



Graphene fiber: a new trend in carbon fibers

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New fibers with increased strength and rich functionalities have been untiringly pursued by materials researchers. In recent years, graphene fiber has arisen as a new carbonaceous fiber with high expectations in terms of mechanical and functional performance. In this review, we elucidated the concept of *sprouted graphene fibers*, including strategies for their fabrication and their basic structural attributes. We examine the rapid advances in the promotion of mechanical/functional properties of graphene fibers, and summarize their versatile applications as multifunctional textiles. Finally, a tentative prospect is presented. We hope this review will lead to further work on this new fiber species.

Introduction

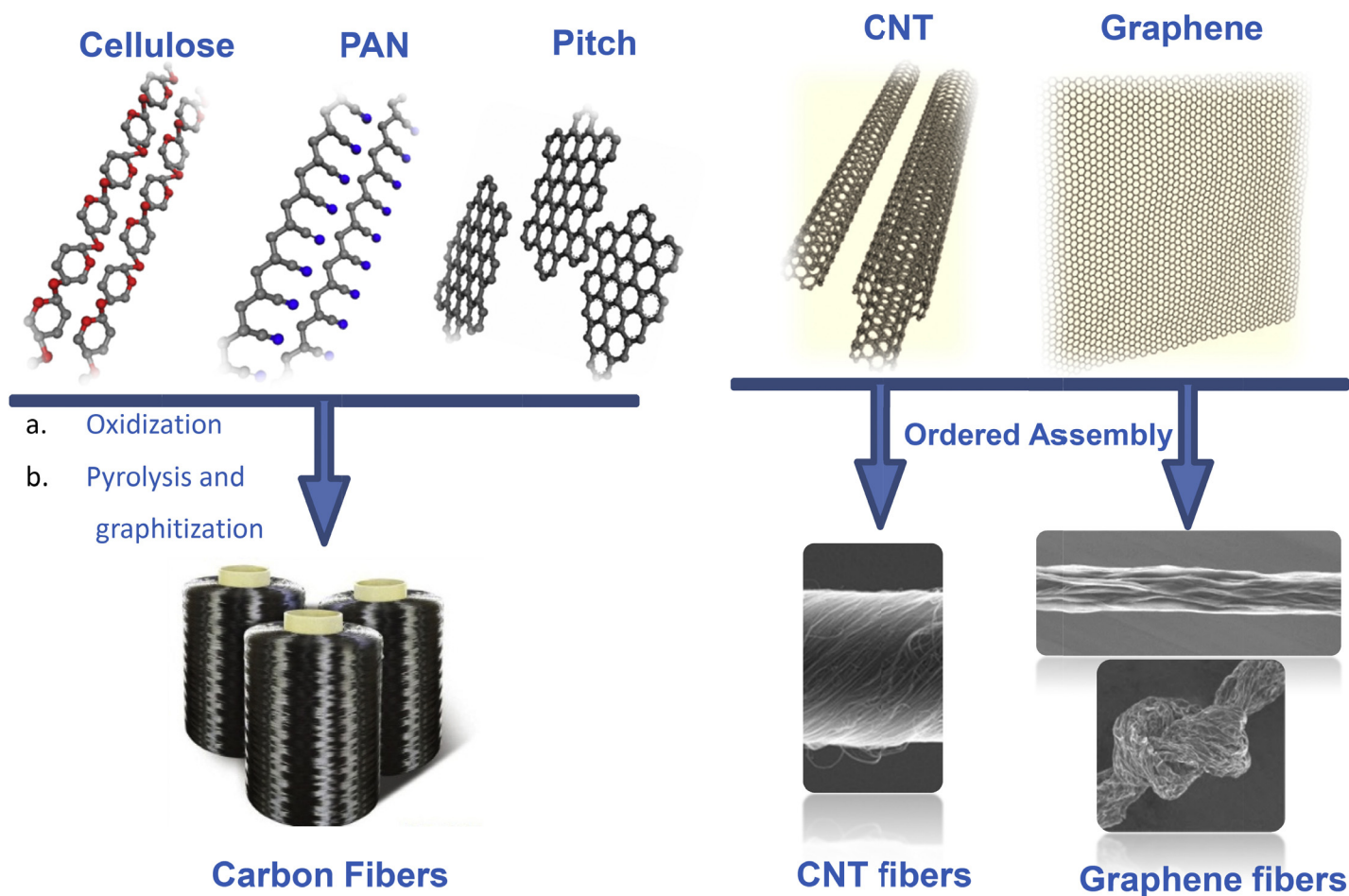
Human ingenuity in the discovery, creation and utilization of fibers not only fulfills primary needs in clothing and shelter, but also promotes important advances in technology and culture. Before the 19th century, natural fiber species that mainly included animal, vegetable, and mineral products, were extensively used and dominated human life. It is such innovation and technical advances in cotton workshops that reformed production and ushered in the First Industrial Revolution [1,2] After natural species, synthetic polymeric fibers were created from petrochemicals, such as Nylon, to meet the rapidly increasing demand for fibers and to complement the limited availability of natural products. Despite vast numbers of commercial fiber species having flooded both industry and daily life, the vigorous search for new ones with better mechanical performance that can bear high stress and rich multifunctionalities for use in increasingly complicated tasks has continued.

Carbon fiber (CF) is a species that permits the integration of high-performance and rich functionalities [3–6]. The creation of CF can be traced back to the pyrolysis of natural cellulose fibers for electrical-light bulbs by Sir Joseph Swan in 1883. CF became widely attractive when teams at the Royal Aircraft Establishment and Rolls Royce, Ltd., promoted CF to the rank of a real high-performance fiber with high mechanical strength (~1.7 GPa) and tensile

modulus (~400 GPa) in the 1960s [7,8]. This almost purely carbonaceous fiber is usually prepared from natural cellulose, synthetic polyacrylonitrile (PAN) and pitch, by carbonization and/or graphitization at high temperatures to eliminate other chemical elements and generate graphitic structures (Fig. 1) [5,6]. The first attractive merit of CFs are the extraordinary mechanical properties; that is, high tensile strength and elastic modulus, which, combined with their lightness in weight, mean they overwhelm steel in enforcement applications as structural components. Beyond their outstanding strength, CFs possess a wealth of functionalities, such as good electrical and thermal conductivities, favorable resistance to chemicals and harsh surroundings, and stability at high temperatures. All of these merits render CFs an indispensable component of many high-tech uses such as aeroplanes, vehicles, and cables, to mention but a few commercial products [3,4].

For material researchers, CF does not represent the end of new fibers, but rather a promising beginning. The principal philosophy underlying all of their attractive merits is the interconnected graphitic structure, which provides extraordinary combined mechanical, electrical, thermal properties. The ideal model counterpart of CF, graphite whiskers, has strengths of up to 20 GPa and electrical conductivity of 1.5×10^6 S/m [9], much higher than ever obtained by CFs (~5.9 GPa and 1.4×10^5 S/m, respectively.) The polycrystalline nature of CFs and the presence of vast grain boundaries confine their properties compared with ideal graphite

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**FIGURE 1**

The precursor system of conventional carbon fibers and the new species including CNT and graphene fibers. Oxidization crosslinking and pyrolysis (and/or graphitization) are employed to fabricate conventional CFs from cellulose, PAN and mesophase pitch precursors. The polycrystalline graphitic structure of CFs is generated from these precursor macromolecules. By contrast, CNT fibers and graphene fibers are fabricated from individual carbon nanotubes and graphene sheets, by a well-controlled macroscopic assembly method.

whiskers. This discrepancy is extremely hard to overcome because all conventional CFs are fabricated by the pyrolysis of organic precursors, which inevitably generates polycrystalline graphitic structures. In this context, great hope for new carbonaceous fibers that can surmount the limitations of conventional CFs has risen from striking developments in the nanotechnology of carbon allotropes, particularly from the discovery of carbon nanotubes (CNT) in 1991 [10] and more recently graphene [11].

CNT and graphene are one- and two-dimensional independent carbon crystals, respectively, with long-range order up to the millimeter scale. Because of the intrinsic covalent connection of sp^2 -hybridized carbon atoms, these two carbon crystals have extremely high mechanical strength, up to 130 GPa tensile strength and 1.1 TPa elastic modulus in the case of graphene, together with the valuable flexibility to accommodate deformation and transcendental conductivity for electrical current and thermal flow [10–14]. Both CNT and graphene are possibly perfect building blocks for new carbonaceous fibers. By contrast to the regeneration of the graphitic structure in the case of conventional CFs, the fabrication of new CNT and graphene fibers should rely on the “bottom-up assembly” concept to fashion individual building blocks into an ordered state with atomic precision (Fig. 1). More importantly, the superior properties of CNT and graphene create

high expectations for the combined performances of their fibers to catch up and even exceed those of conventional CFs.

