Self-Planarization of High-Performance Graphene Liquid Crystalline Fibers by Hydration

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ABSTRACT: Graphene fibers (GFs) are promising elements for flexible conductors and energy storage devices, while translating the extraordinary properties of individual graphene sheets into the macroscopically assembled 1D structures. We report that a small amount of water addition to the graphene oxide (GO) N-methyl-2-pyrrolidone (NMP) dispersion has significant influences on the mesophase structures and physical properties of wet-spun GFs. Notably, 2 wt % of water successfully hydrates GO flakes in NMP dope to form a stable graphene oxide liquid crystal (GOLC) phase. Furthermore, 4 wt % of water addition causes spontaneous planarization of wet-spun GFs. Motivated from these interesting findings, we develop highly electroconductive and mechanically strong flat GFs by introducing highly crystalline electrochemically exfoliated graphene (EG) in the wet-spinning of NMP-based GOLC fibers. The resultant high-performance hybrid GFs can be sewn on cloth, taking advantage of the mechanical robustness and high flexibility.

INTRODUCTION

Since our first discovery of graphene oxide liquid crystal (GOLC) in 2009,1,2 a broad-spectrum of highly aligned graphene-based structures including membranes, films, and aerogels have emerged as promising candidates for the next-generation flexible conductors, transistors, energy storage/conversion, and so on.3,4 Among them, taking advantage of the uniaxial alignment of graphitic layers along the fiber axis direction, graphene fibers (GFs) bear a generic potential to translate the extraordinary properties of the individual graphene sheet, such as superior electrical/thermal conductivity and outstanding mechanical strength, into macroscopically assembled structures.5,6 For the realization of desired outstanding physical properties of GFs, highly aligned parallel stacked GO structure formation is crucial within the fiber geometry, which is obviously endowed by the nematic liquid crystalline (LC) phase.7−9 Graphene oxide (GO) exhibits the aqueous colloidal LC phase owing to the abundant polar oxygen functional groups decorating its basal plane and edge as well as extreme 2D shape anisotropy.2 The oxygen groups are effectively deprotonated in less acidic conditions such that net electrostatic repulsion among neighboring GO sheets stabilizes the colloids of the anisotropic LC phase.10 Recently, organic solvent-based GOLC has been suggested as an important relevant research field, principally owing to the practical limitations of the aqueous dispersion system, such as difficult codispersion of other functional materials and nanomaterials, desired for the hybrid type fibers with diverse additional functionalities.11 In this regard, other well-known solvents for GO, including N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP), have been explored thus far. However, the liquid crystallinity of GO dispersion in the nonaqueous system has been controversial particularly in the presence of other functional materials.12−14

In this work, we realized the hybrid type stable LC dispersion of GO and electrochemically exfoliated graphene (EG) in a nonaqueous solvent system, enabled by the hydration of GO components. NMP is selected as the cosolvent in our hybrid LC systems as it is well-known to be the best solvent for minimal oxidized graphitic carbon, such as EG.15,16 It is noteworthy that a small amount of water (above 2 wt %) in the NMP GO dispersion remarkably promotes nematic LC phase formation along with the highly flat, fully exfoliated GO conformation under hydration. This clarifies the
previous inconsistency in the research results about the GOLC formation in NMP. More significantly, even under wet-spinning through a typical circular shape of the nozzle, relatively slow coagulation of GFs induced by GO hydration evolves the fiber morphology in a more stable flat geometry, which originates from the intrinsic 2D characteristics of GO. Such a spontaneous planarization could enhance the alignment and physical properties of GFs, owing to the well-stacked 2D graphene layer structure with minimal folding or wrinkling. Furthermore, synergistic incorporation of mildly oxidized 2D EG components for hybrid GF formation effectively promotes the electrical conductivity, while maintaining the idealized planar fiber geometry. Interestingly, taking advantage of the genuine higher mechanical flexibility in the basal plane of flat fiber geometry, our hybrid GFs can be readily sewn into a textile structure for wearable devices.

