A Review on Graphene Oxide Two-dimensional Macromolecules: from Single Molecules to Macro-assembly

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Abstract: Graphene oxide (GO), which consists of two-dimensional (2D) sp² carbon hexagonal networks and oxygen-contained functional groups, has laid the foundation of mass production and applications of graphene materials. Made by chemical oxidation of graphite, GO is highly dispersible or even solubilized in water and polar organic solvents, which resolves the hard problem of graphene processing and opens a door to wet-processing of graphene. Despite its defects, GO is easy to functionalize, dope, punch holes, cut into pieces, conduct chemical reduction, form lyotropic liquid crystal, and assemble into macroscopic materials with tunable structures and properties as a living building block. GO sheet has been viewed as a single molecule, a particle, as well as a soft polymer material. An overview on GO as a 2D macromolecule is essential for studying its intrinsic properties and guiding the development of relevant subjects. This review mainly focuses on recent advances of GO sheets, from single macromolecular behavior to macro-assembled graphene material properties. The first part of this review offers a brief introduction to the synthesis of GO molecules. Then the chemical structure and physical properties of GO are presented, as well as its polarity in solvent and rheology behavior. Several key parameters governing the ultimate stability of GO colloidal behavior, including size, pH and the presence of cation in aqueous dispersions, are highlighted. Furthermore, the discovery of GO liquid crystal and functionalization of GO molecules have built solid new foundations of preparing highly ordered, architecture-tunable, macro-assembled graphene materials, including 1D graphene fibers, 2D graphene films, and 3D graphene architectures. The GO-based composites are also viewed and the interactions between these target materials and GO are carefully discussed. Finally, an outlook is provided in this field, where GO is regarded as macromolecules, pointing out the challenges and opportunities that exist in the field. We hope that this review will be beneficial to the understanding of GO in terms of chemical structure, molecular properties, macro-assembly and potential applications, and encourage further development to extend its investigations from basic research to practical applications.

Keywords: Graphene; 2D macromolecules; Macro-assembly

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1. INTRODUCTION

Graphene is a single layer two-dimensional (2D) matter with strong covalently bonded sp² carbon hexagonal networks. Based on its remarkable properties such as high carrier mobility, high thermal conductivity, outstanding mechanical performance, and unique optical and magnetic properties, graphene has emerged...
as a promising material for effective photovoltaic, high-performance energy storage system, durable and flexible conductive electrodes, micro- and macro-mechanics, sensitive chemical sensors and photodetector, memory devices, twistronics, and carbon-based next-generation electronic devices.\[7-10\]

Typically made from chemical exfoliation of graphite, graphene oxide (GO) possesses similar cyclohexane-like network of carbon units in chair configuration like graphene, however, with carbon hexagonal networks decorated by oxygen functional groups.\[7,8\] Each 2D carbon layer of GO molecule consists of sp\(^2\)- and sp\(^3\)-bonded carbon atoms. As a 2D topology polymer, single molecule of GO is easy to be detected and viewed by optical microscopy due to its large lateral size up to tens of hundreds of microns compared to conventional polymers, and it is facile to form nematic and lamellar liquid crystals (LCs) in water and polar organic solvents, related to the functional groups on the surface and its high aspect ratio.\[\text{9,10}\] Therefore, GO appears to be a very important material apart from a precursor of graphene, because of its high dispersibility, tunable functionalization and its easy accessibility to graphene.

Generally, GO can be regarded as either a particle, a molecule or a soft polymer material. The domain size, pH and ionic strength are key parameters determining the colloidal behavior of GO dispersion, which are crucial for guiding the fabricating process of GO-based materials in various applications. Furthermore, atomic or molecular functionalization is an efficient way to achieve the best performance out of graphene and GO by modifying its intrinsic properties and surface chemistry. Probing and quantifying the chemical heteroatom doping and molecular interactions between GO and the target materials (chemical bonding or physical interaction) are crucial for improving performances of graphene-based materials.

Numerous papers have been published to understand the structure and properties of graphene-based materials and explore their applications. Graphene architectures from 0D to 3D including 0D graphene quantum dots (QDs), 1D graphene fibers, 2D graphene films or membranes, and 3D graphene aerogels, foams or fabrics levels have been established. These graphene architectures, as well as their composite materials, possess superior mechanical strength, high electrical transport efficiency, excellent thermal conductivity and unique optical and magnetic properties, etc.

Here, we present a review on GO 2D macromolecules, from single molecular properties to their mass-production scale applications. The development of GO molecular synthesis is discussed, with an emphasis on the size distribution of GO sheets by tuning oxidation conditions. This review article highlights the molecular properties of GO sheets, including colloidal behavior in solvents, viscosity and rheology behaviors, as well as the related affecting factors (e.g., size, pH and cation interaction). Atomic and molecular functionalization of GO sheets can be used to improve the intrinsic properties of graphene and realize designed characters. We then present some examples of macroscopic assembled GO materials, such as fibers, films, foams, and fabrics. GO-based composite materials are also presented in details. We discuss in-depth graphene fibers and their mechanical properties and functional applications, which is one of the most promising candidates for carbon-based materials. We hope that this review can give new views of GO from the point of 2D macromolecules.

2. PREPARATION OF GO

2.1 The Development of GO Fabrication Methods

The development of scalable and low-cost production of high-quality GO is crucial to its commercialization and large-scale applications. Presently, the most common chemical methodology for the preparation of GO is based on strong oxidants under acidic conditions. The preparation of GO by chemical exfoliation usually consists of three key steps: the oxidation of natural graphite, the exfoliation of graphite oxide by sonication to obtain individual sheets, and centrifugation to achieve purified GO. Chemical oxidation of graphite into GO sheets creates functional oxygen-containing groups at the surface such as hydroxyl, epoxy, carbonyl and carboxyl groups. Supersonic or thermal treatment promotes the exfoliation of GO sheets which are previously held together by van der Waals force.\[11\]

Brodie firstly reported the synthesis of GO starting from graphite, potassium chloride and fuming nitric acid.\[12\] This approach requires 4 cycles of oxidation process, washing and drying of graphite, and leads to acid fog evolution from the fuming HNO\(_3\). Then the optimized Staudenmaier-Hofmann-Hamdi method was promoted, where potassium chloride is added to the mixture of concentrated sulfuric acid, nitric acid and graphite.\[13\] However, this method was still limited by the long reaction time and the release of ClO\(_2\) gas from the reaction of chloride and strong acid. In 1958, Hummers and Offeman oxidized graphite with a mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate, which is regarded as the most wildly used method for preparing GO so far.\[8\] The GO synthesized by Hummers’ method shows a bright yellow color, and has a carbon to oxygen atomic ratio between 2.1 and 2.9. The use of H\(_2\)SO\(_4\) and KMnO\(_4\) ensures the complete oxidation of graphite in several hours, and the replacement of HNO\(_3\) with NaNO\(_3\) prevents the acid fog generation. However, Hummers’ method is not an ultimate choice, for it cannot eliminate the NO\(_2\)/N\(_2\)O\(_4\) toxic gases evolution, and the removal of Na\(^+\) and NO\(_3^-\) remains to be solved. Chen et al. found that GO synthesized without using NaNO\(_3\) in Hummers’ method is nearly the same to that prepared by conventional Hummers’ method, without any effects of the yield or oxidation degree of GO.\[14\]

Benzoyl peroxide (BPO) is a strong oxidizer and it can reduce the oxidation time to 10 min while reacting with graphite for the preparation of GO.\[15\] No additional solvent is required due to the low melting point of BPO and it can be used as the solvent directly at the reaction temperature of 110 °C. The intercalated BPO in graphite sheets decomposed upon heating and subsequently released volatile gaseous species, which promoted the exfoliation of graphite and the formation of GO.

A complete conversion of graphite to GO and eliminating the separation process of GO and unoxidized graphite are required in industrial production. Because the degree of oxidation increases faster for small graphite flakes than that for large flakes,\[16\] the filtration of graphite powder to similar
flake size is beneficial to the complete oxidation of graphite in a certain time. During the chemical oxidation, the obtained GO products are largely affected by the degree of oxidation and chemical impurities coming from the source regents and the reactions in the multistep process. A new electrochemical oxidative approach provides an alternative choice for the synthesis of GO, and it prevents the use of toxic chemicals and is free from complicated steps. It shows advantages of low cost, easy operation, environmental friendliness and controllable products. Oxidation and exfoliation of graphite take place simultaneously in an electrochemical cell containing 0.2 mol/L sodium citrate, resulting in GO with carbon to oxygen ratio of 7.6. The degree of oxidation of the produced GO can be controlled by adjusting the electrochemical parameters of the electrochemical process. Recently, Gao’s group established a high-efficiency strategy to convert the polyimide-pyrolyzed industrial carbon wastes into graphene QDs with tunable size through the electrochemical method, which provides a new way for the industrial production of graphene QDs.

To avoid the use of aggressive concentrated acids, a dry mixture of graphite and an oxidant KMnO₄ or (NH₄)₂S₂O₈ was mechanochemically treated by planetary ball milling to get GO with different oxidations degrees. This process via solvent-free method leads to the decrease of graphene size compared to the parent graphite caused by the smearing effect of the graphite layers and the oxidant particles. In addition, it is reported that even chemical-free preparation of graphene oxide can be realized by this dry planetary ball milling process from natural graphite. The atomic concentration ratio of C/O can be controlled by the ball milling time duration.

Significantly, monolayer GO, with the first and the only IGCC (International Graphene Product Certificate Center) certificate, has been manufactured in 10-ton scale by GaoxiTech. The reagent-level products with different lateral sizes have been widely sold in more than ten counties and regions for research and development, which will pave the way to large-scale applications of GO in various industrial and civilian areas.

2.2 Size of GO Sheets

The GO sheets are usually cut into pieces with wide size distribution from tens of nanometers to several micrometers after the oxidation and sonication treatment in the preparation process. The inherent properties of GO vary a lot with its size. In general, larger-size GO (LGO) is believed to be highly desirable for electrical, thermal and mechanical behaviors of the final assembled graphene-based materials because of the high aspect ratio, while molecular-size graphene sheets contribute to the formation of biocompatible functionalized surface in the applications of biosensing and drug delivery. Therefore, the controllable size fractionation of GO is highly desirable for its applications.

The factors that affect the synthesis of LGO include the treatment of parent graphite, oxidation conditions, centrifugation process and pH value. Generally, the breaking of GO sheets occurs unavoidably in the vigorous oxidation and exfoliation processes. The size of obtained GO flakes is usually limited to tens of micrometers regardless of the size of parent graphite if the oxidation and exfoliation processes are not well controlled. By modifying the oxidation and exfoliation in the Hummers’ method, the synthesis of LGO can be realized by choosing large-size parent graphite, mild oxidation condition, and low centrifugation speed in the oxidation process (Fig. 1a).

