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Ultra-high toughness all graphene fibers derived from synergetic effect of interconnected graphene ribbons and graphene sheets

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ABSTRACT

Here, we report a novel strategy for the synthesis of ultra-high toughness all graphene fibers using highly interconnected graphene ribbons (IGRs) and graphene sheets. Due to their interconnected structure and the synergistic effect of graphene ribbons and sheets, the graphene hybrid fiber shows moderate strength of 223 MPa, higher than those of previously reported graphene fibers without adding any other noncarbonous materials. More importantly, the graphene hybrid fiber exhibits an ultra-high toughness of 30 MJ m^{-3}, much higher than those of graphene fiber (0.7 MJ m^{-3}), previously reported graphene based fibers (<22 MJ m^{-3}) and natural nacre (1.8 MJ m^{-3}). The findings from the present study shed fundamental insight on the design of interconnected ribbon strategy addressing the conflict between strength and toughness in graphene materials.

1. Introduction

Graphene, a two-dimensional (2D) monolayer of sp^2-hybridized carbon atoms in a honeycomb lattice, has attracted considerable attention in recent years because of their remarkable electronic, mechanical, and thermal properties [1]. It is well known that graphene acts as the basic building block of all the graphitic carbon materials, therefore, it is crucial for the integration of unique properties of individual 2D nanosheets into macroscopic structures for practical applications, such as 1D fibers [2], 2D films [3,4], and 3D foams [5,6]. Recently, the assembly of 2D graphene nanosheets into 1D continuous graphene fiber is easily achieved by wet spinning of graphene oxide (GO) liquid crystal phases [7–9], dimensionally-confined hydrothermal strategy [10,11], and direct drawing of graphene film [12]. Usually, the irregular shapes and the limited dispersibility of GO, have a significant influence on the microstructures of graphene fibers such as defects, interfacial interaction between graphene sheets, and alignment along a fiber axis direction [13]. Therefore, the strength of as-obtained fibers are rather lower than expected theoretical strength of graphene [14]. To address such a fundamental issue, many efforts have been made to improve the mechanical properties of graphene fibers by chemical cross-linking [15,16], polymer coatings [17], and introducing shear stress on GF [18], as well as using large flake GO [16,19]. Therefore, there are a lot of opportunities in further adjusting the fiber structure, tailoring properties, and exploring new assembling method [2,13]. However, most of these fibers are assembled by 2D graphene nanosheets without adding any other noncarbonous materials *via* strong π-π interaction between each other, their ultimate strain (<3%) and toughness (<5 MJ m^{-3}) of pure graphene fibers are rather low [20,21]. If well designed and tailored graphene fiber with high strength and high toughness, those materials can offer new platforms for a wide range of applications.

To solve this problem, here, for the first time, we report a novel strategy for the synthesis of ultra-high toughness all graphene fibers using highly interconnected graphene ribbons (IGRs) and graphene nanosheets (GNs). Compared with pure graphene fibers, graphene ribbon and sheet hybrid fibers exhibit both higher strength and toughness due to their interconnected structure and the synergistic effect of ribbons and sheets. More interestingly, the as-prepared GN-IGR fibers exhibit both ultra-high ultimate elongation of 22% and toughness of 30 MJ m^{-3}, about 15 and 30 times higher than those of graphene fibers, respectively, superior to those for any other graphene fibers and films currently available [2,22–24].

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2. Experimental

2.1. Synthesis of interconnected graphene oxide ribbons (IGORs)

Graphene oxide (GO) was prepared from natural graphite flakes by a modified Hummers' method as previously described [25]. 100 mL GO suspension (1.0 mg mL^{-1}) was transferred into a spray, and the microdroplets were sprayed into plastic box filled with liquid nitrogen. After that, the as-obtained ice was melt and concentrated to 1.0 mg mL^{-1} IGOR dispersions. For comparison, GO suspensions with different concentrations (0.1, 0.3 and 0.5 mg mL^{-1}) were also used to prepare interconnected GO under the same conditions.

2.2. Preparation of graphene fibers

At first, 8 mL GO suspension (1.0 mg mL^{-1}) was added into 72 mL of IGOR suspension (1.0 mg mL^{-1}). After ultrasonic treatment for 30 min, the suspension was concentrated to 8.0 mg mL^{-1} at 40 °C. Then, the as-obtained IGOR-GO suspension was injected into a silica capillary (0.4 mm inner diameter) by using an injection pump [10]. After sealing up the two ends of the glass pipeline, the glass pipeline as a hydrothermal reactor was heated at 230 °C for 2 h. Finally, the wet fiber was dried in air for 12 h, and named as GN-IGR fiber. For comparison, pure GN fiber and IGR fiber were also prepared under the same conditions.

