



Electrospinning fabrication and *in situ* mechanical investigation of individual graphene nanoribbon reinforced carbon nanofiber



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ABSTRACT

Graphene nanoribbons (GNRs) with opened edges and less structural defects are embedded in polyacrylonitrile (PAN)-based carbon nanofibers (CNFs) by electrospinning followed by stabilization and carbonization. GNRs not only can be used as one-dimensional nanofillers, but also act as nanoplatelet template to promote the formation of graphitic carbon in PAN matrix. X-ray diffraction, Raman spectroscopy and N₂ absorption are used to analyze the microstructure of GNR-reinforced CNFs. *In situ* tensile test using a micromechanical device inside a scanning electron microscope (SEM) is carried out to evaluate the mechanical performance of individual GNR-reinforced CNF. The tensile strength and elastic modulus of CNFs reinforced by 2 wt% GNRs with a diameter of ~160 nm are 3.52 GPa and 70.07 GPa, respectively, which are higher than those of pristine PAN CNFs with similar size, i.e. 2.44 GPa and 28.97 GPa. The rough fracture surface for all GNR-reinforced CNFs suggests that the GNRs can dramatically toughen the fibers. A sword-in-sheath failure is observed in 4 wt% GNR reinforced CNFs, confirming that GNRs are entirely embedded and well aligned along the fiber axis. This study demonstrates the potential of GNRs as a promising reinforcement to improve the formation of graphitic carbon and mechanical performance of CNFs.

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1. Introduction

Carbon nanofibers (CNFs) with high strength to weight ratio are one of the most successful commercialized carbon materials. Owing to their high mechanical strength, unique electrical and good thermal conductivity, CNFs have a wide range of applications, such as carbon based composites, protective textiles, field electron emission sources [1–6]. To date, melt spun [7], gel spun [8,9], and electrospinning [10–12] are generally used to produce CNFs with several popular polymer precursors including polyacrylonitrile (PAN), pitch, and rayon [13,14]. Specifically, the CNFs fabricated from PAN have higher a tensile and compressive strength than the fibers produced from rayon, due to the higher melting point and higher carbon yield of PAN (>50% of the original precursor mass) [14]. Moreover, PAN is much cheaper than pitch [13]. Therefore,

PAN, currently, is the main precursor to fabricate high-performance commercial CNFs [15–18].

For PAN-based CNFs, the mechanical properties of electrospinning nanofibers still do not reach the expectation due to the low crystallinity in preparation. Increasing heat treatment temperature in the steps of stabilization and carbonization can improve the degree of graphitization, further resulting in higher mechanical properties of CNFs [11,12,19–22], while high temperature undoubtedly will increase the product cost. An alternative effective way to improve the mechanical performance of CNFs is to incorporate nanoscale fillers into the polymer matrix, such as carbon nanotubes (CNTs), graphene oxides and graphene oxide nanoribbons (GONRs), which have been used for structural and mechanical reinforcement [2,5,8–10,15,23–27]. Generally it is believed that the dispersion of nanofillers and interactions between nanofillers and PAN matrix play critical roles in optimizing the reinforcement. For example, several covalent grafting methods including acid oxidation, polymer wrapping, and surfactant modified were developed to functionalize the surface of CNTs in order to improve the dispersion of CNTs in PAN and the interfacial

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interaction between two phases [7,9,24,25]. Another reinforcement, graphene oxide nanoribbons (GONRs) with a high length-to-width ratio, which can be longitudinally unzipped from CNTs by a chemical oxidation method. GONRs can provide a large interfacial area for π - π stacking in basal planes with polymer matrix and rich functional groups at the edges, such as carboxylic and hydroxyl groups, which can strongly link GONRs and the polymer matrix together [28,29]. Therefore, GONRs were used as an effective reinforcement in PAN-based electrospun carbon nanofiber yarns [8,10,27,30]. It should be noted that there are a number of structural defects and oxide-functional groups in GONRs, which will largely decrease the mechanical performance of GONRs. In contrast to GONR, graphene nanoribbons (GNRs) with similar opened edges, but less structural defects, which can be easily made from alkali metal intercalated CNTs, have not been investigated as reinforcement in PAN-based CNFs. According to previous reports [1,3,16], the tensile strength of CNFs strongly depends on the diameter. However, the influence of porosity, which acts as structural defects, on the mechanical behaviors of single CNF has not been studied.

Herein, we choose GNRs as one-dimensional nanofillers reinforcing PAN-based CNFs, which are longitudinally split from CNTs by alkali metals. The GNRs not only can be used as the mechanical reinforcement in PAN-based CNFs, but also act as nanoplatelet templates to promote the nucleation of graphitic domains in PAN matrix. We systematically studied the effect of GNRs on the graphitic crystallinity, specific surface area and porosity at different content. Moreover, we carried out *in situ* tensile tests in a scanning electron microscopy (SEM) to quantitatively measure the mechanical properties of individual GNR-reinforced CNFs. The effect of GNRs at different weight fraction and porosity of CNFs on the mechanical performance of individual CNF was studied as well. Our findings prove that GNRs are one of the most promising reinforcements to synthesize CNFs with high strength in a facile and scalable synthesis technique.

