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Wet-spinning of multifunctional graphene fibers using graphene oxide liquid crystals

Rouhollah Jalili

University of Wollongong, rjalili@uow.edu.au

Seyed Hamed Aboutalebi

University of Wollongong, sha942@uowmail.edu.au

Dorna Esrafilzadeh

University of Wollongong, dornae@uow.edu.au

Roderick L. Shepherd

University of Wollongong, rods@uow.edu.au

Jun Chen

University of Wollongong, junc@uow.edu.au

See next page for additional authors

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Wet-spinning of multifunctional graphene fibers using graphene oxide liquid crystals

Abstract

The recent discovery of liquid crystalline (LC) behavior of graphene oxide (GO) dispersions in various organic, and aqueous media brings added control to the assembly of larger structures using the chemical process approach.[1-3] The LC state can be used to direct the ordered assembly of nanocomponents in macroscopic structures via simple methods like wet-spinning.

Keywords

multifunctional, fibers, spinning, oxide, wet, liquid, crystals, graphene

Disciplines

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Authors

Rouhollah Jalili, Seyed Hamed Aboutalebi, Dorna Esrafilzadeh, Roderick L. Shepherd, Jun Chen, Sima Aminorroaya-Yamini, Konstantin Konstantinov, Andrew I. Minett, Joselito M. Razal, and Gordon G. Wallace

Wet-Spinning of Multifunctional Graphene Fibers Using Graphene Oxide Liquid Crystals

Rouhollah Jalili¹, Seyed Hamed Aboutalebi², Dorna Esrafilzadeh¹, Roderick L. Shepherd¹, Jun Chen¹, Sima Aminorroaya-Yamini², Konstantin Konstantinov², Andrew I. Minett³, Joselito M. Razal¹, and Gordon G. Wallace¹

¹Intelligent Polymer Research Institute and ARC Centre of Excellence for Electromaterials Science; ²Institute for Superconducting and Electronic Materials, AIIM Facility, Innovation Campus, University of Wollongong, North Wollongong, NSW 2522; ³Laboratory for Sustainable Technology School of Chemical and Biomolecular Engineering, University of Sydney, Sydney NSW 2006 Australia

gwallace@uow.edu.au; rjalili@uow.edu.au

INTRODUCTION

The recent discovery of liquid crystalline (LC) behavior of graphene oxide (GO) dispersions in various organic, and aqueous media brings added control to the assembly of larger structures using the chemical process approach.^[1-3] The LC state can be used to direct the ordered assembly of nanocomponents in macroscopic structures via simple methods like wet-spinning.^[3]

Here, we developed a scaleable fabrication route to produce graphene fibers via a facile continuous wet-spinning method. We develop solid understanding in the required criteria to correlate processability with LC behavior, aspect ratio and the dispersion concentration to provide a viable platform for spinning of LC GO. We demonstrate a striking result that highlights the importance of GO sheet size and polydispersity in generating wet-spinnable LC GO dispersions from very low spinning dope concentrations (as low as 0.075 wt. %). The new knowledge gained through rheological investigations provides a sound explanation as to why continuous spinning of binder-free GO fibers is enabled by the LC behavior at this very low concentration.

EXPERIMENTAL

Wet-spinning experiment was involved injecting LC GO dispersion into a coagulation bath to produce the gel-state GO fiber. Dried GO fibers were obtained by washing the gel-state GO fibers with water, then 25 vol. % ethanol or acetone and then air-drying the fiber under tension at room temperature. Reduction of GO fibers (rGO) was carried out by overnight annealing at 220 °C under vacuum.

RESULTS AND DISCUSSION

Based on our previously described GO synthesis protocols^[2] and completely eliminating the sonication previously deemed necessary in the complete exfoliation of GO sheets, we have produced ultra-large GO sheets with lateral size of up to ~100 μm (Figure. 1). SEM survey of GO sheets confirmed that the majority of the lateral GO sheet sizes are in the tens of micrometers domain with an average lateral sheet size of 37 μm.

Aqueous GO dispersions at concentrations ranging from 0.10 to 5.00 mg ml⁻¹ were examined using polarized optical microscopy and displayed that nematic phase start to form at GO concentrations close to 0.25 mg ml⁻¹.

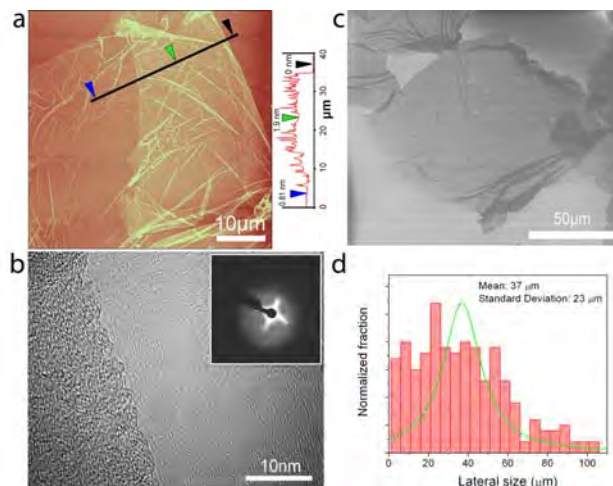


Figure 1. As-prepared GO dispersions predominantly contain giant monolayer GO sheets. (a) AFM image of a large GO sheet with lateral size >75 μm. Inset shows the height profile derived from the marked line in the AFM image showing monolayer GO sheet thickness of ~0.81 nm. (b) High-resolution TEM image of monolayer GO sheet and the corresponding electron diffraction pattern (inset). (c) Representative SEM images of GO sheets present in as-prepared GO dispersions contain GO sheets with lateral size as large as 100 μm, (d) The corresponding lateral size distribution of GO sheets (the diameter of an equal-area circle).