CNT fibers can be fabricated by two methods; wet-spinning of CNT fluids or dry-spinning of CNT forests/cotton. Dry-spun CNT fibers generally have superior properties to wet-spun ones. To date, considerable efforts have yielded materials with combined properties comparable to those of CFs [15–18]. More impressive are their rich functionalities, which already exceed conventional CFs. These advances have been summarized in many reviews that readers can refer to [15–17], so it is unnecessary to repeat them further here.

Since its initial development in 2011, graphene fiber (GF) has become another promising carbonaceous fiber [19]. In this review, we mainly focus on newly sprouted GFs, describing their concept, strategies of fabrication, structural attributes, mechanical properties and functionalities. A tentative prospect in the vicinity of GFs is also presented. We hope that this review provides a comprehensive introduction to GFs and, attracts more efforts to achieve further progress in this new fiber species.

The new concept of GFs

In 2004, a significant experiment based on an extremely simple principle, by Novoselov and Geim *et al.*, announced the existence of

graphene as the first freestanding 2D crystal [11]. Since then, graphene has become one of the most important nanomaterials and has attracted worldwide attention in fundamental condensed matter physics and materials extending from the nano to macroscopic scale [12–14]. Graphene has extraordinary mechanical properties, including a record tensile strength (~ 130 GPa), elastic modulus (1.1 TPa) and notable flexibility, and excellent electronic transport performances such as extremely high electric conductivity ($\sim 10^8$ S/m), carrier mobility ($200,000$ cm²/V s) and ampacity ($1\text{--}2$ GA/cm²). Other attractive properties of graphene encompass its high thermal conductivity (5000 W/m K), good stability against chemicals and high temperatures, atomic thickness and valuable others. These recent advances have renovated the understanding of graphitic materials, together with their fabrication. For example, starting from solvated graphenes, graphene films/papers can be easily fabricated by many sophisticated solution-processing methods and they exhibited many favorable properties in mechanics and electronics. Graphene papers are much stronger than commercial graphite die-cast foils [20,21]. Additionally, graphene gave a fresh concept for the field of 3D frameworks. A typical example is graphene aerogel, which is created by bridging these thinnest building blocks and exhibits the extremely low density of a gas but in a solid state [22].

As discussed above, the outstanding performances of conventional CFs are primarily because of the interior graphite crystallites consisting of turbostratically interconnected graphene. In their established structural model, the size (width L_a and thickness L_c) of graphite crystallites together with their alignment and interaction play a key role in their performance (Fig. 2). However, further improvement in their combined performance is confined by their inherent polycrystalline nature of limited size and faulty alignment. Graphene sheets are actually 2D carbon monocrystals with a lateral size extending from dozens of microns, even to sub-millimeters, far larger than the size (smaller than 20 nm) of the graphene substructure in the turbostratic graphite of CFs. Principally, the scaling of graphite crystallite size allows enhancement of the combined performance of fibers. Provided that graphene is

engineered into macroscopic fibers, the extremely long-range covalent crystalline nature is able to eliminate grain boundaries in the lateral direction to the utmost extent, which may bring about a breakthrough in the limitations of CFs.

Strategies to fabricate GFs from graphite

The building block of 2D topological graphene has extreme asymmetry in its structure and properties, and its attractive mechanical and electronic attributes are in the planar direction (note that, although we acknowledge the existence of graphene ribbons and quantum dots, in this review, graphene means graphene sheets unless specifically stated otherwise). Making GFs from graphene building blocks is actually a process of regularly aligning graphene sheets continuously in a uniaxial direction along which the asymmetrical merits of graphene are translated into macroscopic properties [23]. Because of the unmeltable nature of graphene, it is inconceivable to process graphene into neat fibers by the melt spinning processes for some polymeric fibers such as nylon. In addition, the lack of entanglement of 2D graphene also excludes the throwing method employed in ancient spinning for cotton threads and dry-spinning used to make CNT fibers from CNT aligned forests or cottons. Thus, the production of GF must utilize the strategy of solution assembly, which resembles the wet-spinning of polymeric fibers such as Kevlar and CNT fibers.

To fabricate GF in a continuous manner and achieve sufficiently high quality further, there are three prerequisites that must be fulfilled.

- (i) *Scalable synthesis of solution-processable graphene.* Graphite, whether mineral or synthetic, is an abundant source of graphene that can be commercially obtained in tons; different from chemically synthetic methods to produce graphene in large area such as chemical vapor deposition (CVD) which is especially suitable for electronic devices. The huge mass of graphene obtained from graphite is significant to the scalability of graphene macroscopic materials, such as composites, films, papers and certainly fibers [24]. To circumvent the poor dispersibility of pristine graphene in

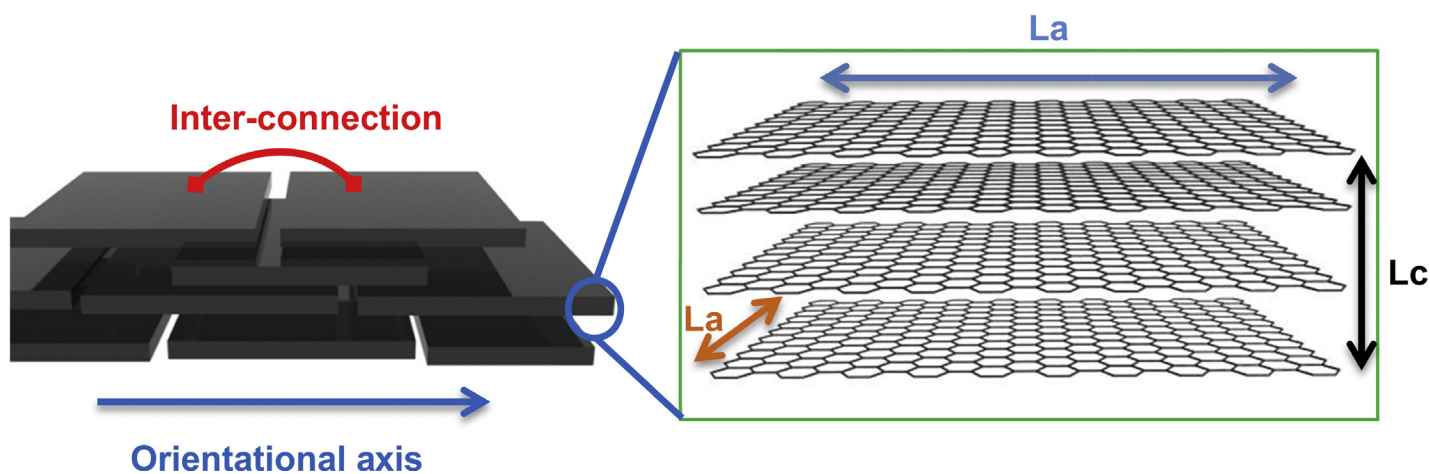


FIGURE 2

Lamellar crystalline structural model of graphitic materials. The whole structure encompasses a two-level hierarchy: (a) lamellar graphite crystal platelets at the nano or sub-micro scale. The orientation degree and inter-connection among these crystals platelets are critical to the performance of macroscopic materials, including fibers, films and bulks; (b) lamellar graphene sheets consist of graphite crystals at the atomic scale, with characteristic parameters of lateral width (L_a) and perpendicular thickness (L_c).

common solvents, chemical functionalization has been proposed to introduce functional groups onto graphene and render the functionalized graphene with good dispersibility and resultant processability by fluid assembly [24–29].

- (ii) *Continuous regular alignment of graphene.* The task of aligning dispersive graphene into its continuous solid form can be divided to two stages: pre-alignment in the fluid state and the subsequent phase transformation to regular alignment in the solid state. In the frame of traditional lyotropic liquid crystals (LCs) of asymmetrical colloids [30], the combination of high asymmetry and engineered high enough dispersibility of graphene determines the spontaneous formation of LCs with orientational or positional orders, that is, the pre-alignment in the fluid state. Subsequently, starting from graphene-based LCs, the wet-spinning process may be an optimal choice to make continuous GFs. Similarly, tuning critical control factors of the wet-spinning process should generate the optimal alignment of graphene in the solid fibers.
- (iii) *Re-engineering of bonds among graphene building blocks.* The relatively weak van der Waals interactions between graphene sheets make graphite a popular lubricant and enable the exfoliation of graphene. Conversely, they become the weak points that confine the enhancement of the performance of assembled graphene materials. Thus, beyond the simple creation of GF, the re-engineering of the bonding among graphene building blocks is necessary to optimize GF performances, which is critical to push GF to a high level comparable to conventional CFs and CNT fibers.