2. Experimental section

2.1. Materials

PAN (Mw = 150,000) was obtained from Scientific Polymer products. Inc. Analytical pure *N,N*-dimethyl formamide (DMF) was received from Chengdu KESHI Chemical Co. Ltd. The GNRs were prepared from CNTs with Na/K alloy by the method as described previously [29]. The layer number of GNRs is in the range of ~30–45, the width is ~100–200 nm and the length is ~3–5 μm .

2.2. Synthesis of GNRs reinforced CNFs

Before the step of electrospinning, PAN was completely dissolved in DMF to get 6 wt% PAN/DMF solution, then GNRs was added to the above solution at different weight fractions from zero to 4 wt% and then dispersed by tip ultrasonic vibration at 80 W for 20 min and continuously stirring at 250 rpm for 1 day at 298 K to obtain a homogeneous solution. We provide four pictures of the solution of PAN in DMF with 4 wt% GNRs at different time. As shown in Fig. S1, there is no precipitate out after dispersion even for three days, indicating that GNRs are homogeneously dispersed in the PAN/DMF solution. The electrospinning device was a horizontal type (Model DFS-L-01), which was provided by Beijing Tech-Nova technology co. Ltd. The obtained black solution was placed in a 5 mL syringe with a capillary tip in the diameter 1 mm. During the electrospinning, the nanofibers were collected on a high speed of 700 rpm rotating roller, which was covered with an aluminum foil. The applied voltage was 20 kV, the flow rate of solution was 1.2 mL h⁻¹, and the spinning distance between the tip and the

collector was 20 cm. All the electrospinning were carried out at 27 ± 2 °C and at less than 40% relative humidity.

Then the as-spun nanofibers were dried at 80 °C under vacuum for 12 h, followed by the stabilization at 300 °C for 3 h in air and carbonization at 850 °C for 3 h in nitrogen to produce the final GNRs reinforced CNFs.

2.3. Microstructure characterization

In order to analyze the effect of GNRs embedding in the microstructure, Raman spectra were examined on a micro-Raman spectroscopy (LabRAM HR Evolution) using 532 nm incident radiation. X-ray diffraction (XRD) patterns were recorded on DMSX-2500 PC X-ray spectrometer with Cu K α radiation ($\lambda = 1.5406$ Å) at a scanning speed of 4° min⁻¹. The specific surface area and the pore structure of the samples were examined by nitrogen adsorption measurements (Belsorp Mini) at 77 K. The morphology was observed by field emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM, LIBRA 200 FE at 200 kV).

2.4. Mechanical characterization

The as-synthesized CNFs were first loaded onto a piece of silicon wafer with 20 nm Au on surface. The silicon wafer together with CNFs was placed under an optical microscope equipped with an objective lens (20 \times) and an eyepiece (15 \times). Generally, the nanofibers with diameter of 60–80 nm are barely seen, while those with diameter ~100 nm can be easily located and picked up with a fine tungsten probe (The Micromanipulator Co. Model: 7A) which is installed to a mechanical arm operated by hand. The weak van der Waals force makes it possible to attach individual CNF to the probe. To load a CNF onto the micromechanical device, the CNF should rub against the device several times, then the CNF came off and laid across the gap. The alignment of the CNFs can be tuned by slightly pushing the end of CNF. The CNFs with different diameters were placed onto the micromechanical devices with good alignment. Both ends of CNF were anchored onto the device shuttle with two drops of epoxy. In case of the epoxy flowed over the CNF, the epoxy was cured 15 min at ambient condition before use. The micromechanical device together with CNF was attached onto an aluminum stub using crystal bond (a commercial wax). The tensile test of an individual CNF was conducted in a SEM (FEI Quanta 400, FEI). A quantitative Agilent in SEM nanoindenter was used to actuate the device and also to measure the load and displacement independently. The fracture surfaces of all tested CNFs were examined after mechanical failure.

3. Results and discussion

Fig. 1 displays a schematic diagram for the preparation of GNRs reinforced CNFs using an electrospun method. The GNRs were prepared through splitting CNT by alkali metal (Na/K) source [29]. The obtained GNR had integral graphitic structures, active carboanionic edges and less defects.

The GNRs and PAN were then dissolved in *N,N*-dimethylformamide (DMF) to form a homogeneous solution, as shown in Fig. S1. The GNRs can act as nanoplatelet templates to promote the formation of graphitic carbon in vicinity of PAN matrix. Then nanofibers were electrospun on a high speed rotating roller with a 1.2 mL h⁻¹ feed rate at 20 kV. Subsequently, the nanofibers were stabilized in air at 300 °C for 3 h and further carbonized in nitrogen at 850 °C for 3 h to finalize GNRs reinforced CNFs.

SEM, TEM and Raman were used to analyze the microstructure of GNRs-reinforced CNFs in detail (Fig. 2). The TEM image of

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