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Paper-like N-doped graphene films prepared by hydroxylamine diffusion induced assembly and their ultrahigh-rate capacitive properties

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ABSTRACT

An approach as "hydroxylamine diffusion induced assembly" has been developed to fabricate N-doped graphene paper-like films (NG-P) and composite films containing multiwalled carbon nanotubes (NG-MWCNT-P). The obtained films have been characterized by using X-ray photoelectron spectroscopy, X-ray diffraction spectroscopy and scanning electron microscopy. The results indicate that the N atoms have doped into the graphene sheets and the interplanar distance between the graphene sheets decreases with the increment of the thermally treated temperature. The films of NG-P prepared at 100 °C are flexible and exhibit a maximum tensile stress of about 70.5 MPa and a Young's modulus of about 17.7 GPa, and the films of NG-P thermally treated at 300 °C (NG-P300) have high thermal conductivity of about 3403 W m^{-1} K^{-1}. However, the NG-MWCNT-P film exhibits a relatively weaker tensile stress compared with NG-P. The electrochemical measurements show that the NG-P300 possesses excellent ultrahigh-rate capacitive properties, and that the specific capacitance and the impedance phase angle of the capacitor can reach to about 318 μF cm^{-2} and -77.1° respectively at frequency of 120 Hz. Simple measurements on NG-MWCNT-P show that it has specific capacitance of about 90 F g^{-1} based on one electrode and the capacitor possesses the high-rate capability.

1. Introduction

Graphene, a kind of two-dimensional carbon material constructed by layers of sp^2-bonded carbon, exhibits applications in such fields as electronics [1], composite materials [2–5], catalysis [6,7], energy generation [8,9] and storage [10–12] owing to its extremely mechanical strength, exceptionally high electrical conductivity and thermal conductivities [13–15]. The graphene produced through chemically reducing graphene oxide (GO, obtained from graphite) is considered to be the simpler, more effective and inexpensive approach to achieve large-scale use [16] although methods of mechanical exfoliation, epitaxial growth and chemical vapor deposition [17,18] can be used to prepare high-quality graphene. However, chemically reduced GO (rGO) dissolved in water will occur an irreversible coagulation, which has blocked to fabricate bulk graphene-based materials from rGO.

Up to date, considerable efforts have devoted to prepare or assemble graphene micro-/nano-architectures in order to extend their applications. For example, graphene paper-like films have been prepared by two-step method: GO films are prepared by vacuum filtration or liquid-air assembly firstly, and then the GO films are reduced by reducing agent or thermal treatment [19–21]. However, the lack of a simple, general and technologically feasible route to produce graphene films with large area is still a major obstacle for large-scale applications. Besides the morphology control, chemical doping and etching are other effective approaches to tailor the properties of graphene and greatly expand the applications [22]. Among numerous potential dopants, N is considered to be an excellent element because of its comparable atomic size and five valence electrons available to form strong valence bonds with C atoms. Compared with the N-doping approaches performed under harsh conditions such as chemical vapor deposition, segregation growth, arc-discharge and plasma treatment [23–26], N-doped graphene synthesized by solution-phase process is considered to be the feasible approach due to its simplicity, low-cost and larger-scale production [27–29]. Hydroxylamine as N source possesses relatively lower toxic properties than the widely-used hydrazine hydrate [30], but it is rarely used as the chemical reductant and dopant to prepare N-doped graphene [31].

It is well known that GO can be considered as a kind of macromolecule with hydroxyl and epoxide functional groups on the basal plane, carbonyl and carboxyl groups at the edge [32,33].

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The dispersion of GO can be coagulated under the action of salt, acid, base and other reagents. For example, the oxygen-containing groups of GO can interact with reagents containing amine or hydroxyl groups to form precipitate or gel. Furthermore, two kind of liquids or solutions with different densities can not quickly blend when the heavy liquid is carefully injected into the bottom of the light liquid without stirring even if the both liquids are miscible, for example water and ethanol.

According to the above-mentioned factors, we can develop a feasible approach named as "hydroxylamine diffusion induced assembly (DIA)" to prepare N-doped graphene paper-like films in large scale. Using this process, the N-doped graphene films will be conveniently produced by directly injecting GO suspension into the bottom of ethanol solution of hydroxylamine, then the GO coagulate slowly to form shaped assembly at room temperature with the help of hydroxylamine flocculants, finally the desired N-doped graphene films are obtained after the evaporation of the solvent under heating. Up to the present, the researches on the ultrahigh-rate capacitive properties of paper-like graphene films are still rare [34–36] although many literatures have focused on their mechanic properties or use on substrates [2,19–21]. In this paper, the paper-like N-doped graphene (NG-P) films have been prepared through DIA process and the materials have been characterized and their capacitive properties have also been measured in detail.

2. Experimental

2.1. Materials

Natural graphite powder (325 mesh) was purchased from Tianjin Guangfu Research Institute. Hydroxylamine hydrochloride was obtained from Tianjin North Fine Chemical Co., Ltd., and all other chemicals were of analytical grade. GO was prepared by oxidizing the natural graphite powder according to the method reported in literatures [7,19], the GO dispersion was diluted to about 5.0 mg mL^{-1} and treated under the ultrasonication for 10 min before use. Hydroxylamine was generally prepared by reacting equal molar hydroxylamine hydrochloride with potassium hydroxide in ethanol solution and used instantly (see Supporting Information).