Below 0.25 mg ml⁻¹, GO dispersions were completely isotropic and un-spinnable (i.e. GO sheets simply spread into the coagulation bath). At higher concentration (between 0.25 to 0.75 mg ml⁻¹), transition of biphasic to fully nematic phase is observed (i.e. when isotropic and nematic phases co-exist). This biphasic concentration range only demonstrated partial spinnability in fiber spinning processes. This partial spinnability is characterized by the weak cohesion of the GO dispersion upon injecting in the coagulation bath, which resulted in short lengths of gel-state GO fibers. Also observed in this concentration range is that the nematic phase volume fraction (ϕ_{nem}) increased with GO concentration. Using GO concentration of ≥ 0.75 mg ml⁻¹, when fully nematic phase forms, in fiber wet-spinning resulted in long lengths of robust gel-state fibers. GO concentrations of 0.75 mg ml⁻¹ to 5 mg ml⁻¹ showed similar ease of spinnability by following coagulation methods: non-solvent precipitation,

dispersion destabilization using acid, base or salt solutions, ionic cross-linking using divalent cations, and coagulation by amphiphilic or oppositely charged polymers.

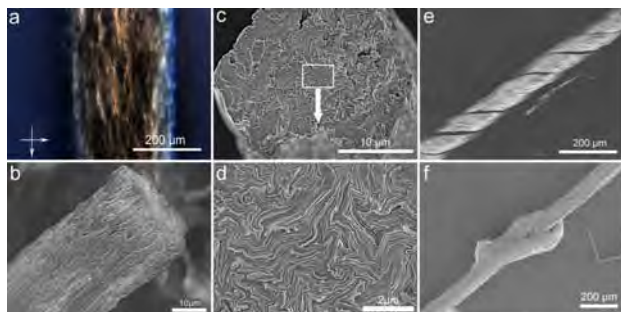


Figure 5. (a) Polarized optical micrograph of as-spun gel-state GO fiber showing birefringence. Birefringence properties confirmed ordered LC domains were formed and preserved during spinning process (arrows show polarizers direction). SEM images of an as-spun GO fiber showing (b) Corrugated surface and (c) Near-circular cross-section. (d) Close-up SEM image of the cross-section of GO fiber shown in b revealing GO sheet planes that are oriented along the fiber axis. (e-f) SEM images of crumpled and knotted rGO yarns showing their flexibility.

As-spun GO fibers prepared by ionic cross-linking and polyionic complexation (using the positively charged polymer, chitosan) displayed the highest mechanical properties with Young's modulus (E), ultimate strength (δ) and toughness (T) of 22.6 ± 1.9 GPa, 442 ± 18 MPa and 4.8 J g^{-1} , respectively. Apart from chitosan, coagulation in CaCl_2 which exploits ionic cross-linking using divalent cations (Ca^{2+}) also resulted in fibers with extraordinary mechanical properties ($E = 20.1 \pm 2.1$ GPa, $\delta = 412 \pm 30$ MPa and $T = 4.8 \text{ J g}^{-1}$). The best as-spun GO fiber strength (~ 442 MPa) is higher than previously reported GO and rGO -based materials such as GO papers (~ 120 MPa),^[4] RGO/PVA fibers (~ 120 MPa),^[5] LC GO fibers (~ 102 MPa),^[6] stretched "ultrastrong" GO fibers (364 MPa),^[7] fibers produced from graphene nanoribbons (378 MPa),^[8] hydrothermally converted rGO fibers (~ 180 MPa) and thermally reduced rGO fibers (420 MPa).^[9] In terms of modulus, the GO fiber (22.6 GPa) is inferior to the highest modulus of GO paper (42 GPa)^[4] and fibers produced from graphene nanoribbons (36.2 GPa),^[8] but the difference in breaking strain is substantial (3.2 % for GO fiber vs. ~ 0.4 % for GO paper and 1.1% for fibers produced from graphene nanoribbons) resulting in toughness (4.8 J g^{-1}) considerably higher than both.^[4, 8] The strength of as-spun GO fiber is also much higher than single yarns of pure multi-walled CNTs (~ 250 MPa).^[10] It should be noted that the GO used in this study is much larger compared to "giant GO"^[7] ($37 \mu\text{m}$ in this study vs $18 \mu\text{m}$), which is the basis of the enhanced improvement

in mechanical properties attained in the current study. Although this reduction method was effective as evidenced by increase in the electrical conductivity ($\sim 250 \text{ S m}^{-1}$), the mechanical properties were found to be lower compared to the parent GO fiber.

CONCLUSION

The promising properties of GO and rGO fibers presented here are potentially applicable in many specialized technical applications. Fundamental understanding of the GO dispersion chemistry and rheology, the associated fiber spinning processes, and the resultant material properties, presented here along with one-step production of rGO fibers will provide scope for the development of next generation advanced GO/rGO-based fiber architectures and associated technologies. The simplicity and the scalability of the processes described here will enable safe and cost-effective large-scale production of GO/rGO fiber to find a place in the smart fiber industry (i.e. fibers that integrate applications in energy, environmental monitoring and biomedical engineering).

KEYWORDS

Graphene oxide, liquid crystal, fiber, multifunctional textiles

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