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Graphene in Macroscopic Order: Liquid Crystals and Wet-Spun Fibers

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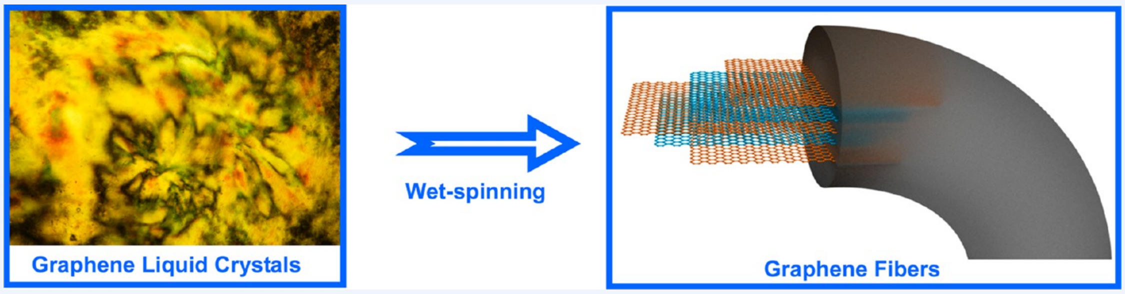

CONSPECTUS: In nanotechnology, the creation of new nanoparticles consistently feeds back into efforts to design and fabricate new macroscopic materials with specific properties. As a two-dimensional (2D) building block of new materials, graphene has received widespread attention due to its exceptional mechanical, electrical, and thermal properties. But harnessing these attributes into new materials requires developing methods to assemble single-atom-thick carbon flakes into macroscopically ordered structures. Because the melt processing of carbon materials is impossible, fluid assembly is the only viable approach for meeting this challenge. But in the meantime, researchers need to solve two fundamental problems: creating orientational ordering in fluids and the subsequent phase-transformation from ordered fluids into ordered solid materials. To address these problems, this Account highlights our graphene chemistry methods that take advantage of liquid crystals to produce graphene fibers.

We have successfully synthesized graphene oxide (GO) from graphite in a scalable manner. Using the size of graphite particles and post fractionation, we successfully tuned the lateral size of GO from submicron sizes to dozens of microns. Based on the rich chemistry of GO, we developed reliable methods for chemical or physical functionalization of graphene and produced a series of functionalized, highly soluble graphene derivatives that behave as single layers even at high concentrations.

In the dispersive system of GO and functionalized graphenes, rich liquid crystals (LCs) formed spontaneously. Some of these liquid crystals had a conventional nematic phase with orientational order; others had a lamellar phase. Importantly, we observed a new chiral mesophase featuring a helical-lamellar structural model with frustrated disinclinations. The graphene-based LCs show ordered assembly behaviors in the fluid state of 2D colloids and lay a foundation for the design of ordered materials with optimal performances.

Using the wet-spinning assembly approach, we transformed prealigned liquid crystalline dopes into graphene fibers (GFs) with highly ordered structures. We extended the wet-spinning assembly strategy to polymer-grafted or mixed graphene LCs to obtain hierarchically assembled, continuous nacre-mimetic fibers and hybridized graphene fibers. Both the neat GFs and the composite fibers are strong, flexible, electrically conductive, and chemically resistive. Multifunctional fibers that are both flexible and modular could be a key for applying atomically thin graphene in real-world materials and devices such as supercapacitors and solar cells. Therefore, we have opened a brand-new avenue for transforming mineral graphite into high performance, multifunctional GFs and offered an alternative strategy for the fabrication of carbon fibers. We hope that this Account and further efforts in the field will guide researchers toward the macroscopic assembly of graphene and its real-world applications.

1. INTRODUCTION

Order Brings Strength. This intuitive insight is not only greatly significant in our daily experiences, for example, strong threads aligned from fluffy cottons, but also rapidly advancing nanotechnologies. It is this concept that guides the design of macroscopic ordered materials with optimal performances integrated from unsymmetrical nanoparticles with fascinating properties. To utilize nanoeffect properties and, sometimes, circumvent the unmeltable nature of nano building blocks, fluid assembly methodology for ordered structures was proposed to effectively bridge the gap between nanoscopic and macroscopic scale, as convincingly demonstrated by advanced materials of one-dimensional (1D) carbon nanotubes (CNTs) and two-dimensional (2D) mineral clays.[1,2]

Over the past decade, graphene, the paradigmatic 2D carbon crystal, has germinated as an attractive building block with a cornucopia of marvelous properties, for the design and fabrication of high performance macroscopic materials with multifunctionalities.[3,4] By the very fluid assembly methodology,

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considerable intelligent efforts have created rich graphene macroscopic materials hitherto, involving 2D (films/papers) and three-dimensional (3D) forms (aerogels) with versatile uses in extensive applications (Figure 1).[4−7] To promote the efficient applications of graphene forward, however, was hindered by the lacking of facile yet effective fluid assembly for their macroscopic ordered structures. It is the challenge that not only suppresses the optimal translation of fascinating properties of individual graphene components as superior macroscopic performances, but also defies the dreamed graphene fibrous materials in 1D form.

In this Account, we describe the newly sprouted concept to realize graphene macroscopic ordered materials, especially graphene fibers (Figure 1), passing through graphene chemistry and graphene liquid crystals (LCs) with macroscopic ordering in fluid state. The whole presented system consists of three logical sections: (1) solvated graphene derivatives with highly stable dispersibility by graphene chemistry; (2) rich lyotropic liquid crystalline behaviors of well-soluble graphene derivatives; (3) wet spinning LCs for graphene fibers (GFs), either neat or hybridized. The strategy, "Graphene Chemistry−Liquid Crystals−Graphene Fibers", represents a fresh philosophy to effectively assemble individual graphene sheets into ordered macroscopic materials. Moreover, graphene fibers have emerged as an important type of graphene-based material, promising versatile uses as high-performance fibers and functional textiles.