RESULTS AND DISCUSSION

Hydrophilic GO with abundant oxygen functional groups is known to be readily dispersed in deionized water while exhibiting a colloidal LC phase. By contrast, it is difficult for electrically conductive EG to form a stable aqueous dispersion with the lesser amount of hydrophilic functionalities (see Note S1 and Figure S1).17 While EG flakes are mixed in aqueous GOLC solution, agglomerated EG flakes destabilize the LC phase by hindering the intersheet orientational ordering and subsequently make it hard to perform continuous wet-spinning of fibers (Figure S2).18 Instead, we prepared various compositional ratios of highly concentrated GO/EG mixtures, up to 100 wt % of EG, in NMP, a well-known dispersion solvent for pristine graphene. It is noteworthy that it is hard for pristine graphene to form a highly concentrated stable dispersion in NMP due to the strong π−π interaction among layers. By contrast, our choice of mildly oxidized graphene sheets, in the form of EG, is more adequate for the stable spinning of GFs.

We spun GO/EG hybrid fibers from the mixture dope of GO and EG in NMP with and without a small amount of water, as schematically represented in Figure 1a. Interestingly, the addition of water in GO/EG dope leads to the noticeable modification in the cross-sectional shape, stacked microstructure, and mechanical properties of the chemically reduced GFs. NMP rich GO/EG (3:1 w/w) hybrid dope (water content ∼1 wt %) with crumpled configuration yields approximately circular cross-sectional GFs (Figure 1b,c). This wrinkled GF shows relatively low tensile strength (186 MPa) and Young’s modulus (29.6 GPa) (Figure 1d). By contrast, 8 wt % of water addition induces planar GFs (Figure 1e,f) with enhanced tensile strength (597 MPa) and modulus (70.9 GPa), which correspond to 420% and 339% increases from those of wrinkled GFs, respectively (Figure 1g). The low-
high-magnification SEM images of multiple GFs represent the pronounced difference in the fiber structures according to the amount of water in the GO/EG NMP spinning dope (Figure S3). Notably, this dramatic enhancement of physical properties by spontaneous planarization of fiber structure is hardly anticipated from conventional wet-spun polymer fiber spinning, which generally favors a circular cross-section to minimize the surface energy.

For a systematic understanding of the morphological variation of GFs in the presence of water, we investigated flake orientation and configuration in the GO/EG dispersions. Water in a GOLC aqueous solution could be effectively removed and exchanged with NMP using a rotary evaporator, while minimizing the aggregation and reduction of GO sheets (Figure S4). Due to the inherent low dispersibility of GO in NMP, the solvent exchanged dispersion revealed the sedimentation of GO sheets after 2 weeks. Interestingly, the colloidal stability of the GO NMP dispersion could be noticeably improved with the addition of water. We could confirm that a small amount of water (2 wt %) induces a highly stable GO NMP dispersion (Figure 2a). Significantly, while the anhydrous GO NMP dispersion shows no optical birefringence (Figure 2b), 2 wt % water addition leads to a typical Schlieren texture indicating the LC phase under polarized optical microscopy (POM) (Figure 2c). It is noteworthy that, without a careful anhydrous experimental condition, a trace amount of water can be readily introduced in the LC phase in the GO NMP dispersion from surrounding ambient humidity or insufficient solvent exchange (Figure S5 and Movie S1). The instant formation of a birefringence texture by adding a water droplet on an anhydrous GO NMP dispersion represents that water is an important parameter for forming an organic solvent based GOLC (Movie S2). In order to further confirm the formation of the LC phase by introducing a small amount of water in the GO NMP dispersion, small-angle X-ray scattering (SAXS) analysis was conducted (Figure S6). The stretched SAXS pattern indicates the nematic LC phase of the GO NMP dispersion with 2 wt % water.8 On the other hand, the anhydrous GO NMP dispersion has a relatively isotropic SAXS circular pattern, which represents the isotropic state without alignment in a particular direction.