To fabricate GF from graphite, the “graphene LC-wet-spinning” system has been established in recent years and is becoming a reliable method to obtain continuous GFs as monofilaments, tows and yarns (Fig. 3). A series of GFs with high performances and

multifunctionalities has been developed. Importantly, many attempts have been made to understand the basic relationship between structure and properties. We now summarize these advances in detail and describe the deduction of a perspective for these new carbonaceous fibers.

Graphene LCs

LCs of asymmetrical colloids and macromolecules with ordered structures and the fluid attribute are key to their fluid assembly for ordered structures and materials, typically exemplified by CNT and liquid crystalline polymers. The 2D topology of graphene undoubtedly satisfies the basic asymmetrical structural factor for the formation of LCs, whereas, the remaining challenge lies in its limited dispersibility that originates from its barren surface with poor interaction with solvents. This dilemma can be resolved by either finding good solvents to directly exfoliate graphite and stabilize the resultant graphene, or using chemical modifications to weaken the interlayer van der Waals attractions, enhancing interactions with solvents and its dispersibility.

Some common organic solvents with surface energy similar to that of pristine graphene (such as dimethylformamide and *N*-methylpyrrolidinone) can exfoliate graphene from graphite with the aid of sonication, but are only stable at very low concentrations (typically far lower than 1 mg/mL) and only for small graphene with lateral sizes in the submicron range [31]. To date, chlorosulfonic acid, a good solvent for CNT, is the only reported good solvent that can directly solve graphite into graphene in a spontaneous manner (Fig. 4A). This super acid strongly protonates graphite and the resultant negatively charged graphene remains stable in it at high concentrations of up to 20 mg/mL. The observation of birefringence of graphite-chlorosulfonic acid dispersion indicated the formation of graphene LCs [32]. Deduced by a similar principle, graphene salts synthesized from alkali metal

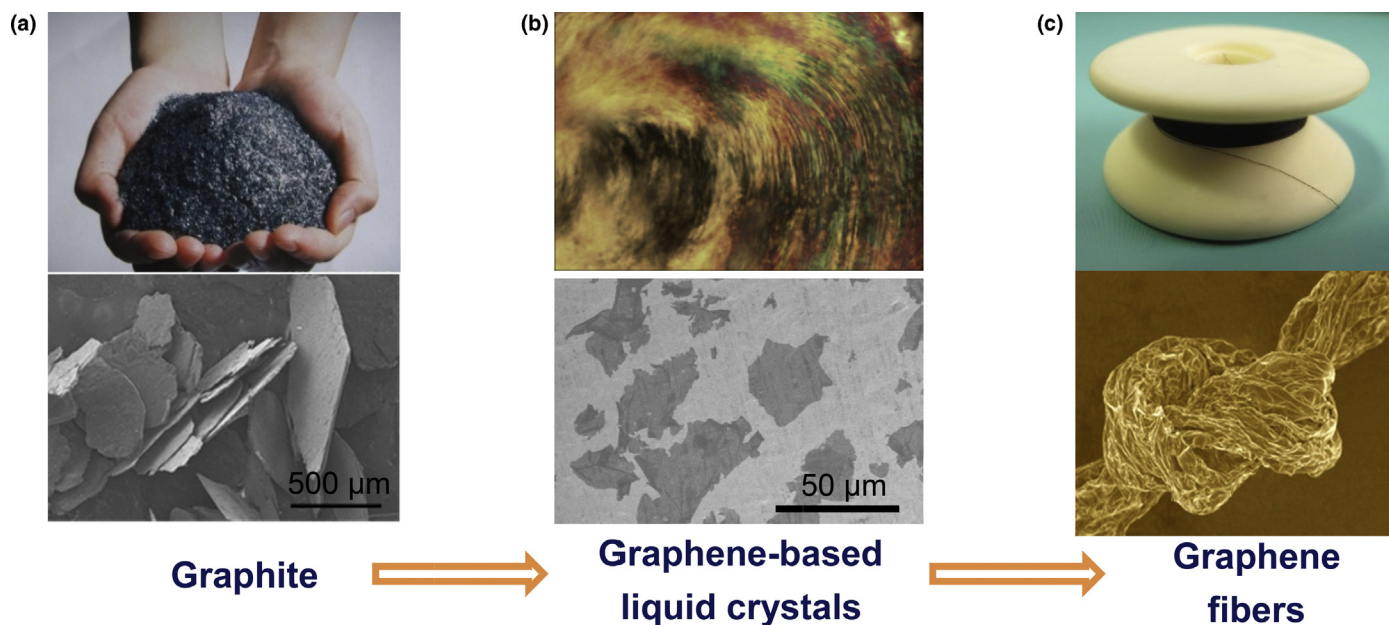


FIGURE 3

The road from graphite to GFs. In the first step, graphite crystals (a) are exfoliated to individual graphene sheets, usually by chemical modification. The modified graphene sheets form liquid crystals in solvents with orientational or positional order (b). In the second step, wet-spinning assembly is employed to make continuous graphene fibers (c) from these graphene-based liquid crystals, which transform orders from the fluid state to orders in the solid state.

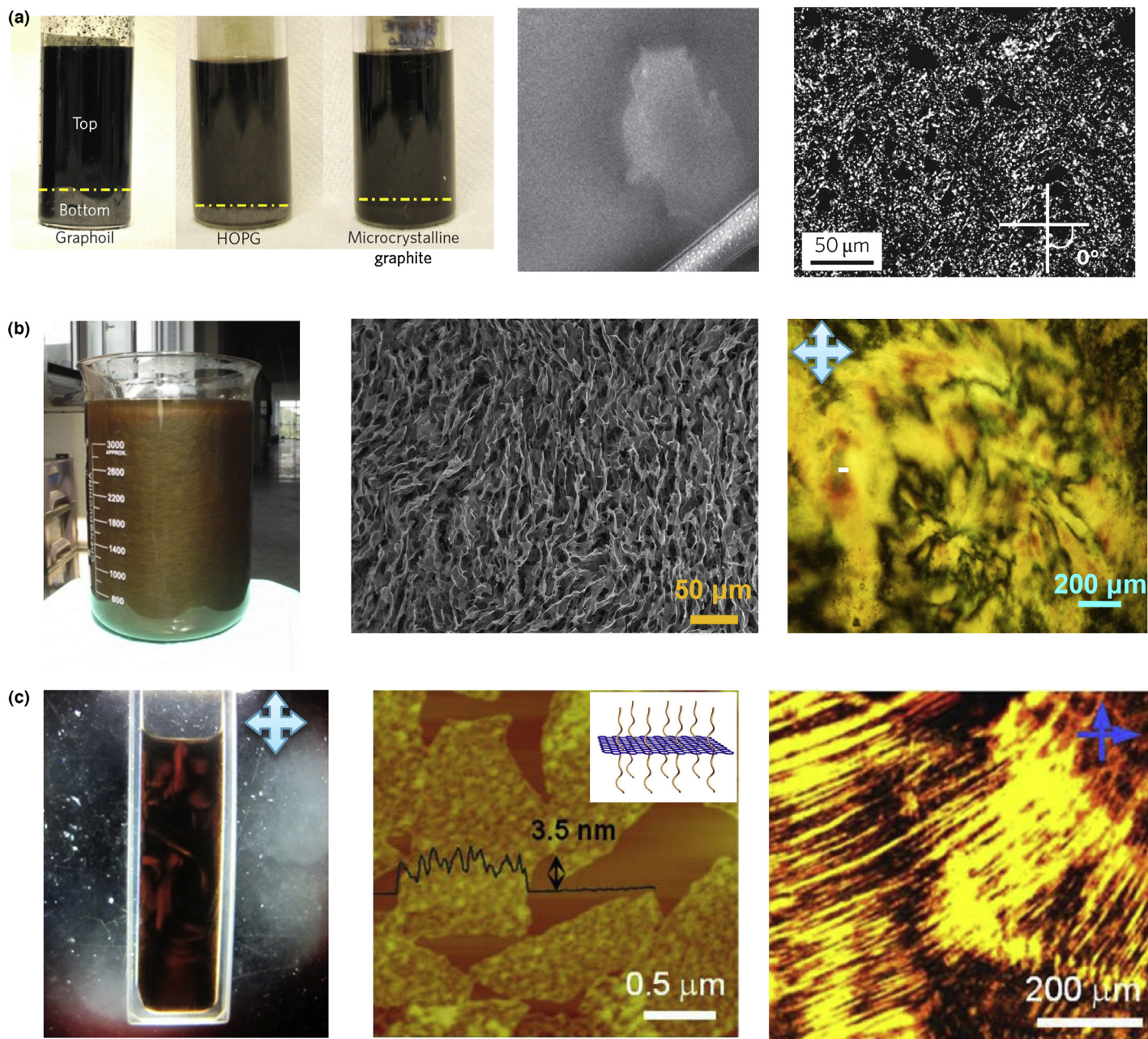


FIGURE 4

Liquid crystalline system of graphene and modified graphenes. (a) Liquid crystal of pristine graphene in super acid. Graphite can simultaneously dissolve in super acid, and is exfoliated into single layer graphenes that form nematic mesophase as the concentration increases. (b) GO liquid crystal. The rich functional groups make GO dispersible in water and polar organic solvents. GO performed rich mesophases with structural orders (the middle panel) depending on the concentration and size distribution of GO sheets, including nematic (optical texture in right panel), lamellar and chiral ones. (c) Modified graphene liquid crystals, including linear, hyperbranched polymers and, ligand modified graphenes.

or halogen intercalated graphite could be another feasible protocol to make pristine graphene LCs in more hazardous surroundings than superacid [32–35].

