

Liquid Crystals of Graphene Oxide: A Route Towards Solution-Based Processing and Applications

Jizhen Zhang, Shayan Seyedin,* Zhoujie Gu, Nisa Salim, Xungai Wang, and Joselito M. Razal*

The liquid crystalline behavior of graphene oxide (GO) has enabled the design of facile and effective solution processing methods for assembling highly ordered macroscopic graphene structures, further expanding the development of novel graphene-based devices. In this progress report, first the preparation of liquid crystalline graphene oxide (LCGO) with a particular emphasis on different approaches to improve the oxidation efficiency and to control the GO sheet size is discussed. Then the use of LCGO dispersions in the solution processing of 1D, 2D and 3D architectures with highly tailored microstructures is covered. The LCGO composites are also reviewed as an important part of novel graphene-based multi-functional materials. Finally, various applications of LCGO are discussed to highlight the critical role of LCGO in expanding the applications of graphene. Based on these systematic discussions, an outlook on the future directions, challenges, and opportunities in this field is provided.

The discovery of liquid crystalline (LC) GO by various research groups^[9,12–14] has offered opportunities for the fabrication of graphene-based macroscopic assemblies with unique micro-structural orders. Fibers,^[10,15–18] ribbons,^[19] films,^[20] and aerogels^[11,15] made from LCGO have shown remarkable electrical and mechanical properties outperforming those obtained from disordered GO (non-LC GO) widening the already diverse application spectrum of graphene and GO. A topical search in Web of Science Core Collection using graphene oxide and liquid crystalline as search terms showed over 130 papers on the synthesis, processing and applications of LCGO in the last five years with over 2450 citations. Notably, more than 58% of these papers were published in 2015 and 2016 indi-

cating the rapid growth of interest in LCGO. It should be noted that due to the restrictive nature of the search terms used, a large number of related works may have been omitted. Moreover, some researchers may have used LCGO without referring them in the title or keywords and these literatures may not have been accounted for using this simple survey.

In this progress report, we first describe the oxidation mechanisms of the various GO synthesis approaches and how the knowledge on improving the oxidation efficiency and the control of sheet size have been utilized to obtain GO dispersions that display LC behavior. We then discuss the various solution processing methodologies that have been developed in generating various graphene-based architectures including 1D fibers, 2D papers, films and coatings, and 3D hydrogels, aerogels and foams. These areas are discussed to specifically highlight the advantages of LCGO towards the processing of neat (pure) and LCGO-based composites and their applications in many important areas including the development of novel materials for energy storage, optoelectronics and electro-optical switching, to name a few. We also discuss our opinion on the knowledge gaps and the opportunities that these gaps create to further advance this important and exciting field.

1. Introduction

Graphene, the wonder material of 21st century with a unique combination of remarkable mechanical, thermal, electrical, and electrochemical properties, has summoned an enormous attention for use in diverse range of macroscopic assemblies with novel functionalities.^[1–5] The advances in graphene synthesis and processing in the past decade have enabled the fabrication of graphene-based fibers (1D), coatings, papers, and films (2D), as well as aerogels, hydrogels, foams, and sponges (3D). Such diverse arrays of structures have catered for a wide range of applications from energy storage to tissue engineering. Graphene oxide (GO), the oxidized form of graphene monolayer platelet with abundant oxygenic groups (e.g., carboxyl, carbonyl, epoxy, hydroxyl), has shown excellent hydrophilicity, dispersibility and stability in polar solvents^[6–9] making it a popular precursor for fabricating graphene-based assemblies.^[7,10,11] GO can then be reduced (rGO) via chemical or thermal treatments during or after processing to recover the desired properties of graphene such as electrical conductivity.

J. Zhang, Dr. S. Seyedin, Z. Gu, Dr. N. Salim,
Prof. X. Wang, Prof. J. M. Razal
Institute for Frontier Materials
Deakin University
Geelong, VIC 3220, Australia
E-mail: shayan.seyedini@deakin.edu.au;
joselito.razal@deakin.edu.au



2. Synthesis

GO synthesis has been inspired by the synthesis of graphite oxide that dates back to over 150 years ago. The most common

DOI: 10.1002/ppsc.201600396

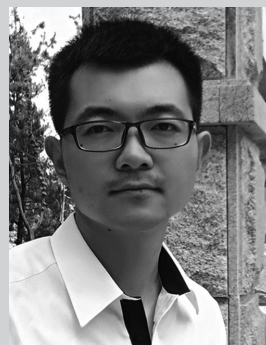
route for GO synthesis is the Hummers' method that is about 60 years old.^[21] In a typical Hummers' method, a graphite source is oxidized using an oxidizing agent in an acidic medium and the mixture is then appropriately washed and collected as a powder or dispersion. Despite having been used for GO synthesis for a long time, the mechanism of Hummers' method has not been fully understood until recently.^[22–24] The synthesis conditions have been found to significantly affect the properties of GO such as average sheets size and defects. For example, by replacing graphite powder as the starting material with expanded graphite and eliminating the sonication step, GO with an average lateral sheet size of $\approx 37\ \mu\text{m}$ has been attained that spontaneously formed LC in water.^[18,25] This section will discuss in detail the important advances in GO synthesis with focus on LCGO preparation.

2.1. Synthesis Mechanism

The methods developed for LCGO synthesis is similar to those of the GO albeit with some modifications to induce the LC feature. Hence, the synthesis of GO is discussed here first and strategies to obtain GO with LC property are then explained. The conversion of bulk graphite into GO according to the Hummers' method generally occurs in three steps (**Figure 1a**): i) formation of graphite-sulfuric acid intercalation compound (GIC), ii) GIC conversion into oxidized pristine graphite oxide (PGO), and iii) reaction of PGO with water to yield GO with a characteristic yellowish brown color.^[24] It is important to note that the reaction can be stopped at any step and the corresponding intermediate product can be isolated, characterized and stored under appropriate conditions.

In the first step (the conversion of graphite into a GIC via intercalation), H_2SO_4 does not spontaneously intercalate into graphite because of the positive Gibbs free energy of the reaction. The GIC can be produced only by means of anodic or chemical oxidation using persulfate or sodium nitrate. GIC was found to form by exposing graphite to an ammonium sulfuric acid $[(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4]$ solution.^[27] This step was found to be reversible with no evidence of chemical oxidation. The electrochemical potential of the surrounding medium generally dictates the intercalation rate of H_2SO_4 .^[23] The GIC formation is manifested by the characteristic deep-blue color of the graphite flakes and can be identified by the suppression of the 2D band (the D-peak overtone) in Raman spectra. Despite the simplicity of this observation, this step has largely been neglected in recent GO literature and has never been systematically utilized to study the mechanism of GO formation.^[24] The influence of eliminating this step on the oxidation efficiency remains unknown as some recent reports have directly mixed graphite flakes with H_2SO_4 without the addition of persulfate or sodium nitrate.^[28,29]

The second step, i.e., GIC conversion into PGO (also called step I oxidation) involves the diffusion of the oxidizing agent into the graphite galleries.^[22,30] PGO powder could be obtained by washing the sample with organic solvents.^[22] The characterization of PGO showed that the sulfur-containing impurities were covalently bound or strongly absorbed onto the GO sheets.^[31] The unoxidized areas in the center of the flake



Jizhen Zhang received his BS and MS degrees from Qingdao University in 2012 and 2015 respectively. He is currently a PhD scholar at Deakin University under the supervision of A/Prof Joselito Razal. His current research is on the development of wearable 2D material-based energy storage devices.



Shayan Seyedin is an Associate Research Fellow at Deakin University. He received his PhD from the University of Wollongong (2014) for his work on advanced fiber spinning of novel organic electroactive nanocomposites for wearable strain sensing. His current work is focused on the synthesis and processing of

novel 2D nanomaterials and the development of advanced functional fibers for wearable energy storage. He is the recipient of an Alfred Deakin Postdoctoral Fellowship and several other awards.



Joselito M. Razal is an Associate Professor at Deakin University and a recipient of Australian Research Council Future Fellowship. He was awarded with a PhD in Chemistry in August 2005 by The University of Texas at Dallas for his work on super-tough carbon nanotube fibers at The Alan G MacDiarmid NanoTech Institute. Prior to

moving to Deakin University in March 2014, he spent 8 years at the University of Wollongong where he worked on various electromaterials including graphene for energy and bionics applications. His research now focusses on developing novel nanomaterials and fibers for use in smart wearable devices and intelligent fabrics.

appeared dark under transmitted light and blue-colored under reflected light (**Figure 1b**). Both the cross-planar oxidation and the edge-center oxidation were found to occur in this stage.^[26] The cross-planar oxidation can result in periodic cracking of the graphene sheets thereby reducing the lateral flake size (**Figure 1c**). Consequently, the reaction time and the amount of oxidant are closely related to the quality and structure of

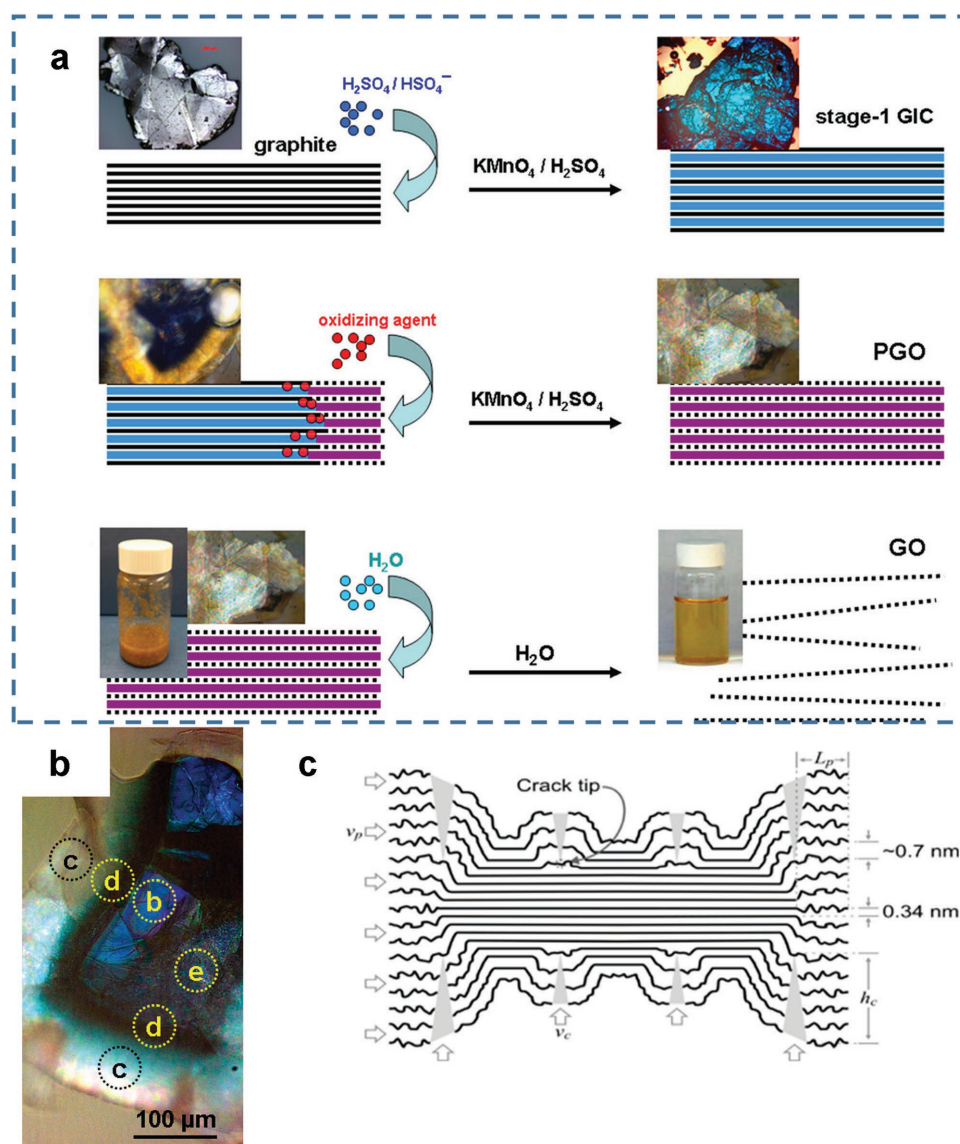


Figure 1. a) Schematic illustrations of conversion of bulk graphite into GO with corresponding sample images at each step, b) optical microphotograph of a graphite flake at the oxidation stage (step I oxidation); the clear edge-to-center front-like propagation of the reaction is an indication that the rate of diffusion of the oxidizing agent into the graphite interlayer galleries is lower than the rate of the chemical reaction itself. Reproduced with permission.^[24] Copyright 2014, American Chemical Society. c) Schematic illustration of crack propagation and penetration of oxidizing solution during the oxidation of a graphite particle. Reproduced with permission.^[26] Copyright 2011, American Chemical Society.

GO that is produced. It has been observed that increasing the amount of oxidant and prolonging the oxidation decreased the GO sheet size from $\approx 59\,000$ to $\approx 550\text{ nm}^2$.^[32] Moreover, the decrease in sheet size also reduced the dispersibility of GO, confirmed by an increase in the zeta potential of the GO dispersion with the oxidation level.^[33] The second step takes about two thirds of the time for GO synthesis. Hence, further understanding of the critical factors affecting the oxidation rate could help to improve the overall efficiency of the GO synthesis.

The third step, the conversion of PGO into monolayer GO after exposure to water, involves the hydrolysis of covalent sulfates and the exfoliation of multilayer graphite oxides.^[22,34]

Another important reaction in this stage is step II oxidation which is further oxidation that occurs after the second step.^[30] It has been found that increasing the reaction temperature and prolonging the reaction time of the step II oxidation can result in a large number of hydroxyl groups in GO and thereby creating more defects within the GO sheets, affecting the thermal stability of GO and the properties of the resultant thermally reduced GO.^[30] These results further highlight the importance of parametric control in the oxidation process as they directly influence the quality of the GO products. We found that the GO synthesis methods used in the literature varied widely resulting in GO with different qualities and properties. **Table 1** summarizes the synthesis and properties of GO in various works.

Table 1. Summary of the experimental details for the GO synthesis.

Shape	Graphite		Media	Step I oxidation			Step II oxidation			C/O ratio	GO sheets			Ref.		
	Size [μm]	Amount [g]		KMnO ₄ [g]	Temp. ^{a)} [°C]	Temp. ^{b)} [°C]	Time [h]	Water [ml]	Temp. [°C]		Time [h]	I _D /I _G	Mean size [μm]		2θ [°] or d-spac. [Å]	Yield [g]
Flake	44	100	H ₂ SO ₄ (2.3 L) NaNO ₃ (50 g)	300	<20	35	0.5	4600	98	0.25	2.1–2.9	–	–	–	188	[21]
	≈300	0.5	H ₂ SO ₄ (60 ml)	1.5	<20	40	5	300	40	1	–	0.93	38.0 ± 16.3	10.3°	≈0.96	[28]
	150	3.0	H ₂ SO ₄ (69 mL) NaNO ₃ (1.5 g)	9.0	<20	35	0.5	400	98	0.4	≈0.64	–	–	8.0 Å	1.2	[35]
	150	3.0	H ₂ SO ₄ (69 mL) NaNO ₃ (1.5 g)	9.0 + 9.0	<20	35	7 + 12	400	0	–	≈0.59	–	–	9.0 Å	4.2	[35]
	150	3.0	H ₂ SO ₄ /H ₃ PO ₄ (9:1, 400 ml)	18.0	35–40	50	12	400	0	–	≈0.45	–	–	9.5 Å	5.8	[35]
Powder	150	3.0	H ₂ SO ₄ (138 ml)	18.0	0–10	35	2	2000	45–95	2–8	–	1.0–1.2	8.8–15.3	9.8–10.9°	–	[30]
	≈1	1.0	H ₂ SO ₄ (23 ml)	3.0	<20	40	1	300	95	0.25	–	0.89	1.7 ± 1.0	11.0°	≈1.52	[28]
	≈50	1.0	H ₂ SO ₄ (30 ml)	3.0	<20	40	3	300	40	1	–	0.95	14.9 ± 8.3	10.5°	≈1.13	[28]
	40	10.0	H ₂ SO ₄ (1.5 L)	60.0	<10	35	2	500	–	2	–	–	2.1	–	–	[9]
	≈44	1.0	H ₂ SO ₄ (23 mL)	3.0	0–20	40	0.5	50 + 150	–	–	2.27–2.49	0.86–0.94	1–20	11.3–12.0°	–	[36]
Expanded graphite	–	2.4	H ₂ SO ₄ (92 ml)	12.0	<5	35	2	200	48	2	2.47	–	~20	–	–	[37]
	<20	2.0	H ₂ SO ₄ (45 mL)	3.0–6.0	<20	35	2	90	–	–	0.31–0.25	≈1.0	–	10.1–10.9°	–	[33]
	–	1.0	H ₂ SO ₄ (200 ml)	10.0	–	–	–	200	Ice bath	–	~1.3	0.85–0.89	32.7	10.1°	–	[14]
	>300	1.0	H ₂ SO ₄ (200 mL)	5.0	Room temp.	Room temp.	24	200	Ice bath	–	0.33	>1	>50	3–6.5 Å	–	[17]
	≈50	5.0	H ₂ SO ₄ (100 ml)	15.0	Ice bath	Room temp.	0.5	400	90	1	2.5	–	~15	–	–	[38]
–	5.0	H ₂ SO ₄ (100 ml)	15.0	Ice bath	Room temp.	≈0.33	400	90	1	–	–	–	11.2°	–	–	[39]
–	≈300	5.0	H ₂ SO ₄ (115 mL) NaNO ₃ (2.5 g)	15.0	Ice bath	35	0.5	230	98	0.25	–	–	23	≈10°	–	[40]

^{a)}Temperature during the addition of water; ^{b)}Temperature after the addition of water.