In order to understand NMP-based GOLC formation behavior by a small amount of water, additional analyses related to the conformation change of dispersed GO sheets were conducted. Partially dark lines in the transmission electron microscopy (TEM) images of GO flakes, obtained from the anhydrous NMP dispersion, indicate a randomly wrinkled sheet configuration without water (Figure S7a). A high-resolution TEM image presents that the GO flakes are folded several times to form up to a few tens of layers (Figure S7b). By contrast, the sheets from the water-assisted GO NMP dispersion exhibit a highly planar configuration without a significant wrinkle in the basal plane (Figure S7c,d). This behavior is similarly understood by the evolution of polymer
chain conformation from collapsed to stretched states according to the solvent—polymer interaction.\textsuperscript{20} Moreover, optical microscopy (OM) and scanning electron microscopy (SEM) investigation represent that GO flakes in NMP/water cosolvent repulse each other to have a stable dispersion state, whereas partially agglomerated flakes are observed in the anhydrous NMP GO dispersion (Figure S8). For an LC phase formation, stably dispersed 2D GO sheets are desired to have a flat configuration for a high shape anisotropy. While it is hard for the anhydrous GO NMP dispersion with a partially restacked and crumpled GO configuration to form LC ordering, the addition of water effectively exfoliates and planarizes GO sheets to form a stable LC phase even in the same concentration.\textsuperscript{21}

Our observation signifies that a small amount of water can largely enhance the solubility of GO in NMP by hydration. Anhydrous NMP (40.1 mN/m) and hydrophilic GO (62.1 mJ/m\textsuperscript{2}) have a relatively low affinity with a large mismatch of surface energy (Table S1).\textsuperscript{22−24} Furthermore, the low dielectric constant of NMP (32.6), which induces weak charge interactions with polar oxygen groups of GO, is also responsible for a poor colloidal stability.\textsuperscript{14} Thus, a crumpled GO configuration is favored in the GO NMP dispersion with a multilayer stacked state owing to the dominant intrashell affinity. This wrinkled sheet morphology together with the absence of the LC property yields a crumpled GF. Although water has a relatively high surface tension (72.7 mN/m) and dielectric constant (80.4), adding only 2 wt % water in the NMP GO dispersion could not significantly reduce the difference of surface tension and alter the dielectric constant of cosolvent.\textsuperscript{5,26} However, GO sheets can readily be hydrated with the introduction of water, even a small amount, facilitated by the effective hydrogen bonding between oxygen functional groups of GO and water molecules. Since water and NMP are highly miscible, the hydrated surface of the GO sheet can act as an intermediate layer, resulting in a high colloidal stability in NMP even exhibiting a stable LC phase with a highly planarized sheet conformation. Notably, EG, which has a size similar to GO, does not have an LC phase even when hydrated (detailed explanations are given in Note S2 and Figure S9). Nonetheless, our NMP-based GOLC can act as a template of nematic ordering to prepare the GO/EG hybrid LC dispersion by introducing EG flakes (Figure 2d).

Figure 2e shows the morphological diagram for the cross-section of chemically reduced GFs with the different mixing ratios of GO/EG/water. For a precise identification of the influence from EG on the typical properties of GFs, we used the nonsolvent precipitation method for the coagulation of GFs.\textsuperscript{12,27} As-spun GO fibers from anhydrous NMP dope are easily broken during the wet-spinning process (Figure S10). By contrast, along with the water addition over 2 wt %, GFs could be continuously spun into fibers. Furthermore, the cross-section morphology is dramatically changed from a crumpled circular to flat shape above 4 wt % of water addition. Since the spun fibers are stuck together in the coagulating solution over the 10 wt % of water addition to NMP dope (this phenomenon will be explained later), it is difficult to obtain a single GF for the evaluation of physical properties. Notably, no noticeable morphology change is observed in the GFs spun from pure EG-based spinning dope with a similar amount of water. In the case of GO/EG hybrid fibers, EG content has a detrimental effect on the planarization. In fact, GO planarization is observed with 25 wt % EG content but requires more than 8 wt % water addition. Furthermore, when EG content is over 25 wt %, the dumbbell-shaped cross-sectional morphology becomes dominant with a relatively high amount of water.