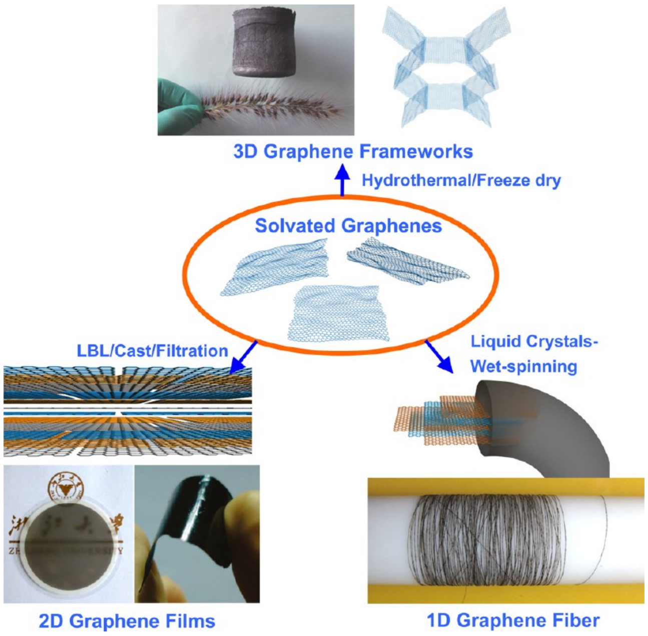


Figure 1. Macroscopic fluid assembly for 3D frameworks with ultralow density (Reprinted with permission from ref 5. Copyright 2013 John Wiley and Sons), ordered 2D thin film for filtration (Reprinted with permission from ref 6. Copyright 2013 John Wiley and Sons), self-standing paper (Reprinted with permission from ref 15. Copyright 2010 American Chemical Society), and 1D graphene fiber from solvated graphenes. The different colors of graphene in film and fiber models are designed for clarification.

2. CHEMICAL EXFOLIATION: SCALABLE APPROACH TO HIGHLY SOLUBLE GRAPHENE DERIVATIVES

To meet the ever-growing demand of graphene, predictably in tons in the near future, one good choice is to acquire from the bountiful mineral graphite by physical and chemical exfoliation.[8] Physical methods involve the exfoliation of graphite in choice solvents under external forces, in some cases, with the aid of surfactants, which results in the favorable high electrical quality but the limited size and poor dispersibility of graphenes. Chemical methods enable the introduction of functional groups onto graphene to overcome the interlayer van der Waals attraction and enhance the solvation, thereby achieving stable dispersions in desired solvents.[8−16] One of the most reliable chemically exfoliated graphenes is graphene oxide (GO), the single layer of graphite oxide crystals. The multifarious merits of GO, for instance, facile and scalable production, fine dispersibility, rich chemistry, and versatile conversion to graphene, exactly set the basis for considerable researches in graphene macroscopic materials.[4,8]

2.1. Graphene Oxide with Controllable Sizes

Through severe oxidization of graphite, the obtained graphite oxide typically possesses C/O ratio around 1.2−1.5, interlayer spacing about 0.9 nm increasing from 0.34 nm of graphite, and distinctive brown color for the deteriorated conjugated electron system.[9−19] Graphite oxide can easily disassemble to single layered GO in water and polar solvents, stabilized by electrostatic repulsion and solvation with solvent molecules. As a direct evidence of the single layered dispersion of GO, its average thickness was usually lower than 1 nm in AFM characterizations (Figure 2c).[14] Significantly, the facile chemical operation involved makes the preparation of GO scalable, for example, 3 L GO aqueous dispersions at 5 mg/mL, 15 g of GO in total, can be synthesized in one pot by a modified Hummers method (Figure 2b).[17−19]

From the molecular viewpoint, GO can be deemed to be a kind of 2D macromolecule merely with covalent bonds in the planar backbone. The covered area, or lateral size of GO, represents its molecular weight, and the distribution in size

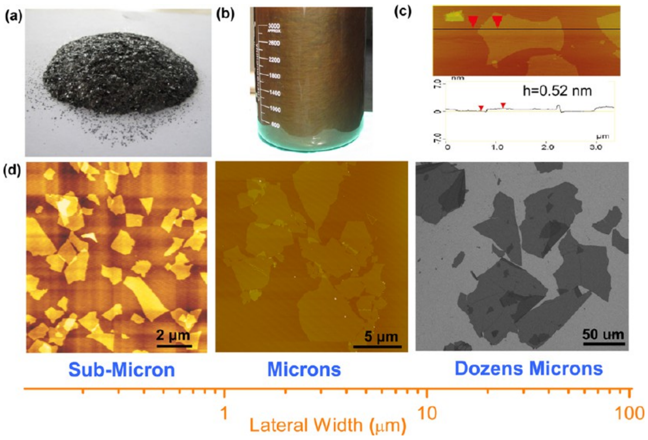
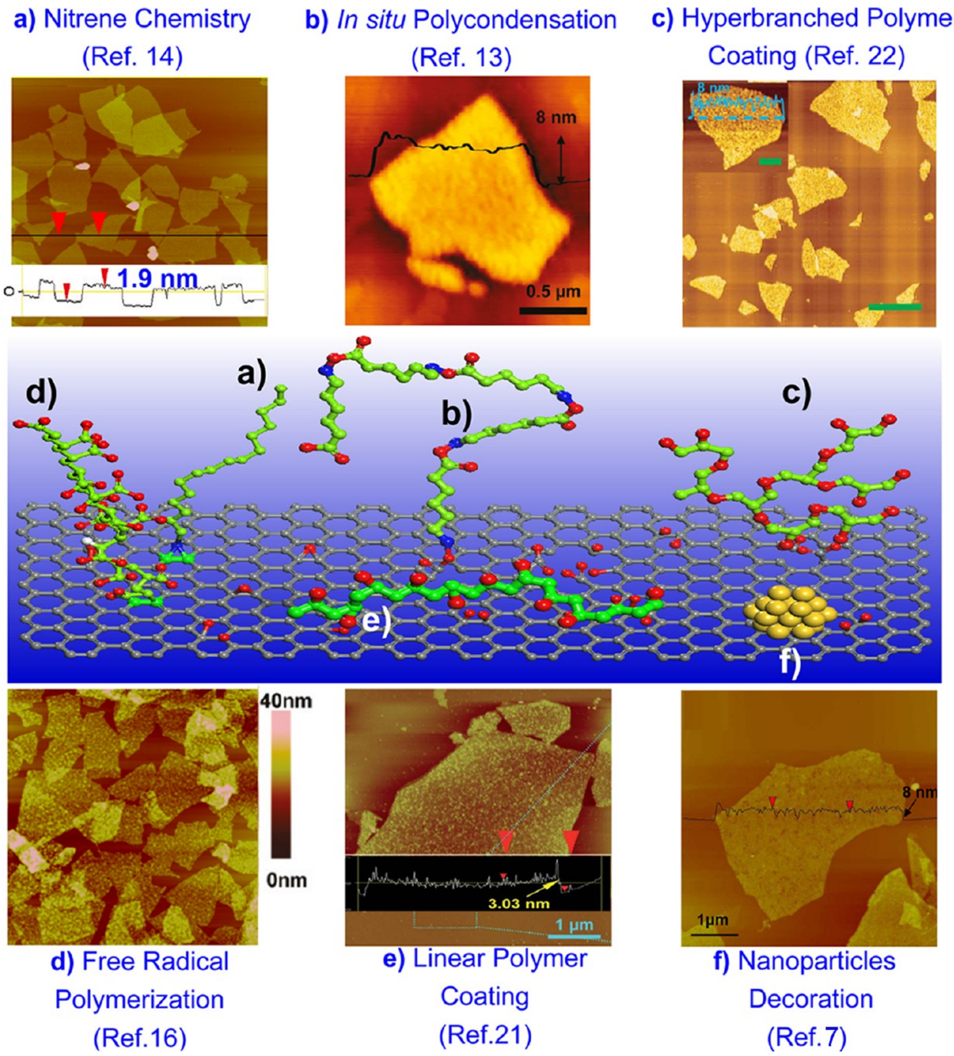