2.2. Modifications of the Typical Synthesis Route for LCGO

LC is a stable state of materials with properties between those of conventional liquids (anisotropic phase) and those of solid crystals (isotropic phase).^[41–43] Generally, the existence of LC phases can be distinguished by its specific optical properties (such as birefringence) under a polarized optical microscope (POM). The formation of LC in GO suspension relies on three main factors: GO concentration, average aspect ratio of GO sheets, and the liquid environment, such as pH or ionic concentration.^[44] It has been found that the GO suspensions with highly exfoliated and sufficiently large sheets show an isotropic-nematic phase transition with increasing concentration indicating a lyotropic LC behavior.^[9,13] This transition typically consists of the formation of a biphasic mixture (coexistence of isotropic and nematic phases) at a threshold concentration. The LC transitional concentrations can be predicted according to the Onsager theory (Equation (1)) for the hard disc-like lyotropic liquid crystals:^[13]

$$\phi \approx \frac{4T}{W} \quad (1)$$

where ϕ is the volume fraction of LC transition, and T and W are the thickness and lateral width of 2D circular colloids, respectively. This indicates that highly exfoliated GO sheets with large lateral width tend to form nematic phase because of the low ϕ . The biphasic mixture transitions into a fully nematic phase with highly ordered GO sheets with increasing the GO concentration (Figure 2a).^[45] For instance, the isotropic-biphasic phase transition for monolayer GO sheets with the thickness of ≈ 0.8 nm and average lateral width of ≈ 2.1 μm occurred at the concentration of ≈ 0.03 wt.% and the full nematic phase was obtained at ≈ 0.5 wt.%.^[9] For LCGO with average sheet area of 10 000 μm^2 (≈ 50 times larger than the previous example), the full nematic phase concentration was observed to be as low as ≈ 0.1 wt.%.^[14] Experimental results also showed that the transitional concentrations were lower than the theoretically predicted values based on the

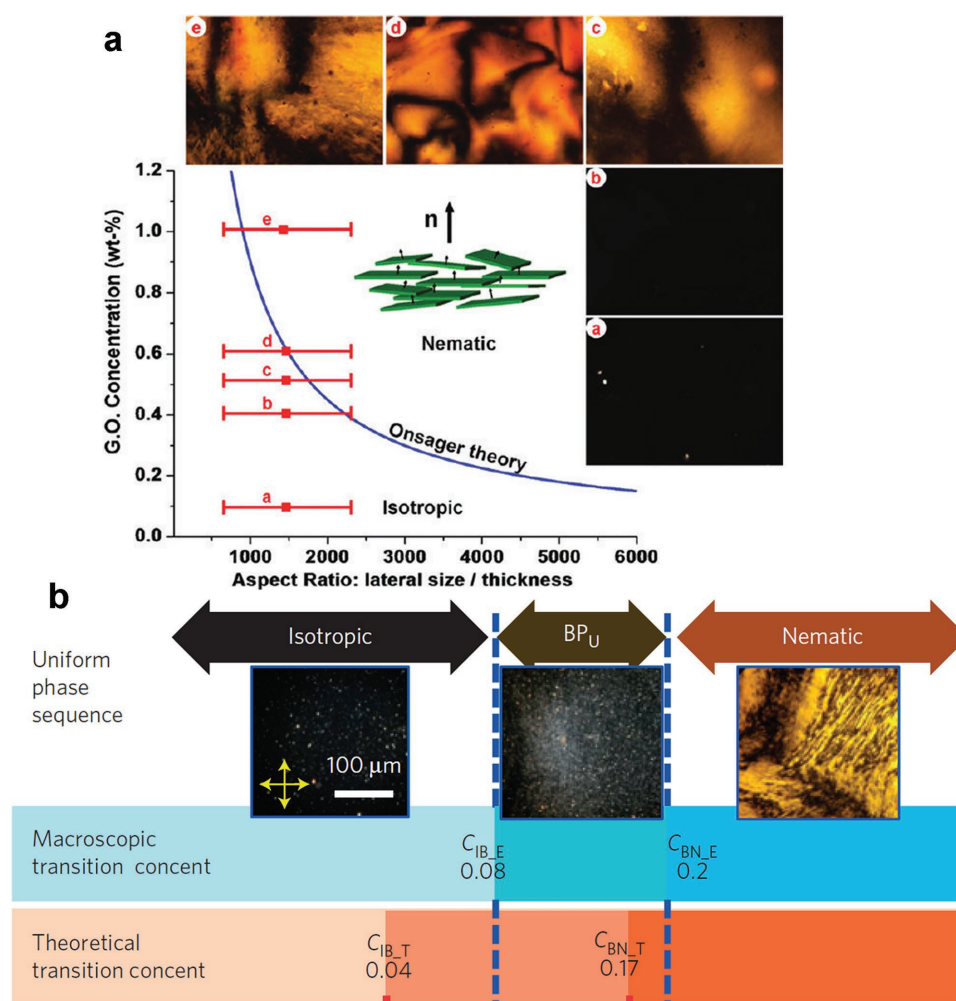


Figure 2. a) Graphene oxide liquid crystal phase diagram; images are optical micrographs of bulk GO aqueous phases under crossed polarizers showing birefringence characteristic of nematic phase at GO concentrations of greater than ≈ 0.4 wt.%. Reproduced with permission.^[45] Copyright 2011, American Chemical Society. b) The uniform sequence of phases determined experimentally (corresponding phase transition concentrations: $C_{IB,E}$, $C_{BN,E}$) and theoretically ($C_{IB,T}$, $C_{BN,T}$). Reproduced with permission.^[50] Copyright 2014, Nature Publishing Group.

hard-disc model (Figure 2b). This discrepancy has been attributed to the flexible nature of the monolayer GO sheets and their polydispersity in size.^[35] Apart from the aspect ratio of GO, removing the acidic or ionic impurities and the unexfoliated graphite oxide particles in the dispersions are also crucial for realizing the LC behavior.^[13] This is because the low pH and the high ionic concentrations result in GO aggregation. It was shown that even low salt (NaCl) concentrations (<0.4 M) results in the LC domains being formed at higher GO concentrations.^[9] With increasing salt concentration, the biphasic GO suspension initially turned into an isotropic phase and then flocculation occurred. In another study, a 2 wt.% GO dispersion with a pH value of ≈ 11 showed no birefringence implying that the LC phase of GO is disrupted in alkaline conditions.^[46] The LC behavior of GO is also sensitive to the types of cations. For example, a high NaOH concentration (>0.044 M) led to the formation of flocculated GO while the similar concentration of KOH did not disrupt the LC property of GO even at a low GO concentration.^[47] These works suggest an efficient LCGO synthesis method is the one that can control not only the sheet size but also the purity particularly when lowering the phase transition concentration becomes critical.^[48] The mechanism of LC formation in GO suspensions have been thoroughly reviewed and interested readers please refer to previous literatures for further details.^[44,48,49]

2.2.1. Improvement of Oxidation Process

The yield and quality of the exfoliated GO monolayers depend on the degree of oxidation during the synthesis. Based on the above discussed oxidation mechanisms, the following three areas are where the oxidation process could be modified to result in a variety of LCGO products: i) pre-oxidation of graphite,^[9,37,51] ii) alternative graphite sources,^[14,17,25] and iii) alternative oxidizing agents.^[52,53]

2.2.1.1. Pre-Oxidation of Graphite: Potassium permanganate (KMnO_4) has proven effective in converting graphite into graphite oxide.^[2,11,17,21,54] However, its slow diffusion rate in the interlayer of graphite restricts the production of GO. The pre-oxidation of graphite with $\text{K}_2\text{S}_2\text{O}_8$ and P_2O_5 is a common process to improve the oxidation efficiency.^[21,29,51] Using this approach, LCGO with an average lateral width of $\approx 2.1 \mu\text{m}$ have been synthesized.^[9] Compared with the conventional GO prepared by Hummer's method, which generally features a deep brown color, low transmittance, weak fluorescence, and low zeta potential (-25 to -30 mV), the GO prepared by the modified method shows an orange color and has a higher transmittance, a stronger fluorescence (≈ 4 -fold higher than the Hummer's GO), and a more negative zeta potential value (-64 mV). The pre-oxidation process was later improved by using impure MnO_2 .^[37] The oxidative and intercalative Mn ions (mainly Mn^{3+}) produced by the reaction of impure MnO_2 with concentrated H_2SO_4 and P_2O_5 resulted in an enhanced exfoliation and oxidation of graphite during the pre-oxidation. The GO suspensions showed a high yield of single-layer large-sized sheets (average size up to $\approx 20 \mu\text{m}$) and were stable in a wide range of concentrations.

2.2.1.2. Alternative Graphite Sources: The average lateral size and size distribution of the GO sheets were found to vary with the graphite source.^[13] For example, expanded graphite have been used to replace the conventional graphite to improve the oxidation/exfoliation process.^[17,38,55,56] Ultra large GO sheets with aspect ratios higher than 30 000 were achieved.^[57] The use of expanded graphite as an alternative starting material avoided the need for the pre-oxidation process in Hummers' method thereby expedited the GO synthesis process.^[17]

2.2.1.3. Alternative Oxidizing Agents: Aside from the low efficiency of the currently available oxidants, the conventional GO synthesis methods involve potentially hazardous chemicals with inherent release of poisonous gases and carry explosion risks. Recently an iron-based green oxidant K_2FeO_4 has been used to prepare large monolayer GO sheets (average lateral size $\approx 8 \mu\text{m}$) with nearly 100% yield within a short reaction time of ~ 1 hour.^[52] The GO obtained using this method also showed LC properties. In contrast to the Hummers' method that generates a huge amount of heavy metal pollutants (e.g., Mn^{2+}) and explosive intermediate products (e.g., Mn_2O_7^+), the eco-friendly K_2FeO_4 was claimed to release harmless by-products. By spray drying the GO dispersion, GO powder was also obtained that could be spontaneously re-dissolved in water or organic solvents to form a stable LC phase.^[58] However, this method has been questioned recently as ferrate (VI) ions are extremely unstable in water, especially in acidic environments.^[53] The fast decomposition of water may not allow ferrate (VI) ions to oxidize graphite into GO. Only the impurities (such as KNO_3 and KClO_3) present in some commercial ferrates (VI) can slightly oxidize graphite surfaces. Consequently, further experiments are required to confirm the suitability of this new oxidizing agent.

2.2.2. Size-controlling of LCGO

As mentioned previously, average sheet size of GO is a critical factor influencing the transitional concentrations from isotropic phases to nematic phases. It should be noted that the LC behavior of aqueous GO dispersion has been realized by the complete removal of the sonication process or using only mild sonication exfoliation of graphite oxide solutions,^[13,14] suggesting that large GO sheet size plays a major role for the formation of LCGO. The purpose of size-controlling is to obtain uniform and desired average GO sheet size. The popular approaches to control the GO sheet size are outlined as follows.

2.2.2.1. Controlled Synthesis: One way to control the GO sheet size is to select a suitable graphite source. GO dispersions with different sheet sizes ranging from 1.7 ± 1.0 to $38.0 \pm 16.3 \mu\text{m}$ have been produced by using graphite powders with different flake sizes.^[28] The use of expanded graphite was also found to be a good option to prepare large GO sheets (see section 0). Research on the oxidation process suggested that the cross-planar oxidation could result in periodic cracking of graphene sheets and reduce the lateral GO size.^[26,30] Therefore, a balance between controlling the

oxidation rate and sheet size is necessary to obtain GO with a suitable range of sheet sizes.

2.2.2.2. Physical Post-processing: Size controlling of GO can also be achieved by physical post-processing, such as centrifugation, filtration, and sonication. For example, centrifugation has been used to separate large GO sheets (average area $\approx 272.2 \mu\text{m}^2$) from small-sized sheets (average area $\approx 1.1 \mu\text{m}^2$).^[59] Filtration through track-etched membranes has also been used to realize size fractionation.^[60] Recently, a facile size selection method was developed based on the spontaneous separation of large-sized GO flakes ($>20 \mu\text{m}$) within the biphasic LC region.^[61] However, a long standing time (1–2 weeks) is typically required for the separation of the large GO flakes. On the other hand, sonication is also a powerful and rapid method to control the GO sheet size after the synthesis; however, it is only possible to decrease the sheet size of GO using the sonication.^[25,26,55]

2.2.2.3. Chemical Methods: The chemical approaches for GO size selection usually involve selective sedimentation of GO sheets using chemical agents or organic solvents. Large GO sheets have larger hydrophobic planes and fewer hydrophilic oxygenated groups on their surface and are more easily precipitated than the smaller sheets. In one study, GO sheets with lateral dimensions larger than $40 \mu\text{m}^2$ were selectively precipitated at a pH value of ≈ 4.0 .^[62] In another work, it was found that the dispersibility and stability of GO sheets were strongly correlated with the C–O content of GO and that the lateral dimensions of GO sheets decreased inversely with the degree of oxidation.^[63] This finding enabled the separation of GO sheets into four groups, i.e., sheet size $d > 25 \mu\text{m}$, $15 \mu\text{m} < d < 25 \mu\text{m}$, $5 \mu\text{m} < d < 15 \mu\text{m}$, and $d < 5 \mu\text{m}$. The long standing time, the relatively complicated procedure, and the use of a large amount of organic solvent can impose some limitations to this approach. Moreover, the use of additives may impart unwanted properties to the GO sheets and can therefore require additional steps to remove the additives.

2.3. LCGO in Organic Solvent

Although direct exfoliation of graphite oxide to GO has been reported in some organic solvents, there are inconsistencies regarding the features of organic solvents capable of exfoliating graphite oxide.^[64] For example, it was found that graphite oxide could be dispersed in *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran, and ethylene glycol to obtain single-layer GO sheets via sonication.^[65] However, it is worth noting that the GO dispersions in organic solvents obtained by intense sonication contained GO with relatively low sheet sizes that prevented the LC formation.^[66] Using a solvent-exchange approach through centrifugation of the LCGO aqueous dispersion and redispersion into the desired solvent, stable LCGO dispersions were obtained in a wide range of polar organic solvents overcoming the practical limitations imposed on LCGO processing by only using the aqueous dispersion.^[67] LCGO showed similar birefringence in different solvents, but the isotropic to nematic phase transition concentration was found to be dependent on the solvent type.

3. LCGO Solution Processing

The assembly of graphene macroscopic structures largely rely on solution processing techniques. The limited dispersibility of graphene sheets in appropriate solvents has imposed significant challenges in the solution processing-based assembly of graphene. The abundant functional groups of GO offers a very high dispersibility, stability, and processability in water as well as in a wide range of organic solvents, making it a preferred precursor for fabricating graphene-based assemblies. The structures fabricated using the GO dispersions generally consist of randomly ordered sheets. Nevertheless, structural ordering is deemed necessary or at least beneficial for many applications. For instance, GO fiber fabrication is facilitated by achieving highly aligned GO sheets along the fiber axis. Also, microstructural order is largely associated with superior performance in macroscopic scale such as mechanical properties, electrical conductivity, and thermal conductivity. The discovery of LCGO afforded new solution processing routes to the assembly of highly ordered graphene architectures with extraordinary mechanical, electrical, and electrochemical properties. This section focuses on the recent progress in solution processing of graphene to a wide range of assemblies, i.e., fibers (1D), coatings, papers, and films (2D), as well as aerogels, hydrogels, foams, and sponges (3D), and highlights the advantages offered by LCGO.

3.1. Wet Spinning of 1D Graphene Fibers

Fiber is one of the most appealing macroscopic structures to utilize the fascinating properties of graphene as it can lead to the fabrication of multifunctional graphene-based textiles with a wide range of applications in wearable electronics, biomedical monitoring, optical displays, sensing, and communication. However, because of the lack of suitable rheological properties, weak inter-sheet interactions, and/or the absence of sheet interlocking in graphene and GO, the realization of graphene fibers has been impeded until recently. The large LCGO flakes offer exceptionally high inter-sheet interactions and with their high flexibility, they can easily crumple and fold to form fibers. Notably, the presence of the pre-ordered LC domains in the LCGO dispersion offers a unique advantage in fiber spinning over non-LCGO dispersions. The shear applied during the extrusion of the LCGO dispersion through a nozzle facilitates the alignment of the LC domains of GO along the fiber axis; a mechanism used in nature for spider silk fiber fabrication.^[68]

The common method used to produce graphene-based fibers is by wet-spinning the LCGO dispersion (Figure 3a). The wet-spinning method involves injection of the GO dispersion into a chemical/solvent bath (coagulation bath) through a nozzle (spinneret) and then washing, drying, and collecting the fibers. There are several requirements to ensure the spinnability of the LCGO dispersion, i.e., the ability to form continuous fibers.

Firstly, the LCGO spinning formulation must have the suitable rheological properties. To achieve spinnability, LCGO dispersions should have storage modulus to loss modulus ratio (G'/G'') of more than 1, typical of viscoelastic soft solids or gels.^[69] High shear rates (frequencies) resulting from high flow

rates or small spinnerets will require dispersions with higher G'/G'' . The suitable rheological properties of the LCGO dispersion can be easily achieved by adjusting the concentration. GO sheet size was also found to adversely affect the rheological properties and the spinnability of the GO dispersion.^[25] For instance, the GO dispersion with average lateral sheet size of $\approx 37 \mu\text{m}$ exhibited fully nematic LC behavior and suitable rheological properties at $\approx 2.5 \text{ mg mL}^{-1}$ for the formation of continuous fibers. However, when the average lateral GO sheet size decreased to $< 1.5 \mu\text{m}$, the GO dispersion at $\approx 2.5 \text{ mg mL}^{-1}$ showed isotropic or biphasic properties with Newtonian liquid-like rheological behavior that was unsuitable for fiber spinning.