During the wet-spinning of GFs, a coagulating solvent, such as ethyl acetate or acetone, extracts NMP for solidification. The morphological evolution of the GF cross-section is closely related to the extraction rate of spinning dope solvent similar to the typical polymer-based fibers.\textsuperscript{28,29} The increase of water content in the GO NMP spinning dope from 1 to 10 wt % delays the coagulation time of GO fibers from 10 s to 2 min, respectively (Figure S11). Coagulation rate is largely affected by imbibition rate, which is governed by the surface tension and viscosity of solvents. Normally, in order to successfully coagulate wet-spun fiber by the solvent extraction process, the imbibition rate of coagulant should be higher than that of the dispersion solvent.\textsuperscript{12,30} Therefore, the high ratio of imbibition rate for acetone/NMP (=1.76) ensures an elevated driving force related to solvent extraction, leading to the fast coagulation rate of GFs. The combination of acetone/water has a low imbibition rate ratio (=0.96) even smaller than 1, which hinders the solidification process of GFs and consequently delays the extraction rate of NMP/water cosolvent in spun fiber volume. Additionally, the chemical structure of dispersion materials can also influence the coagulation rate of fiber. Hydrated GO with abundant oxygen functional groups strongly interacts with NMP, leading to a slow extraction rate. By contrast, EG bearing less oxygen functionalities relatively weakly interacts with NMP and results in a fast extraction of NMP (Figure S12). Moreover, owing to this difference in chemical characteristics, EG fiber has a relatively faster drying time than GO fiber for the evaporation of trapped polar coagulant in the fiber, which is undesirable for the stabilization of fiber morphology and strength together with the deterioration of graphene ordering.

Figure 2f schematically compares the morphological evolution of GF cross-section mechanisms depending on solvent extraction rate by using the case with NMP dope containing 8 wt % of water. The rapid solvent extraction from EG-based fiber induces the restacking of EG flakes while maintaining the original circular cross-section of the nozzle. By contrast, hydrated GOs under a slow NMP extraction may have mobility within the gel-state fiber with residual NMP. Therefore, anisotropic planar GO sheets can be spontaneously rearranged into a parallel stack flat fiber morphology, which is more favored due to the genuine 2D shape anisotropy of constituting 2D sheets.\textsuperscript{9} It is noteworthy that, in the typical wet-spinning of polycrylonitrile (PAN) fibers for the conventional carbon fiber production, the circular shape of fibers is normally generated for the minimal surface energy at a slow coagulation rate. Interestingly, PAN fibers with non-circular rather flat cross-sections could also be produced upon a fast coagulation process, which is attributed to the anisotropic radial deformation caused by inhomogeneous phase separation.\textsuperscript{29,31} However, our flat GF has a much more planar morphology compared to the anisotropic PAN fiber owing to the extraordinary geometry of 2D GO sheets with high aspect ratio. In the case of GO/EG hybrid fibers, while the outer surface of fiber solidifies rapidly, NMP still remains in the core of the fiber such that the internal structure can be rearranged into a flat morphology, yielding dumbbell-shaped fibers. Notably, pure GO fiber (3 wt % water) also forms a similar dumbbell shape, verifying that the edge of the
dumbbell fiber is caused by the controlled coagulation rate rather than segregation of EG and GO sheets. Elongation of the planar part of dumbbell GFs along with water content verifies the intermediate characteristic between circular and flat GFs (Figure S13). It is noteworthy that the spontaneous planarization of GFs is possible only without cross-linking agents in the coagulation nonsolvent. When a small amount of CaCl₂ is dissolved in the coagulation bath, a relatively round shape of GFs is generally yielded, even for the 8 wt % water added GO NMP dope (Figure S14). Ca²⁺ ions induce a rapid cross-link among neighboring GO sheets by ionic bonds to prevent any opportunity for the rearrangement.

Raman spectroscopy was carried out for the characterization of GFs after chemical reduction. Along with EG content, the \( \frac{I_D}{I_G} \) ratio decreases from 1.75 to 1.34, signifying a gradual reduction of defects in the hybrid GFs (Figure 3a, Figure S15 and Table S2). While the decrease of the \( D' \) band (1610 cm⁻¹) represents less damage formation in the carbon crystalline structure, the increase of 2D peaks (2700 cm⁻¹) indicates the growth of crystalline graphitic structures. These observations confirm that EG plays a synergistic role to address the inherent limitation for the chemical reduction of GO.