Figure 2. Photos of natural graphite (a) and prepared GO LC dispersion in 3 L (b). (c) AFM height image of GO single layer. (Reprinted with permission from ref 14. Copyright 2010 American Chemical Society.) (d) Single layered GO with tunable sizes from submicrometers to dozens of micrometers. (Reprinted with permission from refs 17−20. Copyright 2010 American Chemical Society; 2011 Nature Publishing Group; 2013 John Wiley and Sons.)



a) Nitrene Chemistry (Ref. 14)

b) *In situ* Polycondensation (Ref. 13)

c) Hyperbranched Polymer Coating (Ref. 22)

d) Free Radical Polymerization (Ref.16)

e) Linear Polymer Coating (Ref.21)

f) Nanoparticles Decoration (Ref.7)

Figure 3. Chemical grafting and physical modification for single layered graphene derivates, as demonstrated by their typical AFM images. Reprinted with permission from refs 7, 13, 14, 16, 21, and 22. Copyright 2010 American Chemical Society (refs 13 and 14); 2011 and 2013 RSC (refs 7 and 21); 2012 Science China Press; 2013 Nature Publishing Group (ref 22).

corresponds to the molecular weight distribution. These two parameters of GO are greatly significant to the performances of macroscopic materials. Through the choice size of raw graphite and post fractionation by isopycnic differential centrifugation, GO series were established to have tunable lateral size ranging from submicrometers to several micrometers and giant size up to dozens of micrometers even approaching 100 μm, as shown in the size spectrum of GO in Figure 2d.[17−19]

2.2. Functionalized Graphenes (FG)

From the precursory GO to the final graphene, chemical and thermal reductions involved elimination of the pendant oxygen functional groups and restoration of the favorable properties of graphene, but brought annoying poor dispersibility simultaneously. To relieve this dilemma, functionalization of graphene is necessary. Before graphene, the same strategy has long been applied to enhance the dispersibility of carbonaceous nanoparticles for processable uses. Since 2004, the author, Gao, and co-workers have addressed considerable efforts on the chemical functionalization of CNTs, including in situ polycondensation, controllable in situ atom transfer radical and ring-opening polymerizations, and click and nitrene chemistries,[20] all of which now become importantly preparative experiences for chemical functionalization of congeneric graphene.

In principle, the chemically active sites of GO can be roughly classified into two categories: the oxygen containing functional groups and conjugated domains as sp^2 hybridized electron system. Therefore, the chemistry of GO can also be divided into two aspects.[9−19,21−24] Figure 3 shows our established modification methods to synthesize well-soluble, single-layer FGs.

The first involves the chemistry of hydroxyl, epoxy, and carboxyl groups on GO sheets. Small and giant reactive molecules have been covalently grafted onto GO basal planes and defective edges with weight fractions of 19−50%.[9] Additionally, the oxygen containing sites could serve as nucleating points to prepare multifunctional graphene hybridized by nanoparticles with tunable density and size.[10−12] We developed an effective "in situ polycondensation" method to make nylon 6-grafted graphene which improves the tensile strength of nylon composite. In early 2011, we found GO could form rich by about 110% at only 0.1 wt % loading.[13] Besides covalent grafting, GO and chemically reduced graphene (CRG) were physically functionalized with both linear and dendritic polymers such as PVA (poly (vinyl alcohol)) and hyperbranched polyglycerol (HPG) via hydrogen-bonding. The sufficiently adsorbed polymer content up to 64 wt % enabled CRG to be well dispersed as single layers in water and polar organic solvents at high concentrations (>50 mg/cm^3).[21,22]

The second reactive site of GO involves C═C double bonds. Free radical chemistry, such as nitrene chemistry and free radical polymerization, was employed to modify graphene effectively. In the case of nitrene chemistry, small molecules and polymer chains with active azido moieties were covalently grafted onto GO by [2 + 1] cycloaddition with C═C bonds at high temperature, which brought in situ thermal reduction of GO simultaneously.[14] As to the free radical polymerization, a family of FGs grafted by more than ten kinds of vinyl polymers was established, covering from hydrophilic PSSNa (sodium sulfonated polystyrene) to hydrophobic PS (polystyrene), and from amorphous PMMA (poly(methyl methacrylate)) to crystalline PAN (polyacrylonitrile).[16,23,24] Detailed investigations suggested the "grafting to" mechanism as active radical terminals in the generated polymer chains reacted with C═C sites of GO. The high density grafting of polymeric chains (1.6×10^4 chains/μm^2) rendered graphene fine dispersibility in water and desired organic solvents, keeping stable in single layer state up to high concentrations (>15 mg/cm^3). The polymer-grafted graphenes are expected as well-compatible nanofillers for universal polymers, and also interestingly behaved as new building blocks of 2D brushes to construct graphene macroscopic materials.[16]

3. ORDERED FLUIDS: LYOTROPIC LCS OF GO AND FGS

In the theoretic frame of colloidal LCs, 2D topological nanoplatelets with high asymmetry should form lyotropic LCs above a critical concentration, the empirical value of which is deduced as $\Phi \approx 4h/D$ (where Φ is the volume fraction, h and D denote the thickness and lateral width of 2D colloids, respectively).[25] The pristine graphene exfoliated from graphite was found to form LCs above 1.8 mg/cm^3, but in the harsh chlorosulfonic acid.[26] Looking for graphene mesophases in more exercisable mild solvents, even harmless water, relies on GO and its well-dispersible chemical derivatives.