Enhanced oxidation such as high temperature and extra amount of oxidant means increased hydroxyl and epoxy groups in the carbon networks of GO. These oxygen-containing groups increase the interaction between GO sheets, which makes GO sheets easy to cleave and results in the decrease of the size of GO sheets. Therefore, the reaction conditions should be designed less vigorous to minimize the cracking of GO sheets. By utilizing a density-functional theory (DFT) approach, Li et al. proposed GO unzipping model initiated by the formation of epoxy groups on the surface of graphite oxide. Once two epoxides are formed on the opposite ends of a carbon hexagon, more epoxy rings along a straight line are introduced and increased hydroxyl and epoxy sites, and the interaction energy between graphene layers. LGO sheets are maintained only if the core of the graphite is fully oxidized by the penetrating solution before the crack reaches the middle of the particle. In addition to prevent the excess usage of oxidants and multiple oxidation processes, expanded graphite (EG) was demonstrated to be beneficial to the preparation of LGO at low oxidant dosage, because of its high solvent-accessible surface areas.

In addition, strong ultrasonic treatment is not suggested for the synthesis of LGO, because the sonochemical effects and generated ultrahot gas bubbles cause breaks of C=C and C―O―C bonds and the cracking of GO sheets. The size of GO sheets decreased with the increase of sonication time. Qi et al. found that the post-ultrasonication treatment of LGO also results in the decrease of the size, which has a Gaussian distribution depending on the ultrasonication time. The high temperature, rapid cooling and high pressure provided by ultrasonication treatment ensure the breakage and exfoliation of GO sheets, as well as the enhanced oxidation degree of GO sheets. Furthermore, GO sheet with narrow size distribution can be efficiently controlled by varying the centrifugation speed. Small-size GO (SGO) with a size of several hundreds of nanometers is obtained in the GO supernatant at a high centrifugation speed. LGO remains in the precipitate at the bottom of the centrifuge tube, and it can be collected by repeated centrifugation-dispersion steps.

Because the properties and functions of GO sheets greatly depend on their lateral size and size distribution, it is important to control the size of GO sheets in the preparation process and develop the methods for size fractionation of GO. The size fractionation can be realized by pH adjustment, controlled directional freezing method, centrifugation technique, filtration treatment through membranes, polar-solvent-selective natural deposition method, non-gel electrophoresis technique, circular-flow-assisted fractiona-
Pristine GO sheets were mainly stabilized by the polar and charged ionized functional groups through electrostatic repulsion, which prevent the aggregation in aqueous medium. Here, the size fractionation of GO can be realized by adjusting the pH value of GO aqueous solutions. On the one hand, SGO sheets have a higher solubility than LGO because of the higher density of ionized carboxyl groups of the SGO sheets than the large ones as a result of more edges. On the other hand, the solubility of GO sheets in water decreases with the decrease of pH value because the electrostatic repulsion force is weakened by the protonation of the ionized carboxyl groups. Therefore, the GO colloidal dispersion can be separated into two portions by adjusting the pH to a proper value among the “pH window” (3.34−4.24) (Fig. 1d). Wang et al. showed the efficient separation of this method, with GO sheets mostly larger than 40 μm and smaller than 50 μm in two parts with narrow size distribution (Fig. 1e). A controlled directional freezing method of GO aqueous dispersions was developed for the size fractionation of GO nanosheets both experimentally and theoretically. In this case, GO sheets are adsorbed on the surface of ice crystals via hydrogen bond interactions, and then stratification of GO sheet occurs at the ice growth front. Therefore, the size distribution of GO was controlled by the growth rate of the freezing front. Besides, Chen et al. reported a cheap and efficient filtration method based on the exclusive passing through track-etched filter membrane with a given pore size. Furthermore, based on the different dispersibility and stability of GO with various sizes in polar solvent, the separation of varisized GO sheets can also be obtained.

Quantum confinement occurs when decreasing the GO $sp^2$...
domain size to less than 10 nm. Based on the moderate photoluminescence (PL) signal, non-toxicity, cell permeability, and tunable band gap, GO QDs extend their application in cellular imaging, biosensors, drug delivery, catalyst, photo- and electronic-related fields. The nano-size graphene can be fabricated by various physical and chemical methods, as summarized in the article by Liu et al.\[38\] They employed graphite nanoparticles with a diameter of 4 nm as starting materials to prepare graphene oxide quantum dots (GOQDs) and reduced GOQDs (rGOQDs). GOQDs and rGOQDs possess green and blue luminescence, due to defect states with oxygenous functional groups and intrinsic states in the high-crystalline structure, respectively (Figs. 1f and 1g).\[38\] The photoluminescent GOQDs linked with DNA aptamer can capture target Pb\(^{2+}\) for trace lead detection associated with the fluorescence quenching of the GOQD caused by the electron transfer from GOQD to Pb\(^{2+}\) upon UV irradiation.\[39\] Furthermore, the doping of nitrogen atoms in the GOQD (NGOQD) frame changes the p-conductivity type to the n-conductivity type of NGOQD, which makes partial nitrogen-doped GOQDs p-n junctions possible for applications in electronic devices.\[40\]

3. MOLECULAR PROPERTIES OF GRAPHENE OXIDE

3.1 Chemical Structure

GO can be regarded as a kind of 2D macromolecule which consists of graphene-like carbon panel and oxygen functionalized groups (Fig. 2). The oxygen-containing groups are covalently bonded to carbon frameworks and convert them from sp\(^2\)-hybridized state to sp\(^3\)-hybridized state. Graphite presents perfect carbon hexagonal networks on a 2D atom-thin plane. After the aggressive oxidation and sheet exfoliation, GO sheets are obtained with oxygen functional groups and holes, as evidenced by TEM images (Figs. 3a–3c).\[41\] The oxygen functional groups consist of hydroxyl and epoxide species on the carbon planes, and carbonyl, carboxyl, and lactol groups at the defects, holes, and edges. Among them, carboxyl and carbonyl groups, which are formed via the intense oxidation cleavage of C—C bonds, are usually accompanied by the formation of structural defects. C—O related functional groups can be removed upon chemical reduction, leading to a recovered graphitic structure. The functional groups of GO sheets can be controlled by tuning the oxidation conditions in the preparation processes. For instance, Chen et al. reported that the GO fabricated by an optimized recipe by skipping the addition of water during the oxidation steps possessed a lower C=O defect region compared to the GO sample prepared by modified Hummer’s method, and it also had a higher C/O ratio and lower fraction of un-oxidized C=C skeleton compared to the GO obtained from a low-temperature reaction (~5 °C).\[42\] GO sheets treated with concentrated nitric acid solution possess nanopores with diameters from several to hundreds of nanometers. It was found that a large number of carboxyl groups were located at the edges of the nanopores.\[43\]

GO presents holes and defects compared to a perfect graphene sheet, which provides GO with special intrinsic properties. The rich functional groups endowed GO with amphiphilic behavior and make it reactive such as easy-doping. Its high solubility, liquid crystal behavior and easy accessibility compared to graphene offer GO competitive advantages to practical applications.\[44\]

C 1s X-ray photoelectron spectroscopy (XPS) spectrum of GO molecule prepared by modified Hummer’s method can be divided into three peak profiles, carboxyl, carboxyl, and lactol groups centered at ~289.2 eV, hydroxyl and epoxide species at 286.5 eV, and nonoxidized C species at ~284.8 eV. The O 1s spectrum consists of peaks at ~532–533 eV related to hydroxyl, epoxide and H\(_2\)O species, and peaks at 529–531 eV corresponding to carboxyls, carboxyls, and lactols (Fig. 3e).\[44\] Polarized near-edge X-ray absorption fine structure (NEXAFS) provides an evaluation of electronic corrugations in graphene based on the directionality of the graphene π cloud. Three additional spectral features centered at ~286.7, 288.7, and 289.8 eV are detected between n’ (~285.2 eV) and δ * (~293.2 eV) resonances along with a shoulder at ~287.5 eV (Fig. 3f).\[45\] The resonances in the intermediate region (between the n’ and δ * peaks) are attributed to functional groups of GO molecules. DFT calculations also indicated a homogeneous distribution of epoxy and hydroxyl species on GO sheets, and the presence of small amounts of intercalated water molecules, ether groups, and doubly oxidized carbon species (Fig. 3g).\[46\] Because of the presence of oxygen-containing groups and the sp\(^3\)-hybridized carbon which is slightly above and below the

![Fig. 2](https://doi.org/10.1007/s10118-021-2515-1)
original graphene atoms, the monolayer GO sheet is thicker than monolayer graphene sheet, with a thickness of ~1.0 nm.

Chemical reduction by hydrazine and subsequent annealing under 550 °C leads to the reduction of oxygen functionalities and restoration of the original sp² bonding character which has been lost in the oxidation process. However, the area of holes of rGO increases compared to GO due to the release of CO and CO₂ during annealing (Fig. 3b). [41] NEXAFS reveals the increase of the relative intensities of the π* and σ* resonances and integrated π* intensity after chemical reduction of GO, indicating its significant recovery of π-conjugation. [45] Minimizing the oxidation-induced defects/holes and restoring the structure of graphene are crucial to realizing the full potential of graphene materials assembled by GO sheets. Therefore, we have employed an ultrahigh temperature thermal treatment on GO sheets and found that the voids and defects can be healed, and the obtained graphene films show an almost perfect graphite-like lattice structure in scanning tunneling microscope (STM) image (Fig. 3d).

3.2 Polarity and Solvation

GO sheets consist of a basal plane which is essentially a network of hydrophobic polyaromatic islands of unoxidized benzene rings and hydrophilic acidic groups at the edge. The polar surface properties of GO are usually determined by the oxygen-containing groups at GO surface, which contributes to the basic and acidic character of pristine GO molecules. Therefore, GO can be dispersed easily in polar organic solvents because of the functional groups on the surface, such as carboxylic acid, hydroxyl and epoxide groups.

GO is verified to be dispersed in solvents such as N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), ethylene glycol and their mixture solvents such as ethylene glycol/water mixtures with long-term stability. [46,47] Besides, GO is not stable in ethanol or isopropanol due to the strong hydrogen bonding between GO interlayers induced by the oxygen functional groups and its two-dimensional morphology. [48] The dispersion behavior of GO is related to parameters such as dipole moment, surface tension, Hansen and Hildebrand solubility parameters. [49] Park et al. obtained homogeneous colloidal suspensions of rGO in a wide variety of organic solvent systems, and found that solvents with δH+δP (polarity and hydrogen bonding cohesion) in a range of 13–29 show good rGO dispersion. [50] Furthermore, Neklyudov et al. demonstrated that the solubility of GO and the stability of the as-formed solutions depend not just on the solute and solvent cohesion parameters, but mainly on the strong hydrogen bonding interactions established between GO functional groups and solvent molecules. [51] By the DFT and quantum theory of atoms in molecules (QTAIM) theoretical calculations, the hydrogen bond energy between GO functional groups and solvent molecules follows the order of water>methanol>ethanol, in accordance with the experimental trend.
GO sheets usually appear as negatively charged entities due to the acidic groups, and the water dispersity and hydrophilicity of GO have been mainly attributed to the ionizable edge $\text{COOH}$ groups. Therefore, GO can be regarded as an amphiphilic regent with a hydrophobic basal plane and hydrophilic edges. Kim et al. found that GO behaves like both a molecular and a colloidal surfactant. GO shows an ability to adsorb on interfaces and lower the surface or interfacial tension, creating highly stable Pickering emulsions of organic solvents like solid particles. It can also process insoluble materials such as graphite and CNTs in water through $\pi-\pi$ attractions like a molecular dispersing agent (Figs. 4a–4c). They also employed Brewster-angle microscopy (BAM) surface imaging technique to investigate the enrichment of GO at liquid/liquid interfaces. No scattering points were observed at the surface of GO suspension, indicating that no GO was present at the interface. After chloroform was applied and evaporated, bright spots appeared in the BAM image, confirming the enrichment of GO at liquid/liquid interfaces (Figs. 4d and 4e). Similarly, BAM images also show the GO enrichment at liquid/air interfaces. Based on the surface activity of GO suspension, it can be utilized for the fabrication of surfactant-free Langmuir-Blodgett (LB) GO monolayers, which harvests the full potential for large-scale device fabrication. Be-
sides, smaller GO sheets should be more hydrophilic due to their higher charge density resulting from the edge —COOH groups, which was proved by the increasing potential of GO dispersion after sonication.

