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RAPID COMMUNICATION

Scalable non-liquid-crystal spinning of locally aligned graphene fibers for high-performance wearable supercapacitors

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Abstract
One-dimensional graphene fibers have attracted increasing interests due to their extraordinary mechanical strength, electrical conductivity and flexibility compared with two-dimensional graphene films/papers and three-dimensional foams/hydrogels/aerogels. Here, we developed a scalable non-liquid-crystal spinning process for the production of continuous graphene fibers with tailored structure for high-performance wearable supercapacitors. These fibers possessed surfaces with bark-like fine microstructure and different shaped cross-sections with locally aligned dense pores, depending on the jet stretch ratio (***R***) during spinning. Owing to this unique structure facilitating the access to, and diffusion of electrolyte ions, the specific capacitance reached 279 F g^{-1} (340 F cm^{-3}) at a current density of 0.2 A g^{-1} (0.244 A cm^{-3}) in 1 M H_2SO_4 when $R=1.0$. A flexible solid-state fiber supercapacitor assembled from these fibers showed a specific capacitance and energy density of 226 F cm^{-3} and 7.03 mWh cm^{-3} at 0.244 A cm^{-3}, respectively. We further demonstrated the proof-of-concept of wearable energy-storage by sewing three solid-state yarn supercapacitors in series into a textile, which was able

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to power a light-emitting diode for more than 5 min after being charged. This non-liquid-crystal spinning strategy could be extended to the assembly of other two-dimensional nanomaterials into macroscopic fibers for applications in micro-devices, wearable electronics and smart textile.

Introduction

Graphene materials have attracted considerable attention from scientists and engineers, owing to their ultrahigh specific surface area, extraordinary mechanical, optical, electrical and thermal properties, together with their scalable low-cost production from natural graphite [1]. They have promising applications in energy storage devices [2–7], electronic components [8,9], functional nanocomposites [10–12], water treatment [13,14], hydrogen storage [15,16], etc. In most of these cases, graphene materials are used in the macroscopic forms of powders/particles [15,16], two-dimensional (2D) coatings/films/papers [2,3], or three-dimensional (3D) gels/foams [5,6,14], while one-dimensional (1D) macroscopic fibers of graphene were not reported until 2011 [17,18]. Graphene fibers are flexible, have high mechanical strength and electrical conductivity, and exhibit processing versatility [17,19,20]. Just like carbon fibers, they could be processed by twisting, weaving and knitting into light and flexible ropes, belts, fabrics and even 3D scaffolds. Similar to carbon nanotube (CNT) fibers [21], which have been widely explored in micro-/wearable energy devices [22–25], sensors [26,27] and actuators [28,29], graphene fibers would extend the capabilities of graphene in these fields, and could provide better performance [30,31] at a lower cost due to the significantly higher specific surface area of graphene.

Efforts have been devoted to prepare graphene fibers for miniature and wearable energy-storage applications, including the drawing assembly of graphene films [18], hydrothermal assembly of a graphene oxide (GO) dispersion in a pipeline or capillary column [20,32], and wet-spinning assembly of a liquid-crystal (LC) GO dispersion in water followed by reduction [17,19,33–35]. Among these, wet-spinning is the most scalable way to produce continuous long graphene fibers, yet it faces two challenges. The first one is to achieve a simple continuous spinning process compatible with industrial production. The continuous production of GO fibers is crucial for achieving uniform quality (e.g., the diameter and profile of their cross-section) and large-scale application. Because of the low concentration of a GO dispersion necessary for spinning [17,19,34], a large amount of water remains in wet GO fibers, leading to adhesion between the fibers after drying, which is a big issue for the production of bobbins of graphene fibers. The second challenge is the effective control of the structure of graphene fibers for high-performance energy-storage application. It is the surface morphology and inner structure that determine the mechanical, electrical and especially electrochemical performance of graphene fibers. For example, an all-graphene core-sheath fiber, prepared by deposition of electrochemically reduced GO on the surface of a hydrothermally assembled GO fiber, shows a significantly higher capacitance than the pristine core fiber due to the large exposed surface area of the 3D-porous sheath [30]. Though conventional LC spinning can produce long graphene fibers, they often have a coarse surface with extended, slightly wrinkled, hydrophobic RGO sheets [17,33], and have a cross-section composed of compactly stacked, folded RGO sheets [19,33,34]. These structural characteristics are detrimental to the capacitive performance because of their poor affinity to aqueous electrolytes and the limited electrolyte ion diffusion inside those fibers [31]. In order to avoid this disadvantage, various fillers, such as CNTs and MoS_2, have been introduced to inhibit the restacking of RGO sheets and to create porous structures, resulting in hybrid fibers with enhanced specific capacitance but lower mechanical strength and higher costs [32,36,37]. To the best of our knowledge, simultaneous control of the surface morphology and internal structure of unfilled neat graphene fibers for high-performance wearable supercapacitors in a continuous spinning process has not been achieved to date.

Here we report a simple, scalable non-liquid-crystal (NLC) spinning method for the production of continuous RGO fibers with tunable structure for wearable supercapacitors. The resulting fibers possessed a macroscopic smooth surface with a willow-bark-like fine microstructure and a tunable pore structure with locally aligned RGO sheets over the radial plane, which could favor the access to, and fast diffusion of electrolyte ions. Owing to this unique structure, these undoped all-graphene fibers demonstrated excellent electrochemical performance compared with either neat or hybrid graphene fibers and CNT hybrid fibers prepared by conventional methods.

Experimental section

Preparation of RGO fibers

Graphite oxide was prepared by the oxidation of colloidal graphite with an average size of around 2 μm (Shanghai Yifan Graphite Co. Ltd) using the Hummers' method [38]. The weight ratio of graphite:$NaNO_3$:$KMnO_4$ was 1:1:5 and the oxidation time was 5 h. Graphite oxide (2 g) was added to deionized water (98 g) and sonicated for 1 h at an output power of 20 W using a digital ultrasonic processor (S-450D, Branson). The resulting 2 wt% dispersion was centrifuged at 5000 rpm for 10 min to remove unexfoliated particles. The supernatant with a pH value of 2 became more viscose after being left stationary for 6 h, and is denoted as the pristine