3.1. GO Nematic and Lamellar Liquid Crystals

In 2010, we found GO could form rich liquid crystals such as nematic and lamellar mesophases.[17] The nematic phase was subsequently reported by other groups worldwide,[27] which was shortly reviewed in ref 28. These findings presented sophisticated understandings on GO mesophases in the modern language of LCs, beyond the observation of optical birefringence of graphite oxide colloids as early as 1930s.[29]

GO dispersive system performed the typical lyotropic liquid crystalline behavior, i.e. the increasing concentration leads to the formation of mesophases, substantially driven by the competition between orientational entropy and excluded volume entropy. As convincible evidence of nematic LC, GO (D ~ 2.1 μm) dispersion began to exhibit Schlieren textures upon increasing to 3 mg/cm^3 and formed stable mesophases at 5−8 mg/cm^3 in POM (polarized optical microscopy) inspection (Figure 4). The orientational ordering together with disclination defects of GO nematic LCs were also confirmed by quantitative small-angle X-ray scattering (SAXS), visual SEM and TEM, real-time fluorescent microscopy, and rheological investigation.[17] Following the nematic mesophase, the high-level lamellar one of GO was detected after further increasing the concentration above 10 mg/cm^3, mainly evidenced by the integral multiple scattering peaks in SAXS tests (Figure 4).[17]

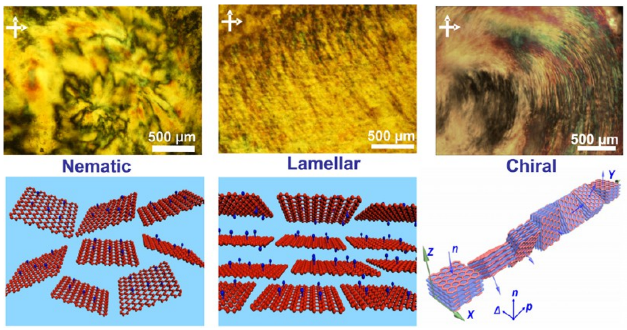


Figure 4. Typical optical textures of GO LCs (nematic,[17] lamellar,[17] and chiral[18] mesophases) and their corresponding structure models. (Reprinted with permission from refs 17 and 18. Copyright 2011 American Chemical Society and 2011 Nature Publishing Group.)

Just after 2 years since 2011, the GO nematic LC family has extended to include GO sheets with lateral width from submicrometers to several micrometers and giant GO (GGO) with dozens of micrometers,[17,19,27,28] and GO nanoribbons (GNRs).[30] The lateral size together with its size distribution of GO were revealed as pivotal factors to their liquid crystalline behaviors: the larger size, higher aspect ratio, and thus lower critical concentration at which phase transition begins (for example, 0.04 vol % for GGO with aspect ratio above 10^4);[27] the more narrow size distribution indicates the more narrow concentration range of phase transition and more regular alignment.[19] This conclusion guides us to prepare GGO and their LCs with low concentration and viscosity, which specifically benefits the fluid processing for continuous macroscopic materials.

3.2. GO Twist-Lamellar Mesophase: A New Chiral LC of 2D Colloids

Besides the ordinary nematic and lamellar mesophase, one may wonder that what new mesophases can form in the newly emerged GO liquid crystalline system?

In the narrowly distributed GO sheets system, we discovered a new chiral liquid crystal (CLC) as GO concentration further increases to 0.38 vol % following the nematic phase at 0.23 vol % (Figure 4).[18] Three important characteristics of this new mesophase were revealed: (1) fingerprint-like texture with aligned bands, indicating the regular rotation of director vectors; (2) strong optical activity; (3) quasi-long-range lamellar ordering, of which the interlayer spacing (d) decreased from 112.2 to 32.7 nm with GO concentration increasing from 0.38 to 2.12 vol %, specifically, conforming a linear function as $d = h/\Phi$.

As far as we know, the GO CLC is the first chiral mesophase of 2D colloids. The attractive puzzle is that how do 2D colloids form the specific mesophase. Cryo-fracture SEM revealed the interior helical-lamellar structure with continuously rotated direct vectors, which conforms the fingerprint like optical textures (Figure 5). In geometry, the lamellar structure and continuous helical attribute should be compromised by frustrated disclinations with rotated vectors, rationalizing the conceived "helical lamellar" model of CLC of 2D colloids (Figure 5e). The electrostatic repulsion between GO sheets boundaries is the dominant interaction in GO CLCs, and therefore, this can be seen as the reason for the twisting of

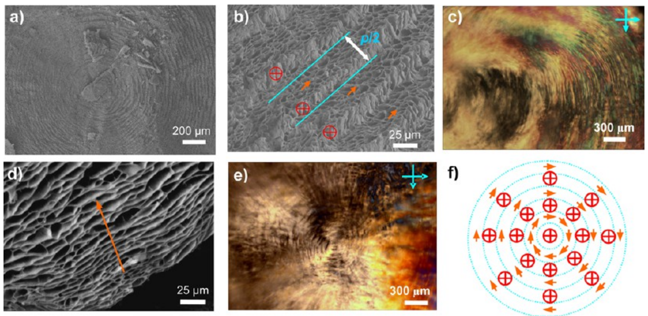


Figure 5. (a,b,d) Cryo-SEM images of GO CLCs with helical-lamellar structures. (c,e) Corresponding fingerprint-like texture of GO CLC and their director vector field (f). (Reprinted with permission from ref 18. Copyright 2011 Nature Publishing Group.)

adjoining sheets boundaries. This deduction was evidenced by experiments in which the increasing ionic concentration screened the electrostatic repulsion, brought deterioration to the liquid crystalline structure, and, as expected, gradually reduced the optical activity of GO CLCs to complete zero.[18]

3.3. FG LCs

After GO, many exemplars of FG LCs were established, and the LC family has included linear PVA wrapped, hyperbranched HPG wrapped, vinyl polymer PAN grafted and surfactant stabilized FGs.[21−24,31]