Generally, it is difficult to disperse hydrophobic graphite or graphene sheets in water without the assistance of surfactant. However, Li et al. demonstrated that chemically converted graphene (CCG) can also readily disperse in aqueous solution to generate stable graphene colloids, without the need for either polymeric or surfactant stabilizers.\(^\text{53}\) pH, the electrolyte concentration, and the content of dispersed particles have been considered in this experiment. Ammonia is added into the reducing solution to increase the pH to around 10, to obtain maximal charge density on the as-prepared graphene sheets. Similar to the original GO dispersion, the obtained CCG sheets remain separated and well dispersed in the aqueous solution. The Tyndall effect test of CCG in which a laser beam passes through CCG colloidal solution shows a discernible track as a result of light scattering, proving the stability of colloidal CCG dispersion (Fig. 4f). In addition, both GO and rGO dispersion show long-term stability in different solutions (Fig. 4h).\(^\text{46}\) Compared to GO, rGO presents greater interaction with non-polar solvents such as chloroform, toluene, and chlorobenzene. Besides, metal salts and acids should be completely removed because the residual electrolytes destabilize the resulting dispersions by neutralizing the charges on the GO sheets. Adding an electrolyte solution to CCG dispersion causes destabilization of the dispersion, and immediate coagulation occurs if sodium chloride is added into a CCG dispersion (Fig. 4g). The influence of adding cations to GO dispersion will be discussed in the next part.

Pristine graphene is generally difficult to disperse in common solvents like water due to the hydrophobic interaction. Although surfactant-free single-layer graphene can be dispersed in water efficiently by mixing graphene oxide solution in tetrahydrofuran (THF) with degassed water and subsequently evaporating THF,\(^\text{54}\) the complicated and time-consuming process hinder the industrial application of graphene. Benefitting from the oxygen functional groups on the surface, functionalization of GO with other groups can be achieved to realize designed properties, especially the dispersal of other materials in organic solvents, and miscibility with polymer matrices. Recently, the solvation behavior of graphene oxide nanosheets in water is employed for probing the critical nucleus size for ice formation (Fig. 5a).\(^\text{57}\) The size of GO nanosheets contained in the water droplets has a significant impact on ice nucleation, which gives experimental evidence on the existence of the critical ice nucleus. Koltonow et al. proposed that GO sheets in water are neither crumpled nor collapsed, with or without poor solvent.\(^\text{58}\) Planar GO sheets can align to form a nematic liquid crystalline phase due to their high aspect ratios and excellent dispersity in water, as first reported by Xu et al.\(^\text{59}\) and Kim et al.\(^\text{60}\) Under poor solvent conditions such as acetone, ethanol, 2-propanol, and ethylene glycol, the GO dispersions still exhibited a strong birefringence under cross polarized configuration (Figs. 5b–5d). The observation through cross-polarizers of a piece of sediment obtained from the slow addition of poor solvent clearly shows that the alignment of the GO sheets in the sediment is parallel to the wrinkles (Figs. 5e and 5f). It is suggested that face-to-face restacking is preferred and it provides an efficient way for sheets to hide their surfaces from poor solvents.

In addition, Tang et al. reported the formation of GO nanoscrolls (Fig. 5g) in both aprotic solvents (pyridine and DMF) and protic solvents (methanol, ethanol, isopropyl alcohol, acetic acid, and isobutyric acid), but the yields vary with the solvents.\(^\text{59–61}\) The formation mainly occurs in the sediments after sonication for hours. The scrolling behavior is controlled by ζ potential, dipole moment, and Hansen solubility parameters of the solvents. Similarly, large GO nanoscrolls are facilitated to form in the solvents with the relatively small dipole moment and less negative ζ potential. Besides, the sedimentation rate of the GO sheets from the suspension is controlled by the dipole moment for the aprotic solvents and Hansen solubility parameters for the protic solvents, which determine the average number of the included sheets per scroll.\(^\text{59}\)

GO can maintain its morphology and structure in solvent with long-term stability. However, most dried GO powders on the market are insoluble, or difficult to recover its original morphology in the solvent, indicating that the structure of GO has changed in the drying process. Gao’s group revealed a “swelling-dissociation-stretching” behavior of flower-shaped dried GO powder while redispersing the GO particle in solvents on a molecular level (Figs. 5h–5j): (1) the interaction between GO layers is weakened since water permeates into GO particles, and GO particles expand significantly; (2) the GO particles keep on swelling until the interlayer distance is large enough, and then the highly crumpled GO layers start to peel off; (3) the single GO sheets with wrinkles and ridges gradually stretch to a plane in order to lower the surface energy.\(^\text{62}\) The fluctuant morphology (e.g., swelled particles, crumpled flakes, flat sheets, as well as their intermediates) of GO powder is controllable to form alignment, and post-buckling of graphene materials on prestrained or responsive substrates.\(^\text{63–66}\) GO sheets in good solvents can collapse to hierarchically wrinkled conformations triggered by poor solvents, which has been proved to be an efficient way to control the structure and performance of their macroscopically assembled materials. Xiao et al. tracked the real-time structural evolution of collapsing behavior in the gelation and drying process of GO film by POM and optical microscopy (Fig. 6a).\(^\text{67}\) The stretching of wrinkles and their intertwined network in collapsed GO and graphene papers account for their rubber-like mechanical behavior.

According to Landau-Ginsburg theory of phase transitions, rich conformations were predicted including flat, crumpled, folded, compact, anisotropic tubular and globular phas-
Previous experimental investigations were limited because graphite oxide with large thickness was usually taken as the model material. Recently, Wang et al. established a conformational phase map of 2D GO macromolecules in solution using single-layer GO sheet as the experimental model, based on theoretical simulation and experimental observations. The conformational phase map was summarized in the potential energy landscape predicted by coarse-graining molecular dynamics (CGMD) simulations (Fig. 6b). In this phase map, GO macromolecules exhibited rich conformations, including anisotropic folds (II) and isotropic crumples (III) as intramolecular phases which were transformed from the flat (I) phase, as well as intermolecular phases of flat stacks (IV), multiple folds (V) and multiple crumpled (VI). Experimental observations were carried on by tuning the intramolecular and intermolecular interactions in three modes: (1) the self-avoidance mode (the introduction of poor solvents), (2) the short-range attraction mode (Ca$^{2+}$-crosslinking), (3) the long-range attraction mode (mild chemical reduction with hydrazine). By combining the theory with experiments, Wang et al. found that self-avoidance and short-range attraction tend to induce anisotropic folding transitions, while long-range attraction leads to globular crumpling transitions. The self-avoidance mode (poor solvent introduction) and the short-range attraction mode (Ca$^{2+}$-crosslinking) make the flat phase of GO (labelled as I) transit into an anisotropic fold (phase II), while the long-range attraction mode via hydrazine reduction leads to a transit to isotropic globally-crumpled phase (phase III). At
high concentrations (above 1 mg/mL), three intermolecular phases were observed, i.e., flat stacks (IV), multiple folds (V) and multiple crumples (VI), which were induced by the self-avoidance mode, the short-range attraction mode and the long-range attraction mode, respectively (Fig. 6c). The conformational phase map of 2D GO macromolecule offers a guidance to precisely control multiscale condensed conformations of other 2D macromolecules and their macroscopic materials.

3.2.2 pH-dependent behavior

The amphiphilicity of GO can be tuned by pH via adjusting the degree of ionization of $-\text{COOH}$ groups at the edge of GO sheets. Molecular dynamics (MD) simulation shows that pH-dependent behavior of GO aqueous solution is related to the degree of deprotonation of the carboxyl groups at the edges of GO sheets. GO does not behave like conventional surfactants in pH 1 and 14 aqueous solutions. As shown in Fig. 7(a), the surface tension continues to decrease gradually with increasing GO concentration at pH 1. GO aggregates are non-micelle-like. It is suggested that GO sheets tend to be concentrated at the water-air interface instead of staying in the bulk aqueous phase. At low pH, the carboxyl groups of GO

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flakes are protonated so that the GO sheets become less hydrophilic and form suspended aggregates, while at high pH, the deprotonated carboxylic groups are hydrophilic, making individual GO sheets prefer to dissolve in bulk water like a regular salt, stabilized by electrostatic repulsions between the ionized carboxylic groups. Wu et al. demonstrated that both the degree of deprotonation of the carboxyl groups at the edges and the electrostatic repulsion between the ionized carboxyl groups are responsible for the increased stability of GO solution at high pH (Fig. 7a). As a result, GO aqueous solution is visually homogeneous with a dark-brown color at pH 14 but presents a precipitate which remains dispersed and stable in the solution at pH 1 (Fig. 7a inset). Besides, Bouchard et al. demonstrated that pH did not have a notable influence on the stability of GO at pH from 4 to 10. Because the pH observed from aquatic environment is usually 5–9, pH has minor effects on the fate and transport of GO suspensions.

As we mentioned in the previous part, rGO sheets can also be well dispersed in water due to its highly negatively charged properties that result from ionization of the carboxylic acid and phenolic hydroxyl groups on GO sheets. Similarly, the stabilization of rGO sheets is attributed to electrostatic repulsion. Therefore, as the ionization of carboxylic acid groups is strongly related to pH, the zeta potential of the rGO dispersion is pH dependent. Li et al. reported that the zeta potential of CCG aqueous solution is below −30 mV when the pH is greater than 6.1 and it reaches −43 mV when the pH approaches 10 (Fig. 7b). CCG solution with potential values more negative than −30 mV are generally considered to yield sufficient mutual repulsion to maintain the stability of dispersion by electrostatic repulsion. Residual acid originated from the preparation of GO is harmful to GO and rGO dispersion, and it should be completely removed.