Alternatively, chemical functionalization can effectively enhance the stable dispersibility of graphene [24]. Graphene oxide (GO), a single layer of graphite oxide crystal, has become one of the most widely accessible chemical precursors to graphene and has been employed in many applications, especially those with a high mass requirement [36]. Owing to the plentiful oxygen-containing functional groups on its surface, GO has versatile dispersibility not only in water but also in many polar organic solvents

such as DMF and NMP. In principle, the remaining 2D topology of GO together with its excellent dispersibility renders the spontaneous formation of LCs. The question for GO LCs received affirmative answers sympathetically until 2011 [23,37–41]. The first several reports on GO LCs outlined their basic notion (Fig. 4b): (1) The phase transition from isotropic to mesophases is dependent on the dispersive concentration and the aspect ratio of GO, approximately conforming to the classic Onsager's LC theory, more specifically, higher aspect ratio means lower critical concentration at which LC forms. (2) GO LCs possess ordered structures but with disclinations, including orientational order in the

nematic phase, quasi-positional order in the lamellar phase, and twist-lamellar structure in chiral mesophase.

Aside from the utility of GO LCs in the fabrication of ordered structures, GO LCs also exhibited interesting optical responses. The GO chiral mesophase exhibited strong optical activity and absorbed circularly polarized light with specific chirality [23]. Li *et al.* reported that GO LCs behaved as photonic crystals and reflected light with a specific wavelength depending on their concentration [42]. Shen *et al.* found that dilute GO dispersions possessed the largest Kerr coefficient in molecular LCs, and the alignment can be controlled by a weak electric field, which may makes GO LCs useful as electro-optical devices [43].

The lability of GO suggests its preferred usage as a reliable chemical precursor of graphene. Generally, in real-world applications, GO should be converted into graphene by chemical and thermal reductions to eliminate functional groups and restore its conjugated structure [44,45]. To avoid irreversible precipitation, chemical modifications are employed to keep good dispersibility. Through modifications, once graphene keeps stable when dispersed in solvents at a high enough concentration, LCs should form. To date, macromolecules with linear and hyperbranched molecular architectures have been grafted onto reduced graphene, and, these effectively modified graphenes with good dispersibility exhibited rich liquid crystalline behaviors as in the case of GO (Fig. 4c) [46–51]. Similarly, surfactant-wrapped chemically reduced graphene was prone to form LCs as its dispersive concentration increased [52].

Graphene-based mesophases can be seemed as liquid crystalline hosts of versatile guests from solvated nanoparticles such as CNT, metallic nanowires, and quantum dots, to polymers with linear or hyperbranched molecular architectures [23]. As expected, these multicomponent graphene-based LCs are useful to fabricate hybridized graphene-based materials with ordered structure, just resembling the significance of neat graphene LCs for neat graphene ordered materials.

Wet-spinning process for GFs

The transition from LCs to fibers is a familiar concept in polymer science and technology. Even pitch-based CFs are melt-spun from pitch mesophases. In this context, the discovery of graphene-based LCs points to the possibility of fabricating continuous GFs by the wet-spinning method. Our first attempt in 2011 demonstrated the practicability of wet-spinning GF from GO LCs [19]. The experiment outlined the following basic processes in obtaining wet-spun GFs: (1) extruding LCs into coagulation baths with uniaxial flow; (2) phase transition by coagulation with solvents exchange; (3) solidification by evaporating solvent; and (4) chemical and/or thermal reduction. The whole process is depicted in Fig. 5.

In the first section, extrusion forces GO LC dopes through spinning pipes with uniaxial flow. Importantly, this common process unifies the random alignment of GO LCs in 3D space along the flow direction and fashions GO sheets oriented along the resultant fiber axis [53,54]. SEM characterizations showed distinct differences in GO LCs between the still and flowing states. The flow-induced alignment of GO dispersions revealed their rheological attribute as typical shear flow. In the second section, coagulation baths using solutions compatible with solvents of GO LCs but

incompatible with GO sheets, such as aqueous solutions with acids, bases, diverse salts that screen the electrostatic repulsion of GO sheets [55], and some organic solvents such as ethyl acetate with a poor capability to disperse GO sheets [56–58] were chosen. After solvent exchange, GO liquid crystalline gel fibers formed with maintaining the structural integrity by hydrogen bonding between GO sheets or ions crosslinking. During the drying section, GO gel fibers underwent shrinkage in the radial direction. The interior GO sheets folded in the same direction but remained aligned along the fiber axis. In the last section, chemical or thermal reduction was employed to transform GO fibers to GFs, which allowed the optimal expression of the outstanding mechanical, electronic, and thermal merits of graphene in the macroscopic performances and functionalities of GFs.

Recent efforts have provided qualitative understanding of the wet-spinning of GFs. Coagulation baths were chosen depending on the solvents of GO LC dopes, for example, ethanol/water mixture with Ca^{2+} ions was suitable for aqueous dopes [55] and ethyl acetate was used for DMF-based dopes [56–58]. The stretching operation is believed to be important to achieve high alignment of GO sheets and to help the formation of compact structures [57]. To obtain the highly compact structure of the final GFs, chemical reduction by hydriodic acid was found to be better than other chemical reagents such as hydrazine hydrate and sodium borohydride, which generate porosity and reduce mechanical performances [59,60]. Based on these qualitative understandings, forthcoming systematic investigations are needed to establish a sophisticated wet-spinning process for GFs with high enough quality. We should quantitatively connect the experimental parameters (graphene size and distribution, dope concentrations, spinning rate, coagulation time, diffusion coefficient, stretching ratio, collecting rate, and solidification temperatures, among others) with the structural parameters (alignment degree, density, layered grain size, among others) to obtain the performance of GFs.

Besides wet-spinning, there have emerged some alternative methods for the fabrication of GFs from GO dispersions [61–74]. For example, Dong *et al.* proposed a dimensionally confined hydrothermal strategy for GFs [66]. In their report, GO dispersions in pipelines were subjected to a hydrothermal step and were extruded to get GF followed by drying and further thermal annealing. Hu *et al.* developed a metal-wire templated assembly method to make graphene microtubes, and demonstrated the possibility of designing a janus structure that consists of different functionalizations on the inside and outside walls [67]. Jang *et al.* used an electrophoretic self-assembly method to draw fibers from dispersions of graphene nanoribbons [68]. Chemical reduction-induced self-assembly was also used to make GFs from GO hydrogel fibers [69,70]. Despite the different concrete operations, these alternative methods have a similar principle to the wet-spinning process, including the use of a relatively high concentration of GO feed dispersions (that may imply the formation of LCs) and continuous flow to ensure the continuous alignment of graphene sheets along the fiber axis.