Secondly, an efficient solidification mechanism is required. In wet-spinning, solidification is typically carried out by using an appropriate coagulation bath composition. The coagulation of the LCGO dispersion can follow one or a combination of any of the mechanisms below:

- i. precipitation using non-solvent such as ethyl acetate^[70,71] and acetone^[18]
- ii. dispersion destabilization using acid, base or salt solutions such as NaOH or KOH or H_2SO_4 in water, ethanol, or methanol,^[10,18,72,73] hexadecyltrimethylammonium bromide,^[40,74] and glacial acetic acid^[46]
- iii. ionic cross-linking using divalent cations such as CaCl_2 in water or in water/ethanol,^[18,40,56,73,75] and CuSO_4 in water/ethanol^[73]
- iv. coagulation by amphiphilic or oppositely charged polymers such as chitosan^[18]

The coagulation mechanism plays a crucial role in determining the morphology of the GO fiber ultimately affecting the fiber properties. It was found that the fast coagulation rate could result in an irregular fiber cross-section with a porous morphology. GO fibers with more regular cross-section shapes and packed morphologies are obtained at slow coagulation rates.^[17] Hence, it is possible to achieve GO fibers with the tailored morphology by simply tuning the composition of the coagulation bath.

Xu et al. produced the first neat GO fibers by wet-spinning its aqueous LC dispersion and achieved several meter-long fibers (Figure 3b).^[10] The as-spun GO fiber exhibited a Young's modulus (E) of 5.4 GPa, tensile strength (σ) of 102 MPa, and elongation at break (ϵ) of 6.8–10.1%. After chemical reduction with hydroiodic acid, the rGO fiber showed an electrical conductivity (γ) of up to $\approx 250 \text{ S cm}^{-1}$. The GO fibers were also incorporated into loosely woven patterns by hand (Figure 3c). Later reports achieved further enhanced mechanical and electrical properties in the graphene-based fibers. It can be summarized that the enhancement of the GO fiber properties rely on three key principles: i) increasing the alignment of the GO sheets and LC domains by methods such as drawing during fiber spinning, ii) promoting higher interactions between the sheets by introducing stronger bonds, and iii) minimizing defects within the fiber such as voids and achieving fibers with packed morphology and regular (more circular) cross-sections. These factors are closely related to the properties of the GO such as sheet size and LC as well as to the fiber spinning conditions such as the coagulation rate.

By using a GO source with larger sheets (average lateral size of $\approx 18.5 \mu\text{m}$) GO fibers were achieved that showed more than 80% increase in tensile strength ($\sigma \approx 185 \text{ MPa}$) compared to the first report on the GO fiber that used GO with average lateral sheet size of $\approx 0.8 \mu\text{m}$.^[73] When CaCl_2 or CuSO_4 were used as the coagulating agent instead of KOH, the tensile strength of the GO fiber was further improved to $\approx 259 \text{ MPa}$. Here, the enhancement in mechanical properties came predominantly from the stronger bonds between the GO sheets achieved by the formation of cross-links using divalent cations. GO fibers with even higher mechanical properties ($E \sim 6.3 \text{ GPa}$, $\sigma \approx 365 \text{ MPa}$, and $\epsilon \approx 6.8\%$) were achieved by wet-drawing the fibers inside the rotary coagulation bath through selectively positioning the spinneret.^[73] The electrical conductivity of the rGO fibers (after post-processing chemical reduction using HI) also increased to $\approx 410 \text{ S cm}^{-1}$ (from $\approx 250 \text{ S cm}^{-1}$) after drawing. The increased alignment of the GO sheets and LC domains as a result of drawing resulted in the enhancement of mechanical and electrical properties of the fiber. Following the same principles and using ultra large GO sheets (average lateral size $\approx 37 \mu\text{m}$), GO fibers with record E of $\approx 22.6 \text{ GPa}$ and σ of $\approx 442 \text{ MPa}$ were later produced.^[18] By employing a dry-jet wet-spinning method, which introduces an air-gap between the spinneret and the coagulation bath (Figure 3d), much higher alignment of the GO sheets and LC domains can be achieved compared to the conventional wet-spinning method leading to flexible and tough GO fibers (Figure 3e).^[56] In wet-spinning, because the spinneret is immersed in the coagulation bath, the solidification of the spinning solution occurs immediately after the extrusion. As a result, the alignment of the GO sheets and LC domains in the fiber is limited and is reflective of the shear-induced alignment achieved in the spinneret. However, in dry-jet wet-spinning, drawing of the GO solution in the air gap under the gravitational force prior to the solidification can result in a much higher alignment of the GO sheets and LC domains. The enhanced mechanical properties achieved by using the dry-jet wet-spinning method enabled the GO fibers to be knitted into various knitted structures using a conventional knitting machine for the first time (Figure 3f).

Apart from the alignment and interactions of the GO sheets and LC domains, defects in the fiber can often lead to lower mechanical and electrical properties. The main form of defect in the GO fiber is the presence of microscopic voids which could easily initiate a break resulting in early failure of the fiber.^[72] The defects in the fiber are associated with the ineffective assembly of the GO sheets mainly due to the rapid coagulation and drying which result in collapsing the structure into a fiber before sufficient time is given to the GO sheets to find the most suitable arrangements within the fiber. Increasing the GO concentration from $\approx 28 \text{ mg mL}^{-1}$ to $\approx 52 \text{ mg mL}^{-1}$ and applying a higher shear force during the spinning was found to decrease the amount of voids in the fiber leading to an increase in the packing density from ≈ 0.20 to $\approx 0.33 \text{ g cm}^{-3}$.^[72] This decrease in defects led to an increase in σ (from ≈ 75 to $\approx 320 \text{ MPa}$) and E (from ≈ 3.1 to $\approx 11.6 \text{ GPa}$) in the GO fiber. Decreasing fiber diameter can also reduce voids and defects within the fiber. Fibers with a smaller diameter could be produced either by using a spinneret with a smaller hole or by increasing the draw ratio during spinning. Decreasing the diameter of the

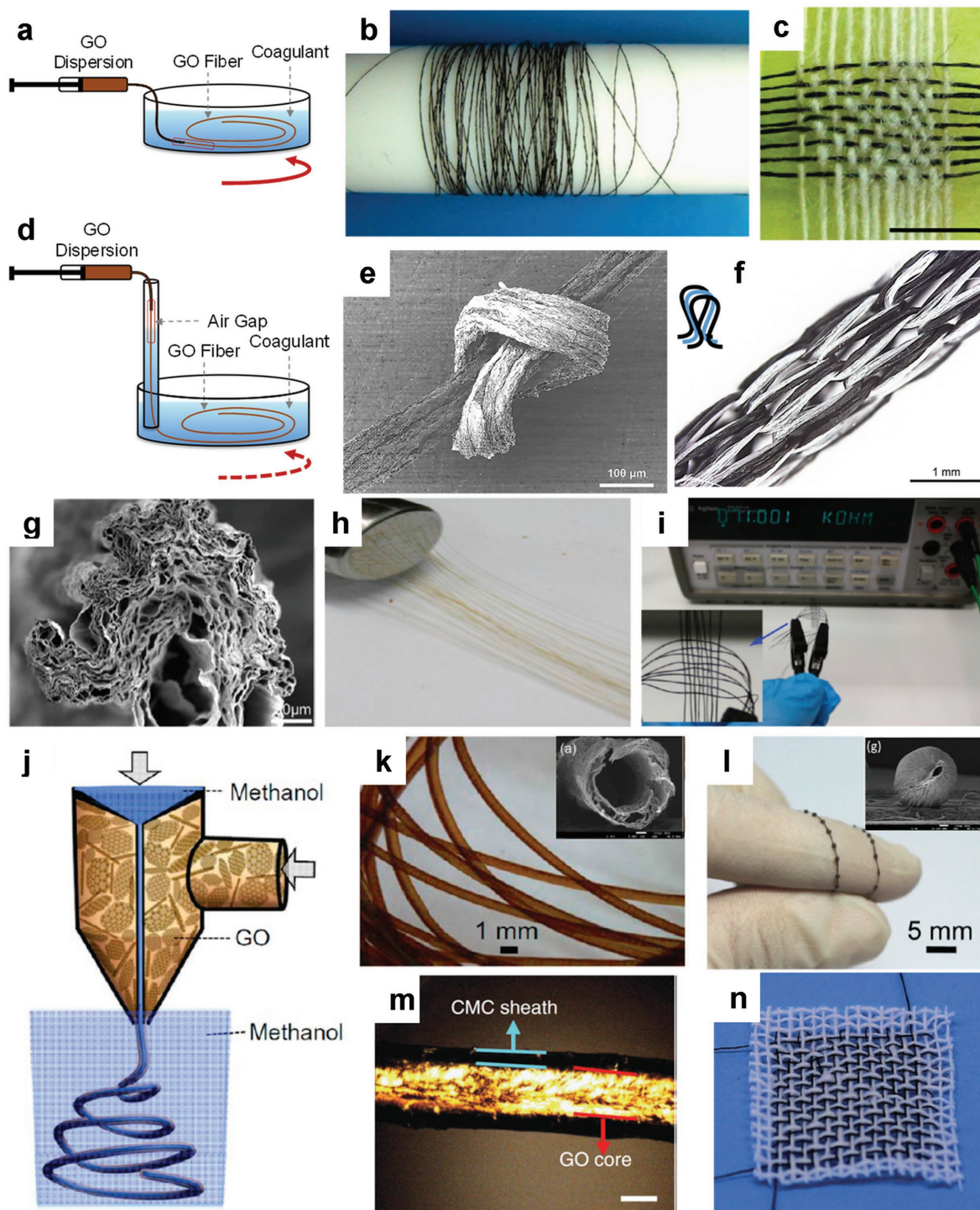


Figure 3. a) Schematic illustration of a typical lab-scale wet-spinning setup used in the fabrication of LCGO fibers. Reproduced with permission.^[56] Copyright 2015, Nature Publishing Group. b) 4 m long wet-spun LCGO fiber on a spool, c) hand-woven graphene fibers together with cotton yarns. Reproduced with permission.^[10] Copyright 2011, Nature Publishing Group. d) Schematic illustration of LCGO dry-jet wet-spinning used to fabricate e) flexible and tough GO fibers that could be used to make f) knitted textiles. Reproduced with permission.^[56] Copyright 2015, Nature Publishing Group. g) Cross-section scanning electron microscopy (SEM) images of porous LCGO fiber fabricated by wet-spinning of a slightly acidic dispersion into an acetone coagulation bath, h) LCGO porous yarn, i) conductive textile made from hand-weaving the LCGO porous yarn. Reproduced with permission.^[17] Copyright 2014, American Chemical Society. j) Schematic illustration of a coaxial two-capillary spinneret used to make k) GO hollow fibers, l) a necklace-like GO structure. Reproduced with permission.^[76] Copyright 2013, American Chemical Society. m) Core-sheath structure of GO/CMC fiber under polarized-light optical microscopy, n) two intact coaxial fibers woven with cotton fiber. Reproduced with permission.^[77] Copyright 2014, Nature Publishing Group.

graphene oxide nanoribbons (GONR) fiber from ≈ 60 to ≈ 30 μm resulted in increasing σ and E from ≈ 25 to ≈ 378 MPa and from ≈ 2.4 to ≈ 36.2 GPa respectively.^[70] The coagulation rate and the solvent-exchange process also affect the formation of voids in the fiber.^[72] At high coagulation rates, GO fibers with irregular cross-sectional shape and with a high number of pores and voids are produced that are associated with poor mechanical properties. By carefully controlling the coagulation rate through the use of appropriate coagulating agent and composition, it is possible to produce fibers with less voids and defects that have higher mechanical properties.^[56]

Chemical and thermal treatments also significantly impact the properties of the GO fibers. Post-spinning chemical reduction treatment using HI^[73] or thermal annealing at 1500 °C^[70] resulted in electrical conductivities of ≈ 410 and ≈ 285 S cm⁻¹, respectively. The chemically reduced GO fiber also showed higher mechanical properties (41% and 70% higher σ and E) compared to the as-spun fiber.^[73] Due to the removal of oxygen-containing groups of GO and enhanced π - π interaction between the sheets, the inter-layer distance decreased from ≈ 0.88 nm to ≈ 0.37 nm with the chemical reduction. Furthermore, chemical reduction was also found to result in a decrease in the fiber diameter and an increase in compactness. Thermal annealing at 1500 °C under tension led to a higher sheet alignment along the fiber axis and enhanced the mechanical properties of the GO fiber.^[70] Fiber spinning and GO reduction can also occur in one step by using an alkaline coagulation bath (such as NaOH and KOH).^[18]

Recently, it has been shown that it is possible to produce graphene fibers with high thermal, electrical, and mechanical properties by achieving an intercalated compact fiber structure through the addition of 30 wt.% small-sized GO (average lateral size ≈ 0.8 μm) to the large-sized GO (average lateral size ≈ 23 μm).^[40] The large GO sheets formed a highly ordered arrangement and the small GO sheets filled the spaces and voids. After high-temperature treatment at 2850 °C, the graphene-based fiber showed outstanding E and σ of ≈ 135 GPa and ≈ 1080 MPa respectively, a remarkable γ of ≈ 2210 S cm⁻¹, and a high thermal conductivity of ≈ 1290 W m⁻¹ K⁻¹. Healing the defects in the lattice structure and removal of the oxygen functional groups by high-temperature annealing resulted in the formation of graphitic crystallites that increased in size with the annealing temperature giving rise to the enhanced mechanical, electrical, and thermal properties of the graphene fiber. In another work, by further managing the defects at atomic, nanoscale and microscale levels, graphene-based fiber with the record E of ≈ 282 GPa, σ of ≈ 1.45 GPa, and γ of ≈ 8000 S cm⁻¹ has been achieved.^[78] The fiber fabrication consisted of i) utilizing the LCGO dispersion in wet-spinning with continuous stretching to maximize the alignment of the sheets along the fiber axis, ii) decreasing the fiber diameter to ≈ 1.6 μm by controlling the concentration of spinning dope and the internal diameter of the spinneret, and iii) high-temperature annealing (at 3000 °C) to achieve graphene-like atomic structures.

Wet-spinning is a facile technique to achieve graphene fibers with tailored structures such as porous, hollow, coaxial, and ribbon-like fibers. For instance, it is possible to produce fibers with high porosity by simply changing the coagulation rate.

Porous GO fibers were produced continuously by extruding the concentrated LCGO dispersion into liquid nitrogen followed by freeze-drying.^[15] The porous fibers showed uniform alignment of the GO sheets that inherited from the orders in the LCGO dispersion offering high specific surface area of ≈ 884 m² g⁻¹, reasonable mechanical properties ($E \approx 350$ MPa, $\sigma \approx 11.1$ MPa, and $\epsilon \approx 6.2\%$), and good electrical conductivity (up to ≈ 49 S cm⁻¹) after reduction by HI. In another work, using a slightly acidic (pH ≈ 3) LCGO spinning dispersion and an acetone coagulation bath, highly porous GO fiber with a very high specific surface area of ≈ 2605 m² g⁻¹ was produced (Figure 3g).^[17] The porous GO fiber was found to be mechanically robust ($E \approx 29$ GPa and σ of ≈ 60 MPa) and exhibited a moderately high γ of ≈ 25 S cm⁻¹ after thermal annealing. GO fiber yarns were also prepared by using a multi-orifice spinneret and were then handwoven into a textile (Figure 3h,i).

GO hollow fibers were also produced by implementing a coaxial two-capillary spinning strategy (Figure 3j,k).^[76] KCl methanol solution was used in the coagulation bath. The GO dispersion was extruded through the outer channel of the spinneret to the bath and the coagulating agent was injected through the inner channel. By choosing an appropriate spinneret design and changing the GO concentration, both the wall thickness (≈ 0.55 – 8.0 μm) and the outer diameter (≈ 400 – 620 μm) of the GO hollow fiber could be tuned. Furthermore, a necklace-like hollow GO fiber consisting of connected microspheres was obtained by replacing the coagulating solution in the inner channel with the compressed air (Figure 3l).^[76] The coaxial wet-spinning assembly approach was later employed to fabricate sodium carboxymethyl cellulose (CMC)/GO sheath-core fibers (Figure 3m).^[77] This work also reported the fabrication of cloth supercapacitors interwoven from individual intact fiber electrodes (Figure 3n).

GO ribbons were also produced by using a customized wet-spinning set-up. A glass rod was placed in the rotating coagulation bath of chitosan solution to which GO dispersion was injected.^[79] Graphene ribbons with tailored morphology (oriented, partially oriented, or with random wrinkles) were produced that were woven into fabric showing promise for a range of applications such as textile supercapacitor electrodes. It was recently shown that it is possible to produce GO fibers from non-LC dispersions.^[46] By adding NaOH to LCGO (≈ 20 mg mL⁻¹), a basified GO dispersion with a pH of ≈ 11 was obtained that in contrast to the original LC dispersion did not show LC behavior. The GO fiber made from the non-LC dispersion showed disordered distribution of GO sheets as opposed to highly ordered sheets in fibers made from the LCGO dispersion.

3.2. Papers, Films, and Coatings

Arguably the most widely studied graphene-based macroscopic assemblies are the 2D structures such as papers, films, and coatings. The common approaches used to fabricate these structures from graphene dispersions include filtration, coating, printing, and solution spinning.