3.2.3 Interlayer interactions by cations
Adding cations to GO can cause the destabilization of GO dispersion. Immediate coagulation occurs if sodium chloride was added into a chemically converted graphene dispersion. Yang et al. investigated colloidal behavior of GO in the presence of nine different cations, and they found that the destabilizing ability of cations follows the order of $\text{Cr}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Ag}^+ > \text{K}^+ > \text{Na}^+$. The destabilizing ability of metal cations is consistent with their adsorption affinity with GO determined by their electronegativity and hydration shell thickness. Based on the Schulze-Hardy rule, cations with higher valence possess higher charge screening capability, and the same valent cations should produce similar charge screening effects. However, it is found that heavy metal cations destabilized GO suspension more aggressively than common cations: $\text{Pb}^{2+}$, $\text{Cu}^{2+}$, $\text{Cd}^{2+}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{Ag}^+ > \text{K}^+$, $\text{Na}^+$. Therefore, Schulze-Hardy rule is not the single factor that contributes to the colloidal behavior of GO. Attachment efficiency (a) and adsorption isotherms of cations, which originate from hydration shell thickness of the metal cations and electronegativity, are used to normalize the aggregation kinetics and adsorption behavior of GO respectively (Fig. 8a), both of them determining the colloidal behavior of GO sheets. GO aggregation and stability in the aquatic environment follows Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and Schulze-Hardy rule.

Based on the colloidal behavior of GO affected by adding salt, Yeh et al. found that multivalent aluminum ions facilitated the crosslinking of GO assembled films prepared by filtration using AAO, making the membranes stable and intact in water. Neat GO membranes do disintegrate in water because GO sheets become negatively charged on hydration and the membrane should disintegrate due to electrostatic repulsion (Fig. 8d). However, during filtration, $\text{Al}^{3+}$ releases from AAO, and efficiently crosslinks the sheets in the dried state, especially in the dispersion with low pH value (Fig. 8e). Calcium ions are also reported as gelators to enable readily direct writing monolithic lattices under ambient surroundings.

Three types of cross-linking interactions were proposed by Wu et al. that may cause the aggregation of GO sheets by multivalent cations (Fig. 9a): (1) the edges of the GO sheets being bridged through chelating carboxylicate groups; (2) intercalating between the GO basal planes through either weak alkoxide or dative bonds; (3) cross-linking hydrogen bonds being formed among the surface oxygen functional groups and the interlamellar water molecules. Wu et al. summarized two fundamental interacting modes between GO sheets for their colloidal behavior in the conditions of adding cations and tuning pH (adding $\text{H}^+$): edge-to-edge and face-to-face modes (Fig. 9b). The aggregation of GO sheets by adding multivalent cations is induced by the strong cross-
linking of GO sheets, therefore, edge-to-edge is the dominant interaction mode of GO aggregation in this case. While adding H+ to GO dispersion, –COOH groups at the edge were protonated, leading to a decrease of electrostatic repulsion. van der Waals interaction and the residual n-conjugated domains in GO sheets are the main factors that contribute to the aggregation via face-to-face mode.\(^\text{(73)}\)

Recently, Gao’s group investigated the dynamic dispersion stability of GO suspension with ions, and they observed a re-dispersion behavior of GO in concentrated Fe\(^{3+}\) solution rather than permanent aggregation.\(^\text{(76)}\) The redispersion phenomenon is caused by the specifically strong electrostatic shielding effect and the coordination attraction between Fe\(^{3+}\) and functional oxygen groups (Figs. 9c and 9d): (1) in the absence of Fe\(^{3+}\), GO dispersion remains stable because the repulsion potential energy (\(E_r\)) is larger than the adsorption potential energy (\(E_a\)); (2) as Fe\(^{3+}\) was loaded on the denser layer, \(E_a\) decreased, leading to the flocculation of GO sheets; (3) increasing Fe\(^{3+}\) continuously occupies the coordinated sites on GO sheets until the GO sheets are stabilized; at \(P_e>1\), GO sheets are oriented along the flow direction. While \(\phi<\phi_c\) and at Pecllet number \(Pe = \gamma a/D_0<1\), GO sheets are randomly oriented; at \(Pe>1\), GO sheets are oriented along the flow direction. The dispersion is arranged randomly oriented and breaks down while applying a flow at \(Pe>1\). Then GO sheets start to self-arrange when the flow is arrested (\(Pe=0\)), and recover the initial cluster configuration after sufficient resting time. Moreover, Naficy et al. found that the rheological behavior of GO sheets varies considerably with dispersion concentration.\(^\text{(81)}\) Ultra-large GO sheets (with a high aspect ratio of \(\sim\) 4.5 × 10\(^9\)) were employed as the model material to study the viscoelastic properties of GO sheets. Four distinct regions are summarized: viscoelastic liquid (with GO concentration: \(\sim 0.05 – 0.25\) mg/mL), in which considerable elastic component still exists, and this behavior enables electrospray and spray-coating; transition to viscoelastic soft solid (with GO concentration: \(\sim 0.25 – 0.75\) mg/mL), in which GO sheet disper-

3.3 Viscosity and Rheology Behavior

The rheology behavior of GO dispersion is intimately related to the characteristics of material, processing of the system, and structure design of GO-based composites. Probing and quantifying the rheology behavior of GO sheets is crucial to guiding the fabricating methods of GO-based materials, such as electro-spraying, spray coating, filler, ink-printing techniques, etc.

In this part, we report recent progress on the shear rheology of both aqueous GO dispersions and GO-based composite materials, as well as the external factors which affect the rheology behavior such as pH and adding salt. We also refer to the review of Del Giudice et al.\(^\text{(80)}\) for the shear rheology of both GO and GO-based materials. The rheological behavior of GO aqueous dispersion at different volume concentrations can be classified as follows: (1) Oscillatory linear flow properties. When \(\phi<\phi_c\) (\(\phi_c\) is the critical volume or mass concentration), viscous response prevails over the elastic response; when \(\phi>\phi_c\) elastic response prevails over the viscous response. (2) Steady shear flow properties. When \(\phi<\phi_c\) and at Pecllet number \(Pe = \gamma a/D_0<1\), GO sheets are randomly oriented; at \(Pe>1\), GO sheets are oriented along the flow direction. (3) Transient shear flow properties. Only the case \(\phi<\phi_c\) is considered. The dispersion is arranged randomly oriented and breaks down while applying a flow at \(Pe>1\). Then GO sheets start to self-arrange when the flow is arrested (\(Pe=0\)), and recover the initial cluster configuration after sufficient resting time.
**Fig. 9** (a) GO aggregation caused by cross-linking of GO sheets by divalent cations (Mg^{2+} and Ca^{2+} were selected as examples) and (b) proposed aggregation modes of GO nanosheets. (Reprinted with permission from Ref. [73]; Copyright (2013) American Chemical Society). (c) Schematic showing the evolution of electric double layer (EDL) on the surface of GO sheets in Fe^{3+} solution and (d) the corresponding diagram of GO-Fe^{3+} dispersion. (Reprinted with permission from Ref. [79]; Copyright (2020) Elsevier).
digation, Vallés et al. demonstrated the importance of interactions between graphene and polymer and the dispersion of the flakes in the matrix in the graphene-polymer system. The viscosities and percolation thresholds of the composite system can be tuned by changing either the surface chemistry of the flakes or the nature of the polymer.

The rheological behaviors of GO inks are crucial for direct ink writing (DIW), especially 3D printing technology. To realize DIW printing with GO inks, three criteria have been demonstrated by Gao’s group: (1) the ink has to keep homogeneous to prevent its clogging in the nozzle; (2) the elastic modulus of the GO ink should be large enough to pass through the nozzle stably; (3) the shear modulus of GO ink should be relatively low under high shear stress, in order to leave the nozzle.

It is also revealed that strong alkaline solutions contribute to fast deoxygenation of GO and result in stable aqueous rGO suspensions.\textsuperscript{[86]} Hydrazine reduction greatly enhances the electrical performance of GO films. However, immersing GO films in hot aqueous hydrazine solutions (80 °C) usually results in film fragmentation and delamination. Hydrazine vapor reduction provides an alternative scheme,\textsuperscript{[87]} but the thickness of hydrazine reduced GO films expand more than 10 times, and the films are too rigid to bend. Stiffening and disintegration occur after chemical reduction by hydrazine or NaBH₄. Hydrazine reduction greatly enhances the electrical performance of GO films. However, immersing GO films in hot aqueous hydrazine solutions (80 °C) usually results in film fragmentation and delamination. Hydrazine vapor reduction provides an alternative scheme,\textsuperscript{[87]} but the thickness of hydrazine reduced GO films expand more than 10 times, and the films are too rigid to bend. Stiffening and disintegration occur after chemical reduction by hydrazine or NaBH₄. Hydrazine reduction greatly enhances the electrical performance of GO films. However, immersing GO films in hot aqueous hydrazine solutions (80 °C) usually results in film fragmentation and delamination. Hydrazine vapor reduction provides an alternative scheme,\textsuperscript{[87]} but the thickness of hydrazine reduced GO films expand more than 10 times, and the films are too rigid to bend. Stiffening and disintegration occur after chemical reduction by hydrazine or NaBH₄.

3.4 Reduction

An ideal reduction process should fulfil the requirement of both oxygen functional group removal and the recovery of sp² conjugation. Until now, a variety of reduction approaches have been developed, including chemical reduction, thermal treatment, Joule heating, microwave, photoreduction, electrochemical reduction, hot press reduction, and so on.

Chemical reduction using hydrazine hydrate is a conventional method for synthesizing reduced graphene oxide in large quantities. This method is efficient to remove the oxygen functional groups on the surface of GO. Epoxide opening reacts with hydrazine and further reacts via the formation of an aminoaziridine moiety, and finally forms a double bond through thermal elimination of diimide.\textsuperscript{[88]} It is also revealed that strong alkaline solutions contribute to fast deoxygenation of GO and result in stable aqueous rGO suspensions.\textsuperscript{[86]} Hydrazine reduction greatly enhances the electrical performance of GO films. However, immersing GO films in hot aqueous hydrazine solutions (80 °C) usually results in film fragmentation and delamination. Hydrazine vapor reduction provides an alternative scheme,\textsuperscript{[87]} but the thickness of hydrazine reduced GO films expand more than 10 times, and the films are too rigid to bend. Stiffening and disintegration occur after chemical reduction by hydrazine or NaBH₄.
driodic acid (HI) provides an alternative to hydrazine hydrate for GO reduction. The obtained rGO films reduced by HI show good flexibility and improved tensile strength. Hydrohalic acids including HI and HBr can effectively catalyze the ring-opening reaction of epoxy groups on GO and convert them into hydroxyl groups, and the halogen elements can be easily removed from the carbon basal plane because of the low binding energy between a carbon and a halogen atom (Br or I).\[89\]

