) was drop-wise added and yellow colloid was formed. Then, the mixture was transferred into a dialysis tubing (14,000 MWCO Daltons, Fisher Scientific) to dialyze in deionized water for 7 days till the pH was close to 7. The dialyzed sample was stored in a refrigerator and denoted in short for GO.

2.2. Preparation of aniline modified GO

Aniline ($C_6H_5NH_2$, 5 ml, Fisher Scientific) was dispersed into 15 mL ethanol, followed by adding 20 g GO colloid in a ball mill jar (100 mL). The mixture was grinded by a planetary ball mill (PMQW0.4 L, Nanjing Chishun Science & Technology Co., Ltd.) at 450 rpm for 30 min. Then, the grinded mixture was transferred into a petri dish (100 × 1 mm, Fisher Scientific) and dried naturally. The dried product was denoted as GO-PANi.

2.3. Preparation of aniline modified graphene

Aniline modified graphene was prepared using a magnetically enhanced dielectric barrier discharge system schematically illustrated in Fig. 1.The system consisted of a quartz container, a vacuum pump, a vacuum gauge, a mass flow controller, two copper electrodes (~2 × 2 cm) attached to the outside surface of the quartz container (inner surface distance: 2.5 cm), a set of magnets that generated a magnetic field of ~1500 Gauss parallel to the electrodes surfaces, and a 13.56 MHz RF power supply with a matching network. Modeling of the discharges and the resulting plasma characteristics will be discussed later. To prepare aniline modified graphene, 200 mg of GO-PANi was placed in the quartz tube in between the electrodes. Then, the system was evacuated down to ~10 mTorr and purged with the process gas (10% methane in Ar) for five times to ensure the residual air in the
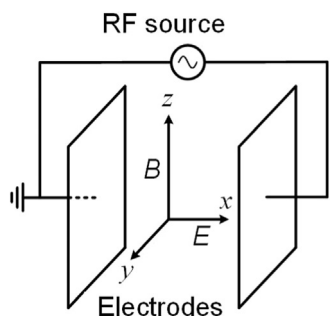

Fig. 1. The schematic diagram of the magnetically enhanced dielectric barrier discharge system used for producing the aniline modified graphene.

tube was negligible. After that, the gas pressure was set to ~80 mTorr by adjusting the mass flow controller. Then the RF power was turned on, starting with 20 W input power, and the matching network was tuned to achieve almost zero-watt reflection power. The RF power was then gradually increased to 45 W, at which the GO-PANi was exfoliated. After the exfoliation, the RF power was turned off and the vacuum system was vented to collect the exfoliated sample denoted as r-GO-PANi-CH_4. It was worth noting that exfoliating of GO-PANi in CH_4 plasmas at the same 80 mTorr pressure would require a much higher RF power of 120 W if no magnetic field was applied.

2.4. Preparation of flexible supercapacitors

Carbon cloth (MPL Carbon Cloth, Fuel Cell Earth) that served as current collector was cut into 2×1 (length × width) cm^2 pieces and cleaned by alcohol, acetone, and distilled water in turn. After that, slurry of the electrode materials made of r-GO-PANi-CH_4, acetylene black and PTFE with a mass ratio of 8:1:1 was pressed onto the carbon cloth; the carbon electrode area was 1 × 1 (length × width) cm^2. The electrodes were subsequently dried in an oven at 60 °C for 12 h. PVA-H_2SO_4 electrolyte was prepared by mixing 2 g of poly vinyl alcohol (PVA) powder and 2 g concentrated sulfuric acid with 20 mL of DI water. The mixture was subsequently heated to 100 °C under vigorous stirring until the solution became clear. The prepared electrodes were immersed into the gel electrolyte for 10 min and then put into a fume hood for 24 h to allow the electrolyte to cure into solid. Then, two of the electrodes were pressed together with the edges sealed by silicon glue. For convenient measurements, metal wires were connected to the electrodes with conductive silver paste.

2.5. Physical characterization

The microstructures of the samples were characterized by X-ray diffraction (XRD) (Rigaku Smartlab, Rigaku Americas, Inc. USA). The morphologies of the plasma exfoliated graphene were confirmed by transmission electron microscopy (TEM) (JEM-2200FS, JEOL, Japan) at an acceleration voltage of 200 kV. Raman spectra were obtained on a Horiba LABRam confocal Raman system with an excitation wavelength of 532 nm from a diode pumped solid-state laser. X-ray photoelectron spectroscopy (XPS) was performed on an SSX-100 system (Surface Science Laboratories, Inc.) equipped with a monochromated Al K_a X-ray source. An optical spectrometer (FLAME-T-XR1-ES, Ocean Optics, Inc. USA) was used to record the plasma emission spectra.

2.6. Electrochemical characterization

Electrochemical measurements, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were conducted on an Autolab electrochemical work station (PGSTAT128N, Metrohm). The galvanostatic charge/discharge tests were performed on a battery test system (BTS series, NEWARE, China).

2.7. Modeling of magnetically enhanced dielectric barrier discharges

A fluid plasma model was developed to verify the effects of the magnetic field and guide the design of the magnetically enhanced dielectric barrier discharge. The model was equivalent to a parallel plate dielectric barrier discharge. Hence, a one-dimensional model was valid. N_2 gas was used in the model to demonstrate the effects of the magnetic field and avoid unnecessarily complicated chemical reactions in the plasmas. The details of the modeling process are described in S1 section in the Supplementary document.

The above models of plasma discharges with and without a magnetic field were established in a commercial software COMSOL [28]. The species considered in the nitrogen plasmas were electrons, N_2^+, N_2^*, N^+ and N. where N_2^* was an equivalent excited state of N_2