Vacuum filtration of colloidal dispersions of GO has been used to prepare free-standing GO papers with the thickness of

$\approx 1\text{--}30\text{ }\mu\text{m}$ and E of $\approx 32\text{ GPa}$.^[7] The effective load distribution achieved through the large interaction surfaces between the GO sheets and their wrinkled morphology at the submicrometer scale resulted in higher mechanical properties of the GO papers compared to other carbon- and clay-based papers. In another work, chemically converted graphene (CCG) dispersion was prepared as the first surfactant-free stable aqueous colloid of reduced GO and processed into free-standing films (thickness $\approx 10\text{ }\mu\text{m}$) using vacuum filtration.^[6] The CCG films were bendable and exhibited γ of $\approx 72\text{ S cm}^{-1}$ without the need for further treatments. Such conductive, robust ($E \approx 35\text{ GPa}$), and flexible graphene-based papers are attractive platforms for practical applications. The use of GO with LC properties has shown to be beneficial in GO paper formation as it allows for the self-assembly into a highly aligned and layered structure without the need for external aligning force such as the one used in the vacuum filtration technique (Figure 4a,b).^[14] Such microstructural order have led to graphene-based films with enhanced electrical and mechanical properties.^[59]

Coating techniques can be used to achieve ultra-thin graphene films down to the thickness of several nanometers. Free-standing GO films have been produced by drop-casting, displaying high σ ($\approx 382\text{ MPa}$), good ϵ ($\approx 4.3\%$), and high γ ($\approx 350\text{ S cm}^{-1}$).^[80] Drop-casting is a facile approach to produce GO films and can be potentially used to make large area films. However, the films obtained using this technique are often non-uniform and inconsistency of fabrication is an issue. Spin-coating offers an alternative route to fabricating more uniform graphene-based coatings and can be used to produce transparent films.^[81] Highly uniform graphene films can also be fabricated by dip-coating^[82] and spray-coating.^[83] Large area and patterned GO films with controlled thicknesses were achieved by applying templates during the spray-coating process followed by electrochemical reduction of the GO layer resulting in γ of $\approx 85\text{ S cm}^{-1}$.^[84] Spray-coating offers a straightforward way to fabricate graphene-based devices such as flexible integrated circuits. GO dispersion has also been processed into free-standing, large area, highly flexible, and conducting films using a simple bar coating approach and used as a high-performance supercapacitor.^[85] Roll-to-roll coating is another interesting approach that can be used to fabricate graphene coatings in large scale suitable for industrial applications.^[86]

Printing techniques can also be used to fabricate graphene films with the desired patterns. Printing requires graphene ink formulations that have suitable rheological properties to enable droplet formation and impingement on a substrate.^[87,88] Inkjet printing was used to print inks made from liquid exfoliated graphene ($\approx 80\%$ with $\approx 20\%$ ethylene glycol) in NMP and transparent and conductive patterns were fabricated with $\approx 80\%$ transmittance and low sheet resistance of $\approx 30\text{ k}\Omega\text{ cm}^{-2}$.^[87] Printing techniques can be easily scaled-up for large-area patterned graphene-based film manufacturing. However, processing graphene into compatible additive-free ink formulations has proven to be challenging. Due to the low viscosity and unsuitable rheological properties of the liquid exfoliated graphene, inks prepared using these graphene dispersions contained additives. These additives however, can negatively impact the properties of graphene such as electrical conductivity. The facile tunability of the rheological properties of the LCGO

dispersions provides an effective route to printing GO patterns because by simply changing the LCGO concentration, suitable inks can be achieved that can be readily printed without the need for any additives (Figure 4c,d).^[69]

The above graphene-based films were mainly produced on small scale (in the range of centimeter) via the time- and energy-consuming methods such as filtration, coating, etc. that cannot be used for continuous film fabrication limiting their practical applications. The discovery of LCGO has enabled the continuous film fabrication via a customized wet-spinning technique (Figure 4e).^[20] Using an LCGO dispersion, a 20 m long, 5 cm wide GO film was produced at a speed of 1 m min^{-1} . The film thickness was controlled by adjusting the width of the spinneret to make GO films with thicknesses ranging from ≈ 1.5 to $\approx 10\text{ }\mu\text{m}$. The wet-spun GO films showed tightly packed and highly aligned GO sheets with the mechanical properties suitable for weaving into mat-like fabrics or for scrolling into fibers (Figure 4f,g). The wet-spinning technique was also used to continuously fabricate ordered graphene hydrogel films with open pores using LCGO.^[19]

3.3. Hydrogels, Aerogels, and Foams

Apart from fibers, films and papers with compact structures, graphene-based 3D assemblies such as aerogels with high porosity are another interesting types of macroscopic architectures that are suitable for a range of practical applications such as energy storage and catalysis. The pioneering work in this area by Xu et al. reported a self-assembled graphene hydrogel via a one-step hydrothermal method, i.e., heating the GO dispersion sealed in a Teflon-lined autoclave at $180\text{ }^{\circ}\text{C}$ for 12 h.^[89] The graphene hydrogel was composed of well-defined interconnected 3D porous networks with pore sizes ranging from submicrometer to several micrometers. The graphene hydrogel contained $\approx 97.4\text{ wt.}\%$ water and showed a compressive elastic modulus of $\approx 290\text{ kPa}$ and a γ of $\approx 4.9 \times 10^{-3}\text{ S cm}^{-1}$. When three of the graphene hydrogels with a diameter of $\approx 0.8\text{ cm}$ were placed next to each other, they could support a 100 g weight. In another work, by freeze casting of the partially reduced GO, ultralight graphene-based cork-like monoliths were produced as opposed to the randomly oriented porous structure obtained by directly freezing the GO dispersion.^[90] The cork-like graphene monolith with a density of $\approx 5.1\text{ mg cm}^{-3}$ could be compressed to $\approx 80\%$ strain with complete recovery after the load removal and displayed a γ of $\approx 0.12\text{ S cm}^{-1}$. Using LCGO as the source, graphene-based aerogels with long-range ordered microstructures were produced (Figure 4h,i) that led to the enhanced mechanical and electrical properties.^[47] By increasing the pH of the LCGO dispersion and using a hydrothermal reduction and then freeze drying, a highly ordered graphene foam with a low density of $\approx 13.2\text{ mg cm}^{-3}$ was obtained. The ordered graphene foam showed a high elasticity upon repeated compression to 60% over 500 cycles and an increase in γ from ≈ 0.21 to $\approx 0.42\text{ S cm}^{-1}$ when compressed to 60%.

LCGO also enabled the production of three-dimensional graphene aerogel cylinders with aligned pores via a facile and scalable wet-spinning process using liquid nitrogen as the coagulating agent (Figure 4j).^[15] The GO porous cylinder

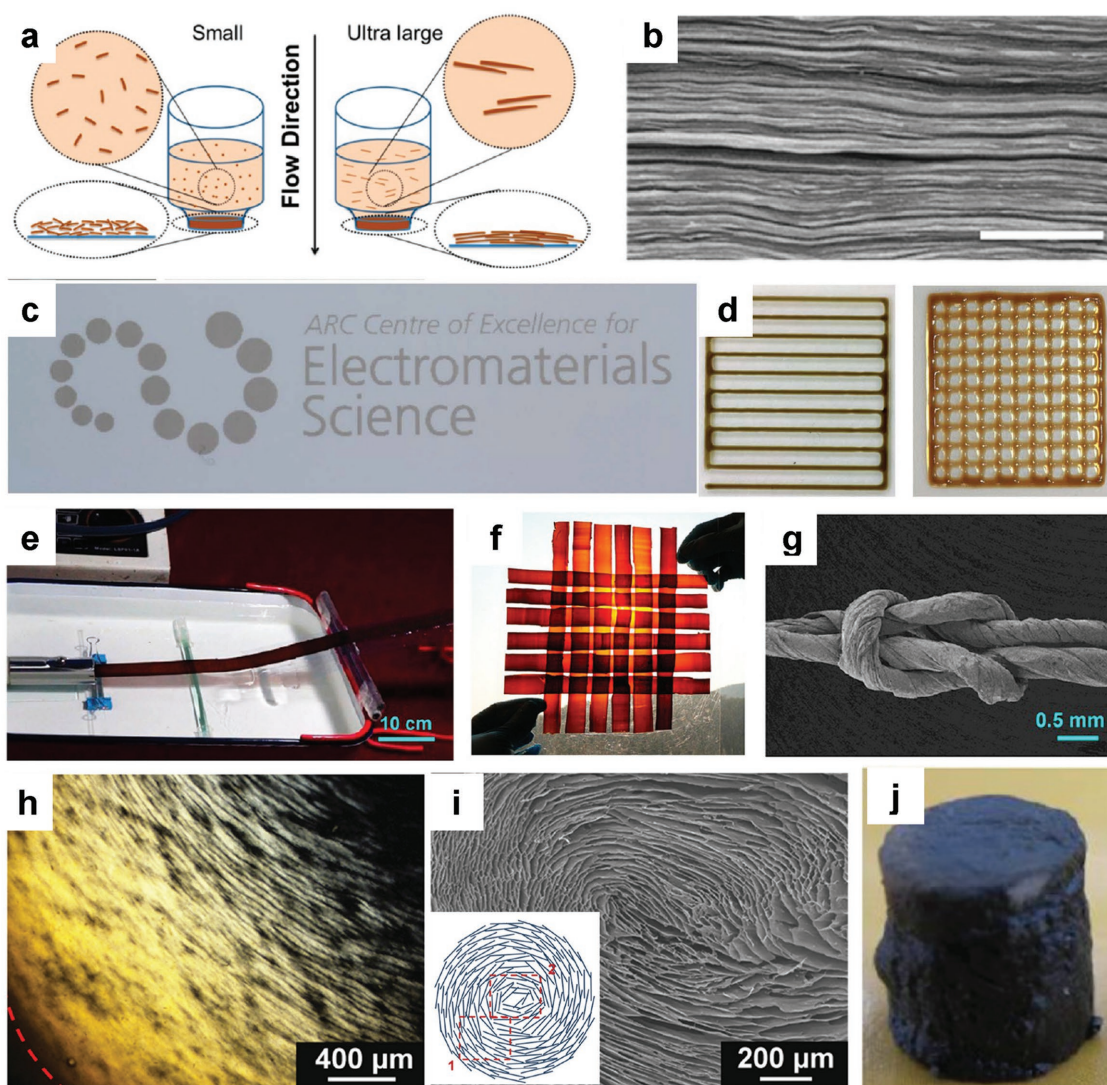


Figure 4. a) Schematic illustrations of self-assembly process of GO sheets with different sizes during vacuum filtration, b) cross-section SEM image of GO paper obtained from large sheets. Reproduced with permission.^[59] Copyright 2012, American Chemical Society. c) An ink-jet printed pattern and d) extrusion printed patterns using LCGO dispersions with suitable rheological properties. Reproduced with permission.^[69] Copyright 2014, Royal Society of Chemistry. e) Experimental setup used for wet-spinning of continuous GO film, f) hand-woven fabric of the wet-spun GO film, g) wet-spun GO film scrolled into fiber and then knotted. Reproduced with permission.^[20] Copyright 2014, American Chemical Society. h) Long-range ordered microstructure of LCGO used to fabricate i) graphene-based aerogel with tailored arrangement of graphene sheets.^[47] Copyright 2016, Wiley-VCH. j) Photograph of rGO porous cylinders. Reproduced with permission.^[15] Copyright 2012, American Chemical Society.

(diameter of ~ 1 cm) showed a very low density of $\approx 71 \text{ mg cm}^{-3}$, a high compression modulus of $\approx 3.3 \text{ MPa}$, and a γ of $\approx 20 \text{ S cm}^{-1}$ (based on porous fiber with diameter of $\approx 100 \mu\text{m}$) after chemical reduction using HI. The graphene-based porous cylinder could support $>20\,000$ times of its own weight without breaking.

Advances in 3D printing have also enabled the fabrication of graphene-based 3D constructs such as scaffolds and aerogels. Similar to 2D printing, formulating a suitable ink, that has proven to be challenging, is critical for achieving 3D printed graphene architectures. A printable graphene-based ink formulation was prepared by functionalizing GO with a branched copolymer surfactant and gluconic- δ -lactone to lower the pH of the suspension.^[91] Various freestanding and stable GO 3D structures such as filament piles, rings, or woodpiles

with different shapes were built that maintained their shapes after printing. The structures were subsequently freeze dried to remove water and were thermally treated (at $900\text{--}1000^\circ\text{C}$ in Ar/H_2 atmospheres) to reduce GO and decomposing other additives. The 3D printed graphene-based structures showed a density of $\approx 6 \text{ mg cm}^{-3}$, E of $\approx 0.13 \text{ MPa}$, up to $\approx 96\%$ recoverable deformation at 20% strain, and a γ of $\approx 0.4 \text{ S cm}^{-1}$. A 3D printable composite graphene ink was also prepared by adding 40 vol.% polylactide-co-glycolide to graphene dispersion.^[92] The resulting ink could be printed into 3D arbitrarily shaped scaffolds with filaments ranging in diameter from ≈ 100 to $\approx 1000 \mu\text{m}$. Other 3D printed objects such as custom-sized nerve graft conduits and 3D-printed skull were also developed. When two 3D printed open-mesh cylinders were incorporated in

series, an LED light was turned on upon passing the current. It was also shown through *in vitro* studies that the 3D printed graphene composite structures supported the viability of multiple, distinct cell types such as adult mesenchymal stem cells. All of the above examples used an additive to prepare 3D printable graphene-based inks with suitable rheological properties. The need to add other components to the ink can result in a complicated and lengthy processing and deviation from the actual properties of graphene. LCGO dispersions offer suitable rheological properties for a range of extrusion-based processing. It is expected that using LCGO can promote additive-free ink formulation suitable for 3D printing.

4. LCGO Composites and Hybrids

The unique LC feature of LCGO in conjunction with the large flake size (in the order of tens of micrometers) provide suitable platforms for the incorporation of a wide range of compounds (Figure 5a) such as polymeric chains, 0D nanoparticles, 1D nanorods, nanotubes, and nanowires, and other 2D nanomaterials such as clay and metal oxide nanosheets. Not only the highly exfoliated flakes of large size have high aspect ratios ($>10^4$) desirable for composites and hybrids, but also the distinctive LC property of GO can induce microstructural orders ultimately leading to graphene-based composite and hybrid architectures with remarkable mechanical, electrical, and thermal properties.

This section will discuss the various approaches for fabricating graphene-based composites and hybrids and will provide an overview of the important achievements in this area with the main focus on LCGO composites and hybrids.

4.1. Preparation of LCGO Composites and Hybrids

Three main approaches, e.g., melt-compounding, solution mixing, and covalent bonding, have been reported in the literature to prepare graphene-based composites and hybrids and are also applicable to LCGO.

4.1.1. Melt-Blending

Melt-blending involves mixing graphene, GO, or LCGO with melt thermoplastic polymers and is a facile processing route to prepare graphene-based polymer composites. This method enables the large-scale production of graphene composites, however, it typically results in poor dispersion of graphene flakes in the polymer matrix often leading to relatively low composite strengths and poor electrical conductivities. For example, polycarbonate (PC)/functionalized graphene sheets (FGS) composites with a loading of up to ≈ 3 wt.% were produced by mixing PC and FGS and then melt compounding the mixture at 250 °C.^[93] When compared with the melt-compounded PC/graphite composites, the FGS flakes were better dispersed in the PC/FGS composites. Melt-compounding was also used to prepare polyethylene terephthalate (PET)/graphene composites.^[94] The exfoliated graphene flakes in NMP was first filtered

and dried to obtain graphene powder and then mixed with PET at loadings of up to ≈ 0.1 wt.% using melt compounding at 260 °C. Isolated graphene flakes were observed by the transmission electron microscopy (TEM) observation of the PET/graphene composite at ≈ 0.1 wt.% loading. Also, protruding graphene flakes were seen in scanning electron microscopy (SEM) analysis of the fractured surface of the composite indicating that the graphene flakes were well dispersed within the PET matrix. An alternative approach is adding graphene to the polymer melt.^[95]

4.1.2. Solution-Mixing

Solution mixing is a versatile approach to prepare graphene-based composites and hybrids, which typically involves adding the graphene dispersion to the solution or dispersion of a secondary component (e.g., polymers, carbon nanotubes, other nanomaterials). For example, polyvinyl alcohol (PVA)/graphene polymer composite has been produced by directly exfoliating graphite in PVA aqueous solution up to a graphene loading of ≈ 1 wt.%.^[96] PVA acted as a stabilizer and assisted the dispersion of graphene in the composite. In another study, polyurethane (PU) was dissolved into the CCG dispersion in DMF and polyurethane PU/CCG composite fibers were produced by wet-spinning the formulation.^[97] SEM observation of the fiber cross-section showed excellent dispersion of CCG in PU even at the high loading of 12.5 wt.%. Compared with melt-blending, the solution-mixing approach offers better graphene dispersion in the polymer matrix or the secondary component. For instance, polyethylene (PE)/TRG composites prepared by solution mixing contained fully exfoliated and well-dispersed graphene flakes while poorly dispersed and aggregated graphene flakes were observed for the melt compounded composite.^[98]

The solution-mixing method has also been extensively used to prepare LCGO composites and hybrids. As the result of the templating role of LC phases in LCGO, the guest compounds localize in the interlayer channels between the sheets, forming a host-guest composite or hybrid LCs. The first LCGO composite was made from a poly(acrylic acid) (PAA)/LCGO aqueous dispersion (weight fraction of PAA/LCGO = 5:0.1) (Figure 5b).^[13] This composite maintained the birefringence property of the parent LCGO. The SEM observation of the hand drawn PAA/LCGO fiber showed that GO platelets were aligned along the stretch direction (Figure 5c). Solution-mixed PVA/LCGO composite films and fibers were also produced using vacuum filtration and wet-spinning, respectively.^[99] In another study, nacre-mimetic hyperbranched polyglycerol (HPG)/LCGO composite fibers with highly ordered hierarchical structures were produced using the solution mixing approach followed by wet-spinning.^[100] Because of the confining effect of the LCGO sheets, the phase separation between LCGO and HPG was avoided resulting in a uniform brick and mortar (B&M) structure (Figure 5d,e).