Long polymer chains coated on graphene, either by covalent grafting or physical adsorption, offer entropic repulsion to suppress the irreversible aggregation of graphene and, therefore, endow graphene a good solubility in favorable solvents. Exemplified by the case of HPG-wrapped graphene, the adsorbed hyperbranched molecules brought a high hydroxyl density to the modified graphene sheets, approaching 35−260 hydroxyl groups per 1000 carbon atoms. As a result, HPG-coated graphene displayed good dispersibility in polar solvents even after long-time hydrothermal reduction at 160 °C and, moreover, spontaneously formed LCs rather than annoying precipitation.[22]

In the cases of linear PAN and poly(glycidyl methacrylate) (PGMA) covalently grafted graphene, the partially remaining oxygen containing groups and the grafted polymer chains simultaneously provided electrostatic repulsion and entropic repulsion among graphene sheets. This system performed rich liquid crystalline behaviors, including nematic and CLC mesophases.[23,24]

Besides the promotion of the LC formation, there is another significance of graphene chemistry to be emphasized: its capability in tuning the chemical composition aids the design of interlayer interactions between solvated graphene sheets and the upgrading of macroscopic properties of the final assembled materials.

4. ORDERED MATERIALS: WET-SPINNING OF NEAT GFS

4.1. The Concept: From Graphene LCs to Continuous GFs

Graphene fiber is the much dreamed macroscopic material of graphene in 1D form. GF in continuity should be assembled by regular alignment of individual graphene and is hoped to possess marvelous attributes of graphene components. By fluid assembly, the continuous alignment of graphene in the solid state can be deduced from the ordering in the fluid state; that is to say, graphene LCs ensure the preparation of GFs with continuously regular alignment.

The finding of GO and FG LCs puts the concept to fabricate GFs by wet-spinning into practice. Since our first try of wet-spinning of GFs,[18] many efforts have been endeavored to upgrade their combined performances (e.g., mechanical strength, electrical conductivity, and functional uses), and moreover, extending this concept has obtained a rich family of graphene-based fibers, including neat GFs, biomimetic composite fibers, and hybridized fibers.[19,21−24,32−34]

4.2. Neat GFs

Employing the similar principle of wet-spinning for polymeric fibers, the continuous injection of liquid crystalline GO dispersions into coagulation baths, generates continuous GO fibers (GOFs). After chemical reduction, GO fibers turned into GFs, strictly speaking, reduced GFs. The wet-spun GOFs and GFs inherit the orientational ordering of the flowing GO liquid crystalline dopes and, therefore, keep the continuity and possess good mechanical performance. The mechanical strengths of the first made GOF and GFs were measured as 102 MPa at 6.8−10.1% ultimate elongation and 140 MPa at ~5.8% elongation, respectively. Notably, these fibers are so flexible that can be fastened into tight knots without any breakage, and integrated into conductive patterned textiles with other threads (Figure 6).[18]

Our first try with GF has justified the wet-spinning philosophy. However, the huge gap between mechanical strengths of macroscopic fibers and the constituent graphene sheets is eager to be bridged. By analogy of the structural model of GFs with well-established polymeric fibers and CNT fibers, three strategies, from atomic to macroscopic scales, are deduced to be able to upgrade the mechanical strength of GFs: (1) increasing the interlayer interaction by introducing high energy bonds, either covalent or noncovalent; (2) decreasing the structural defects, such as graphene sheets boundaries, voids, and foreign impurities; (3) enhancing the regular alignment of graphene sheets along the fiber axis.

Following these three principles, the availability of GGO sheets offers an opportunity to enhance mechanical strength of fibers thereof. From GGO LCs in aqueous and organic

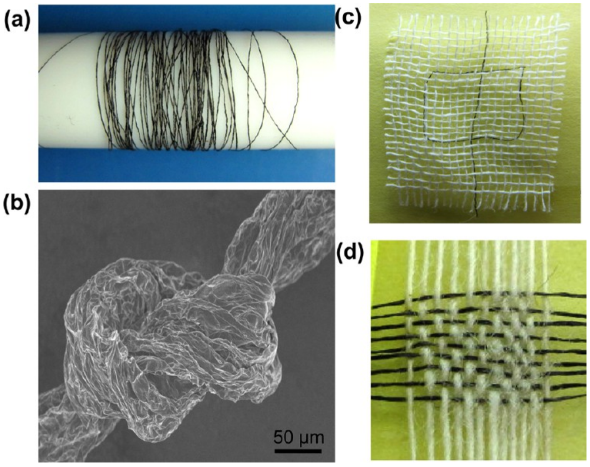


Figure 6. (a) Meters long macroscopic GOFs. (b) SEM image of a graphene fiber knot. The knitted pattern (c) and mat of graphene fibers (d). (Reprinted with permission from ref 18. Copyright 2011 Nature Publishing Group.)

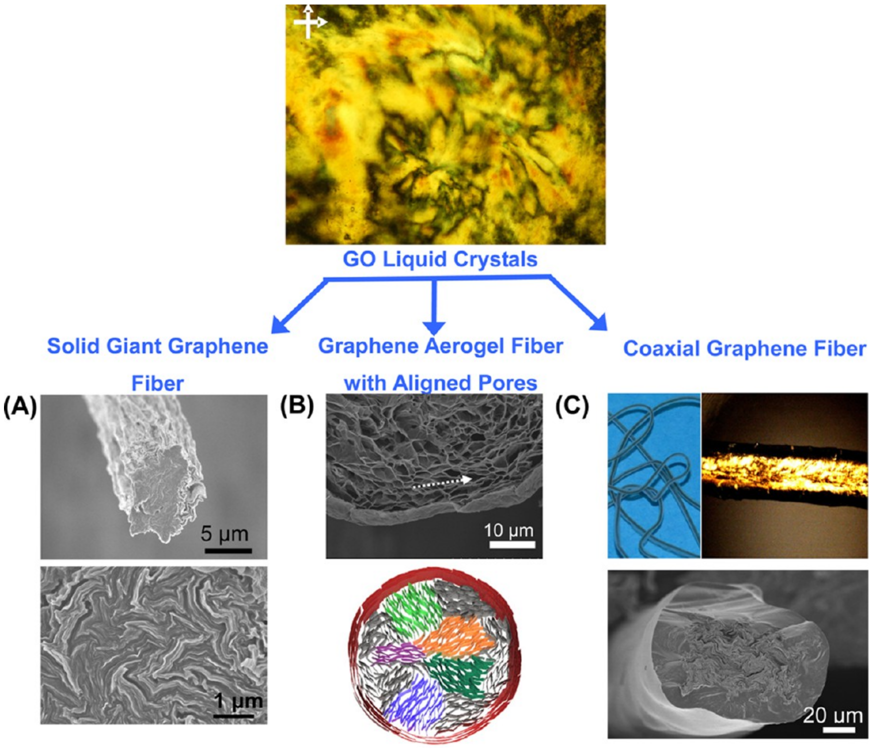


Figure 7. Preparation of strong graphene fibers from GGO LCs (A) (Reprinted with permission from ref 19. Copyright 2013 John Wiley and Sons), graphene aerogel fibers with aligned pores by freezing dry spinning (B) (Reprinted with permission from ref 34. Copyright 2012 American Chemical Society), and coaxial polymer-graphene fibers (C, unpublished figures).