The TGA curves of pristine graphene, hydrazine reduced graphene, thermally reduced graphene and GO are shown in Fig. 11(a). The weight loss up to 150 °C is caused by the evaporation of water, and that from 150–310 °C is due to decomposition of carboxyl groups, and that above 310 °C is mainly attributed to carbonyl groups.\[89\] It suggests that after chemical or thermal reduction, the amount of adsorbed water decreases and the obtained rGO is more thermally stable than GO. XPS provides the information about the composition, degree of oxidation and kind of oxygen species of GO and rGO sheets. The oxygen content of GO decreases after thermal or chemical reduction. For instance, the sp² peak increases, while C=OH and C=O peaks decrease after thermal reduction (Figs. 11b and 11c). Yang et al. investigated the O1s/C1s ratio obtained from XPS of rGO after thermal treatment under argon, a mixture of argon and hydrogen and ultra-high vacuum, and found that GO underwent a partial reduction at temperature even as low as 200 °C.\[89\] C K-edge NEXAFS spectra at magic angle (54.7°) provide the information of electronic structure upon chemical defunctionalization of GO. The collected relative intensities of the π* and σ* resonances (I_{π*}/I_σ*) enhanced upon chemical reduction of GO, indicating significant recovery of π-conjugation (Fig. 11d).\[89\]

Raman spectroscopy is a tool to characterize the physical and chemical properties of graphene, such as the identification of graphene, GO and rGO, checking the number of graphene layers, and the investigation of graphene-based heterostructures. D peak can be used to identify the defect of graphene-based materials including disorder and holes, as

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**Fig. 11** (a) TGA of pristine graphene (curve 1), hydrazine reduced graphene (curve 2), thermally reduced graphene (curve 3) and GO (curve 4). High-resolution XPS C 1s spectra of (b) GO and (c) thermally reduced GO. (Reprinted with permission from Ref. [89]; Copyright (2010) Wiley). (d) C K-edge NEXAFS spectra at magic angle (54.7° incidence) for eight GO and rGO films, variously reduced using NaBH₄, hydrazine, and phenylhydrazine. (Reprinted with permission from Ref. [45]; Copyright (2012) American Chemical Society). (e) Polarized Raman spectra of graphene fiber annealed at different temperatures. (f) Crystalite size in perpendicular and parallel directions to the fiber axis after thermal treatment at different temperatures. (Reprinted with permission from Ref. [94]; Copyright (2015) American Association for the Advancement of Science). The (g) thermal and electrical conductivity, (h) XRD patterns and (i) Raman spectra of graphene films annealed at different temperatures (from 20 °C to 3000 °C). (Reprinted with permission from Ref. [95]; Copyright (2017) Wiley).
well as the degree of oxidation. D band (around 1350 cm\(^{-1}\)) is assigned to the breathing mode of \(\kappa\)-point phonons of A1g symmetry. G peak (around 1582 cm\(^{-1}\)) is related to the stacking order of graphene layers. In addition, other external factors such as strain, stress, temperature and magnetic fields also show significant influence on the electronic and vibration properties, which can also be shown by Raman spectroscopy.\(^{[91]}\)

Thermal conductivity is usually determined by phonon transport in the strong covalent sp\(^2\) lattice vibrations,\(^{[92]}\) and electrical conductivity is dominated by the delocalized \(\pi\)-bond. Therefore, highly aligned sp\(^2\) graphene sheets are required for superior electrical and thermal transport properties, while functional groups and sp\(^3\) bonds usually act as electron- and phonon-scattering centers, greatly hindering the electrical and thermal transport of graphene materials. The defects and chemical residue are the keys to determining whether GO is well reduced. The phonon- and electron-scattering centers caused by lattice vacancies and residual functional groups after thermal treatment at a relatively low temperature significantly deteriorate the thermal and electrical properties. Besides, the chemical reduction of GO solution tends to introduce defects, vacancies and dislocations to the obtained rGO material, as well as the functionalization of its surface, edge, and basal plane. High-temperature thermal treatment is beneficial to the healing of defects and the removal of chemicals in the basal plane of GO sheets. With the increase of temperature, oxygen-containing functional groups are removed by a simultaneous conversion from sp\(^3\) to sp\(^2\) carbon in the graphitic lattice. The rGO films can achieve a high thermal conductivity of 1043.5 W/(m·K) as the temperature reached 1200 °C.\(^{[93]}\) Xin et al. reported graphene fibers composed of large-size graphene sheets and small-size graphene sheets through high-temperature treatment (2850 °C), with excellent electrical and thermal conductivities up to 2.21×10\(^5\) S/m and 1290 W/(m·K), respectively.\(^{[94]}\)

High-temperature thermal treatment contributes to the formation of the submicrometer crystallite domain on graphene sheets. The increase of thermal treatment temperature leads to the removal of defects (oxygen functional groups, nanocavities, and sp\(^3\) carbon bonds) and crystallization, as evidenced by the diminishment of D band and change of 2D band.\(^{[94,95]}\) After thermal treatment over 2000 °C, the D peaks are usually undetectable (Fig. 11e), suggesting a defect-free structure of graphene. High-temperature carbonization allows the growth of crystalline graphitic domains (Fig. 11f), harvesting the simultaneous improvement of thermal and electrical conductivities (Fig. 11g). Annealing at 2800 °C with sufficient time leads to the construction of AB stacking structure of graphene (Figs. 11h and 11i). AB stacking is the most common and stable stacking type of graphene-based materials, e.g. graphite. It means that the empty centers of the hexagonal carbon network are occupied by the carbon atoms of the adjacent layers.

Besides, GO can also be reduced by photochemical reactions with the assistance of photocatalysts such as TiO\(_2\),\(^{[96]}\) ZnO,\(^{[97]}\) and BiVO\(_4\).\(^{[98]}\) For example, charge separation occurs on the surface of TiO\(_2\) under UV irradiation, and holes are scavenged to produce ethoxy radicals in the presence of ethanol, while electrons are accumulated and reduce GO sheets to rGO.

To avoid the use of toxic chemicals and massive energy consumption, other unconventional heating approaches have been utilized to realize thermal reduction including Joule heating,\(^{[99]}\) laser pulse,\(^{[100]}\) and microwave irradiation.\(^{[101]}\) The nature of the reduction of GO by laser pulse is photochemical reduction. The oxidation degree of as-reduced graphene has strong dependences on the output power of femtosecond laser.\(^{[100]}\) Joule heating generates high temperature at the junction point where the high resistance located, while traditional thermal treatment heats the whole space of the furnace. It can efficiently raise the temperature to 2750 K in less than 1 min of annealing time, providing the graphene with crystalline structure and ultrahigh electrical conductivity of up to 3112 S/cm.\(^{[102]}\)

Reducing GO using 1- to 2-s-long microwave pulses is a simple and rapid method for preparing high-quality graphene.\(^{[101]}\) GO possesses a good ability of microwave absorption due to its functional groups. The absorption of microwaves and fast quenching lead to rapid heating of the GO. Oxygen functional groups are almost entirely removed after microwave reduction, which results in the formation of highly ordered structure. Raman spectrum reveals graphene-like features of GO after microwave treatment with sharp G and 2D peaks and a nearly absent D peak. In other words, microwave-induced reduction of GO causes desorption of oxygen functional groups and reordering of the carbon basal plane.

Different from approaches based on thermal treatment, electrochemical reduction of GO relies on the direct electron transfer between the electrode and GO sheets, and this method avoids the addition of harsh and toxic chemicals.\(^{[103−105]}\) The oxygen functional groups of GO sheets can be successfully removed by the electrochemical reduction process, making electrochemical reduction a low-cost, rapid, high-yield, and environmentally friendly approach for GO reduction.

4. ATOMIC AND MOLECULAR FUNCTIONALIZATION OF GO

4.1 Atomic Chemical Doping

Chemical oxidation of graphite into GO sheet creates functional oxygen-containing groups at the surface (hydroxyl, epoxy, carboxyl, and carboxyl groups) and corresponding polar surface properties. To achieve designed properties, the reactive groups are usually used to functionalize GO sheets with various groups, such as atoms, small molecules, and polymer branches. Atomic and molecular functionalization provide efficient ways to achieve the best performance out of graphene or GO. Actually, graphene oxide itself can be regarded as the covalent functionalization of graphene by oxygen atoms. In this part, we mainly focus the atomic and molecular functionalization of GO sheets, through the reconstruction of carbon lattice and modification of surface chemistry of GO, while details of covalent or noncovalent functionalization of graphene/GO with polymer matrix will be discussed in Part 7, where the interaction forces inside the composites are presented. Heteroatom doping can efficiently reconstruct the sp\(^2\)-bon-
ded carbon atoms, induce polarization of electron density at the carbon-heteroatom bonds, and tailor the surface chemistry interaction, leading to the modification of electrical properties and chemical activity of graphene. The chemical doping of heteroatoms induces defects into the graphene plane and provides additional active sites for chemical reactions, changes the conductivity of GO, and also benefits the control of the n- and p-type semiconducting electronic properties, as well as engineering its bandgap and magnetic effect. Atomic radicals provide sufficient energy to overcome the thermodynamic and kinetic barriers to covalently bonding with the basal plane of carbon networks but lack the energy required to break the C–C bonds that will destroy the carbon lattice.\textsuperscript{[106]} For instance, n-type electrical doping can be obtained by replacing carbon atoms with nitrogen atoms in graphene frameworks.

Three forms of N doping were proposed in graphene carbon frameworks, i.e. sp\textsuperscript{2} hybridized graphitic N, pyridinic N, and sp\textsuperscript{3} hybridized pyrrolic N (Fig. 12a).\textsuperscript{[107]} Graphitic N induces the replacement of carbon atoms in the hexagonal rings, and benefits the conductivity of graphene, while pyridinic and pyrrolic N provide active defect sites in favor of the chemical or electrochemical process. XPS N1s spectrum of nitrogen-doped graphene prepared by annealing at 800 °C of GO with melamine reveals mainly four peaks (Fig. 12b), with lower binding energy located at about 398.2 and 399.5 eV corresponding to pyridine-like and pyrrole-like nitrogen, peak at 400.8–401.3 eV resulting from graphitic nitrogen substituted of carbon atoms, and high energy peak at 402.3–402.9 eV attributed to oxidized nitrogen.

Various nitrogen sources have been used for N doping of GO/graphene, including melamine,\textsuperscript{[108]} ammonia,\textsuperscript{[107,109]} and...
(NH₄)₂CO₃. During thermal annealing of GO in an ammonia atmosphere, oxygen groups in GO were responsible for C=N bond formation, and the reduction, exfoliation of GO and nitrogen doping occurred simultaneously in this process. Compared to high-temperature thermal treatment, plasma-assisted downstream microwave technique enables the reaction at near room temperature, and provides a high-level amount of nitrogen doping. Thiourea can be used as both the N and the S source, and directly annealing GO with thiourea in argon leads to N and S co-doping, which makes graphene an efficient metal-free oxygen reduction reaction (ORR) electrocatalysts for energy conversion and storage devices. Moreover, co-doping of cobalt and nitrogen offers graphene excellent electrocatalytic activity for ORR both in alkaline and acidic solution.

Nitrogen doping of rGO provides this material with improved electrical properties, along with enhanced chemical reactivity. The doped nitrogen atoms change the local density of states around the Fermi level, providing graphene with energetically low-lying frontier molecular orbitals as well as a pronounced stabilization of the lowest unoccupied molecular orbital (LUMO). The formation of a delocalized conjugated system with nitrogen atoms and the sp²-hybridized carbon frameworks is favorable for its electrocatalytic activity. The heterostructure of p-doped pristine GO and n-type N-doped GO triggers effective exciton separation and charge transfer under solar light irradiation, achieving high photosynthetic H₂ generation performance from overall water-splitting (Fig. 12d). In addition, the doped nitrogen atoms can serve as coordination and reduction sites of metal ions, such as gold ion aqueous solution (HAuCl₄)₃. Due to the terminal carboxylates, gold nanoparticles are believed to coordinate with the nitrogen site by electrostatic interaction.