The advancement of LCGO processing in organic solvents^[67] has further allowed the fabrication of various LCGO-based composites. Our group reported the production of PU/LCGO composite fibers by mixing of the PU solution with LCGO dispersion in DMF and wet-spinning the formulation in isopropanol.^[55,102]

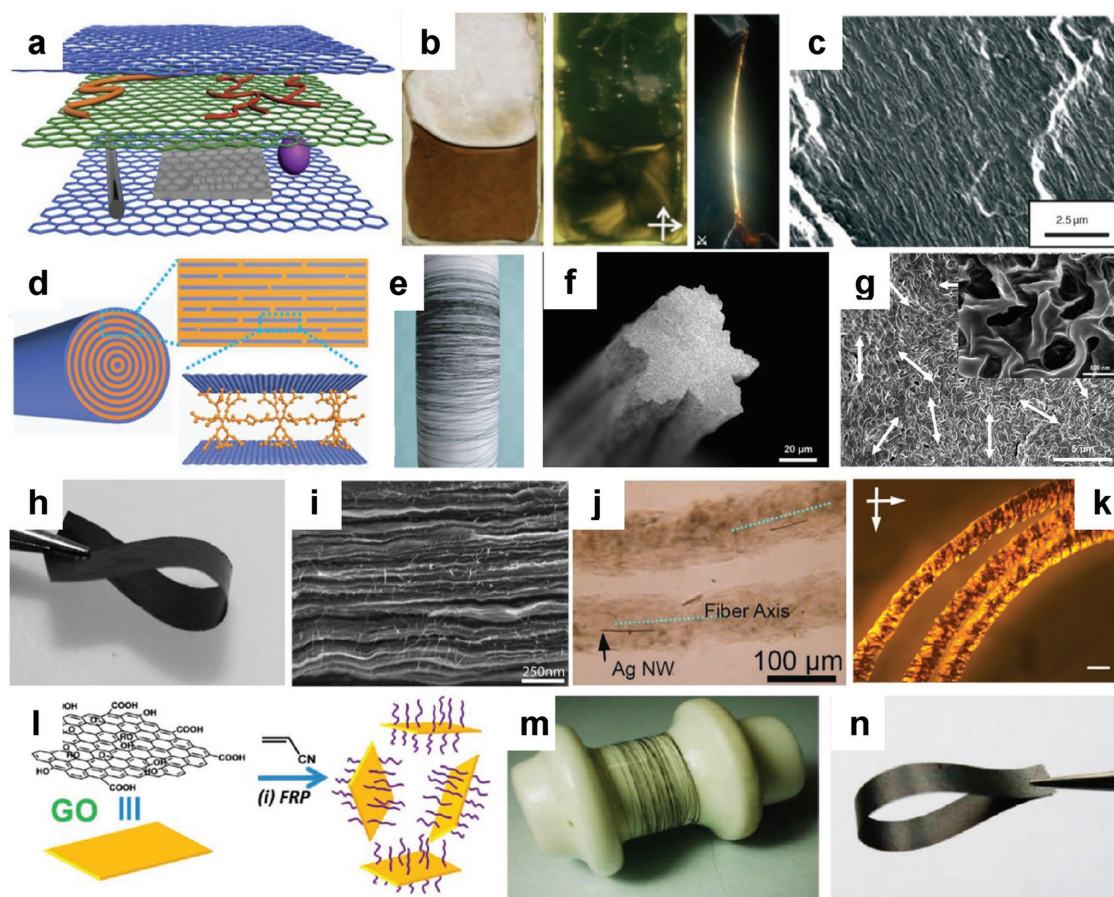


Figure 5. a) Schematic illustration showing that LCGO can host a wide range of compounds such as polymeric chains as well as 0D, 1D, and 2D nano-materials. Reproduced with permission.^[101] Copyright 2015, Elsevier. b) PAA/LCGO mixture without and with crossed polarizers and the hand-drawn gel composite fiber, c) highly aligned GO morphology along the PAA/LCGO fiber axis. Reproduced with permission.^[13] Copyright 2011, Wiley-VCH. d) Schematic illustration of the B&M structure in e) wet-spun nacre-mimetic HPG/LCGO composite fiber. Reproduced with permission.^[100] Copyright 2013, Nature Publishing Group. f) Wet-spun PU/LCGO composite fiber with g) highly aligned microstructure. Reproduced with permission.^[102] Copyright 2016, Wiley-VCH. h) flexible free-standing LCGO/SWCNT hybrid paper and i) a representative SEM image of (h) showing SWCNTs between the highly aligned sheets in LCGO. Reproduced with permission.^[67] Copyright 2013, American Chemical Society. j) LCGO/Ag nanowire hybrid fibers. Reproduced with permission.^[103] Copyright 2013, Wiley-VCH. k) LCGO/MMT nanoplatelets composite fibers. Reproduced with permission.^[104] Copyright 2015, American Chemical Society. l) Synthesis of PAN-grafted GO building blocks by in situ free radical polymerization of acrylonitrile in the presence of GO, m) fiber and n) film prepared from PAN-grafted GO. Reproduced with permission.^[105] Copyright 2013, American Chemical Society.

Due to the spinnability of both PU and LCGO, it was possible to make fibers with very high LCGO loadings. The retained LC behavior of homogeneous PU/LCGO dispersion indicated very high compatibility between the two components. The directional alignment of the LCGO domains in the PU/LCGO fiber suggested that the ordered domains were maintained in the fiber after wet-spinning (Figure 5f, g). Post-spinning annealing treatment at 180 °C was later used as a means to partially reduce the LCGO component in the fibers.^[102]

LCGO was also used in the preparation of novel hybrid systems. For example, by mixing up to ~5 wt.% of bismuth oxide (Bi_2O_3) nanotubes with LCGO dispersion and then wet-spinning the formulation, LCGO/ Bi_2O_3 hybrid fibers were produced.^[106] Despite the precipitation and aggregation of the neat Bi_2O_3 nanotubes in water, they remained very well dispersed in the presence of LCGO and did not interrupt the LC property of the parent LCGO. The preparation of LCGO/SWCNT hybrid films with up to ~10 wt.% of SWCNT was facilitated by

solution mixing of LCGO and SWCNT in organic solvents such as CHP (Figure 5h,i).^[67] The advantage of using LCGO dispersions in organic solvents lies in the compatibility of LCGO and SWCNT dispersions thus preventing the SWCNT aggregation and eliminating the further sonication step to obtain highly dispersed SWCNT in LCGO. Further examples include solution processing of LCGO with Fe_3O_4 ,^[20] Co_3O_4 ,^[107] and NiO nanoparticles,^[107] LCGO/MWCNT,^[108] LCGO/Ag nanowires (Figure 5j),^[103] LCGO/montmorillonite (MMT) nanoplatelets (Figure 5k),^[104] LCGO/transition metal dichalcogenides (TMD) nanosheets,^[109] and LCGO/MWCNT/NiO ternary hybrid system.^[110]

4.1.3. Covalent Bonding

The oxygen-containing functional groups on the surface and edges of GO and rGO sheets can be used in a variety of ways

for covalent attachment of polymers or other species. The covalent functionalization approach is typically useful to prepare graphene-based polymer composites and is carried out using two main methods named as “grafting-to” and “grafting-from”. In grafting-to, polymer chains are covalently linked to the GO sheet by appropriate functionalization of the GO sheets or the polymer. In contrast, in the grafting-from method, the polymer chain is directly grown on the GO sheets. The grafting-to method has been used to prepare polyester/GO composite via the esterification between hydroxyl groups of polyester and carboxyl groups of GO.^[111] The grafted GO was then reduced by vitamin C and coagulated with methanol. Interestingly, unlike GO or rGO that are insoluble in chloroform, acetone, and tetrahydrofuran, the polyester/GO and polyester/rGO composites were found to be soluble in these solvents and remained well dispersed for two months. The grafting-from method has been used to prepare graphene-based composites with poly(dimethylaminoethyl acrylate), PAA, and polystyrene via reversible addition fragmentation chain transfer (RAFT) polymerization on pyrene-functionalized graphene precursor.^[112] It was shown that by simply controlling the monomer feed, the length of the polymer chain could be tailored. This is an effective strategy to achieve graphene-based composites with desired properties. In another study, covalent attachment of poly(ϵ -caprolactone) (PCL) onto chemically converted graphene (CCG) was compared with solution-mixing approach.^[113] The covalently attached PCL/CCG showed enhanced homogeneity with very well-dispersed graphene nanosheets and improved solution processability compared to the solution-mixed composite.

This approach has also been used to prepare polymer-grafted LCGO composites. In a pioneering work, polyacrylonitrile (PAN) chains were covalently grafted onto LCGO sheets (GO-g-PAN) via a simple free radical polymerization resulting in the PAN content of up to ~25.8 wt.% (Figure 51-n).^[105] The GO-g-PAN had good dispersibility in DMF and dimethyl sulfoxide (DMSO) similar to PAN and showed birefringence property. The high-quality dispersion of GO-g-PAN enabled further solution processing of the composite into fibers and papers. The soft interlayer of PAN grafts between neighboring graphene sheets created a B&M structure seen in nacre. No obvious phase interface was found between the graphene bricks and polymeric mortar as opposed to the composites obtained by non-covalent approaches. Using the same principle, poly(glycidyl methacrylate)-grafted LCGO composite were also prepared.^[114]

Compared to the traditional blending approach that can lead to phase separation of graphene and polymer, covalent functionalization is an effective strategy to achieve highly dispersed graphene in polymer matrices. This is due to the covalent and uniform immobilization of polymer chains on the surface of individual graphene sheets that can result in homogeneous composites at molecular levels. The polymer grafting renders the composite soluble or dispersible in organic solvents typically not achievable for pristine graphene or GO. The covalent bonding can also preserve the LC property of LCGO promoting the production of highly ordered composites with B&M structures. By controlling the degree of functionalization or polymerization, composites with the desired graphene contents can be produced.

4.1.4. Other Methods

In situ polymerization is another approach to fabricate graphene-based polymer composites. In this approach, graphene is mixed with a monomer which is then polymerized to yield a composite. Polyaniline/graphene composites were produced by the in situ polymerization of aniline in GO dispersion in acidic conditions followed by chemical reduction of GO and reoxidation and reprotonation of the reduced polyaniline.^[115] It was observed that polyaniline nanofibers were absorbed on the surface of graphene and were filled between the graphene sheets resulting in a homogeneous composite at the nanometer scale. Nylon 6/graphene composites with up to ~10 wt.% graphene were also produced by in situ polymerization of caprolactam in the presence of GO.^[116] GO was thermally reduced to graphene during the polymerization. The nylon/graphene composites were processed into fibers by melt spinning and the composite fiber showed a 2.4-fold increase in E and a 2.1-fold increase in σ compared to the neat nylon fiber. Similarly, in situ polymerization was used in conjunction with simultaneous thermoreduction of GO to prepare polyester/rGO composite with enhanced properties.^[117] Highly aligned polydimethyl siloxane (PDMS)/LCGO composites have also been prepared by uniaxially aligning the GO sheets through geometric confinement followed by freeze-drying and then infiltration with PDMS.^[118] The composite displayed well-integrated GO sheets within the PDMS matrix and was robust even after repeated bending.

Melt blending, solution mixing, and in situ polymerization methods were compared in the preparation of PU/graphene composites obtained from two graphene sources, i.e., thermally reduced graphene (TRG) and isocyanate-treated GO.^[119] Solution processing was found to be a more effective approach for obtaining well-distributed graphene sheets throughout the PU matrix than the melt processing. Graphene composites that were in situ polymerized with PU appeared better dispersed and interconnected than other composites. However, surprisingly the mechanical reinforcement in the composite prepared by the in situ polymerization approach was not as pronounced as the solution mixing. This was attributed to the reduced interchain hydrogen bonding in the PU matrix. Surface modification with isocyanate was found to be an effective approach to prepare highly dispersed GO sheets in solution mixing.

4.2. Properties of LCGO Composites and Hybrids

As discussed in the previous sections, the inter-sheet space in LCGO can be used to accommodate various guests such as polymer chains to obtain composites with highly ordered microstructures. Research in this area has been focused to produce high performance composites with enhanced mechanical properties and/or with electrical conductivity. Kim et al.^[13] have reported PAA/LCGO composite using the solution mixing approach. Although, electrical or mechanical properties of the PAA/LCGO composites were not reported, this work helped pave the way to realizing a wide range of LCGO based composites. LCGO was later used to prepare HPG composite papers and fibers with B&M layered structures.^[120] HPG/LCGO paper at ~34 wt.% HPG (~66 wt.% LCGO) showed an E of

≈ 12.2 GPa, a σ of ≈ 128 MPa, and an ε of $\approx 1.6\%$ with a γ of $\approx 1.8 \times 10^{-3}$ S cm $^{-1}$ (in reduced form). The composite fibers prepared from HPG and LCGO showed higher mechanical properties ($E \approx 10.0$ GPa, $\sigma \approx 145$ MPa, and $\varepsilon \approx 1.5\%$) and electrical conductivity ($\gamma \approx 48.8 \times 10^{-3}$ S cm $^{-1}$) than the paper form. This enhancement in properties is caused by the flow-induced alignment of the LCGO sheets and domains. By further aligning the LCGO sheets and treatment with glutaraldehyde that formed bridges between -OH groups of HPG and LCGO, HPG/LCGO fibers with significantly enhanced mechanical properties, i.e., $E \approx 20.9$ GPa, $\sigma \approx 652$ MPa, $\varepsilon \approx 4\%$ and toughness (T) ≈ 14 MJ m $^{-3}$, were achieved that upon reduction with HI and acetic acid, showed an electrical conductivity of ≈ 52.6 S cm $^{-1}$. PVA/LCGO composite fibers displayed $\approx 95\%$ enhancement in tensile strength ($\sigma \approx 161$ MPa) at ≈ 34.2 wt. % LCGO compared to the pure PVA fiber ($\sigma \approx 86$ MPa).^[99] After LCGO reduction with HI, the PVA/LCGO composite fibers showed electrical conductivities of up to ≈ 3.5 S cm $^{-1}$. This work demonstrated that it is possible to make composites with high filler loadings and still achieve tough and conducting composites.

PAN/LCGO composite fibers produced by grafting PAN onto LCGO sheets showed remarkable mechanical properties ($E \approx 8.3$ GPa, $\sigma \approx 452$ MPa, $\varepsilon \approx 5.4\%$, and $T \approx 12.3$ J cm $^{-3}$) at 25.8 wt.% PAN (74.2 wt.% LCGO) that were found to be significantly higher than those of composites achieved by simple blending approach ($E \approx 2.6$ GPa, $\sigma \approx 160$ MPa, $\varepsilon \approx 6.2\%$, and $T \approx 4.9$ J cm $^{-3}$).^[105] The PAN/LCGO composite fibers could provide suitable precursors for the fabrication of PAN-based commercial carbon fibers. Poly(glycidyl methacrylate)-grafted LCGO composite fiber showed a σ of ≈ 440 MPa at ≈ 62 wt.% of LCGO.^[114] The σ of the polymer-grafted LCGO composite fiber was 2.5 times higher than that of the neat LCGO fiber, 733 times higher than that of the neat polymer fiber, and 5 times that of the blend composite. The composite fibers also showed remarkable chemical resistance against 98% sulfuric acid and a range of organic solvents.

LCGO has also been used to prepare conducting elastomeric composites. PU/LCGO composite films that were electrically conductive at a very low percolation threshold of ~ 0.16 wt.% have been produced.^[121] As the result of using LCGO in composite preparation, a high degree of orientation of graphene sheets were achieved that led to composite films with highly anisotropic properties.

For a range of advanced technological applications such as stretchable electronics and wearable sensors, it is highly desirable that the addition of conductive fillers to elastomeric hosts provides not only electrical conductivity, but also stiffness and strength. Using organic solvent based LCGO to achieve the compatibility of PU and LCGO, our group developed multifunctional conductive elastomeric fibers that were also stiff, strong, and tough.^[55,102] Compared to the PU composite fibers obtained from carbon black (CB), SWCNT, and CCG,^[97] PU/LCGO composite fiber showed significantly higher mechanical properties and a lower percolation threshold of electrical conductivity. When LCGO was used as the filler, the rate of reinforcement (calculated as $dE/d\phi$, ϕ filler volume fraction) was found to be in excess of 16 GPa, which is significantly higher than that of PU composites reinforced with SWCNT, CCG, and CB (≈ 6.5 , ≈ 2.1 , and ≈ 0.1 GPa, respectively). Unlike other

PU composites, it was noted that LCGO did not interrupt the strain induced crystallization behavior of PU soft segment, suggesting the preferential reinforcement of LCGO towards the hard segment domains. The solvent exfoliated graphene (SEG)^[122] which is ≈ 40 times smaller than LCGO, required a loading of ≈ 40 wt.% to achieve a comparable reinforcement with ≈ 2.9 wt.% LCGO. Consequently, the high loading of SEG resulted in ≈ 10 times decrease in ε and more than 20 times decrease in T in respect to PU while the LCGO loading to achieve the same level of reinforcement did not affect ε or T . The reduced PU/LCGO fibers showed strain sensing property through changing the resistance response during cyclic stretching with a large sensing range of up to $\approx 75\%$ suitable for application in wearable body movement monitoring. Careful analysis of the mechanical properties of PU/LCGO composite fibers showed a large dependence on GO sheet size and LC property of the dispersion.^[55] The PU/GO composite fiber (GO loading ≈ 2.9 wt.%) with large sheets exhibited a superior ≈ 80 -fold reinforcement (enhancement of stiffness) compared to the PU fiber, and this reinforcement decreased with GO sheet size (≈ 60 -fold for medium sheets and ≈ 20 -fold for small sheets).