Table 1. Mechanical Properties of Neat Graphene Fibers

species	tensile strength (MPa)[c]	Young's modulus (GPa)	failure elongation (%)	electrical conductivity (S/m)	toughness (MJ/m^3)	ref
GOF	102	5.4	6.8−10.1	[b]	~10.3[a]	18
GF	140	7.7	~5.8	2.5 × 10^4	~9.52[a]	18
GGO fiber ($CaCl_2$)	364.4	11.2	6.8	[b]	~24.7[a]	19
	412 ± 30	20.1 ± 2.1	3.2	[b]	~6.3[a]	32
	214 ± 38	47 ± 8.1	0.61 ± 0.1	[b]	1.3[a]	33
RGG fiber ($CaCl_2$)	501.5	11.2	6.7	4.1 × 10^4	~33.5[a]	19
GNR fiber	378.0 ± 5.0	39.9	1.10 ± 0.13	2.8 × 10^4	~3.8[a]	30

[a] Estimated values deduced from the tensile curves in the references. [b] No available data. [c] Strength was based on the measured section area of fiber samples. It is more appropriate to express the strength as specific stress (N/tex), for irregular shapes of spun graphene fibers.[33]

solvents, continuous GGO fibers and GFs were fabricated by wet-spinning with the wet stretching operation unit, which was realized by the overwhelming collecting velocity than extrusion velocity.[19,33] Both GGO fibers and their reduced GFs had regular alignment of the constituent graphene sheets along the fiber axis, evidenced by the alignment of wrinkles on fiber surfaces and the densely compacted laminates on fiber sections (Figure 7A). Compared with GFs assembled from GO with several micrometers width, GGO fiber and GFs showed enhanced mechanical strengths, which tested as 180 MPa at ~7.5% elongation and 303 MPa at ~6.4% elongation, respectively (Table 1).[19]

Learning from the delicate biological materials, the introduction of coordinating cross-linking can enhance the interlayer interaction of constituent graphene sheets and therefore improve the strength of fibers. During wet spinning process, the choice of coagulation baths with divalent ions, such as Ca^{2+} and Cu^{2+}, simultaneously introduced coordinating bonds as cross-linking factors in the final fibers. The spun GGO fiber and reduced GGO (RGG) fibers cross-linked by Ca^{2+} ions performed enhanced mechanical strengths up to the record 412 MPa at 3.2% elongation[32] and 501 MPa at 6.7% elongation,[19] respectively. Together with the enhanced mechanical performances, the electrical conductivity was improved to 3.8−4.1 × 10^4 S/m, for the enlargement of graphene sizes and their optimized regular alignment.[19]

Aside from these three strategies listed above, some encouraging reports demonstrated that conventional thermal treatment is also a good choice to upgrade the performance of GFs. Thermal annealing at 1050 °C gave one magnitude improvement in strength to graphene nanoribbon fibers, increasing from 33 to 383 MPa.[30] As to the graphene sheets fibers, Qu and co-workers reported that thermal treatment at 800 °C promoted a 130% increasing in tensile strength of GFs, from 180 to 420 MPa.[37]

4.3. Porous or Coaxial GFs

Controlling the coagulation conditions and nozzle types brought special porous structures to GFs.[34] In the spinning process, we employed liquid nitrogen as coagulation bath, followed by freeze-drying, to prepare graphene aerogel fibers

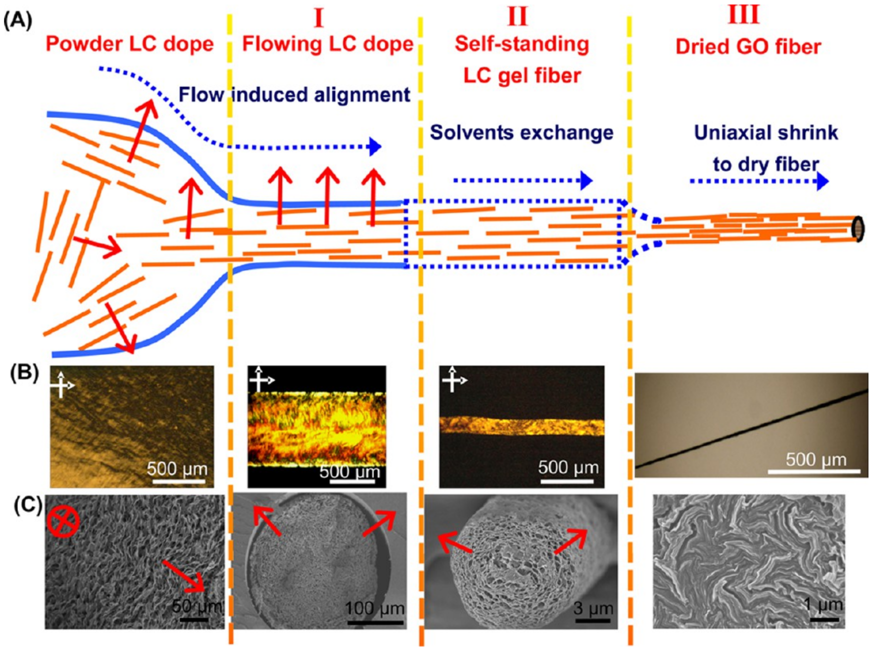


Figure 8. The structural evolution (A) and experimental track in the spinning process (B,C). The upper row indicates the enhanced alignment process under uniaxial flow during the spinning (I), from the powder GO LC with different orientation ordering to the regular alignment of the flowing GO LC dope, GO LC gel fibers (II), and final dried GOFs (III). The red arrows denote the direct vectors. The middle and bottom rows are the tracking results by POM (B) and visual SEM (C) on the fiber sections. Reprinted with permission from refs 19 and 34. Copyright 2013 John Wiley and Sons and 2012 American Chemical Society.