X-ray photoelectron spectroscopy (XPS) analysis was also performed at various GO/EG ratios. High-resolution C 1s peaks of air-dried GFs exhibit the gradual decreases of the carbons linked to oxygen with EG addition (Figure 3b). After HI vapor treatment, oxygen functional groups such as C—O (epoxy and hydroxyl, \( \sim 286.7 \) eV) and C=O (carbonyl, \( \sim 288.3 \) eV) were effectively removed at a low reaction temperature of 70 °C (Figure 3c). Notably, the C/O atomic ratio of the pure EG-based fiber (C/O = 11.13) is significantly higher than that of the pure GO-based fiber (C/O = 8.84) (Figure S16).

Crystalline structures within GFs are characterized by X-ray diffraction (XRD). We named the chemically reduced GFs with various mixing ratios of GO/EG/water as GE\( X_1 X_2 X_3 \), where \( X_1 \) and \( X_2 \) represent the compositional ratio of GO/EG, and \( X_3 \) is the weight percent of water in the original NMP dope. In cases of pure GO or pure EG-based fibers, we denoted these as GO\( X_3 \) or EG\( X_3 \), respectively. In the XRD spectra of GFs (Figure 3d, Table S3), a single peak at \( 2\theta = 9.93° \) indicates a large intersheet spacing, the typical characteristic of GO fiber (\( \sim 0.890 \) nm) with abundant oxygen functional groups at the edge and basal planes of graphene. Low-temperature (70 °C) HI vapor treatments lead to the \( 2\theta \) peak shifts to 24.17° and 24.04° for GO\( X_1 \) and GO\( X_8 \), respectively (interlayer distance: \( \sim 0.368 \) and \( \sim 0.370 \) nm). The noticeable difference of \( 2\theta \) peak shape between GO\( X_1 \) and GO\( X_8 \), including peak broadness, confirms the role of water for the enhancement of sheet alignment in the GFs. Considering the original interlayer distance of pristine graphite (\( \sim 0.335 \) nm), the interlayer distance of the pure EG-based fiber (\( \sim 0.356 \) nm, \( 2\theta = 24.99° \)) is still high with minor residual oxygen functionalities. EG\( X_8 \) shows a similar broadness of the \( 2\theta \) peak with EG\( X_1 \), suggesting the negligible influence of water on the graphene alignment. Interestingly, instead of
displaying two distinct peaks, the reduced GO/EG hybrid fiber shows a single broad peak, illustrating the homogeneous distribution of reduced GO and EG flakes within the fiber volume.

For a quantitative analysis of the degree of graphene layer alignment, an azimuthal scan of wide-angle X-ray scattering (WAXS) was performed.\(^9\)\(^{35}\) GFs spun from pure GO dope show improved alignment from the (002) scattering plane with the addition of water, while no noticeable change is observed for pure EG-based fibers (Figure 3e). The azimuthal scan profile of GEw318 narrower than GEw311 presents the significant role of water for layer alignment particularly in the hybrid LC state (Figure 3f). Herman’s orientation functions \((f)\) were calculated from the azimuthal scan profiles.\(^{36}\) Up to 25 wt % of EG, a high order parameter over 0.9 is attained in the presence of water, demonstrating highly aligned structures driven by the LC nature. Above 50 wt % of EG, the alignment of GFs decreases without LC characteristics.

Electrical and mechanical properties for various compositional ratios of GFs were compared with the water contents of 1 and 8 wt %. GO fiber has no electrical conductivity without a postreduction process (Figure S17), whereas the as-spun EG fiber showed a weak electrical conductivity (158 S cm\(^{-1}\)). HI treatment recovers the electrical conductivities of all fibers (Figure 4a). GFs from the pure GO dope with water additive show a large improved conductivity among highly aligned graphene layers. Furthermore, electrical conductivity is proportionally enhanced with EG content obviously due to the less amount of residual functionalities and defects compared to GO.