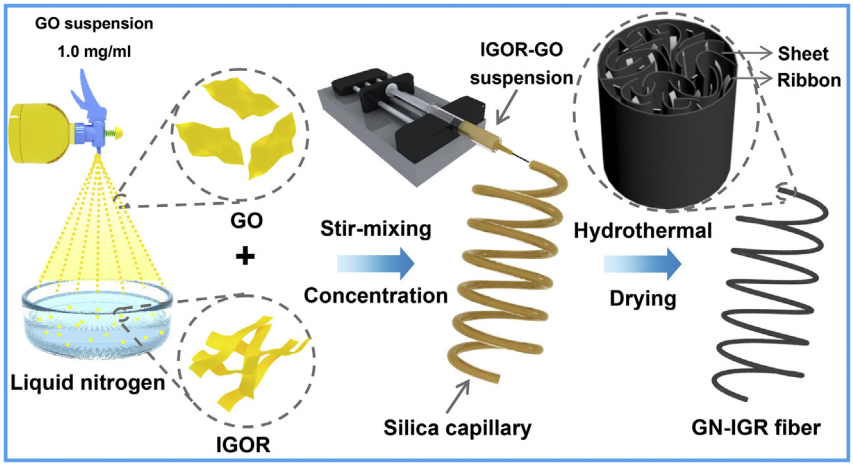
2.3. Characterizations

The morphology of the powders and fabricated fibers were examined by scanning electron microscopy (SEM, SU70-HSD) and transmission electron microscopy (TEM, Tecnai F20). XRD patterns were recorded on a Rigaku TTR III X-ray diffractometer at 40.0 kV and 20 mA with Cu Kα radiation (λ = 0.154 nm). Raman spectra were conducted on a Jobin-Yvon HR800 Raman spectrometer with 532 nm wavelength incident laser light. The tensile properties of the GN, IGR and GN-IGR fibers were measured for 5 samples for each fiber using a tensile tester (Shimadzu AGS-X) at a strain rate of 1 mm min^{-1} with a gauge length of 5 mm. All of the samples for the tensile test were cut into the fibers with length of 20 mm. The diameters of the fibers were measured by SEM observation. All data were collected as the failure occurred at the middle region of the testing fibers. Electrical properties tests were measured by CHI660E electrochemical workstation.

3. Results and discussion

Interconnected graphene ribbons (IGOR) was prepared by a "spraying-rapid freezing" approach (Scheme 1 and See Experimental section) as reported by our previous work [26]. Scanning electron microscopy (SEM) images of the IGORs show the interconnected ribbon network. Simultaneously, there are some wrinkles on the basal plane of ribbons due to the shear stress between the ice crystals and GO sheets (Fig. 1a). TEM image further confirms the interconnected structure of the IGORs (Fig. 1b). It is worth noting that the concentration of GO suspension has a great effect on the microstructures of the assembly. For example, the GO nanosheets are easily assembled to nanoscrolls due to the shear stresses or uneven surface tension induced by the evaporation of the solvent [27], when the GO concentration is less than 1.0 mg mL^{-1} (Fig. 1c–e). With an increasing GO concentration up to 1.0 mg mL^{-1}, GO exhibits a ribbon-like structure (Fig. 1a). It may be due to the reason that ice crystals with ultrafast growth rate can pierce into the surface of GO sheet, and subsequently cut the sheet into ribbons by the edge of ice pillars during the growth of ice crystals [26]. Moreover, the distribution of GO nanosheets is very complex in the liquid drops, GO sheets are separated, interconnected and stacked, resulting in the formation of the ribbons with different modes after "spraying-rapid freezing" process, such as knot (Fig. 1f), twine (Fig. 1g), and buckling (Fig. 1h).

After confined-hydrothermal treatment of IGORs suspension, the as-obtained IGRs fiber has a diameter of 43 ± 3 μm (Fig. 2a and Fig. S1). The as-prepared fibers can be easily tied into a knot or twisting (Fig. S2), demonstrating their excellent flexibility. It is worth mentioning that the buckled graphene ribbons each other are assembled along the axial direction (Fig. 2b and c). Moreover, the surface of the IGR fiber displays tortuous and wrinkled structure constructed by interconnected graphene ribbons (Fig. 2c), which is beneficial for the enhanced ductibility at high stress. IGOR suspension was injected into a silica capillary using an injection pump, GO ribbons easily arranged along the axial direction of the capillary. It can be clearly seen that bunched graphene ribbons have a width of 200 nm (Fig. 2c, marked by parallel dotted lines). Whereas, the surface of the GO derived fiber (GN fiber) exhibits densely stacked graphene sheets (Fig. S3). When GO is incorporated into the IGR fiber, the GN-IGR fiber seems denser than that of IGR fiber due to the consolidation of the ribbons by graphene sheets (Fig. 2d). Further SEM images of GN-IGR fiber confirm that the bunched ribbons are embedded into sheets (Fig. 2e, f and Fig. S4),



Scheme 1. Graphical illustration for the formation process of graphene sheet/ribbon hybrid fibers.