Neat GF

With the aim of a new CF in mind, neat GF has been continuously fabricated by wet-spinning together with chemical and/or thermal

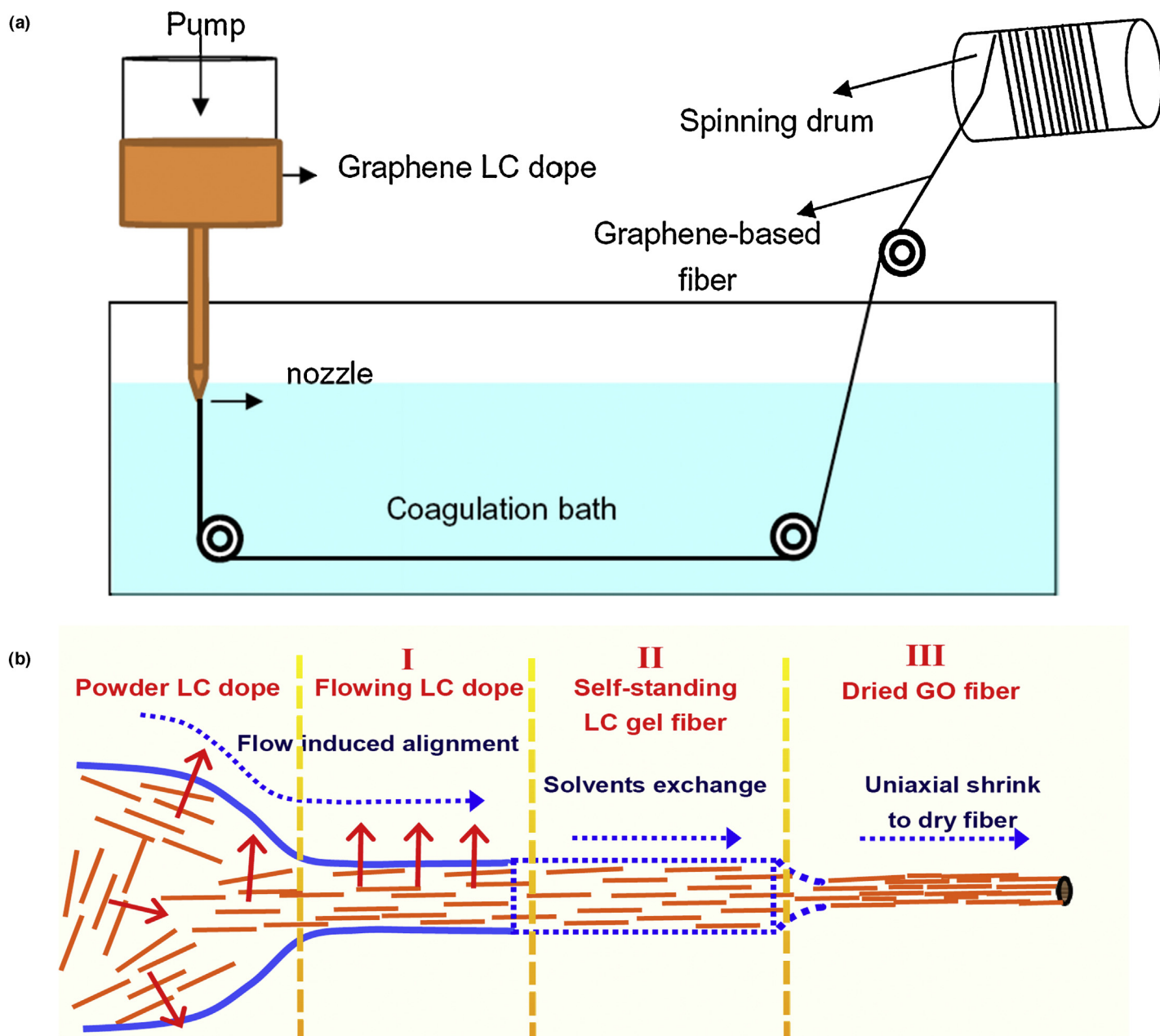


FIGURE 5

Liquid crystal-based wet-spinning for GF. (a) The schematic wet-spinning process from GO liquid crystals to fibers in a continuous manner. (b) The structural evolution in the spinning process, which indicates the enhanced alignment process under uniaxial flow during the spinning (Section I), from the powder GO LC with different orientation ordering to the regular alignment of the flowing GO LC dope, GO LC gel fibers (Section II) and final dried GO fibers (Section III). The red arrows denote direct vectors.

reduction when employing neat GO LCs as raw materials [19,53,55–57,66]. The chemical composition of GF primarily consists of carbon, oxygen and affiliated hydrogen elements. Depending on the reduction extent, the carbon content of neat GF ranges from 80% to 99%. Chemical reduction by reagents such as hydrazine hydrate and hydriodic acid usually give around 80% carbon, and thermal annealing especially at high temperature above 800°C raises the value up to 95%, approaching that of conventional CFs [53,66].

Neat GF consists of well-aligned graphene sheets only along the fiber axis. Its structural order involves two correlated aspects: the alignment along the fiber axis and the layered attribute in the fiber

radial direction (Fig. 6). Graphene sheets with a folding morphology are well-aligned along the fiber axis, and their lateral size and degree of alignment play key roles in the optimal expression of expected properties and, as a result, guide the improvement of the performance. After the first GF was made of GO and corresponding graphene sheets with lateral sizes of several microns, the availability of GO with giant size (GGO) of up to one hundred microns has rendered the creation of GF from these giant materials, by wet-spinning GGO LCs [39,41]. Several experiments in Refs. [55–58] confirmed this trend: the enlargement of graphene lateral size promoted the combined properties, not only in mechanical strength but also in electronic functionalities. GFs made from

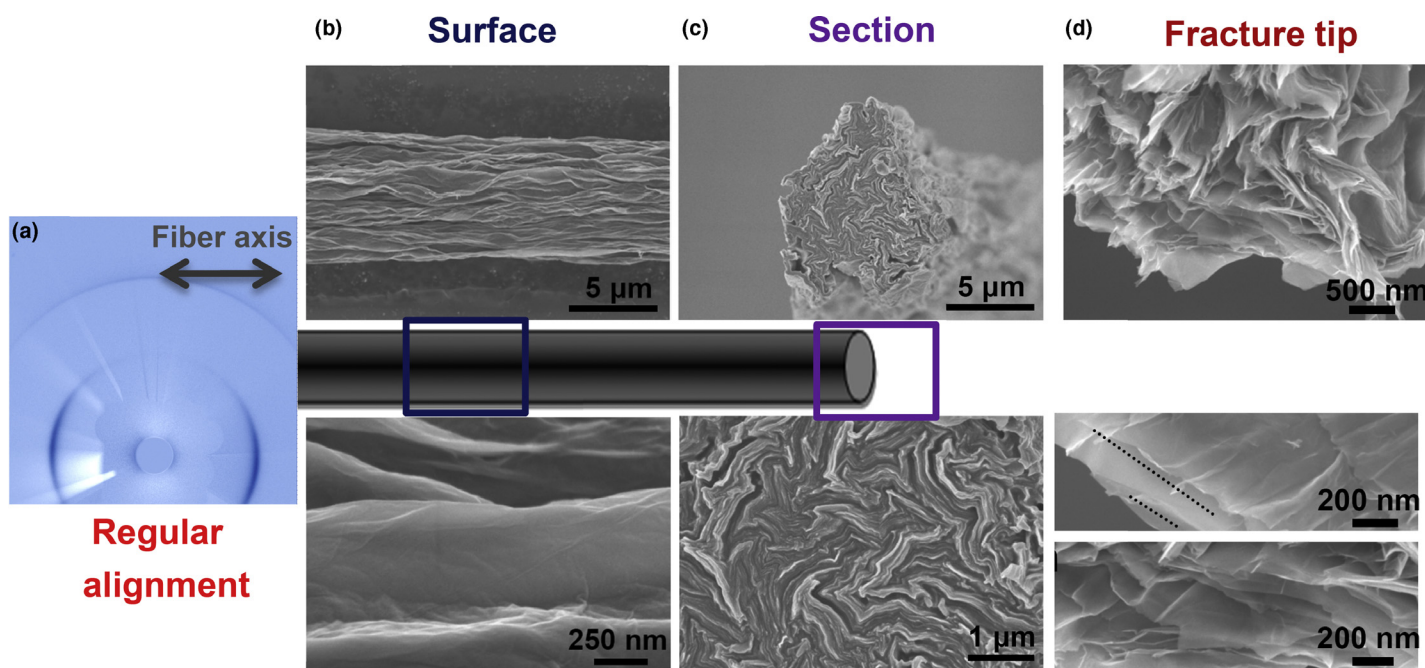


FIGURE 6

Microstructural attributes of GF. Graphene sheets are well-aligned along the fiber axis, as demonstrated in the 2D XRD pattern (a, unpublished result). (b) On the GF surface, wrinkles that originate from radial shrinkage during drying are well-aligned along the fiber axis. (c) Lamellar structure of graphene-assembled bricks on the section. (d) Lamellar graphene sheets at atomic scale identified at the fracture tips.

GGO exhibited higher mechanical strength (0.5 GPa) and electrical conductivity (4.1×10^4 S/m), superior to those (140 MPa and 2.5×10^4 S/m) of GF spun from GO LC respectively. As to the alignment, the stretching operation in the whole wet-spinning process has been shown to be important and raised the elastic modulus of GF up to 47 GPa [57].