The tensile strength and Young’s modulus of hybrid GFs follow close relationships with the orientation order parameter (Figure 4b,c). Because of the genuine LC alignment of hydrated GO as well as the rearrangement into a flat parallel-stack structure in the coagulant process, GEw318 exhibits the highest mechanical properties. Interestingly, because of the synergetic effect from liquid crystalline GO and highly crystalline EG, it shows higher properties than GOw8. The larger average lateral carbon crystallite dimensions \((L_a)\) of reduced EG components (=12.5 nm) compared to reduced GO (=9.57 nm) could contribute to the enhanced mechanical properties mediated by stronger π−π interlayer interaction.\(^{37,38}\) Additionally, hydrated GO can maintain the high degree of graphitic layer alignment in GFs by acting as an LC template under the spontaneous layer planarization behavior.

This outstanding mechanical strength and modulus of the flat GF morphology are attributed to the maximized face-to-face interactions and highly ordered graphene layers.
face interaction among highly planar graphene flakes relying on LC ordering (Figure 4d). It is noteworthy that effective enhancements of GF properties spun from the flat shape nozzle have been reported recently, suggesting that the planar structure is a desirable morphology for the high-performance GFs. By contrast, the GFs with a crumpled and randomly oriented layer structure without the LC phase reveal poor mechanical strength and modulus (Figure 4e). Although the circular GF spun from hydrated GOLC (2 wt % water content) shows enhanced physical properties compared to the corrugated round shape of fiber owing to the relatively less folded sheets, its mechanical strength and modulus are lower than those of the flat GF generated by the spontaneous flattening process (Figure S18). Randomly orientated graphitic layers with bends, folds, and wrinkles, caused by the inherently mismatched geometries between the circular cross-section of fiber volume and constituting anisotropic 2D sheets, should be responsible for the unavoidable deterioration of fiber properties.9

From our systematic comparison of material properties (Figure S19), GEw318 constitutes the optimized GF composition for high conductivity (527 S cm−1) and strong tensile strength (597 MPa). This hybrid fiber synergistically combines outstanding electrical conductivity and mechanical strength, compared to the previously reported chemically reduced GF without metal additive (Figure 4f, Table S4). Additionally, in order to compare the mechanical flexibility according to the reduction method for GEw318, high-temperature annealed GFs (TAGFs) were prepared by thermal reduction at 1000 °C under an Ar atmosphere. GEw318 well maintains the fiber structure after 1000 bending and releasing cycles with a bending radius of 6 mm owing to the halogenation substitution reaction by HI reduction, yielding a liquid phase byproduct rather than gas (Figure S20). By contrast, TAGF is easily fractured even after a single bending cycle with a larger bending radius, which is principally due to the defective porous inner structure induced by the volume expansion under the thermal reduction process accompanied by the release of gaseous byproducts (Figure S21). The surface observation after the bending test indicates that HI treated GEw318 has an intact surface without any fracture. Interestingly, the surface wrinkles are significantly removed by the stretching effect under bending (Figure S22). Notably, GEw318 exhibits a constant electrical current flow upon the 1000 cycles of bending with an applied potential of 10 V, revealing a potential for lightweight and flexible carbon-based cables (Figure 4g). The obtained outstanding mechanical properties of HI reduced GEw318, especially 1243% higher average fracture toughness (4.23 MJ m−3) compared to TAGF (0.37 MJ m−3), endow the genuine mechanical flexibility and stability under the bending test.

Eventually, our GEw318 could be successfully sewn into fabrics and transformed into curved yarn fiber, exhibiting the genuine compatibility with wearable electronics (Figure 4h, Figure S23). Our GFs could also be applied as a flexible electrode for fiber type supercapacitors. For the promoted electrical conductivity and redox capability, a conductive polymer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), was coated at the surface of GEw318 via simple dip coating. SEM images of the resulting fiber represent a homogeneous PEDOT:PSS coating at the fiber surface (Figure S24a,b). A H2SO4 post-treatment was employed for the further enhancement of the electrical conductivity (Figure S24c). When the resultant fibers are utilized for fiber supercapacitors, a high volumetric capacitance is attained along with excellent capacitance retention for different bending angles, establishing its potential in flexible wearable electronics (Figure S25).