with aligned pores core and densely compact shell (Figure 7B). The unique core–shell structure and regular alignment of GO sheets gifted high specific tensile strength (188 kN m kg^{-1}), fine compress strength (3.3 MPa) and high specific surface area (884 m^2 g^{-1}) to the aerogel fibers simultaneously, which relieves the intrinsic conflict between porosity and strength to a certain extent. Additionally, the inside pores in aerogel fibers offered space to be filled by functional guest particles (Pt or Ag nanoparticles) or polymers, providing GFs more useful multifunctionalities.[34] Coaxial spinning of GO dispersions has created continuous coaxial GFs featured with graphene core and polymer shells or CNT core and graphene shell for promising use of yarn supercapacitors (Figure 7c).

4.4. Observation and Control of Wet-Spinning

LC based wet-spinning process for GFs is essentially the phase transformation from ordered fluids to ordered solids, of which the efficiency is important to the performances of final solid fibers. Tracked by POM and visual SEM, we summarized the qualitative understanding on this phase transformation as shown in Figure 8.[17−19,21−24,34−36] The journey from the precursory GO LC to final fiber comprises three episodes. The first (I) is the flow-induced unidirectional alignment of GO sheets to homogenize orientational orderings along the flow direction, against the random distribution in three dimensions of aligned domains in the still GO LC. The second (II) is solvents exchanging between coagulation baths and dopes, which makes solvated GO interconnect to each other to form self-standing gel fibers. In this step, the wet-drawing promotes more regular alignment of GO along the fiber axis. The last (III) is the drying procedure. The evaporation of solvents brings the radical shrinkage of gel fibers, the buckling of GO sheets, and final compact stacking of solid GOFs with typical wrinkled surface morphology.

The understanding of the wet-spinning gives important hints for spinning GFs. Two important control factors on their structure and macroscopic performances have been exploited in recent investigations, including coagulation and bath stretching. The optimal coagulation bath should be chosen to be miscible with solvents of dopes, and further to have a balanced solvent exchanging rate, in order to get the final compact structure of GFs. In the examples of GOFs spun from aqueous LC dopes, ethanol/water mixture with divalent ions was tested as an effective coagulation bath.[19,32,33] As an extremely important operation to every step in the whole wet-spinning process, stretching not only perfects the compact structure of the fibers but also promotes the regular alignment of the constituent graphenes, which was experimentally evidenced by the higher Young's modulus (up to the record 47 GPa)[33] and tensile strength (up to 0.5 GPa)[19] of GFs with stretching during wet-spinning. Until now, previous valuable efforts are far from enough, and the complexity of the wet-spinning process for optimal GFs is still calling more efforts to establish systematical understandings and parametric control system to upgrade their performances to the utmost extent.

5. ORDERED COMPOSITES: CONTINUOUS NACRE-MIMETIC AND HYBRIDIZED FIBERS

Another important member of GF family is graphene composite fibers hybridized with rich guests, including nanoparticles, polymers, and possible countless other components. Recently competitive efforts focused on graphene composite fibers with polymer guests that hold the capability to stabilize the graphene-based LCs and further tune the interlayer interactions.[21−23,38] According to the state of guest components before wet-spinning, the preparation of graphene composites fibers can be divided into two principal categories: (i) host–guest LC approach in which guest components are