The thickness of graphite crystals that are re-assembled from individual graphene sheets is essential as well (observed in the fracture tips), which is reflected in the compactness or density of GF. Recent efforts have mainly been devoted to the control over the wet-spinning and the choice of reduction methods. Appropriate coagulation baths such as ethanol/water calcium ion solutions and stretching were efficient to get compact structure of GFs, but their density of lower than 1 g/cm^3 is still much lower than that ($1.7\text{--}1.9 \text{ g/cm}^3$) of conventional CFs, not to mention that (2.2 g/cm^3) of ideal graphite crystals [55]. Possibly profiting from the sophisticated control system in wet-spinning industrial technology and underlying theoretical understanding, the control system of wet-spinning of GFs will be established in the near future. During reduction, the elimination of oxygen functional groups is prone to cause the exhaust of gas, which inevitably undermines the integrated structure and results in GFs with pores, cracks and poor performance. For this reason, some reductants such as HI and vitamin A were testified more suitable for GF than other common reductants for graphene powders such as N_2H_4 and NaBH_4 [49,55].

In addition to these structural factors, the interlayer interaction among graphene sheets is essential at the atomic scale to dominate the performance of neat GFs. For example, multi-valent Ca^{2+} ions can bridge reduced graphene sheets by forming coordinate bonds with residual oxygen groups, and the introduction of these ions brought a remarkable enhancement by $\sim 65\text{--}100\%$ in the mechanical strength of GFs [55,56]. Ultimately, covalent links with the

highest bond energy are needed to bridge graphene sheets that will enhance the properties of GFs. This extreme protocol does not mean the hard transformation of graphite into diamond; it can actually be achieved by introducing multifunction binders that will couple graphene sheets together by virtue of versatile chemical reactions with basic units of graphene.

Graphene composite fibers and hybridized GFs

In addition to fabricating neat GF, the fluid assembly of graphene into fibers provides the potential to tune components and structures of GFs (also called graphene-based fibers) by wet-spinning graphene-based LCs. In practical terms, GO LCs have been used as an ordered matrix to host many guests ranging from macromolecules with either linear or hyperbranched topology to nanoparticles such as 0D nanodots, 1D carbon nanotubes and nanowires (Fig. 7). The family of graphene-based fibers is growing, and mainly encompasses two categories: biomimetic graphene composite fibers and hybridized GFs.

Biomimetic graphene composite fibers

As graphene has developed into an advanced carbon nanomaterial, it is logical to add graphene to polymeric composites either in bulks or as fibers to enhance their performance and implement functionalities. Example includes graphene-nylon fibers [29], graphene-CNT-PVA fibers [75] and graphene-cellulose fibers [76]. Biomimetic graphene composite fibers are distinct from traditional composites; they possess extremely high graphene content, typically above 50% even exceeding 90%, far more than that (usually below 1–5%) of traditional species. The overwhelming amount of 2D graphene in composite fibers creates their laminated structure that particularly resembles the “brick and mortar” layered attribute of nacre [77], which is the origin of the “biomimetic” prefix. In these nacre-like

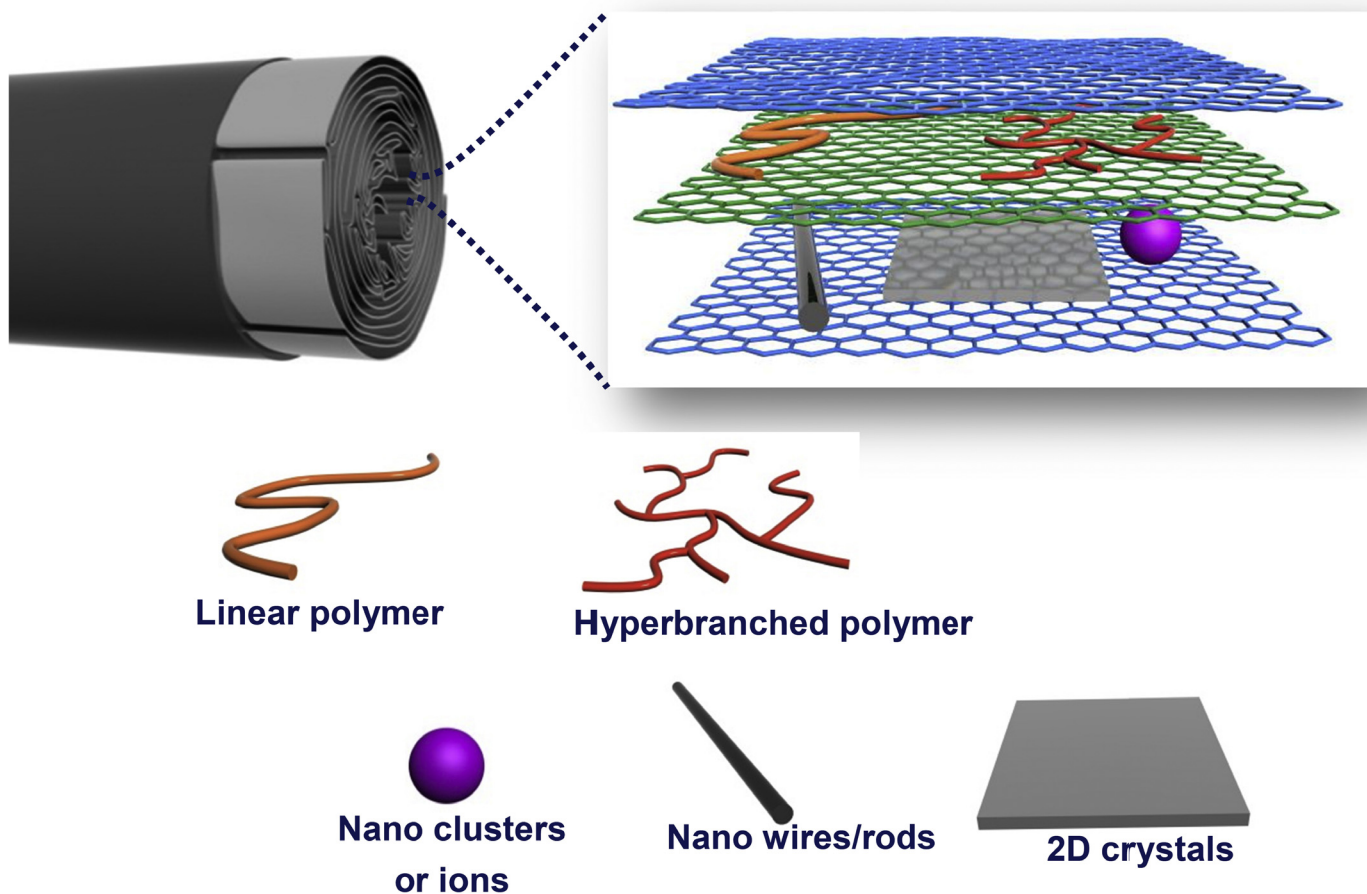


FIGURE 7

Composite and hybridized GFs. Many guests, such as linear and hyperbranched polymers, nano clusters, nano wires/rods, 2D crystals and ions can be introduced into GFs. The graphene composites polymer fibers have nacre-like layered structures and high mechanical strength.

fibers, 2D graphene behaves as bricks and the interlayer macromolecules as mortar, and their mechanical behavior conforms to the classical “tension-shear” model of nacre-like materials.

Two strategies have been developed to fabricate biomimetic graphene fibers continuously based on the state of the guest components, as follows: (1) host-guest LC strategy in which guest components are isolated and (2) building-block approach in which guests are attached on graphene to form independently hybridized graphene building blocks. In the first strategy, polymeric guests were homogeneously mixed with GO in water or other solvents to form GO-based composite LCs as dopes for the wet-spinning of the biomimetic fibers. The ever-reported polymeric guests included linear polymers such as PVA and hyperbranched ones exemplified by hyperbranched polyglycidol (HPG) [46,49]. In the second approach, polymer guests were grafted onto graphene especially through covalent bonds and rendered sufficient dispersibility to form LCs for the wet-spinning of fibers. This approach has generated a rich family of biomimetic graphene fibers that combine linear polymers such as PAN, PVA and hyperbranched ones [47,48,50]. Importantly, the wet-spinning method for graphene composite fibers actually yielded the continuous fabrication of biomimetic nacre-like materials, which was previously confined to a limited size of centimeters.

Merited from their “brick-mortar” structure, biomimetic graphene composite fibers exhibited many favorable properties and

functions. From a mechanical perspective, the interlayer polymeric “mortar” binds graphene sheets together by van der Waals interaction, hydrogen-bonding, or covalent links, which increase the mechanical strength. For example, the multifunctional groups of hyperbranched polymers allow the hydrogen-bond array to tightly connect graphene sheets and the fibers exhibit strength up to 650 MPa, although the mortar bulk alone is extremely weak in strength. The highest strength achieved has already exceeded that of natural nacre and previously fabricated biomimetic nacre-like materials. In terms of functionalities, biomimetic graphene fibers possess good electrical conductivity of approximately 5×10^3 S/m because of the high content of graphene, which is several orders of magnitude higher than that of conventional graphene-based composites. In addition, the compact layered structure allows these fibers to resist chemical erosion by strong acids and bases.