Apart from application in polymeric composites, LCGO has been found to be an excellent host for accommodating various types of fillers such as 0D nanoparticles, 1D nanorods, nanowires, and nanotubes, and other 2D nanosheets. For instance, LCGO/Fe $_3$ O $_4$ hybrid films were produced that showed superparamagnetic property.^[20] LCGO has also been used to fabricate self-aligned LCGO/MWCNT hybrid (weight ratio 3:1).^[108] The LC properties of GO sheets induced spontaneous self-assembly into highly ordered layer-by-layer 3D structures upon simple casting and drying resulting in a hybrid with a high hydrogen capacity of up to ≈ 2.6 wt.%, much higher than the parent LCGO and MWCNT (≈ 1.4 and ~ 0.9 wt.% respectively). Self-assembled layer-by-layer LCGO/SWCNT 3D hybrid architectures containing ≈ 10 wt.% SWCNT showed an E of ≈ 51.3 GPa, σ of ≈ 505 MPa, and ε of $\approx 9.8\%$ that were much higher than the properties of the parent LCGO architecture.^[67] The self-templating role of LCGO has also been used to produce graphene/Bi $_2$ O $_3$ nanotubes hybrid supercapacitor fibers using the wet-spinning technique.^[106]

LCGO has also been used to prepare hybrid microfibers of graphene and a range of TMD nanosheets such as MoS $_2$, TiS $_2$, TaS $_2$, and NbSe $_2$.^[109] It was shown that the hybrid fiber containing only ≈ 2.2 wt.% MoS $_2$ nanosheets showed an improved capacitance (≈ 30 F cm $^{-3}$) compared to the parent graphene fiber prepared from LCGO (≈ 3 F cm $^{-3}$). Hybrid fibers produced by incorporating ≈ 10 wt.% MMT nanoplatelets within LCGO showed a high decomposition temperature (≈ 612 °C) in air with a high residual mass fracture ($\approx 97\%$) at 600 °C out-performing the commercial T700 carbon fibers.^[104]

LCGO can also be used to fabricate ternary composites and hybrids with novel properties. For example, self-assembled ternary hybrid architectures composed of LCGO, MWCNT, and NiO nanoparticles showed an impressive energy storage performance (gravimetric capacitance of ≈ 2074 F g $^{-1}$ tested in a three electrode system).^[110] Similarly, LCGO/PEDOT:PSS/iron oxide nanorods 3D interconnected layer-by-layer hybrid architectures have been produced that showed high gravimetric capacitances of up to ≈ 875 F g $^{-1}$ (volumetric capacitance ≈ 868 F cm $^{-3}$).^[123]

5. Applications of LCGO

Significant efforts have been directed to explore the applications of graphene in various fields such as energy storage,^[124,125] filtration and water desalination,^[126] sensors,^[127,128] optical imaging,^[129] and drug delivery.^[130] This section outlines how the intrinsic structural alignment and anisotropic characteristic of LCGO has broadened the application spectrum of graphene.

5.1. Supercapacitors

LCGO has been widely used to fabricate energy storage devices particularly supercapacitors. Electric double-layer capacitors (EDLCs) and pseudocapacitors are the two main types of widely studied supercapacitors. EDLCs primarily use the charges accumulated on the electrode/electrolyte interface and is mainly associated with carbon-based materials with high specific surface area. The selection and processing of active materials to obtain highly porous structures, large accessible surface area, and high electrical conductivity are crucial to achieve high EDLCs. On the other hand, materials used in pseudocapacitors, such as conductive polymers or metal oxides, typically use Faradaic mechanisms to store charges. Pseudocapacitors can show higher capacitances than the EDLC-based materials; however, they are known to have poor cyclic stability due to the structural degradation of the electrode material during the charge/discharge process.

Theoretical studies suggest that the specific surface area of 2675 m² g⁻¹ for graphene can lead to a specific capacitance as high as ≈550 F g⁻¹ provided that the surface of graphene is fully utilized.^[131] A variety of graphene-based supercapacitors have been fabricated.^[132–140] However, the restacking of graphene sheets was found to significantly reduce their accessible surface area compromising the specific capacitances and energy and power densities of the device.^[141,142]

Generally, high ion-accessible surface area and low ion transport resistance of the electrodes are the crucial factors to the realization of high energy density supercapacitors. A number of strategies have been developed to increase the ion-accessible surface area, such as the use of spacers (e.g., surfactants, nanoparticles, and polymers),^[143–145] template-assisted method,^[146–148] and crumpling the graphene sheets.^[149–151] The discovery of LCGO offered alternative routes to design novel graphene-based electrodes in different forms such as fibers, ribbons, and aerogels. The microscopic ordered structures in graphene electrodes prepared from LCGO compared to the disordered structures from non-LCGO have faster electron transport between graphene sheets giving rise to a higher electrical performance suitable for energy storage applications.^[85] Table 2 summarizes the properties of supercapacitor devices fabricated from LCGO.

One facile approach to achieve graphene electrodes with high energy storage properties is to maximize the electrode surface area. By deliberately inducing a fast coagulation rate in LCGO fiber formation process, graphene fibers with porous structures were achieved that showed high specific surface areas (≈2210 m² g⁻¹) and excellent charge storage capacities (≈409 F g⁻¹ at 1 A g⁻¹).^[17]

An alternative route to enhance the energy storage capacity of graphene based electrodes is to incorporate pseudocapacitive materials. For instance, Bi₂O₃ nanotubes/graphene hybrid fibers assembled into flexible fiber supercapacitors showed a specific capacitance of ≈69.3 mF cm⁻² (at 0.1 mA cm⁻² for single electrode) that was six times higher than the pristine LCGO fiber.^[106] In another example, core-sheath graphene/MnO₂ fibers were produced that combined the pseudocapacitance of MnO₂ with the high conductivity and EDLC of graphene and achieved an aerial capacitance of ≈59.2 mF cm⁻², five times higher than that of the neat graphene fibers.^[152]

Table 2. Electrochemical and mechanical properties of typical LCGO-based electrodes.

Composition	Structure	Reduction method	Electrical conductivity [S cm ⁻¹]	Electrolyte	Specific capacitance at a scan rate	Energy density	Young's modulus/Tensile strength	Ref.
rLCGO	Hydrogel film	Annealed 180 °C	0.007	1 M H ₂ SO ₄	183 F g ⁻¹ at 1 A g ⁻¹ (device)	—	—/0.56 MPa	[19]
rLCGO	Hydrogel film	Hydrazine	0.322	1 M H ₂ SO ₄	203 F g ⁻¹ at 1 A g ⁻¹ (device)	—	—/0.38 MPa	[19]
rLCGO	Porous yarn	Annealed 220 °C	25.08	1 M H ₂ SO ₄	409 F g ⁻¹ at 1 A g ⁻¹ (single electrode)	14 mW h g ⁻¹	>29 GPa/—	[17]
rLCGO	Hydrogel film	Annealed 180 °C	—	1 M H ₂ SO ₄	286 F g ⁻¹ at 1 A g ⁻¹ (device)	—	—/—	[153]
rLCGO/MWCNT/PEDOT:PSS	Hybrid film	Vitamin C	387	—	761 F cm ⁻³ at 5 mV s ⁻¹ (device)	11.4 W h kg ⁻¹	26.1 GPa/252 MPa	[123]
rLCGO/Bi ₂ O ₃ NTs	Hybrid fiber	Annealed 400 °C	—	6 M KOH or 1 M H ₃ PO ₄ (single electrode) PVA/H ₃ PO ₄ (device)	69.3 mF cm ⁻² /17.3 mF cm ⁻² at 0.1 mA cm ⁻² (single electrode/device)	2.9 W h cm ⁻³	—/—	[106]
rLCGO@PANI	Coated fiber	HI	—	PVA/H ₃ PO ₄	66.6 mF cm ⁻² at 0.1 mA cm ⁻² (device)	—	—/—	[75]
rLCGO/CNT@CMC	Coaxial fiber	HI	—	1 M H ₂ SO ₄	239 F cm ⁻³ at 0.1 mA cm ⁻² (single electrode)	—	—/—	[77]

LCGO offers high conductivity and highly ordered and tunable structures suitable for use as fiber-based electrodes for energy storage devices. Fiber electrodes prepared from LCGO showed excellent capacitive performance, high mechanical strength and flexibility suitable for wearable energy devices.^[154]

Besides the compositional parameters, device configurations were also found to affect the energy storage properties of the graphene-based devices. It is well known that increasing the interfacial area will promote the specific capacitance and energy density of supercapacitor devices. However, in the case of solid fibers, only the outer surface of the fiber is effectively accessed by the electrolytes due to the difficult diffusion of the electrolyte to the inside of the fiber. A hollow fiber electrode is expected to produce a higher specific capacitance owing to the additional inner interface of the fiber electrode. For instance, the hollow composite fiber supercapacitor produced from non-LC GO using hydrothermal method revealed a higher areal capacitance of $\approx 304.5 \text{ mF cm}^{-2}$ ($\approx 143.3 \text{ F cm}^{-3}$ or $\approx 63.1 \text{ F g}^{-1}$) at 0.08 mA cm^{-2} compared to the solid composite fiber, i.e., $\approx 189.2 \text{ mF cm}^{-2}$ ($\approx 67.0 \text{ F cm}^{-3}$ or $\approx 50.8 \text{ F g}^{-1}$).^[155] The specific capacitance of the hollow fiber electrode remained almost unchanged after bending for 500 times and was maintained ($\approx 96\%$) after 10 000 cycles.

Using sheath-core configuration is another way to effectively utilize the electrode surface. For instance, CMC/GO sheath-core fibers have been produced and interwoven to form a two-ply yarn supercapacitor that showed a volumetric capacitance of $\approx 114 \text{ F cm}^{-3}$ ($\approx 127 \text{ mF cm}^{-2}$ for aerial and $\approx 3.8 \text{ mF cm}^{-1}$ for length) at the current density of 0.1 mA cm^{-2} (Figure 6a–c).^[77] The electrode performance was further improved (volumetric,

aerial, and length capacitances of $\approx 239 \text{ F cm}^{-3}$, $\approx 269 \text{ mF cm}^{-2}$, and $\approx 8.0 \text{ mF cm}^{-1}$ respectively) by using GO/CNT hybrid in the core. This enhanced electrochemical performance was ascribed to the CNTs preventing the adjacent LCGO sheets from restacking after reduction. Two $\approx 40 \text{ cm}$ long coaxial fibers (used as anode and cathode) were co-woven into a cloth with cotton yarns and the assembled device showed a capacitance of $\approx 28 \text{ mF}$ at the current of 10 mA . Alternatively, the continuous LCGO wet-spun fiber can provide the backbone for creating a coaxial all-graphene fiber supercapacitor.^[156] A coaxial fiber assembly was made by coating a PVA layer (as a separator) on the reduced GO fiber, following the dip-coating of the structure in a GO solution, drying and reducing the outer layer, and further coating a gel electrolyte layer (PVA/ H_2SO_4) on the outside (Figure 6d). The single fiber supercapacitor showed a high specific capacitance of $\approx 182 \text{ F g}^{-1}$ ($\approx 205 \text{ mF cm}^{-2}$) and a high energy density of $\approx 17.5 \text{ }\mu\text{W h cm}^{-2}$ ($\approx 15.5 \text{ W h kg}^{-1}$). Other researchers also obtained fiber-based supercapacitors based on wet-spinning, but it is unclear if LCGO dispersions were used.^[157,158]

LCGO-mediated soft self-assembly is a promising approach for fabricating 2D/3D architectures suitable for energy storage device fabrication. For instance, flexible and free-standing highly ordered graphene hydrogel film with open pores were produced using LCGO.^[19] The reduced LCGO hydrogel film showed a specific capacitance of $\approx 203 \text{ F g}^{-1}$ at 1 A g^{-1} , which is much higher than that of electrodes with disordered graphene sheets ($\approx 111 \text{ F g}^{-1}$) using the same reduction method. The effect of LC phase on the electrochemical properties of the reduced GO films was investigated by comparing films

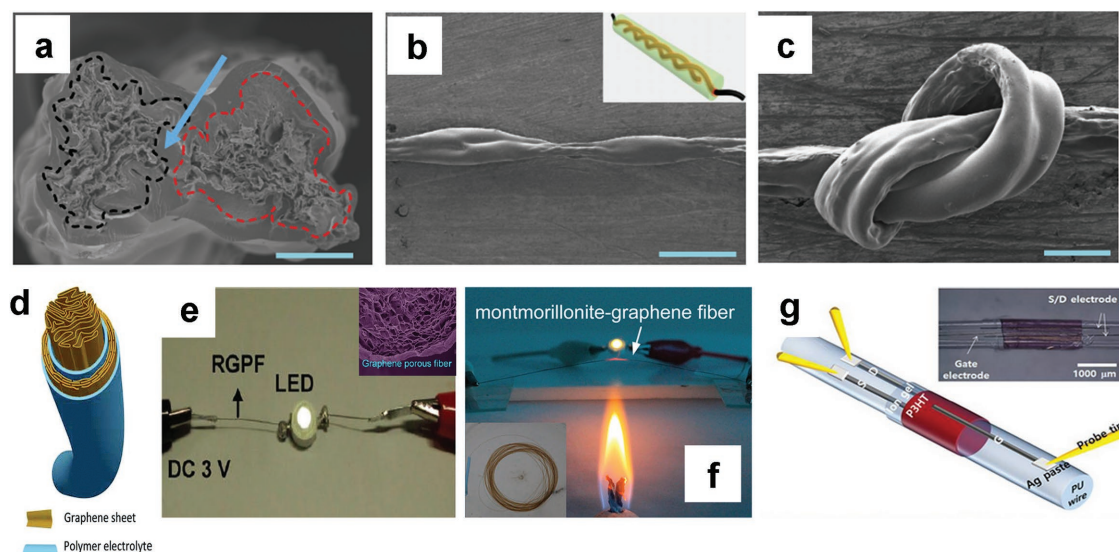


Figure 6. SEM images of a) cross-section and b) side view of a two-ply yarn supercapacitor; the arrow in (a) shows the PVA/ H_3PO_4 electrolyte; inset of (b) shows the schematic illustration of the yarn supercapacitor, c) SEM image of the two-ply yarn supercapacitor knot. Reproduced with permission.^[77] Copyright 2014, Nature Publishing Group. d) the cross sectional structure of a graphene fiber supercapacitor with a core fiber and a cylinder sheath as the two electrodes. Reproduced with permission.^[156] Copyright 2015, Royal Society of Chemistry. e) A constructed circuit using graphene aerogel fiber as lightweight conductive wire; a representative cross-section SEM image of the fiber is shown in the inset. Reproduced with permission.^[15] Copyright 2012, American Chemical Society. f) A circuit constructed by an LED and graphene/MMT (90/10) fiber; the LED works even when the fiber is heated. Reproduced with permission.^[104] Copyright 2015, American Chemical Society. g) Schematic illustration and optical image of a fiber-type transistor based on graphene/Ag hybrid fiber electrodes. Reproduced with permission.^[159] Copyright 2015, Nature Publishing Group.

prepared through blade-coating of LCGO and spray-coating of dilute GO (non-LC).^[153] It was observed that the specific capacitance of the film prepared from LCGO was twice as high as that of the GO film. For a blade-coated film with a mass loading of $\approx 0.115 \text{ mg cm}^{-2}$, the specific capacitance reached $\approx 286 \text{ F g}^{-1}$ in an aqueous electrolyte and $\approx 263 \text{ F g}^{-1}$ in a gel electrolyte. It was found that the trapped water in the LCGO film could play an important role in preventing the restacking of the sheets facilitating the removal of the oxygenated groups during the reduction process. These results indicate that LCGO is favorable for preparing high performance 2D paper-shaped electrodes for supercapacitor devices.

5.2. Electrical and Thermal Conductors

The highly ordered structures obtained from LCGO have led to higher electrical and thermal conductivities than those produced from non-LCGO.^[59,160] For instance, the graphene aerogel fiber produced by freeze-drying the wet-spun porous LCGO showed a high electrical conductivity (up to $\approx 49 \text{ S cm}^{-1}$) that could be used as a lightweight conductive wire (Figure 6e).^[15] In addition, LCGO has been used to host conductive nanowires in order to achieve high electrical properties. The wet-spun LCGO mixed with Ag nanowires ($\approx 20 \text{ wt.}\%$) showed a very high γ of up to $\approx 930 \text{ S cm}^{-1}$ and a high current capacity of $\approx 7.1 \times 10^3 \text{ A cm}^{-2}$ that were respectively ≈ 3 and ≈ 15 times higher than those of the graphene fiber.^[103] Because of the combination of excellent conductivity, high mechanical strength, and fine flexibility, the Ag-doped graphene fibers could be used as good stretchable conductors suitable for soft circuits. The high electrical conductivity ($\approx 35 \text{ S cm}^{-1}$) and good thermal stability of LCGO/MMT hybrid fibers made them suitable candidates for fire-resistant and lightweight conductors (Figure 6f).^[104]

Because of their potentially high thermal conductivities and light weight, graphene-based structures have also been used in thermal management for high-power electronics and portable devices. It was recently found that by intercalating small sized GO (SMGO) sheets into aqueous LC dispersions of large-sized GO (LGGO), fibers with high thermal conductivity and mechanical properties could be achieved.^[40] The optimized graphene fiber with $\approx 30 \text{ wt.}\%$ SMGO exhibited an excellent thermal conductivity of up to $\approx 1290 \text{ W m}^{-1} \text{ K}^{-1}$ after high-temperature treatment. In addition, the thermal transfer rate was much faster for the optimized graphene fiber compared to the pure LGGO fiber and the copper wire.

5.3. Fiber-Shaped Transistors

Recent studies suggested the high potential of graphene and its hybrid fibers as promising candidates for fabrication of wearable electronic devices. For example, flexible fiber-type field-effect transistors were fabricated from graphene/Ag hybrid fibers.^[159] The graphene/Ag hybrid fibers possessed an electrical conductivity of up to $15\,800 \text{ S cm}^{-1}$ and could be cut and placed onto flexible substrates by simply gluing or stitching. Fiber-based transistors were then constructed by embedding the graphene/Ag hybrid fiber electrodes onto conventional

polyurethane monofilaments (Figure 6g). The graphene fiber-based transistor exhibited an excellent flexibility (highly bendable and rollable), high electrical performance (charge carrier mobility of $\approx 15.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off current ratio of more than 10^4), and outstanding device performance stability (stable after 1000 bending cycles).

5.4. Biomedical Application of LCGO

Graphene and GO have been widely used in biomedical applications, such as drug delivery and tissue engineering. The biomedical applications of graphene-based materials have been summarized in recent reviews.^[129,161] LCGO can offer many advantages over non-LC GO and other forms of graphene for biomedical applications. For instance, the larger graphene sheets in LCGO can provide larger interfaces for drug loading and the highly ordered sheets and LC domains can offer natural channels for drug transports. The toxicity studies of wet-spun LCGO/polypyrrole composite fibers after chemical reduction showed that the L929 fibroblasts cultured on fibers had no significant change in cell viability or number.^[162] The high conductivity, mechanical properties as well as cytotoxicity made these composite fibers suitable for a wide range of applications such as cell scaffolding components in implantable devices that require electrical stimulation. Due to the limited works in this area, more research is required to probe the superiority of LCGO over other graphene sources or to reveal its shortcomings.