**CONCLUSION**

Electrically conductive and mechanically robust flat GFs were spontaneously assembled by the synergistic combination of EG with the water-assisted GOLC template. Significantly, highly planar hydrated GO induces a stable NMP-based nematic LC phase as well as spontaneous rearrangement of GFs into a flat fiber geometry with enhanced mechanical and electrical properties. Our hybrid flat GFs present the highest electrical conductivity (527 S cm−1) and outstanding tensile strength (597 MPa) among the chemically reduced GFs without metal additives. Moreover, taking advantage of NMP-based spinning dope with a genuine low-temperature process, further diversification of material properties is anticipated by hybridizing a wide range of new components, such as CNTs, polymers, TMDs, and metal nanowires. As such, our hybrid GFs suggest a great potential in the functional wearable textiles such as fiber type energy-harvesting, energy-storing, and sensing devices.

**EXPERIMENTAL SECTION**

**Synthesis of Graphene Oxide.** Graphene oxide (GO) was synthesized from graphite powder, which was purchased from GSK, using a modified Hummers method. Graphite (1 g) was oxygenated in 40 mL of sulfuric acid (H2SO4) and 5 mL of phosphoric acid (H3PO4) with 3.5 g of potassium permanganate (KMnO4) at 35 °C for 2 h in a sealed vessel. After that, this oxidized graphite solution was transferred to 300 mL ice pellets, followed by the addition of 20 mL of hydrogen peroxide (H2O2). After stirring the solution for 30 min at 300 rpm, it was filtered using a glass filter followed by washing with 1 L of 1 M hydrochloric acid (HCl). Unreacted graphite was removed by centrifuging the solution at 8000 rpm for 30 min. In order to make highly purified neutral graphene oxide, the final product was dialyzed for 2 weeks using dialysis membrane (MWCO: 6000–8000).

**Synthesis of Electrochemically Exfoliated Graphene.** Electrochemically exfoliated graphene (EG) was prepared from graphite foils (0.25 mm thickness) purchased from Alfa Aesar. Two electrode systems were designed using graphite foil as the anode and Pt electrode as the cathode. Electrolyte was prepared by dissolving 3.6 g of Na2SO4 in 250 mL of deionized water. Constant +10 V was applied for 10 min at the anode, which led to the exfoliation of graphite foil into expanded graphite flakes. These flakes were purified by deionized (DI) water in a vacuum filter equipment with an HVLP membrane filter (0.45 μm pore size) and then dispersed in N-methyl-2-pyrrolidone (NMP). The solution was sonicated at high power for 20 min. In order to shuttle down unexfoliated graphite flakes, centrifugation was used at 4000 rpm for 30 min. The supernatant, which is exfoliated graphene, was carefully transferred to another beaker.

**Wet-Spinning GO/EG Hybrid Fibers.** GO dispersion (13 mg mL−1) in NMP was prepared by solvent exchange method using a rotary evaporator. A calculated amount of NMP was added in highly concentrated GO aqueous dispersions, and water was removed using a rotary vacuum evaporator for 2
days, maintaining the temperature of the bath at 28 °C. A calculated amount of NMP was additionally injected at the exchanged GO NMP dispersion to have a concentration of 13 mg mL⁻¹. The same concentration of EG NMP dispersion was prepared by removing solvent using centrifugation at 17 000 rpm for 30 min. In order to make hybrid fibers, prepared EG and GO NMP dopes were mixed with additional DI water by enough vortex mixing. Prepared dopes were spun through a Teflon coated nozzle (diameter = 500 μm) acetone/ethyl acetate bath (according to GO/EG hybrid rate) at 2.3 cm away from the center with constant rotating (17 rpm). The injection rate was fixed at 0.4 mL min⁻¹. Wet-spun fibers were dried at room temperature while maintaining the original gel state length by fixing the end of the fibers.