Hybridized GFs

Through two similar strategies for biomimetic graphene composite fibers, hybridized GFs with other versatile nano-objects with rich functionalities have been fabricated as well [58,66,78–82]. These nano-guests have included 1D metallic nanowires and CNTs, 0D quantum dots and nanoparticles, and extend to 2D nano-platelets such as transition-metal dichalcogenides and 2D crystals. The introduction of rich guests is able to enhance or add

many functionalities in GFs. For example, the binary fiber of graphene and 1D Ag nanowires greatly improved electrical conductivity up to 9.3×10^4 S/m, promising for use as a lightweight conductor [58]. Incorporation of paramagnetic Fe₃O₄ nanoparticles imparted magnetism to GF that can be actuated by an external magnetic field [66,79]. GFs hosted with CNTs showed more favorable uses in supercapacitors than neat GFs because of the synergistic effect between graphene sheets and CNTs [80,81]. Alternatively, post-hybridization of neat GFs can improve their performances as well. For instance, the intercalation of electron donors (alkali and rare earth metals) or acceptors (acids and metal halides) should substantially increase the electrical conductivity of GF, similar to graphite intercalated compounds [83].

Combined properties of GFs

Arising from the outstanding properties of graphene building blocks, it is expected that GF should possess an outstanding simultaneous combination of properties in mechanical, electronic and thermal aspects, through a great deal of effort on GFs (Table 1). Beyond its creation, the mission to enhance the intrinsic properties of GFs has advanced quickly in recent years.

Mechanical properties

The first GF only had a tensile strength of approximately 140 MPa at ~5.8% breakage elongation, but had good flexibility to make tight knots [19]. The huge gap between the mechanical strengths of GFs and the constituent graphene sheets must be bridged. In the analysis of the structural characteristics of GFs, three strategies from atomic to macroscopic scales have been proposed to upgrade mechanical performance: (1) improving the alignment of graphene sheets along the fiber axis; (2) decreasing the structural defects that include sheets boundaries, voids and impurities; and (3) enhancing the interlayer interaction of the constituent graphene sheets by either covalent or noncovalent bonds.

Guided by these ideas, the mechanical strength of GF has risen to the GPa range in a stepwise fashion after only 3 years. Stretching during the wet-spinning process has been employed to enhance

the alignment of graphene sheets, and raised the mechanical performance, especially the ultimate strength of GF, up to 0.5 GPa. Stretching also promoted the compactness of graphene laminates and therefore the elastic modulus to 47 GPa. The enlargement of the lateral size of graphene sheets has been confirmed to effectively diminish defective grain boundaries. To enhance the interlayer interaction on the atomic scale, Hu *et al.* introduced hyperbranched molecules with multifunctional groups into interlayer galleries, and their biomimetic fibers with hydrogen bonding arrays exhibit mechanical strength of ~550 MPa, which was further increased to ~650 MPa after chemical crosslinking [49]. Recently, our lab has achieved a strength of 1.1–1.2 GPa by a combination of methods to increase the alignment of graphene sheets and the compactness of GFs (unpublished results). All of these rapid advances justify the thrilling prospect of GF as a new high-performance carbonaceous fiber.

Electronic performance

Another attractive merit of GFs is their excellent electronic properties, such as high electrical conductivity and current capacity. In the preparative system of GO LC-spinning to produce GFs, post-reduction has been designed to circumvent the deficit in electronic quality that is accompanied by good processability of GO. Jalili *et al.* proposed a mild reduction in coagulation baths of strong alkali base (NaOH) and achieved electrical conductivity of 250 S/m [56]. More intensive reduction was obtained using HI or HBr, which enhanced the conductivity to 4.1×10^4 S/m [55]. Although thermal annealing is more efficient than chemical reduction, direct thermal annealing only yielded conductivity of ($\sim 1 \times 10^3$ S/m) [66], comparable to that by intense chemical reduction. The underlying reasons may be that the carbon loss during thermal annealing (the exhaust of carbon dioxide) can undermine the compactness of GFs. Thus, the combination of chemical reduction and thermal annealing, even graphitization, should improve the conductivity of GFs to the level (10^5 – 10^6 S/m) that has been achieved in graphene films [84], already superior to that of conventional CFs.

TABLE 1

The mechanical properties of neat GFs and biomimetic graphene composite fibers.

Species	Tensile strength (MPa)	Young's modulus (GPa)	Failure elongation (%)	Electrical conductivity (S/m)	Ref.	
GOF	102	5.4	6.8–10.1	–	[19]	
GF	140	7.7	~5.8	2.5×10^4	[19]	
GF-1 (CaCl ₂)	364.4	11.2	6.8	–	[55]	
	412 ± 30	20.1 ± 2.1	3.2	–	[56]	
	214 ± 38	47 ± 8.1	0.61 ± 0.1	–	[57]	
GF-2 (CaCl ₂)	501.5	11.2	6.7	4.1×10^4	[55]	
GF-Ag	300	9.5	5.5	9.3×10^4	[58]	
Graphene-HPG fiber	~555	15.9	3.5–5.6	5.2×10^3	[49]	
Graphene-PAN fiber	452 ± 24	8.31 ± 0.56	4.5–5.4	–	[50]	
Graphene-PVA fiber	162	17.1	1.7–3.0	1.3×10^{-2}	[46]	
Graphene-PGMA fiber	~500	18.8	~3.0	186	[48]	
CNT fibers	Wet-spun	~1000	~120	~1.4	$\sim 2.9 \times 10^5$	[18]
	Dry-spun	1300–8800	78–397	4–8	$\sim 5 \times 10^5$	[17]
Carbon fibers	PAN	3530–7000	230–290	1.5–2.4	5.8 – 7.1×10^4	[4]
	Pitch	2740–4700	343–588	0.7–1.4	0.9 – 1.4×10^5	

"–" No available data.

As the restoration of the graphene structure improves, we are able to further improve the conductivity through molecular doping to increase carrier density or mixing with other benchmark metals such as silver, copper and gold. Doping with Ag ions has pushed the conductivity to 9.4×10^4 S/m, and other dopants (alkali metals, acids) may also possibly work well, as in the case of graphene transparent electrodes [85]. GFs mixed with

benchmark metals can be realized by wet-spinning GO-based LCs with nanoparticles of these metals, and this protocol has been used to fabricate Ag nanowire-hybridized GFs [57].

Potential functional uses of GFs

Because GFs possess many of the outstanding attributes of graphene, they should have many functionalities that can be used in a