5.5. Optoelectronics

Liquid crystalline materials have been widely used in liquid crystal display switching which is known to come from the alignment of the LC molecules with the assistance of an external electric field. Early attempts to induce LCGO alignment under a constant electric field were not successful as the negatively charged GO platelets were found to be prone to electrophoretic migration and subsequent reduction.^[13] Nevertheless, it was later discovered that applying a low-frequency electric field to the GO dispersion at a very low concentration ($\sim 0.1 \text{ vol.}\%$) could result in the phase transition from isotropic to nematic phase.^[50] Based on this knowledge, a few types of electro-optical devices were designed to demonstrate the potential application of LCGO in optical devices.^[50]

5.6. Other Applications

A single GO sheet with its well-defined nanometer pores can be used as a molecular sieve for nanofiltration and desalination.^[163] It has been demonstrated that the shear-induced alignment of nematic phase of GO deposited on a porous substrate could be used for nanofiltration.^[164] In contrast to the membrane composed of disordered GO, the highly ordered membrane produced from the nematic LCGO with stacking periodicity and organized channels showed an enhanced permeability while

facilitating high retention (>90%) of organic molecules. LCGO has also been used to induce partial orientation of organic molecules in NMR analysis and was found to be helpful in producing extremely clean and high quality NMR spectra.^[165]

6. Summary and Outlook

LCGO is a relatively new concept as research in this field has only begun just over five years ago. Hence, there are still plenty of potential opportunities for discovery and incremental advances; from improving the synthesis and processing efficiency, uncovering novel properties of new LCGO-based formulations, to developing novel applications. There are also a few challenges that will need to be addressed to achieve these developments. Based on the recent progress on LCGO, here we highlight some of the opportunities that arise from the challenges in this field.

Firstly, LCGO synthesis require control (from the quality of the starting material through to the sonication step) to ensure GO sheets are highly exfoliated and also have large sheet size and less defects. We found that there is no consensus in the literature on the optimal LCGO synthesis conditions to follow in order to ensure the achievement of LC behavior or large sheets. It is not surprising that the properties of LCGO, e.g., sheet size, elemental components, and I_D/I_G , varied noticeably among different reports. Therefore, a thorough investigation of the synthesis parameters will be very useful in identifying the true parameters required for the reliable achievement of LCGO with known quality. One relatively unexplored area includes investigating the influence of temperature on the intercalation and oxidation steps for producing large GO sheet sizes that have narrow sheet size distribution.

Furthermore, in terms of the LCGO synthesis, the environmental problem becomes a critical issue when the scale of LCGO production is increased. Large amounts of acids and oxidants are typically consumed in the LCGO synthesis and if the use of large amounts of chemicals cannot be avoided, studies on effective recycling and waste treatment strategies will be required.

In terms of processing, the unique LCGO property has enabled the use of a wide range of fabrication techniques and many research groups have shown that LCGO is an efficient starting material to make graphene-based architectures. The microstructural order in LCGO-based macroscopic assemblies has led to superior properties (mechanical, thermal, electrical, electrochemical, etc.) particularly when compared to the non-LC GO source. The key to most processing techniques rely on the understanding of the rheological properties of LCGO. Although there are a few interesting reports on this topic, more detailed understanding of the correlation of the LC behavior and the rheological properties will enable researchers, scientists, and engineers to prepare appropriate LCGO dispersions for the desired solution-based processing technique.

Specifically on fiber spinning, the recent advances on various methods to produce different fiber types have led to significant improvements in fiber properties compared to the initial report. However, there is still room for improvement. For instance, the mechanical properties of graphene fibers have yet to reach

those of the carbon fibers. Preparing a defect-free GO source with suitable sheet size distribution and rheological properties amenable to fiber spinning is the first step towards achieving high strength and high modulus graphene fibers. Detailed control of the spinning parameters such as coagulation bath composition, temperature, flow rate, spinneret size, and draw ratio is also critical to achieve an optimized GO fiber fabrication. In this instance, the coagulating agent in the bath should ideally provide inter-sheet bonds and give rise to the interactions of the adjacent graphene sheets. Furthermore, effective strategies are required to promote the fabrication of ultra-fine graphene fibers with highly packed morphology, circular cross-section, low defects, and high structural ordering. The demonstration of large scale fiber production will also drive the practical application of graphene fibers. Yarns and textiles will provide more suitable platforms for the wide-spread use of graphene fibers and should be paid more attention in future research. In this regard, graphene fibers with high conductivity are required to operate at a sufficient scale essential for the desired applications.

Compared to 1D fiber assemblies, there have been significantly less works on 2D and 3D based assemblies from LCGO. The prominent advantage of the LCGO over non-LC GO is the suitable processability and self-assembly of LCGO into highly ordered 2D and 3D architectures with tailored microstructures. This rationale suggests that graphene-based 2D and 3D assemblies should be further developed to unravel the unique properties that highly ordered GO assemblies can provide. As an example, LCGO has facilitated the preparation of additive-free ink formulations for printing. Further studies to probe the effects of LCGO on the microstructure and properties of 2D and 3D macroscopic assemblies will be useful.

The large sheet size and LC domains of LCGO have also been found to be excellent platforms for accommodating various species such as polymeric chains, 0D nanoparticles, 1D nanorods, nanowires, and nanotubes, and other 2D nanosheets to prepare functional composites and hybrids. The unique long-range orientational ordering of LCGO can be effectively utilized to prepare highly ordered composite and hybrid architectures for mechanical reinforcement, electrical conductivity, and energy storage to name a few.

The outstanding dispersibility of LCGO in water and in organic solvents has enabled its composite and hybrid processability via the simple blending approach. Due to the abundant functional groups on the surface and on the edges, LCGO offers great potential for covalent attachment of polymers or other compounds. Previous works have mostly focused on the blending strategy to produce LCGO composites and hybrids and very little attention has been paid to the covalent attachment strategy. Further advancements in covalent attachment of various components to LCGO are expected to result in composites and hybrids with superior properties.

Although LCGO can lead to structural ordering via self-assembly, this approach might not achieve highly ordered hierarchical microstructures. Utilizing approaches (such as wet-spinning) that induce high alignment to the LCGO and other components in the system can be highly beneficial in achieving enhanced properties (i.e., mechanical, electrical, electrochemical, etc.) of the composites and hybrids.

Many useful properties of LCGO-based materials such as energy storage and sensing are only available after its reduction. Reducing LCGO in the presence of other materials, however, has proven to be challenging as the chemical or thermal treatments required to effectively reduce LCGO may alter the properties of other components in the composite and hybrid or even destroy the structure. Therefore, efforts will need to be directed towards effectively using LCGO in reduced form within composite or hybrid systems. It is also noteworthy that the LCGO-based composites and hybrids produced so far are mostly in small scale. Scaling-up the fabrication to achieve LCGO composites or hybrids in commercially viable forms is of paramount importance.

Various compositions and designs have been proposed to realize the practical applications of LCGO in wearable energy storage devices. The main emphases were on fabricating LCGO fibers with the suitable EDLC properties as well as on integrating pseudocapacitor materials such as conductive polymers and transition metal oxides within the LCGO fibers to achieve enhanced energy storage properties. In order for the LCGO-based fibers to be suitable for wearable electronic devices, the fibers should possess high flexibility and strength as well as sufficiently high electrical conductivity. Hence, detailed understanding of the influence of the compositional and fabrication parameters are critical in achieving fibers with high electrical, mechanical, and electrochemical properties suitable for wearable energy storage devices.

In terms of the design, it has been shown that the fiber electrode structure and configuration play a significant role in charge storage capacity of the final supercapacitor device. Using highly porous or hollow LCGO fibers instead of a solid compact fiber has proven to be beneficial to achieve high energy storage devices. The production of core/sheath LCGO fibers with appropriate electrolyte coating has also been reported as an effective strategy for the fabrication of all-in-one wearable energy storage fibers. Further research should be directed towards fabricating novel electrodes that benefit from the right combination of composition, structure, and electrode configuration.

It can be concluded that the application of LCGO is still in its infancy and there are yet plenty of opportunities to be developed to further expand its applications in other areas such as biomedicine, sensing, and catalysis. Benefiting from the highly aligned graphene sheets of LCGO can be challenging but the large surface area and highly ordered structures of LCGO can offer much more benefits than non-LC GO for many practical applications.

Acknowledgements

J.Z. and S.S. contributed equally to this work. This work is funded by the Australian Research Council (FT130100380 and DP170102859).

Received: December 7, 2016

Revised: January 7, 2017

Published online: February 23, 2017

[1] A. K. Geim, *Science* **2009**, 324, 1530.

[2] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Adv. Mater.* **2010**, 22, 3906.

- [3] Z. Li, Z. Liu, H. Sun, C. Gao, *Chem. Rev.* **2015**, 115, 7046.
- [4] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, 490, 192.
- [5] M. J. Allen, V. C. Tung, R. B. Kaner, *Chem. Rev.* **2010**, 110, 132.
- [6] D. Li, M. B. Müller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.* **2008**, 3, 101.
- [7] D. a. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, *Nature* **2007**, 448, 457.
- [8] S. Park, R. S. Ruoff, *Nat. Nanotechnol.* **2009**, 4, 217.
- [9] Z. Xu, C. Gao, *ACS Nano* **2011**, 5, 2908.
- [10] Z. Xu, C. Gao, *Nat. Commun.* **2011**, 2, 571.
- [11] H. Hu, Z. Zhao, W. Wan, Y. Gogotsi, J. Qiu, *Adv. Mater.* **2013**, 25, 2219.
- [12] N. Behabtu, J. R. Lomeda, M. J. Green, A. L. Higginbotham, A. Sinitskii, D. V. Kosynkin, D. Tsentelovich, A. N. G. Parra-Vasquez, J. Schmidt, E. Kesselman, Y. Cohen, Y. Talmon, J. M. Tour, M. Pasquali, *Nat. Nanotechnol.* **2010**, 5, 406.
- [13] J. E. J. E. Y. Kim, T. H. Han, S. H. Lee, J. E. J. E. Y. Kim, C. W. Ahn, J. M. Yun, S. O. Kim, *Angew. Chem. Int. Ed.* **2011**, 50, 3043.
- [14] S. H. Aboutalebi, M. M. Gudarzi, Q. Bin Zheng, J.-K. Kim, *Adv. Funct. Mater.* **2011**, 21, 2978.
- [15] Z. Xu, Y. Zhang, P. Li, C. Gao, *ACS Nano* **2012**, 6, 7103.
- [16] H. Cheng, C. Hu, Y. Zhao, L. Qu, *NPG Asia Mater.* **2014**, 6, e113.
- [17] S. H. Aboutalebi, R. Jalili, D. Esrafilzadeh, M. Salari, Z. Gholamvand, S. Aminorroaya Yamini, K. Konstantinov, R. L. Shepherd, J. Chen, S. E. Moulton, P. C. Innis, A. I. Minett, J. M. Razal, G. G. Wallace, *ACS Nano* **2014**, 8, 2456.
- [18] R. Jalili, S. H. Aboutalebi, D. Esrafilzadeh, R. L. Shepherd, J. Chen, S. Aminorroaya-Yamini, K. Konstantinov, A. I. Minett, J. M. Razal, G. G. Wallace, *Adv. Funct. Mater.* **2013**, 23, 5345.
- [19] L. Kou, Z. Liu, T. Huang, B. Zheng, Z. Tian, Z. Deng, C. Gao, *Nanoscale* **2015**, 7, 4080.
- [20] Z. Liu, Z. Li, Z. Xu, Z. Xia, X. Hu, L. Kou, L. Peng, Y. Wei, C. Gao, *Chem. Mater.* **2014**, 26, 6786.
- [21] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, 80, 1339.
- [22] A. Dimiev, D. V. Kosynkin, L. B. Alemany, P. Chaguine, J. M. Tour, *J. Am. Chem. Soc.* **2012**, 134, 2815.
- [23] A. M. Dimiev, G. Ceriotti, N. Behabtu, D. Zakhidov, M. Pasquali, R. Saito, J. M. Tour, *ACS Nano* **2013**, 7, 2773.
- [24] A. M. Dimiev, J. M. Tour, *ACS Nano* **2014**, 8, 3060.
- [25] R. Jalili, S. H. Aboutalebi, D. Esrafilzadeh, K. Konstantinov, J. M. Razal, S. E. Moulton, G. G. Wallace, *Mater. Horizons* **2014**, 1, 87.
- [26] S. Pan, I. A. Aksay, *ACS Nano* **2011**, 5, 4073.
- [27] A. M. Dimiev, S. M. Bachilo, R. Saito, J. M. Tour, *ACS Nano* **2012**, 6, 7842.
- [28] J. Chen, F. Chi, L. Huang, M. Zhang, B. Yao, Y. Li, C. Li, G. Shi, *Carbon* **2016**, 110, 34.
- [29] S. Shamaila, A. K. L. Sajjad, A. Iqbal, *Chem. Eng. J.* **2016**, 294, 458.
- [30] J. H. Kang, T. Kim, J. Choi, J. Park, Y. S. Kim, M. S. Chang, H. Jung, K. T. Park, S. J. Yang, C. R. Park, *Chem. Mater.* **2016**, 28, 756.
- [31] C. Petit, M. Seredych, T. J. Bandoz, *J. Mater. Chem.* **2009**, 19, 9176.
- [32] L. Zhang, J. Liang, Y. Huang, Y. Ma, Y. Wang, Y. Chen, *Carbon* **2009**, 47, 3365.
- [33] K. Krishnamoorthy, M. Veerapandian, K. Yun, S.-J. J. Kim, *Carbon* **2013**, 53, 38.
- [34] S. Eigler, C. Dotzer, F. Hof, W. Bauer, A. Hirsch, *Chem. – A Eur. J.* **2013**, 19, 9490.
- [35] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS Nano* **2010**, 4, 4806.
- [36] J. Chen, Y. Li, L. Huang, N. Jia, C. Li, G. Shi, *Adv. Mater.* **2015**, 27, 3654.