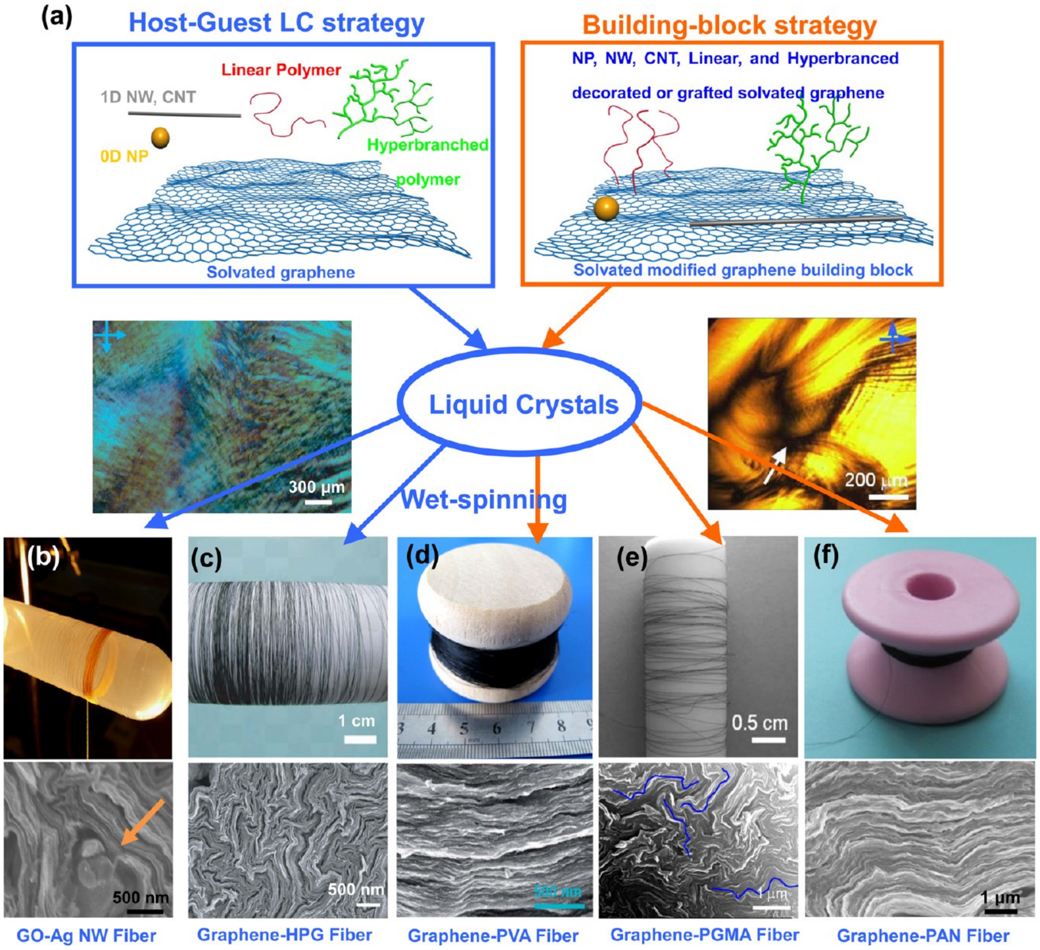


Figure 9. Host–guest LC and building-block strategies for the fabrication of graphene-based composite fibers, including GO-Ag NW fibers (Reprinted with permission from ref 35. Copyright 2013 John Wiley and Sons), graphene-HPG fibers (Reprinted with permission from ref 36. Copyright 2013 Nature Publishing Group) from mixing LC dopes and graphene-PVA (Reprinted with permission from ref 21. Copyright 2013 RSC), graphene-PGMA (Reprinted with permission from ref 24. Copyright 2013 Nature Publishing Group), and graphene-PAN biomimetic fibers (Reprinted with permission from ref 23. Copyright 2013 American Chemical Society) with B&M structures from FG LCs.

Table 2. Mechanical Properties of Graphene Composite Fibers

species	tensile strength (MPa)	Young's modulus (GPa)	failure elongation (%)	electrical conductivity (S/m)	toughness (MJ/m^3)	ref
graphene-HPG fiber	~555	15.9	3.5–5.6	5.2×10^3	~18	36
graphene-PAN fiber	452 ± 24	8.31 ± 0.56	4.5–5.4		4.9	23
graphene-PVA fiber	162	17.1	1.7–3.0	1.3×10^{-2}	4	21
graphene-PGMA fiber	~500	18.8	~3.0	186	7.8	24

isolated by graphene sheets, and (ii) hybrid building block approach in which guest components are attached on graphene to form independent sandwich-like hybrid building blocks (Figure 9a).

5.1. Host–Guest LC Approach

The interspace between graphene sheets in LCs can play the role of hosts to store compatible guests with maintaining their ordered characteristics, making the wet-spinning of continuous composite fibers possible. Choosing polymers as guests, the prepared LC-based wet spun fibers were featured with typical "brick-and-mortar" (B&M) biomimetic microstructures, where graphene sheets are strong "bricks" and polymers are "soft binders". This method overcomes the limitation of requisite templates in previous preparation methods (e.g., layer-by-layer), and serves as a template-free or self-template method to implement the authentic continuality to artificial nacre materials.

Hyperbranched polymers, exemplified by HPG, were chosen as guests into GO LCs, and continuous biomimetic GFs were fabricated by wet spinning assembly methodology. The self-templated regular compact structures of composite fibers and the interlayer adaptive hydrogen bonding array offered by multifunctional groups of hyperbranched guests rendered ultra high mechanical strength (up to 650 MPa) and impressive toughness (up to 18 MJ m^{-3}) of the fibers, which are 4–7 times and 2 orders of magnitude higher than those of natural nacre, respectively (Table 2).[36]

Striking advances have also been achieved in host–guest graphene composite fibers. The binary GFs hosted by 1D Ag nanowires (NWs) greatly improved electrical conductivity up to 9.3×10^4 S/m (Figure 9b). The combination of remaining good flexibility, high mechanical strength, and enhanced electrical conductivities of Ag-GFs proposes the feasibility to make stretchable circuits for promising wearable functional textiles.[35]

5.2. Hybrid Building Block Approach

Hybridized graphene building blocks, ascending from the rich chemistry of graphene derivatives, easily formed lyotropic LCs and, reasonably, can be wet-spun into composite fibers with regular alignment (Figure 9d−f). This strategy has been tested effectively for many established hybridized graphene samples, involving hyperbranched (HPG) and linear (PVA) polymers, coated and linear ones (PAN and PGMA) grafted graphenes. Sharing the common structural attributes of regular alignment of graphene sheets and B&M compact stacking, all of the wet-spun continuous composite fibers from these hybridized 2D building blocks consequently resulted in high mechanical strength (450−500 MPa), fine flexibility, good electrical conductivity, and favorable toughness (∼10 MJ m^{-3}). Additionally, corrosion-resistance against severe acidic (e.g., 98% sulfuric acid) and basic surroundings (e.g., 1 M NaOH) was revealed in these graphene-based nacre-mimetic fibers, still ascribing to the compact layered structures holding together by the multivalent supramolecular interactions.[21−24]

6. CONCLUSIONS AND OUTLOOK

The ordered assembly of graphene has triggered the finding of graphene rich liquid crystalline behaviors and established the brand-new GFs with promising performances and multi-functionalities. As a growing branch in the rush of nano-technology, it is facing a long-term challenge but with an exciting question: how far can we push macroscopic ordered assembly of graphene?

Recent efforts have revealed the rich liquid crystalline behaviors of chemically derivative graphenes, involving conventional nematic, lamellar mesophases and chiral one with helical lamellar model. It is extensively accepted that the rich chemistry of graphene not only compensates its poor dispersibility, but importantly offers a wealth of possibility to control the surface properties, such as type of charge, grafting kind and density. Together with the tunableness in graphene topological shapes (covering from 0D quantum dots to 1D ribbons and 2D sheets) and lateral size, the controllable surface properties of graphene suggest that graphene family can be taken as a role model to explore ordered assembly in fluid physics. Besides the established nematic and chiral mesophases, more novel liquid crystalline behaviors of graphene are hoped to be found in the near future.

The methodology of LC-based wet spinning has harvested a series of graphene-based fibers with ceaselessly upgrading performances and new functional applications.[35,38] It is this methodology that makes the dream to fabricate high performance carbon fibers directly from mineral graphite come true. The next sprouted targets are the promotion of combined performances of GFs, for instance, stepwise upgrading their mechanical strength to approach and even overwhelm that of conventional carbon fibers, or developing GFs with superior toughness and flexibility. This long-term hard duty can be traced back to the de novo design on the precursor graphene size together with distribution, the control over the interlayer interaction of graphene sheets, and last but not least the optimization of the wet-spinning process. Another short-term predictable goal in GFs is to develop their multifunctionalities such as electrical conductivity, thermal conductivity, electromagnetic shielding, chemical-resistance, wearable energy-storage, and sensors for designed applications, which can propel GFs to spectacular heights to swiftly engage into our daily lives.

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Notes

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