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Synthesis of free-standing carbon nanohybrid by directly growing carbon nanotubes on air-sprayed graphene oxide paper and its application in supercapacitor

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ABSTRACT

We report the synthesis of a free-standing two dimensional carbon nanotube (CNT)-reduced graphene oxide (rGO) hybrid by directly growing CNTs on air-sprayed GO paper. As a result of the good integration between CNTs and thermally reduced GO film during chemical vapor deposition, excellent electrical conductivity (2.6×10^4 S/m), mechanical flexibility (electrical resistance only increases 1.1% after bent to 90° for 500 times) and a relatively large surface area (335.3 m^2/g) are achieved. Two-electrode supercapacitor assembled using the CNT–rGO hybrids in ionic liquid electrolyte (1-ethyl-3-methylimidazolium tetrafluoroborate) shows excellent stability upon 500 bending cycles with the gravimetric energy density measuring 23.7 Wh/kg and a power density of 2.0 kW/kg. Furthermore, it shows an impedance phase angle of −64.4° at a frequency of 120 Hz, suggesting good potentials for 120 Hz alternating current line filtering applications.

1. Introduction

Carbon nanotubes (CNTs) [1] and graphene [2] are new nanocarbon materials, which have high electrical conductivity [3,4] and outstanding mechanical properties [5,6], demonstrating great potentials in many applications [7–10]. CNT is a one-dimensional tube, while graphene is a two-dimensional nanosheet. Integration of CNTs and graphene (or its oxygen enriched derivative, graphene oxide, GO) may result in hybridized materials with better performances than their corresponding CNTs and graphene/GO alone. A number of CNT–graphene/GO composites or hybrids have been synthesized using solution processing methods, including in-situ polymerization [11], layer-by-layer self-assembly [12], direct blending [13] and co-electrodeposition [14]. The conductivities of the solution processed composites/hybrids are often unsatisfactory due to incomplete GO reduction, which results in insulating components and ineffective contacts between CNTs and graphene/GO. Alternatively, chemical vapor deposition (CVD) has been used to directly grow CNTs on graphene/GO to synthesize CNT–graphene/GO hybrids. In previous studies, metal catalysts were deposited on graphene/GO to enable efficient CNT growth. Several methods were used for metal nanoparticle deposition, including co-polymer template patterning [15], impregnation [16,17] or e-beam evaporation with Al_2O_3 as a buffer layer [18–20]. Alternatively, synchronous growth of CNT and graphene was reported on FeMgAl layered double oxide flakes [21]. Generally, CNT–graphene/GO hybrids synthesized using CVD methods have better electrical conductivity than those obtained using solution processing methods because of the improved contacts between CNTs and graphene/GO and a more efficient reduction of GO sheets under high temperature CVD [15,18]. However, these CVD synthesized hybrids are often fragile with poor mechanical properties. The addition of polymer elastomers, e.g. poly(dimethyl siloxane), is required to obtain twistable/bendable materials [15].

GO paper can be easily fabricated by stacking layers of GO sheets together [22]. It has exceptional stiffness and strength due to the intrinsic strength of individual GO sheets and the paper's interwoven layer structure [23]. On the other hand, it was reported that vertically aligned CNTs can be synthesized on SiO_2 substrates using a floating catalyst method [24]. By combining the strengths of these two processes, we have developed a new method to synthesize a free-standing two dimensional carbon nanohybrid by directly growing CNTs on air-sprayed GO paper in this study. The synthesis conditions at different metal catalyst precursor (ferrocene, $(Fe(Cp)_2)$ concentrations were optimized. The morphology, surface area, density, and chemical composition of the optimized

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hybrid were studied by a range of characterization techniques. In particular, the conductivity and mechanical flexibility of the hybrid were examined. The hybrids were used as electrodes to fabricate a two-electrode supercapacitor. The electrochemical performances of the assembled supercapacitor, especially its application potentials as flexible devices and 120 Hz alternating current line filtering, were evaluated.

2. Materials and methods

2.1. Synthesis of CNT–rGO hybrid

The CNT–rGO hybrid was synthesized in several steps as illustrated in Fig. 1. Graphite oxide was first prepared by the modified Hummers' method [25,26]. Graphite oxide was then washed with HCl (1 M) and deionized water, afterwards, exfoliated by bath sonication for 30 min. The resulting GO aqueous dispersion was centrifuged to remove large GO aggregates, and GO concentration was calibrated to 0.2 mg/mL. A piece of Cu foil (2×2 cm^2, 99.5%, 0.025 mm thick, Alfa Aesear) was used to support the deposition of GO paper. GO aqueous dispersion (5 mL) is air-sprayed using a spray gun (Badger 200, Badger airbrush Co.) on the Cu foil. After drying in an oven at 80 °C for 8 h, a uniform GO paper was formed. Next, the GO paper was placed in a quartz tube (1 in. in diameter). The quartz tube was heated up at 10 °C/min under Ar flow (50 sccm) to 760 °C, and annealed at this temperature for 10 min. GO would be thermally converted to rGO at this high temperature. $Fe(Cp)_2$ (99%, Sigma) was dissolved in toluene (HPLC grade, Fisher) at various concentrations of 0.5, 1.5 and 4.5 wt% as metal catalyst precursors to initiate CNT growth. The ferrocene solution (3 mL) at different concentrations was injected into the quartz tube with a constant rate of 0.2 mL/min at 760 °C together with a gas mixture of Ar and H_2 (4:1 at 250 sccm). CNTs were grown and anchored on the reduced GO paper. After cooling to room temperature in Ar, the free-standing CNT–rGO hybrid films were peeled off from the Cu foil. The Cu foil can be reused for GO paper deposition. Pure rGO paper obtained after heat treatment without CNT growth was also obtained as a control for characterization.