2.2. Fabrication of the NG-P films

Ethanol solution of hydroxylamine (300 mL, 0.5 mg mL^{-1}) was poured into a container (20.5 × 20.5 × 5 cm, length × width × height) containing a square glass plate with a thickness of 1.1 mm at the bottom. The container was placed into an oven and then adjusted to leveling, and 60.0 mL GO dispersion (5.0 mg mL^{-1}) was then injected into the bottom of the ethanol solution through a glass tube carefully. Subsequently, the container was placed for more than 6.0 h at room temperature, during which the GO sheets were assembled into gel slowly. The temperature of the oven was firstly increased to about 40 °C slowly and kept at this temperature for about 1.0 h. Subsequently, the temperature was raised to 100 °C and kept this temperature until the thickness of the solution in container was about 1.0 mm. The film of NG-P deposited on the glass was removed from the container and heated at 100 °C for 10 h after the solution was evaporated completely. Finally, the film was peeled from the glass substrate carefully and heated at 150 °C for 5 h and 300 °C for 2 h further, and washed by distilled water thoroughly. The samples as-prepared at 100, 150 and 300 °C were named as NG-P100, NG-P150 and NG-P300, respectively. The films of NG-P300 with different thickness were also fabricated by using the same process through controlling the concentration of the injected GO solution. For comparison, GO film was fabricated by using the air-solution assembly method according to literature [20], and then graphene film named as G-P300 was obtained by heating the GO film at 300 °C under nitrogen atmosphere.

2.3. Fabrication of the composite films of N-doped graphene and multiwalled carbon nanotubes (NG-MWCNT-P)

In order to verify the effectiveness of DIA for composites, the film of NG-MWCNT-P was prepared by using the similar process. Briefly, 100 mL ethanol solution of hydroxylamine (0.5 mg mL^{-1}) was poured into a container (10.5 × 10.5 × 5 cm, length × width × height) containing a square glass plate with a thickness of 1.1 mm at the bottom. The container was placed into an oven and then adjusted to leveling. Then 20.0 mL mixture of GO (4.0 mg mL^{-1}) and MWCNTs (1.0 mg mL^{-1}) was injected into the bottom of the ethanol solution through a glass tube carefully. After the layer of GO and MWCNTs has assembled and formed gel (standing for 6.0 h or long), the temperature of the oven was increased to 40 °C and kept this temperature for 2.0 h, the temperature was then increased to about 110 °C to evaporate most of the solvent. Successively the temperature was adjusted to 70 °C and kept at this temperature until the surface of the composite paper has become dried. The sample together with the glass substrate was carefully removed from the container and heated at 100 °C for 10 h. Finally, the composite film was peeled from the glass substrate carefully and heated at 150 °C for 5 h further, and washed by distilled water thoroughly. The samples prepared at 100 and 150 °C were named as NG-MWCNT-P100, NG-MWCNT-P150, respectively.

2.4. Characterization and Measurements

Atomic force microscopic (AFM) images were taken out using a Nanoscope III Multi Mode SPM (Digital Instruments) with an AS-12 ("E") scanner operated in tapping mode in conjunction with a V-shaped tapping tip (Applied Nanostructures SPM model: ACTA), and the images were recorded at scan rate of 2 Hz. The X-ray diffraction (XRD) patterns of the products were recorded on a Bruker D8 Advance X-ray diffraction meter with Cu Kα radiation and graphite monochromator at the scan speed of 5° min^{-1} with a step size of 0.02°. The morphologies of the samples were observed by using a JEOL-JSM-6701 field-emission microscope (SEM) operating at an accelerating voltage of 10 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCAL-ab 220i-XL spectrometer (VG Scientific, England) using a monochromic Al Ka source at 1486.6 eV. Mechanical tests were conducted with an electronic stretching machine (INSTRON test machine 5544). The samples were clamped by using the film clamps with a clamp compliance of about 0.2 μm N^{-1}. All tensile tests were performed in controlled force mode with a preload of 0.001 N and at a strain ramp rate of 0.2 mm min^{-1}. Tensile modulus is determined by fitting the stress-strain plot in the "elastic" regime with a straight line. The thermal conductivities of the samples were measured on a Netzsch LFA 447 nanoflash TM instrument at room temperature.

The fabrications of the capacitors were described as follows: two pieces of nearly identical (in weight and size) NG-P, G-P300 or NG-MWCNT-P were separated by a filter paper soaked with 1.0 M H_2SO_4 or 25% KOH aqueous solution. Before the electrochemical measurements, the slices of N-doped graphene materials were also immersed in electrolyte solution under vacuum in order to make the electrolyte exchange their interior. Two Pt foils were used as the current collectors. All the components were assembled into a sandwiched structure between the two plastic sheets and the structural scheme of the capacitor was showed in Fig. S1. Electrochemical performances of the cells were tested by cyclic voltammetry