Reduction of GO/EG Hybrid Fibers. The air-dried fibers were chemically reduced by exposing hydroiodic acid (Sigma-Aldrich) vapor at 70 °C for 12 h under tension. The reduced fibers were washed with ethanol in succession to remove the remaining HI. To achieve TAGF, the air-dried fibers were kept at 40 °C under vacuum over 24 h and then thermally annealed up to 1000 °C under 100 sccm of Ar flow. The heating rate was about 1.5 °C min⁻¹, and holding time was 1 h. After cooling down to room temperature, TAGF was obtained.

Assembly of Conductive Polymer Coated GF Super-capacitors. PEDOT:PSS was coated on GFs via the dip coating method. The GFs were immersed in aqueous PEDOT:PSS solution for 10 min and washed with ethanol. For the sulfuric acid treatment, the PEDOT:PSS coated GFs were immersed into sulfuric acid for 20 min and then sufficiently washed with DI water. Afterward, GFs were further dried at 120 °C for 10 min. In order to fabricate the solid-state GF supercapacitors, two GFs were placed parallel to each other on a flexible PET film surface. PVA/H₂SO₄ (1 M) was pasted on the GFs and then briefly dried at 50 °C for 1 h to produce all-solid-state supercapacitors.

Characterization. Prepared GO and EG sheets were observed by SEM (Hitachi, S-4800) and AFM (Seiko Instruments, SPA-400) and TEM (FEI Company, Titan cubed G2, 80 kV). For the liquid crystal property measurement, an optical microscope (Leitz, Laborlux 12-Pol) with crossed polarizers was used. The imbibition ratio of coagulant/dispersion solvent was calculated by the following equation.

\[ \text{imbibition ratio} = \left( \frac{\sigma_c \mu_D}{\sigma_D \mu_c} \right)^{1/2} \]

where \( \sigma_c \) and \( \sigma_D \) are the surface tension of coagulant and dispersion solvent, \( \mu_c \) and \( \mu_D \) are the viscosity of coagulant and dispersion solvent. The fibers were characterized by SEM (Hitachi, S-4800), XPS (Thermo VG Scientific, K-alpha), and Raman spectroscopy (ARAMIS, 514 nm). The average lateral carbon crystallite dimensions (\( L_c \)) were calculated by the following formula:

\[ L_c (\text{nm}) = \left( 2.4 \times 10^{-10} \right) \lambda^2 \left( \frac{I_D}{I_G} \right)^{-1} \]

where \( \lambda \) is the wavelength of the irradiated laser, and \( (I_D/I_G) \) is the intensity ratio of D and G bands. XRD and WAXS measurements were carried out at the 4C SAXS II beamline of the Pohang Accelerator Laboratory (Pohang, Republic of Korea) with an X-ray beam wavelength of 0.675 Å. Single GFs was loaded into a polyimide tape sealed holder with exposure for 60 s, while maintaining a sample-to-detector distance of 20 cm. 2D WAXS patterns and azimuthal scan profiles were obtained from the (002) peak in wide-angle X-ray scattering spectra of GFs. Herman’s orientation function \( (f) \) was calculated by the following equation.

\[ f = \frac{1}{2} \left( 3 \int_0^{\pi/2} \frac{I(\phi) \cos^2 \phi \sin \phi d\phi}{I(\phi) \sin \phi d\phi} - 1 \right) \]

\( I \) is the intensity of measured azimuthal peaks, and \( \phi \) is the azimuthal angle. The electrical conductivities of fibers were measured by the 2-point probe method (HiOKI, Card HiTester). Tensile strengths of graphene fibers were investigated using a mechanical testing machine (Instron, 8848) with a 5 N load cell.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.0c00467. SEM, AFM, OM, and POM images; FTIR, Raman, XRD, and XPS data; surface tension and Hansen solubility parameter table; and a performance comparison of GFs (PDF)

Movie S1: in situ POM observation of the anhydrous GO NMP dispersion on open cell slide glass (MP4)

Movie S2: in situ POM observation of the anhydrous GO NMP dispersion with the addition of a DI water droplet (MP4)

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Notes
The authors declare no competing financial interest.

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