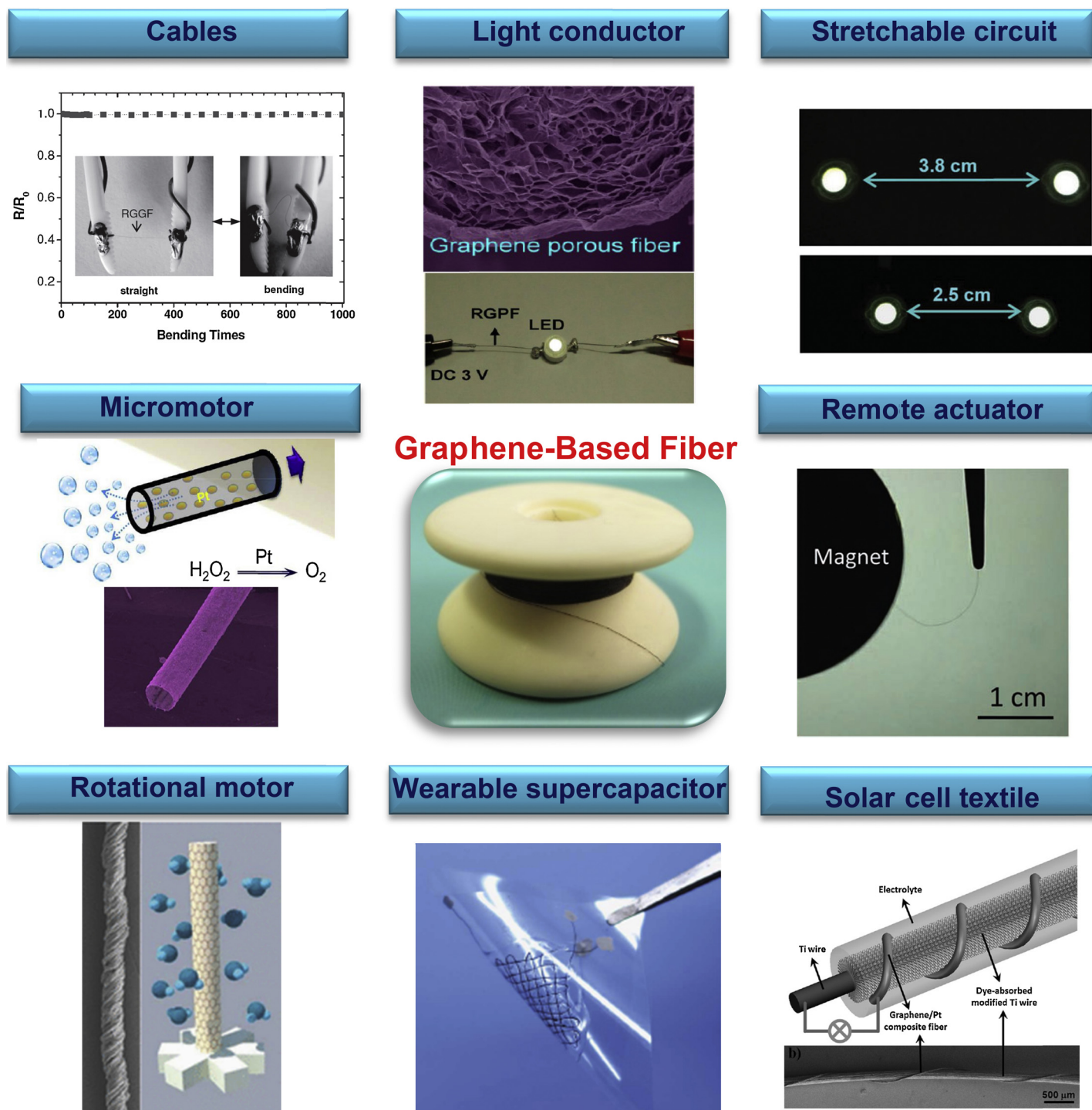


FIGURE 8

Functional applications of GF. The high conductivity of GFs makes them good candidates for lightweight electrical conductors such as cables and flexible wires. By tuning the structure of GF and introducing functional guests, GF can perform rich behaviors of actuation, such as rotation motor and remote actuator. Additionally, GFs can be taken as wearable flexible textiles to be used in supercapacitors and solar cells.

wide variety of functional applications. Apart from the important goal of upgrading the intrinsic properties of GF, considerable effort has been devoted to exploiting their functional uses in products, such as electrical conductors, supercapacitors, actuators and solar cells, all of which indicated the rich functionalities of GFs that surpass those of conventional CFs (Fig. 8).

Lightweight electrical conductors

Highly conductive lightweight GFs are good candidates for wires and cables to carry heavy current. Another advantage of GFs is their valuable flexibility; they can be twisted into tight knots without breaking, which is not possible for conventional CFs. As described in Ref. [52], chemical reduced GFs can be used as conductors to connect prototype devices and batteries. In Ref. [57], Ag-doping enhanced the electrical conductivity and only minimally affected the mechanical strength and flexibility of GFs. Through the “pre-stretching and buckling” strategy, flexible Ag-doped GFs were employed to construct stretchable circuits on rubber substrate, and the resistance remained invariable during 50 cycles of stretching-relaxation. The breakdown current density (ampacity) of this Ag-doped GF was 7.1×10^7 A/m², which should be greatly improved by further thermal annealing and graphitization for practical uses.

Yarn supercapacitors and solar cells

In view of the prospect of using graphene-based films and frameworks as chemical supercapacitors for energy storage, graphene-based fibers have been considered as having potential for becoming useful supercapacitor textiles that are flexible and can be knitted into wearable devices [78,85–93]. The capacitance of GFs was assessed at approximately 100 F/g, and the best result ever reported is 409 F/g because of the highly porous structure of the spun fibers [83]. The introduction of CNTs, single or multi-walled, created extra hierarchical pores in GFs and enhanced their capacitance from 100 F/cm³ to 300 F/cm³ in the case of single-walled CNTs [81]. Other ingredients such as oxides (MnO₂ and Bi₂O₃) and conductive polymers (polypyrrole and polyaniline) also supplemented their pseudo capacitance to the performance of hybridized GFs [78,81–93]. Using a coaxial wet-spinning method, polyelectrolyte-wrapped graphene/CNT core-sheath fibers were designed as safe electrode textiles for direct use in yarn supercapacitors. In addition to their high capacitance (up to 269 mF/cm²) and energy density (3.84 μWh/cm²), the yarn supercapacitor fibers were flexible enough to be interwoven into wearable cloth supercapacitors [90]. As for functional textiles that can generate energy, GFs have been employed to construct photovoltaic wire devices that attained a high-energy conversion efficiency of 8.45% [91]. These energy flexible devices of GFs can be integrated into conventional textile technology for many functional applications.

Smart actuators

Qu's group established a series of smart actuators of GFs, such as self-driven GF tubes, moisture actuators, torsional motors and magnetic-driven springs, by virtue of the design of their structures [94–97]. They used lasers to reduce only one side of GO fibers and obtained GFs with asymmetrically hydrophilic attributes. The remaining GO part was responsive to moisture and drove the

whole GF to bend or curl reversibly [94]. For a torsional motor, they rotated GO gel fibers in the radial direction during the drying process and obtained GO fibers with helically twisted wrinkles on the surface. The twisted GO fibers are able to reversibly respond to moisture by rotation, behaving like a typical rotational motor [95].

Comparison between graphene fibers and carbon fibers

As a new member of carbonaceous fiber, graphene fibers (especially neat) are significantly different from conventional carbon fibers. First, in the aspect of precursor, GFs are prepared from graphite, whereas, conventional CFs can be made from natural or synthetic polymers and small pitch molecules. Second, in terms of fabrication, GFs can be continuously fabricated by the wet-spinning of solvated graphene derivatives, while a combination of spinning, oxidation and thermal pyrolysis is used in the case of conventional CFs. Third, the atomic to micro scale structure of GFs is distinct from that of conventional CFs. GFs consist of well-aligned graphene sheets along the fiber axis, and basic units of CFs are nano-graphite crystals that are interconnected. The lateral crystal size of graphene sheets is much larger than that of CFs, by three orders of magnitude at the most, which can make some GF properties superior to those of CFs controlled by grain boundaries, such as electrical conductivity and thermal conductivity.

Conclusions and perspectives

Graphene fiber is a new high performance carbonaceous fiber with rich functionalities. Its creation significantly demonstrates a novel protocol to fabricate carbonaceous fibers just from mineral graphite. The preparative system of GF has been established in recent years, which encompasses reliable synthesis of solvated graphenes, formation of liquid crystals and wet-spinning for neat or composite GFs. A basic understanding of the structure and properties of GFs has been established preliminarily, and the critical control parameters have also been concluded, including, the lateral size of graphene building blocks, the alignment thereof, and the interaction between them. Guided by these concepts, the combined properties of GFs have been rapidly promoted to a GPa level of tensile strength and electrical conductivity comparable to conventional CFs, promising a thrilling trend toward higher levels on par with or even exceeding CFs.

GFs have demonstrated much more impressive rich functional uses than conventional CFs. These potential applications involved lightweight conductive cables and wires, knittable supercapacitors with high energy density, wearable solar cell textiles, environmentally responsive actuators, micro motors and so on. The functional application of GFs could become pioneering commercial products used in our daily lives, as a typical 1D delegate among forthcoming batches of graphene macroscopic materials.

The recent advances in GFs have urged us to address the central issue, that is, to upgrade its combined performance, mainly mechanical strength and electrical/thermal conductivities. In terms of mechanics, more regular alignment and more compact microstructure can be achieved by the optimization of the spinning process parameters, such as stretching ratio, spinning velocity and so on. In the atomic aspect, the enhancement of interlayer action between graphene sheets should increase the mechanical strength of GF, either by introducing external crosslinking reagents into the interlayer gallery or by partly transforming graphene sheets into

diamond structures [98]. Importantly, the structural model of GF should be established from more detailed characterizations and the corresponding properties.

The optimization of the alignment degree of graphene also promotes the electrical/thermal responses. These functional properties are closely related to the electronic quality of the constituent graphene building blocks. As a result, more effective methods to restore graphene structures to the greatest extent, such as high temperature graphitization, should be sought. Alternatively, we can develop new graphene precursors with reversible functionalization for high enough electronic quality, which is also a central issue in the whole vicinity of graphene. *p*- or *n*-type chemical doping based on the concept of ancient graphite intercalation compounds will considerably increase the carrier density and the electrical conductivity of GFs to surpass graphite materials such as CFs.

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