- [37] J. Sun, N. Yang, Z. Sun, M. Zeng, L. Fu, C. Hu, S. Hu, *ACS Appl. Mater. Interfaces* **2015**, 7, 21356.
- [38] L. Sun, B. Fugetsu, *Mater. Lett.* **2013**, 109, 207.
- [39] F. Pendolino, E. Parisini, S. Lo Russo, *J. Phys. Chem. C* **2014**, 118, 28162.
- [40] G. Xin, T. Yao, H. Sun, S. M. Scott, D. Shao, G. Wang, J. Lian, *Science* **2015**, 349, 1083.
- [41] L. Li, J. Walda, L. Manna, A. P. Alivisatos, *Nano Lett.* **2002**, 2, 557.
- [42] S. Chandrasekhar, in *Liquid Crystals*, Cambridge University Press, Cambridge, **1992**, pp. 1–16.
- [43] T. H. Han, J. Kim, J. S. Park, C. B. Park, H. Ihee, S. O. Kim, *Adv. Mater.* **2007**, 19, 3924.
- [44] R. Narayan, J. E. Kim, J. Y. Kim, K. E. Lee, S. O. Kim, *Adv. Mater.* **2016**, 28, 3045.
- [45] F. Guo, F. Kim, T. H. Han, V. B. Shenoy, J. Huang, R. H. Hurt, *ACS Nano* **2011**, 5, 8019.
- [46] S. Chen, W. Ma, Y. Cheng, Z. Weng, B. Sun, L. Wang, W. Chen, F. Li, M. Zhu, H.-M. Cheng, *Nano Energy* **2015**, 15, 642.
- [47] B. Yao, J. Chen, L. Huang, Q. Zhou, G. Shi, *Adv. Mater.* **2016**, 28, 1623.
- [48] Z. Xu, C. Gao, *Acc. Chem. Res.* **2014**, 47, 1267.
- [49] F. Lin, X. Tong, Y. Wang, J. Bao, Z. M. Wang, *Nanoscale Res. Lett.* **2015**, 10, 1.
- [50] T.-Z. Shen, S.-H. Hong, J.-K. Song, *Nat. Mater.* **2014**, 13, 394.
- [51] N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, A. D. Gorchinskiy, *Chem. Mater.* **1999**, 11, 771.
- [52] L. Peng, Z. Xu, Z. Liu, Y. Wei, H. Sun, Z. Li, X. Zhao, C. Gao, *Nat. Commun.* **2015**, 6, 5716.
- [53] Z. Sofer, J. Luxa, O. Jankovský, D. Sedmidubský, T. Bystroň, M. Pumera, *Angew. Chem. Int. Ed.* **2016**, 55, 11965.
- [54] J. Chen, B. Yao, C. Li, G. Shi, *Carbon* **2013**, 64, 225.
- [55] M. Z. Seyedin, J. M. Razal, P. C. Innis, R. Jalili, G. G. Wallace, *Adv. Funct. Mater.* **2015**, 25, 94.
- [56] S. Seyedin, M. S. Romano, A. I. Minett, J. M. Razal, *Sci. Rep.* **2015**, 5, 14946.
- [57] G. Xin, H. Sun, T. Hu, H. R. Fard, X. Sun, N. Koratkar, T. Borca-Tasciuc, J. Lian, *Adv. Mater.* **2014**, 26, 4521.
- [58] C. Chen, Z. Xu, Y. Han, H. Sun, C. Gao, *ACS Appl. Mater. Interfaces* **2016**, 8, 8000.
- [59] X. Lin, X. Shen, Q. Zheng, N. Yousefi, L. Ye, Y.-W. Mai, J.-K. Kim, *ACS Nano* **2012**, 6, 10708.
- [60] G. Wu, Y. Hu, Y. Liu, J. Zhao, X. Chen, V. Whoehling, C. Plesse, G. T. M. Nguyen, F. Vidal, W. Chen, *Nat. Commun.* **2015**, 6, 7258.
- [61] K. E. Lee, J. E. Kim, U. N. Maiti, J. Lim, J. O. Hwang, J. Shim, J. J. Oh, T. Yun, S. O. Kim, *ACS Nano* **2014**, 8, 9073.
- [62] X. Wang, H. Bai, G. Shi, *J. Am. Chem. Soc.* **2011**, 133, 6338.
- [63] W. Zhang, X. Zou, H. Li, J. Hou, J. Zhao, J. Lan, B. Feng, S. Liu, *RSC Adv.* **2015**, 5, 146.
- [64] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon* **2007**, 45, 1558.
- [65] J. I. Paredes, S. Villar-Rodil, A. Martínez-Alonso, J. M. D. Tascón, *Langmuir* **2008**, 24, 10560.
- [66] S. Dubin, S. Gilje, K. Wang, V. C. Tung, K. Cha, A. S. Hall, J. Farrar, R. Varshneya, Y. Yang, R. B. Kaner, *ACS Nano* **2010**, 4, 3845.
- [67] R. Jalili, S. H. Aboutalebi, D. Esrafilzadeh, K. Konstantinov, S. E. Moulton, J. M. Razal, G. G. Wallace, *ACS Nano* **2013**, 7, 3981.
- [68] F. Vollrath, D. P. Knight, *Nature* **2001**, 410, 541.
- [69] S. Naficy, R. Jalili, S. H. Aboutalebi, R. A. Gorkin III, K. Konstantinov, P. C. Innis, G. M. Spinks, P. Poulin, G. G. Wallace, *Mater. Horizons* **2014**, 1, 326.
- [70] C. Xiang, N. Behabtu, Y. Liu, H. G. Chae, C. C. Young, B. Genorio, D. E. Tsentalovich, C. Zhang, D. V. Kosynkin, J. R. Lomeda, C.-C. Hwang, S. Kumar, M. Pasquali, J. M. Tour, *ACS Nano* **2013**, 7, 1628.
- [71] C. Xiang, C. C. Young, X. Wang, Z. Yan, C.-C. Hwang, G. Cerioti, J. Lin, J. Kono, M. Pasquali, J. M. Tour, *Adv. Mater.* **2013**, 25, 4592.
- [72] L. Chen, Y. He, S. Chai, H. Qiang, F. Chen, Q. Fu, *Nanoscale* **2013**, 5, 5809.
- [73] Z. Xu, H. Sun, X. Zhao, C. Gao, *Adv. Mater.* **2013**, 25, 188.
- [74] H.-P. Cong, X.-C. Ren, P. Wang, S.-H. Yu, *Sci. Rep.* **2012**, 2, 613.
- [75] T. Huang, B. Zheng, L. Kou, K. Gopalsamy, Z. Xu, C. Gao, Y. Meng, Z. Wei, *RSC Adv.* **2013**, 3, 23957.
- [76] Y. Zhao, C. Jiang, C. Hu, Z. Dong, J. Xue, Y. Meng, N. Zheng, P. Chen, L. Qu, *ACS Nano* **2013**, 7, 2406.
- [77] L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy, H. Sun, C. Gao, *Nat. Commun.* **2014**, 5, 3754.
- [78] Z. Xu, Y. Liu, X. Zhao, L. Peng, H. Sun, Y. Xu, X. Ren, C. Jin, P. Xu, M. Wang, C. Gao, *Adv. Mater.* **2016**, 28, 6449.
- [79] J. Sun, Y. Li, Q. Peng, S. Hou, D. Zou, Y. Shang, Y. Li, P. Li, Q. Du, Z. Wang, Y. Xia, L. Xia, X. Li, A. Cao, *ACS Nano* **2013**, 7, 10225.
- [80] M. Zhang, L. Huang, J. Chen, C. Li, G. Shi, *Adv. Mater.* **2014**, 26, 7588.
- [81] H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, Y. Chen, *ACS Nano* **2008**, 2, 463.
- [82] H. G. Jeon, Y. H. Huh, S. H. Yun, K. W. Kim, S. S. Lee, J. Lim, K.-S. An, B. Park, *J. Mater. Chem. C* **2014**, 2, 2622.
- [83] S. Gilje, S. Han, M. Wang, K. L. Wang, R. B. Kaner, *Nano Lett.* **2007**, 7, 3394.
- [84] M. Zhou, Y. Wang, Y. Zhai, J. Zhai, W. Ren, F. Wang, S. Dong, *Chem. – A Eur. J.* **2009**, 15, 6116.
- [85] Y. Liu, B. Weng, J. M. Razal, Q. Xu, C. Zhao, Y. Hou, S. Seyedin, R. Jalili, G. G. Wallace, J. Chen, *Sci. Rep.* **2015**, 5, 17045.
- [86] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Ri Kim, Y. Il Song, Y.-J. Kim, K. S. Kim, B. Özyilmaz, J.-H. Ahn, B. H. Hong, S. Iijima, *Nat. Nanotechnol.* **2010**, 5, 574.
- [87] F. Torrisi, T. Hasan, W. Wu, Z. Sun, A. Lombardo, T. S. Kulmala, G. W. Hsieh, S. Jung, F. Bonaccorso, P. J. Paul, D. Chu, A. C. Ferrari, *ACS Nano* **2012**, 6, 2992.
- [88] B. Derby, N. Reis, *MRS Bull.* **2003**, 28, 815.
- [89] Y. Xu, K. Sheng, C. Li, G. Shi, *ACS Nano* **2010**, 4, 4324.
- [90] L. Qiu, J. Z. Liu, S. L. Y. Chang, Y. Wu, D. Li, *Nat. Commun.* **2012**, 3, 1241.
- [91] E. García-Tuñón, S. Barg, J. Franco, R. Bell, S. Eslava, E. D'Elia, R. C. Maher, F. Guitian, E. Saiz, *Adv. Mater.* **2015**, 27, 1688.
- [92] A. E. Jakus, E. B. Secor, A. L. Rutz, S. W. Jordan, M. C. Hersam, R. N. Shah, *ACS Nano* **2015**, 9, 4636.
- [93] H. Kim, C. W. Macosko, *Polymer* **2009**, 50, 3797.
- [94] O. M. Istrate, K. R. Paton, U. Khan, A. O'Neill, A. P. Bell, J. N. Coleman, *Carbon* **2014**, 78, 243.
- [95] K. A. Anand, T. S. Jose, U. S. Agarwal, T. V. Sreekumar, B. Banwari, R. Joseph, *Int. J. Polym. Mater.* **2010**, 59, 438.
- [96] P. May, U. Khan, A. O'Neill, J. N. Coleman, *J. Mater. Chem.* **2012**, 22, 1278.
- [97] S. Seyedin, J. M. Razal, P. C. Innis, G. G. Wallace, *Smart Mater. Struct.* **2016**, 25, 35015.
- [98] H. Kim, S. Kobayashi, M. A. AbdurRahim, M. J. Zhang, A. Khusainova, M. A. Hillmyer, A. A. Abdala, C. W. Macosko, *Polymer* **2011**, 52, 1837.
- [99] L. Kou, C. Gao, *Nanoscale* **2013**, 5, 4370.
- [100] X. Hu, Z. Xu, Z. Liu, C. Gao, *Sci. Rep.* **2013**, 3, 2374.
- [101] Z. Xu, C. Gao, *Mater. Today* **2015**, 18, 480.
- [102] S. Seyedin, J. M. Razal, P. C. Innis, R. Jalili, G. G. Wallace, *Adv. Mater. Interfaces* **2016**, 3, 1500672.
- [103] Z. Xu, Z. Liu, H. Sun, C. Gao, *Adv. Mater.* **2013**, 25, 3249.
- [104] B. Fang, L. Peng, Z. Xu, C. Gao, *ACS Nano* **2015**, 9, 5214.
- [105] Z. Liu, Z. Xu, X. Hu, C. Gao, *Macromolecules* **2013**, 46, 6931.

- [106] K. Gopalsamy, Z. Xu, B. Zheng, T. Huang, L. Kou, X. Zhao, C. Gao, *Nanoscale* **2014**, 6, 8595.
- [107] A. Chidembo, S. H. Aboutaleb, K. Konstantinov, M. Salari, B. Winton, S. A. Yamini, I. P. Nevirkovets, H. K. Liu, *Energy Environ. Sci.* **2012**, 5, 5236.
- [108] S. H. Aboutaleb, S. Aminorroaya-Yamini, I. Nevirkovets, K. Konstantinov, H. K. Liu, *Adv. Energy Mater.* **2012**, 2, 1439.
- [109] G. Sun, J. Liu, X. Zhang, X. Wang, H. Li, Y. Yu, W. Huang, H. Zhang, P. Chen, *Angew. Chem. Int. Ed.* **2014**, 53, 12576.
- [110] A. T. Chidembo, S. H. Aboutaleb, K. Konstantinov, D. Wexler, H. K. Liu, S. X. Dou, *Part. Part. Syst. Charact.* **2014**, 31, 465.
- [111] Z. Tang, H. Kang, Z. Shen, B. Guo, L. Zhang, D. Jia, *Macromolecules* **2012**, 45, 3444.
- [112] L. Cui, J. Liu, R. Wang, Z. Liu, W. Yang, *J. Polym. Sci. Part A Polym. Chem.* **2012**, 50, 4423.
- [113] S. Sayyar, E. Murray, B. C. Thompson, S. Gambhir, D. L. Officer, G. G. Wallace, *Carbon* **2013**, 52, 296.
- [114] X. Zhao, Z. Xu, B. Zheng, C. Gao, *Sci. Rep.* **2013**, 3, 3164.
- [115] K. Zhang, L. L. Zhang, X. S. Zhao, J. Wu, *Chem. Mater.* **2010**, 22, 1392.
- [116] Z. Xu, C. Gao, *Macromolecules* **2010**, 43, 6716.
- [117] K. Liu, L. Chen, Y. Chen, J. Wu, W. Zhang, F. Chen, Q. Fu, *J. Mater. Chem.* **2011**, 21, 8612.
- [118] K. E. Lee, J. J. Oh, T. Yun, S. O. Kim, *J. Solid State Chem.* **2015**, 224, 115.
- [119] H. Kim, Y. Miura, C. W. MacOsco, *Chem. Mater.* **2010**, 22, 3441.
- [120] X. Hu, Z. Xu, C. Gao, *Sci. Rep.* **2012**, 2, 767.
- [121] N. Yousefi, M. M. Gudarzi, Q. Zheng, S. H. Aboutaleb, F. Sharif, J.-K. Kim, *J. Mater. Chem.* **2012**, 22, 12709.
- [122] U. Khan, P. May, A. O'Neill, J. N. Coleman, *Carbon* **2010**, 48, 4035.
- [123] M. M. Islam, D. Cardillo, T. Akhter, S. H. Aboutaleb, H. K. Liu, K. Konstantinov, S. X. Dou, *Part. Part. Syst. Charact.* **2016**, 33, 27.
- [124] M. Mao, J. Hu, H. Liu, *Int. J. Energy Res.* **2015**, 39, 727.
- [125] L. Chen, Y. Liu, Y. Zhao, N. Chen, L. Qu, *Nanotechnology* **2016**, 27, 32001.
- [126] A. Aghigh, V. Alizadeh, H. Y. Wong, M. S. Islam, N. Amin, M. Zaman, *Desalination* **2015**, 365, 389.
- [127] K. Toda, R. Furue, S. Hayami, *Anal. Chim. Acta* **2015**, 878, 43.
- [128] J. Zhao, G.-Y. Zhang, D.-X. Shi, *Chinese Phys. B* **2013**, 22, 57701.
- [129] J.-L. Li, B. Tang, B. Yuan, L. Sun, X.-G. Wang, *Biomaterials* **2013**, 34, 9519.
- [130] K. Yang, L. Feng, Z. Liu, *Expert Opin. Drug Deliv.* **2015**, 12, 601.
- [131] M. D. Stoller, S. Park, Y. Zhu, J. An, R. S. Ruoff, *Nano Lett.* **2008**, 8, 3498.
- [132] Y. Bai, R. B. Rakhi, W. Chen, H. N. Alshareef, *J. Power Sources* **2013**, 233, 313.
- [133] A. Bello, F. Barzegar, D. Momodu, J. Dangbegnon, F. Taghizadeh, M. Fabiane, N. Manyala, *J. Power Sources* **2015**, 273, 305.
- [134] Q. Chen, Y. Meng, C. Hu, Y. Zhao, H. Shao, N. Chen, L. Qu, *J. Power Sources* **2014**, 247, 32.
- [135] W. Fan, Y.-Y. Xia, W. W. Tjiu, P. K. Pallathadka, C. He, T. Liu, *J. Power Sources* **2013**, 243, 973.
- [136] P. K. Kalambate, R. A. Dar, S. P. Karna, A. K. Srivastava, *J. Power Sources* **2015**, 276, 262.
- [137] C. Gong, Y. He, J. Zhou, W. Chen, W. Han, Z. Zhang, P. Zhang, X. Pan, Z. Wang, E. Xie, *ACS Appl. Mater. Interfaces* **2014**, 6, 14844.
- [138] Y. M. Shulga, S. A. Baskakov, Y. V. Baskakova, Y. M. Volkovich, N. Y. Shulga, E. A. Skryleva, Y. N. Parkhomenko, K. G. Belay, G. L. Gutsev, A. Y. Rychagov, V. E. Sosenkin, I. D. Kovalev, *J. Power Sources* **2015**, 279, 722.
- [139] T. Zhai, X. Lu, H. Wang, G. Wang, T. Mathis, T. Liu, C. Li, Y. Tong, Y. Li, *Nano Lett.* **2015**, 15, 3189.
- [140] Y. Chen, X. Zhang, P. Yu, Y. Ma, *J. Power Sources* **2010**, 195, 3031.
- [141] Y. Huang, J. Liang, Y. Chen, *Small* **2012**, 8, 1805.
- [142] J. Yan, Q. Wang, T. Wei, Z. Fan, *Adv. Energy Mater.* **2014**, 4, 1300816.
- [143] L. Huang, C. Li, G. Shi, *J. Mater. Chem. A* **2014**, 2, 968.
- [144] Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, *ACS Nano* **2010**, 4, 1963.
- [145] N. A. Kumar, H.-J. Choi, Y. R. Shin, D. W. Chang, L. Dai, J.-B. Baek, *ACS Nano* **2012**, 6, 1715.
- [146] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H.-M. Cheng, *Nat. Mater.* **2011**, 10, 424.
- [147] Z. Chen, C. Xu, C. Ma, W. Ren, H.-M. Cheng, *Adv. Mater.* **2013**, 25, 1296.
- [148] J. Zhang, W. Yang, J. Liu, *Electrochim. Acta* **2016**, 209, 85.
- [149] H.-P. Cong, J.-F. Chen, S.-H. Yu, *Chem. Soc. Rev.* **2014**, 43, 7295.
- [150] J. Luo, H. D. Jang, J. Huang, *ACS Nano* **2013**, 7, 1464.
- [151] J. Luo, H. D. Jang, T. Sun, L. Xiao, Z. He, A. P. Katsoulidis, M. G. Kanatzidis, J. M. Gibson, J. Huang, *ACS Nano* **2011**, 5, 8943.
- [152] B. Zheng, T. Huang, L. Kou, X. Zhao, K. Gopalsamy, C. Gao, *J. Mater. Chem. A* **2014**, 2, 9736.
- [153] B. Wang, J. Liu, Y. Zhao, Y. Li, W. Xian, M. Amjadipour, J. MacLeod, N. Motta, *ACS Appl. Mater. Interfaces* **2016**, 8, 22316.
- [154] H. Cheng, Z. Dong, C. Hu, Y. Zhao, Y. Hu, L. Qu, N. Chen, L. Dai, *Nanoscale* **2013**, 5, 3428.
- [155] G. Qu, J. Cheng, X. Li, D. Yuan, P. Chen, X. Chen, B. Wang, H. Peng, *Adv. Mater.* **2016**, 28, 3646.
- [156] X. Zhao, B. Zheng, T. Huang, C. Gao, *Nanoscale* **2015**, 7, 9399.
- [157] Y. Hu, H. Cheng, F. Zhao, N. Chen, L. Jiang, Z. Feng, L. Qu, *Nanoscale* **2014**, 6, 6448.
- [158] T. Xu, X. Ding, Y. Liang, Y. Zhao, N. Chen, L. Qu, *Nanoscale* **2016**, 8, 12113.
- [159] S. S. Yoon, K. E. Lee, H.-J. Cha, D. G. Seong, M.-K. Um, J.-H. Byun, Y. Oh, J. H. Oh, W. Lee, J. U. Lee, *Sci. Rep.* **2015**, 5, 16366.
- [160] C.-Y. Su, Y. Xu, W. Zhang, J. Zhao, X. Tang, C.-H. Tsai, L.-J. Li, *Chem. Mater.* **2009**, 21, 5674.
- [161] B. C. Thompson, E. Murray, G. G. Wallace, *Adv. Mater.* **2015**, 27, 7563.
- [162] K. S. U. Schirmer, D. Esrafilzadeh, B. C. Thompson, A. F. Quigley, R. M. I. Kapsa, G. G. Wallace, *J. Mater. Chem. B* **2016**, 4, 1142.
- [163] R. K. Joshi, P. Carbone, F. C. Wang, V. G. Kravets, Y. Su, I. V. Grigorieva, H. A. Wu, A. K. Geim, R. R. Nair, *Science* **2014**, 343, 752.
- [164] A. Akbari, P. Sheath, S. T. Martin, D. B. Shinde, M. Shaibani, P. C. Banerjee, R. Tkacz, D. Bhattacharyya, M. Majumder, *Nat. Commun.* **2016**, 7, 10891.
- [165] X. Lei, Z. Xu, H. Sun, S. Wang, C. Griesinger, L. Peng, C. Gao, R. X. Tan, *J. Am. Chem. Soc.* **2014**, 136, 11280.