4.2 Molecular Modification

Except for atomic chemical doping of graphene frameworks, surface modification of GO with small molecules and polymer branches is promoted. The electronic structure of graphene is crucial to its applications, especially the development of carbon-based electronics. The direct interaction of GO with electron-donors and electron-acceptors induces modifications of the electronic structure of the obtained graphene. Chemical doping of graphene surface by attachment of gas molecules has proved to endow graphene with gas detecting function based on the changes of electrical conductivity, because the adsorbed molecules act as donors (NH₃, CO, and ethanol) or acceptors (NO₂, H₂O, and iodine), thus changing the local carrier concentration in graphene.

The abundant oxygen functional groups in GO make it possible to assemble GO sheets on other materials. The oxygen-containing groups act as two roles, dispersibility of GO in the aqueous solution and modification of bonding groups in certain chemical reactions. Functionalization of GO with quaternathiophene molecules, dopamine, amine-functionalized polyhedral oligomeric silsesquioxane, polymerized norepinephrine, and γ-aminopropyltriethoxysilane has been reported. For example, Ou et al. assembled GO sheets onto silicon wafers via covalent bonding, through chemical adsorption and subsequent thermal reduction progress. GO can be easily bonded with (3-aminopropyl)triethoxysilane (APTES)-covered silicon wafer through the chemical reaction between oxygenous (epoxy and carboxyl groups) and amine-terminated groups via nucleophilic substitution and amidation, respectively.

5. LIQUID CRYSTALS OF GO

5.1 Introduction to GO Liquid Crystals

Due to the poor dispersibility of pristine graphene in common solvents, it is hard to process graphene in industrial applications. But GO can disperse well in water and other polar solvents owing to its functional groups. Therefore, GO appears as a very important precursor of graphene because of its high dispersibility and it can be easily reduced to graphene. Besides, a great investigation has been attempted to tailor the ordering and orientation of GO and GO-assembling materials. In the long journey of 2D colloids, the phenomenon of flow birefringence has been usually observed in their dispersions, and proven as a flow induced mesophase, including clay and graphite oxide. As early as 1948, Thiele had observed the flow-birefringence of graphite acid (the old name of graphite oxide) when studying its viscosity property, which was considered as the first observation of flow-induced LC of graphite oxide. Till 2011, the stable LC of graphene oxide was re-observed and re-investigated systematically by several groups of Kim, Gao, and Pasquali and Smalyukh.

Afterwards, the liquid crystalline behavior of GO and rGO sheets were also reported by other research teams.

According to Onsager’s theory, if the volume fraction of 2D sheets is higher than a critical value (0=4Τ/W), LCs tend to form in dispersions. Especially, graphene and GO sheets possess a high aspect ratio and anisotropy, with monatomic thickness (Τ) and a micrometer-scale lateral width (W), resulting in the formation of nematic and lamellar liquid crystals in water and polar organic solvents. The LC properties of GO dispersion were directly evidenced by POM, with the stable birefringence spreading through the whole dispersions and displaying vivid Schlieren texture, as well as macroscopic colorful textures observed by the naked eye when the GO dispersions are placed between crossed polarizers (Figs. 13a and 13b), indicating the formation of a uniform nematic phase of GO. Kim et al. monitored the local orientation of the GO LCs by SEM after quickly quenching concentrated liquid-crystalline dispersion in liquid nitrogen. GO platelets were left oriented in the nematic phase and 1/2 disclinations were subsequently dominantly identified after subsequently freeze-drying treatment (Figs. 13c–13e), consistent with the typical disclination morphology. Upon the addition of the ultralarge graphene oxide sheets, lyotropic nematic liquid crystals were obtained, as reported by Aboutalebi et al. GO LCs can also be obtained in a wide range of organic solvents except water, such as ethanol, acetone, tetrahydrofuran, N,N-dimethylformamide, N-cyclohexyl-2-pyrrolidone, etc. In addition, GO LCs dispersions exhibit typical shear thinning and typical colloidal isotropic-nematic phase transition behaviors, which have been described by power law or simple Curreau model.

Gao’s group discovered a new form of chiral liquid crystal (CLC) of GO suspension when the concentration of narrow
size distribution GO increases to 0.38 vol%.[133] Cryo-SEM was employed to visualize the helical structural details of GO CLC, and it confirmed the annual ring-like structures of GO CLC comprised of undulating bands with distinct boundaries. Furthermore, POM for the confined GO CLCs in a cavity also reveals highly regular fingerprint-like and focal conic textures (Figs. 13f and 13g). They proposed the structure mode of CLC of 2D colloidal GO sheets as both continuous lamellar and helical features (Fig. 13h). The electrostatic repulsion between GO sheets is the dominant interaction in GO CLCs. Therefore, the neighboring blocks repel each other due to the negative charges at boundaries and on surfaces of GO sheets. In order to minimize the free energy, rotated conformation was like to form by turning to a certain angle.

Meta-periodicity exists in solids but tends to fade away in fluid states after a short relaxation time because of energetic instability. The achievement of stable meta-periodicity for lyotropic LCs remained a challenge. Jiang et al. fabricated lyotropic liquid metacrystals (LMCs) in colloidal GO LCs by shearing microlithography (SML) (Figs. 14a and 14b).[134] This technology allows the design of crystalline cells by programming the probe movement, covering five Bravais lattices (with translational and rotational symmetry) and quasi-crystals (with rotational symmetry but not translational symmetry), as shown in Figs. 14(c)–14(i). The programmable GO LMCs allow us to construct arbitrary lattices and patterns in liquid 2D space, making it possible for programming solid materials with designed behavior and performance.

LMCs exhibit special relaxation behavior compared to conventional 1D macromolecules. Gao’s group has tracked the fraction of reorientation area \( f \) and the translational order parameter \( S \) over time in a p4mm LMC. The relaxational dynamics follows a relationship of \( f \propto e^{-t^{1/2}} \) and \( S \propto e^{-t^{1/2}} \). The fraction of reorientation area and the translational order parameter over time at various concentration are shown in

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**Fig. 13** (a) POM images between crossed polarizers of GO aqueous dispersions with \( f_m \)'s of 5×10\(^{-4}, 1×10^{-3}, 3×10^{-3}, 8×10^{-3}, \) and 1.0×10\(^{-2}\) (from 1 to 6). The green arrows indicate the disclinations. (b) Macroscopic photographs on crossed polarizers of GO aqueous dispersions with \( f_m \)'s of 1.0×10\(^{-4}, 2.5×10^{-4}, 5×10^{-4}, 1.0×10^{-3}, 5×10^{-3}, 1.0×10^{-2}\), and 2.0×10\(^{-2}\) (from 1 to 7). The stable birefringence of GO aqueous solution indicates a typical nematic phase. (Reprinted with permission from Ref. [9]; Copyright (2011) American Chemical Society. (c, d) Typical nematic schlieren texture of GO LCs dispersion with ±1/2 disclinations and a +1 disclination. (e) SEM of GO LCs in a freeze-dried sample, with blue and red symbols indicating +1/2 and −1/2 disclinations, respectively. (Reprinted with permission from Ref. [10]; Copyright (2011) Wiley). (f) The annual-ring undulating fracture morphology of GO CLC and (g) POM images between crossed polarizers of GO CLCs in lateral domains. (h) Proposed model for one pitch of GO chiral liquid crystals. GO sheets are indicated as pink nets, and the semitransparent blue blocks indicate interlayer water. (Reprinted with permission from Ref. [133]; Copyright (2011) Nature Publishing Group).
Figs. 15(a) and 15(c). For instance, the radial autocorrelation function (ACF) of p4mm GO LMC at 0.09 wt% gradually lost characteristic peaks within 4 h (Fig. 15b). Furthermore, the authors proposed an anisotropic melting behavior of GO LMCs, where the perpendicular vibration against π walls possessed a narrower melting range and higher melting frequency than those of parallel vibration, which reflected the anisotropic strength of crystalline planes.[134]

Pristine GO LCs were mainly stabilized by polar and charged functional groups through electrostatic repulsion. However, in the case of polyacrylonitrile (PAN) grafted GO LCs, the surface charge of GO slightly decreased due to the partial reduction of GO in the polymerization process. Therefore, the delicate balance of GO-g-PAN LCs is mainly attributed to the remaining charge and the free-volume entropic repulsion of grafted polymers. Liu et al. grafted PAN on GO surface for assembling continuous strong nacre-mimetic fibers.[135] The mixed GO-g-PAN sheets were highly dispersible in polar organic solvents. At low concentration, the GO-g-PAN sheets form nematic LCs, and evolve into lamellar LC phase with increasing concentration. The increase of height of the sheets after grafting indicates the covalent bonding between PAN and GO (Fig. 14j).

5.2 Key Parameters
High aspect ratio is essential for the formation of GO LCs. In the case of normal-sized GO sheets, a high concentration is usually required for highly oriented LC. Increasing GO LCs concentration leads to the phase transitions from isotropic to biphasic system and then to a discotic nematic liquid crystal of GO sheets.[126] Besides, increasing the pH value of GO suspension provides a possibility for LC formation at relatively low concentration.[136] Yao et al. observed a well-organized rod-like texture if the suspension contained 0.132 mol/L KOH at GO concentration of 0.5 mg/mL, while the neat GO dispersion showed...
disordered phase at this concentration. At GO concentration of 3.5 mg/mL, GO containing KOH showed much more regular ordered laminar texture than the neat GO (Figs. 16a–16c). K ion was excluded for this phenomenon because K⁺ weakens the electrostatic repulsion between GO sheets and makes zeta potential of GO sheets positively shifted. In contrast, increasing pH value decreases the zeta potential of GO sheets even considering the existence of K⁺, which was caused by the deprotonation of the hydroxyl groups and additional carboxyl groups formation.

As we discussed in Part 3.2, pH and ionic strength are key factors that determine the colloidal behavior of GO dispersion. Therefore, inducing ionic impurities or decreasing the pH value of GO suspension deteriorates the electrostatic repulsion and causes the coagulation of GO suspension. Removal of ionic impurities is crucial for the stability of LC phase. Gao’s group has established the isotropic-nematic solvations and the concentration of the transition to I phase by adding NaCl (Fig. 16e): isotropic (I, mass fraction (f_m) < 2.5 x 10⁻³), nematic (N, f_m > 5 x 10⁻³), and biphasic coexistence (I+N). However, with the addition of NaCl salt, the biphasic phase turns into an I phase initially and solids (S) phase eventually, and the concentration of the transition to I phase by adding salt scales with f_m of GO. The phase evolution is caused by the decreased electrostatic repulsive forces induced by adding salt, which is confirmed by tracking the zeta potentials of the dispersions along with the concentration of salt (Fig. 16f).