2.2. Physicochemical characterization

The morphologies of the hybrids synthesized at different conditions were first examined by scanning electron microscopy (SEM) on a field emission microscope (Joel, JSM-6700F) at 5 kV. Elemental analysis was conducted by energy-dispersive X-ray spectroscopy (EDX) on the hybrids synthesized at different $Fe(Cp)_2$ concentrations. The specific surface area (SSA) of the hybrids and rGO paper was determined by a methylene blue (MB) absorption method following the procedure described previously [27,28]. Briefly, MB was used as a probe molecule. When one MB molecule is adsorbed on graphic materials, it covers about 1.35 nm^2. The carbon material (2.5 mg) was added into a MB solution, which contains MB of the concentration equivalent to half of the amount required to cover the same weight of graphene solid (2630 m^2/g) [29]. After stirring at 300 rpm for 24 h, the carbon material was removed by centrifugation, and the MB concentration was determined by its absorbance at 664 nm. The change of MB quantity in the solution before and after adsorption was used to estimate the SSA of the carbon material. The carbonaceous composition of the hybrids and rGO paper was characterized by thermal gravimetric analysis (TGA) on a TG instrument (PerkinElmer diamond). For a typical test, about 2 mg of the hybrids (or rGO paper) was placed in an alumina pan. The sample was heated to 200 °C and held for 10 min under airflow (100 sccm) to remove moisture. Subsequently, its temperature was continuously raised from 200 to 900 °C at 10 °C/min rate under the airflow. The differential thermogravimetric (DTG) analysis was also conducted on the TG profiles. Raman spectroscopy was employed to validate the characteristics of the carbonaceous species identified in TGA. Raman spectra were recorded on a Renishaw inVia Raman spectrometer using a 514 nm laser. At least five different spots were measured for each sample, and an average of each sample was obtained.

2.3. Electrical conductivity and mechanical measurement

The electrical conductivities of the hybrids and rGO paper were measured using a probe station (Keithley 4200). The hybrids and rGO paper were cut into 10 mm long and 1 mm wide strips. Two copper electrodes were placed at different locations on the strips with a distance of 5 mm between one another. The voltage scan was applied from −0.8 to 0.8 V, and the current responses were recorded to calculate the conductivity (σ, S/m) by $\sigma = L/(RWT)$, where L is the distance between the two electrodes (5 mm), R is the resistance (Ω) measured between the two electrodes, W is the width of the strips (1 mm), and T is the thickness of the strips obtained by SEM. The strips were also bended around a glass tube of 1.2 mm in diameter to test the conductivity stability under mechanical deformation. The mechanical stress–strain curves of the strips were tested using a tensile testing machine (Instron 5543). Three strips were evaluated for each sample.

2.4. Supercapacitor assembly and performance tests

The free-standing hybrids were cut into 1.5×1.5 cm^2 size as electrodes (each electrode is about 0.6 mg). The supercapacitors in this study were comprised of two hybrid electrodes, a separator membrane (Nippon Kodoshi Co.), and ionic liquid electrolyte (1-ethyl-3-methylimidazolium tetrafluoroborate, EMIM-BF_4, Sigma). They were sandwiched and sealed between two layers of parafilm by a hot press in a glove box to isolate air and moisture. Due to the high conductivities of the hybrid electrodes, no metal current collectors are required. Instead, two hybrid strips were used to connect the supercapacitor to the clamps of an electrochemical workstation. The assembled supercapacitors were tested on the electrochemical workstation (CHI 660D). Electrochemical impedance spectroscopy (EIS) analysis was conducted on a potentiostat (VersaSTAT 4). The frequency was varied from 0.01 to 100,000 Hz with 10 mV amplitude, and the applied dc bias potential was at 0 V.

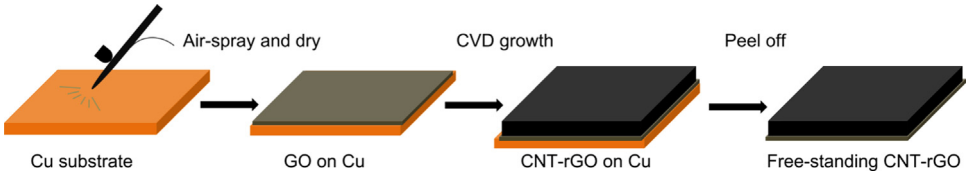

Fig. 1. A schematic illustration of the synthesis procedure of the CNT–rGO hybrids.