CaCl₂ added in the GO LCs dispersion can act as an efficient cross-linker, which turns GO sol into hydrogel to prevent the collapse of GO-based 3D structures, while being applied into direct 3D printing (Fig. 16f). 

5.3 Applications

GO LCs were applied in electro-optic devices due to their tunable degree of ordering and direction of alignment.[127] In addition to electric field, magnetic field and mechanical deformation can also be used for controlling the macroscopic alignment of GO LCs.[10] The formation of GO LCs has been utilized to develop high-performance supercapacitors.[138] The component, defect, structure and interface of GO sheets should be considered during preparation. Guo et al. utilized liquid crystal-derived GO phases as smart stimuli-response materials based on unique anisotropic swelling behaviors of GO LCs.[139] Besides, GO aqueous dispersions possess typical shear flows and show decreased viscosity upon shearing. The prealigned orientation of GO LCs can be directly used for the ordered assembly of macroscopic architectures or composite structures under shear flow.[136,140–143] GO LCs facilitate the design of long-range and ordered structures of graphene-based functional materials and provide these materials with different topologies by controlling the alignment of graphene sheets in the fluid phase. It can be concluded that GO is a living building block in the 21st century (Fig. 17). Until now, the most widely used application of GO LCs is the ordered assembly for the design of ordered materials with optimal performances, which will be discussed in Part 6.
6. MACROSCOPIC ASSEMBLY OF GO

The discovery of GO LCs has built solid new foundations for highly ordered, macro-assembled graphene materials. The assembly is mainly realized through π-π stacking and hydrogen bonding of GO sheets. Moreover, wet-fusing assembly occurs on two GO fibers because of the swelling of fibers and hydrogen bonding at the interface. Until now, a lot of graphene architectures from 1D to 3D levels have been established such as graphene fibers, films, foams (or aerogels), fabrics, as well as their composites with other materials (Fig. 18).

6.1 1D Graphene Fibers

Graphene fibers possess promising applications compared with conventional polymer fibers and metal wires, benefiting from their excellent properties including high electrical conductivity, chemical stability, lightweight and strong mechanical properties. In 2011, Gao and Xu firstly created graphene fibers by the wet spinning of GO LCs in the lab, and opened a new field for high-performance carbonaceous fiber with rich functionalities. Then many reports have been published to understand the structure and properties of GFs and explore their applications. In this part, mechanical strength and flexibility of graphene fibers are demonstrated and their related electrical and thermal transport properties are discussed. Detailed discussions on graphene fibers such as preparation, morphology, properties, and applications are beyond the scope of this review, and an excellent review article on graphene fibers is suggested to follow for interested readers.

6.1.1 Mechanical strength and flexibility

The significant differences between conventional polymeric fibers and 2D graphene-sheets-based fibers lie in the structure of basic constituent units and the interaction mode thereof (Fig. 19). In general, the mechanical performance of polymeric fibers is dominated by the molecular weight, chain-by-chain interaction, defect-free engineering and entanglement, while that of graphene fibers is usually determined by (1) the crystalline graphitic domain size, (2) defect-free engineering of graphene sheets, (3) alignment of graphene sheets and (4) the compactness of graphene layers, as well as (5) hierarchical and multiscale interactions. The interactions inside graphene...
fibers include π-π interaction of graphene sheets on atomic scale, nanoscale interlocked structure caused by wrinkles, and microscale sheet-by-sheet friction. Although the interaction of polymer chains is strengthened by the chain-by-chain interaction and entanglement, the polymeric fibers still suffer from chain sliding under uniaxial tension. In terms of 2D graphene sheet, it can be considered as intermolecular cross-linking of individual “carbon chain”, and the chain-sliding can be effectively inhibited. Meanwhile, the interlocked wrinkles of 2D graphene sheets also block the slippage within the graphene fibers.

Although the mechanical strength of single graphene sheet reaches an ultrahigh value of ~130 GPa, the limited strength of macroscopic graphene materials is still far from being achieved. Efficient strategies are required to minimize the large mechanical performance gap between graphene fibers and individual graphene sheets. Giant GO sheets with extremely high aspect ratio are usually selected as the building blocks for graphene fiber fabrication to reduce defective edges. Xu et al. hold the view that LGO sheets contribute to the improvement of the mechanical performance of the obtained graphene fibers because of the high aspect ratio.21 Among the process of wet-spinning of neat GFs, GO LCs can form regular alignments along the directional flowing field, which is helpful to get continuously assembled GO fibers with highly ordered micrometer-sized structures (Figs. 20a–20d). More recent studies by Xin et al. reveal that the combination of LGO and SGO is beneficial to the fabrication of mechanically strong graphene fibers, with LGO sheets acting as a highly ordered arrangement and SGO sheets filling the space and microvoids (Fig. 20e).94

Afterwards, a conventional high-temperature thermal treatment is introduced to improve the performance of GFs.147 High-temperature annealing contributes to the formation of fine graphene crystallite domain, as well as the removal of defects such as oxygen functional groups, nanocavities and sp3 carbon bonds, resulting in the enhanced mechanical performance of graphene fibers. However, this method may be not suitable for graphene films, because of the formation of “micro-gasbag” inside the GO layers.95

Furthermore, a well-stacked microstructure assembled by directional fluids is the key to outstanding mechanical performance.148,149 A uniform alignment of graphene sheets favors the mechanical strength of assembled graphene fibers in the axial direction. In 2012, Xu et al. presented neat GO aerogel fibers with unique “porous core-dense shell” structure originated from lamellar-ordered GO LCs via spinning assembly strategy and ice-templating strategy, offering

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**Fig. 18** Diagram of GO liquid crystals and their macroscopic assembly to get graphene F4 materials, i.e. fiber, film, foam and fabric.

**Fig. 19** Structural models of polymeric fibers and graphene fibers and the factors for the enhancement of their mechanical strength.

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graphene fibers high specific tensile strength (188 kN·m/kg) and high compression modulus (3.3 MPa). The structure retained during the phase transformation from ordered fluids to ordered solids. Xu et al. further induced a stretching strategy in the whole wet-spinning process to improve the alignment of graphene and the compactness of fibers (Figs. 20f–20h). Therefore, a full-scale synergetic defect engineering method has been proposed to minimize the possible defects of graphene fibers at all levels ranging from atomic to macroscale scales, offering the obtained graphene fibers ultrahigh stiffness of 282 GPa and record mechanical tensile strength of 1.45 GPa in 2016. Recently, Gao and co-workers improved the mechanical strength of graphene fibers to 3.4 GPa via a plasticization spinning strategy. The intercalated plasticizers enable GO fibers to achieve a 580% enhanced deformable plasticity, followed by the flattening of random graphene wrinkles and formation of large crystallite domains.

Fig. 20 (a) Schematic apparatus for wet-spinning GO fibers. (b) A five-meter long GO fiber wound on a ceramic reel. (c) Photograph of the process to twist graphene fibers to yarns. (d) SEM images of the twisted yarn. (Reprinted with permission from Ref. [21]; Copyright (2013) Wiley). (e) Schematics of graphene fibers consisting of LGO and SGO. (Reprinted with permission from Ref. [94]; Copyright (2015) American Association for the Advancement of Science). (f) Schematic illustration of wet-spinning of GO fibers with continuous stretching in two stages, followed by the transformation of GO fibers into graphene fibers through graphitization up to 3000 °C. (g) A close-up snapshot of 50-filament GO fibers extruded from the spinneret in the coagulation bath. (h) A roll of 500-m long 50-filament graphene fibers with a metallic luster. (Reprinted with permission from Ref. [151]; Copyright (2016) Wiley). (i) Photograph of a CNT/rGO hybrid fiber sewn into a rubber band and an attached 3.5-cm long needle. (Reprinted with permission from Ref. [156]; Copyright (2012) Nature Publishing Group). (j) Photo of four-meter-long GO fiber wound on a Teflon drum. (k) SEM image of a tightening knot of graphene fiber. (Reprinted with permission from Ref. [133]; Copyright (2011) Nature Publishing Group).

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Besides, the improvement of the mechanical performance of GO fibers or graphene fibers can be achieved by the ion cross-linking bond introduction between the layers. Previous experimental and theoretical investigations have proposed that adding cation promotes cross-linking bridges between the oxygen-containing groups, and thus leads to the mechanical enhancement of graphene fibers/films.[21,133] The introduction of coordinating cross-linking enhances the interlayer interaction of graphene sheets, leading to the improvement of graphene fiber strength. The wet-spinning technology can be extended to polymer-grafted graphene UCs to obtain hierarchically assembled, nacre-mimetic fibers.[135,134,153] In 2013, Gao and coworkers reported the nacre-mimetic fibers with “brick-and-mortar” microstructure starting from the mixture of GO and PAN, showing excellent mechanical property of graphene fibers with a tensile strength of 452 MPa at that time.[135] Moreover, combining carbon nanotubes and rGO flakes promotes an interconnected network of partially aligned rGO flakes and carbon nanotubes during solution spinning, forming super-tough nanostructured fibers by strong interaction between these two types of carbon components. The assembled CNT/rGO hybrid fiber can be sewn into a rubber band with an 3.5-cm long needle (Fig. 20).[156] Furthermore, nacre-inspired approaches are also suitable for fabricating graphene composite films. Ni et al. applied a long linear chain form 1-aminopyrene (AP) and disuccinimidyl suberate (DSS) to make cross-link adjacent between graphene sheets via n-π interfacial interactions, aiming to enhance the tensile strength of graphene films.[157]

Flexibility is regarded as the one of the most important figures of merit for graphene fiber. It can be twisted together to obtain continuous threads and yarns, which makes flexible and wearable devices such as electronic skins, smart clothes, wearable heater, bendable display, and flexible fiber-shaped supercapacitors, etc.[144] Fig. 20(k) shows a knot made of graphene fiber and it does not break as the knot is tightened. It is suggested that the flexibility results from the locally crumpled structures of individual graphene sheets.[133]

### 6.1.2 Electrical and thermal transport

Except for improving the mechanical strength of graphene fibers, the large and fine crystalline graphitic domain, defect-free engineering of graphene sheets and the alignment of graphene layers also contribute to the superior electrical and thermal transport properties. Fabricating graphene fibers with high strength and electrical/thermal conductivity simultaneously remains a great challenge. For superior electrical and thermal transport properties, highly aligned sp² graphene sheets are required, while sp³ bonds and functional groups usually act as electron- and phonon-scattering centers, which greatly hinder the electrical and thermal transport of graphene.[94,158]

The electrical conductivity of graphene films is dominated by the contact resistance between the graphene sheets. LGO sheets reduce the number of graphene-graphene contacts for a given number of conducting paths. As a result, the large size of GO sheets reduces the total contribution of contact resistance and enhances the conductivity.[159] We believed that LGO sheets contribute to the improvement of the mechanical performance of the obtained graphene fibers, as well as their electrical performance due to the high aspect ratio.[21]

Moreover, thermal annealing heals structural defects in the lattice structure and removes functional groups, greatly improving the electrical and thermal properties.[160] With the increase of annealing temperature, the D band at near 1350 cm⁻¹ in Raman spectra is depressed, suggesting the removal of defects. It is reported that the D band can be no longer evidenced after thermal treatment at 2200 °C or above, meaning the complete removal of defects in graphene.[148] The D band becomes narrow and the 2D band recovers after high-temperature treatment, indicating the crystallization of graphene sheets. As well as its influence on mechanical strength, fine alignment of graphene sheets also contributes to the high conductivity of the assembled graphene structure.[150]

The high flexibility and electrical conductivity of graphene fibers enable various applications among wearable electronic devices and flexible power sources (Fig. 21a).[147,161–169] Much of the research in wearable energy storage devices in the last two decades has examined to meet growing demands in the field of communication, biomedical devices, and entertainment systems.[170] Qu et al. fabricated fiber-shaped supercapacitors using hollow graphene fiber as the electrodes, by incorporating conducting polymer into graphene fibers (Figs. 21b and 21c).[171] Ma et al. introduced external conductive connection “bridges” polydopamine (PDA) into graphene sheets and employed thermal treatment at 1200 °C under inert atmosphere, providing the assembled graphene fiber with high electrical conductivity of 6.6×10⁴ S/m.[154] Other polymers such as polyaniline were used by electrodeposition to fabricate superelastic wet-spun hybrid carbon nanotube graphene fibers for high-performance fiber-based supercapacitor.[172] Gao’s group proposed a coaxial wet-spinning assembly approach to make polyelectrolyte-wrapped graphene/carbon nanotube core-sheath fibers for yarn supercapacitors (Fig. 21d).[173] An ultra-high capacitance of 269 mF/cm² and energy densities of 5.91 mWh/cm² were obtained. Meng et al. reported a hierarchical all-graphene hybrid structure with a highly conductive core and 3D graphene network with a highly-exposed surface, offering the great advantages as flexible electrodes for electrochemical supercapacitor (Fig. 21e).[174] Chen et al. introduced cellulose nanocrystal into GO via non-liquid-crystal spinning followed by chemical reduction to fabricate hybrid fibers.[175] Moreover, the high stretchability and high electrical conductivity of graphene fiber make it favorable wearable heater with an ultrafast electrothermal response and very low operation voltage to access high temperature.[176]

Neat graphene fibers reduced by chemical reduction still showed limited electrical conductivity (σ) only about 0.2×10⁻⁴–4.1×10⁴ S/m, because of the inherent structural defects and residual oxygen-containing groups, as well as the lower carrier density compared to metal (up to 10⁷ cm⁻³). Therefore, increasing the carrier density by doping provides an option to improve the electrical conductivity of GFs. Liu et al. employed a facile two-zone vapor transport method (Fig. 21f) to dope GFs chemically with superior electrical conductivity with various elements, reaching 0.77×10⁶ S/m (GF-FeCl₃), 1.5×10⁷ S/m (GF-Br₂), and 2.24×10⁸ S/m (GF-K).[177] The dopants were sublimated in the lower temperature zone and
diffused to the higher temperature zone where the doping reaction occurred. Moreover, Ca intercalation of graphene fiber provides it with superconducting property, showing a superconducting transition at ~11 K, which is comparable to that of commercial superconducting NbTi wire (Fig. 21g).[178]

6.2 2D Graphene Films
Graphene/GO films have been applied in numerous fields such as electrode of electrochemical capacitors,[179–182] battery separators,[183] cathodes for Al ion batteries,[184–186] ion sieving,[187–189] liquid handing,[190] gas separation,[191] thermal management,[192–194] electromagnetic interference shielding,[195,196] and so on. The mechanical properties of graphene films are quite critical for many applications such as human-motion sensors, flexible electronics and stretchable energy-harvesting devices. A variety of structures are designed to endow graphene films with excellent behaviors such as high tensile strength, favorable Young’s modulus, long durability and rapid recovery while retaining its high conductivity.[197] In this part, we would like to present mainly the mechanical strength, flexibility and thermal transport of graphene films.

The issue of mechanical strength of graphene/GO films has received considerable critical attention in the past decade. Factors influencing the mechanical strength have been explored in several studies, such as denser grain boundary,[198] cross-linking network,[199] modulated plasticization stretching,[200] etc. The efficient cross-linking of neighboring GO sheets is essential for improving the mechanical strength of graphene films,[201] which is also one of the key factors in the case of graphene fibers. Liu et al. have documented that Fe3+ tannic acid complex network served as the “mortar” to stick the GO “bricks” together, which induced the cross-linking of GO sheets and greatly improved the fracture strength and Young’s modulus of GO papers.[198] Recently, Gao and co-workers have achieved graphene paper with superior mechanical properties, with tensile strength of 1.1 GPa and stiffness of 62.8 GPa.[199] In this work, an intercalation modulated plasticization strategy was applied to regulate the spontaneous graphene wrinkles into crystalline orders. Besides, benefiting from the crystalline orders, superior conductive properties were achieved, with high electrical conductivity of 1.1×10^5 S/m and thermal conductivity of 109 W/(m·K).

Leaf spring is a good example of elastic property from daily life, which is usually used in vehicles to support the axle and absorb shocks based on their arch structure of the suspension system. Other similar examples include honeycomb-like structure,[202] microvoids,[203] and natural cork.[204] Finite element mechanical simulation suggests that the arch-shaped structure can sustain large geometric deformation without yielding and recover to its original shape immediately because its true strain is small (Fig. 22a). Learning from the examples from daily life, researchers have developed a series of structures for elastic materials, e.g. a super-elastic carbon-graphene (C-G) monolith with hierarchical lamellar architecture.[205] Hundreds of micrometric arches serve as structural and elastic units of the carbon-graphene composite. The link between adjacent lamellae is crucial for elastic performance because it helps restrict lateral extension and slip of the layers while undergoing vertical compression (Fig. 22b). Besides, the link or interlocking-tile is suggested to promote the thermal and electrical behaviors of graphene films, because it provides a transmission tunnel for thermal and electrical con-

Fig. 21 (a) Schematic illustration of fiber-based micro-supercapacitors integrated into a flexible fabric substrate to power electronics. (Reprinted with permission from Ref. [169]; Copyright (2017) Wiley). Cross-sectional SEM images of the hollow GO/conducting polymer composite at (b) low and (c) high magnifications, respectively. (Reprinted with permission from Ref. [171]; Copyright (2016) Wiley). (d) Two intact coaxial fibers woven with cotton fibers. (Reprinted with permission from Ref. [173]; Copyright (2014) Nature Publishing Group). (e) SEM image of graphene fiber with a core covered with a sheath of 3D porous network-like graphene framework. (Reprinted with permission from Ref. [174]; Copyright (2013) Wiley). (f) Comparison of the specific conductivity of the doped GFs, the doped CNT fibers, the doped CF, and several commonly used metallic conductors. (Reprinted with permission from Ref. [177]; Copyright (2016) Wiley). (g) Temperature dependence of the electrical resistance of Ca intercalation of graphene fiber, showing a superconducting transition at ~11 K. Inset: a photograph of Ca intercalation of graphene fiber with a yellow color. (Reprinted with permission from Ref. [178]; Copyright (2017) American Chemical Society).
ductivity. Yang et al. proposed Maxwell-Wiechert model to describe the dynamic mechanical behavior of graphene films/papers and revealed that relaxation behavior can be relieved by the interlayer crosslinking between adjacent layers (Fig. 22c). Based on the ternary Maxwell-Wiechert model, the stress-time curves of graphene films during stress relaxation can be expressed by the following equation:

$$\sigma(t) = \sigma_\infty + \sigma_1 e^{-t/\tau_1} + \sigma_2 e^{-t/\tau_2}$$

where $\sigma$ refers to the stress, $\sigma_\infty$ refers to the residual stress of graphene films, $\sigma_1$ and $\sigma_2$ and $\tau_1$ and $\tau_2$ are the initial stress and relaxation time of each Maxwell unit.

The mechanically flexible property can be achieved by producing 3D macroporous structure inside graphene films via a breath-figur method. Lee et al. disperses polymer-grafted GO platelets in an organic solvent and exposed the suspension to a stream of humid air. Endothermic evaporation of the volatile organic solvent leads to the packing of aqueous droplets at the surface of the organic solvent. Finally, a special porous morphology of the graphene films forms after drying (Fig. 22d). Huang et al. induced graphene film with microvoids structure by coating hydrazine hydrate solution on GO film followed by confining the film between two alumina plates in order to ensure the controlled expansion of graphene films in thickness. Xu et al. directly reduced wavy GO films electrodes by in situ reducing wavy GO films precoated on elastic tapes without involving film transfer or high-temperature annealing. The rGO electrodes showed excellent electrochemical stability and flexibility for solid-state electrochemical capacitors.

Moreover, the flexibility study of graphene can be extended from 2D films to 3D foams. Qiu et al. fabricated graphene-based cellular monoliths with similar cork-like structure by a simple freeze-casting method. Upon freezing, rGO sheets were rejected and entrapped between neighboring ice crystals to form a continuous network around the ice crystal. As a result, the rGO sheets concentrated at the boundary of ice crystals and aligned along the ice growth direction due to the squeezing effect.

Peng et al. reported super-flexible graphene films with ultrahigh thermal conductivity ($K$), with the assistance of the high-temperature annealing technique. The obtained graphene films present a high thermal conductivity of about 1940 W/(m·K), which is higher than that of copper foil ($K=390$ W/(m·K)) and graphitized polyimide film (GPI, with $K=1750$ W/(m·K)) (Figs. 22e and 22f). The high thermal conductivity of graphene film is mainly attributed to its high crystalline structure and debris-free graphene sheets, because the defects and grain boundaries of the graphene sheets are healed after high-temperature thermal treatment. The high thermal transport property mainly relies on the large crystalline graphitic domain, defect-free and aligned sp² graphene sheets. Besides, the high-temperature annealing graphene film also maintains the highly flexible property, and it can endure 180°-seamless folding for over 6000 cycles and 180°-bending for 1.0 × 10⁵ cycles. This property is determined by the microfolds generated by mechanical pressing, the randomly dispersed and compacted microfolds can be stretched out and deformed to crumples under tension or folding.

6.3 3D Graphene Architectures

The control of GO platelets into 3D structure functional materials is a great issue. 3D graphene architectures such as...
aerogels, fabrics and foams have been developed, which makes them viable candidates for catalysis,[197−211] energy storage,[212−216] gas/ion/dye/wave absorption,[217−221] water harvester from air,[222] hygroelectric generator,[223] solar-thermal energy conversion,[224−226] solar-electron energy conversion,[227] and sensing applications.[228−230]

The fabrication of highly stretchable carbon aerogels (CAs) or foams is crucial to their uses for growing demands in wearable devices, stretchable electronics, and smart manufacturing. Jiang et al. fabricated graphene CAs from GO-based ink by a facile ion-induced gelation method. CaCl$_2$ was added to GO sol as an efficient cross-linker to turn GO sol into printable gel ink (Figs. 23a–23c).[84] With trace addition of Ca$^{2+}$ ions as gelators, aqueous GO sol converts to printable gel ink. The ions prevent the collapse of 3D structure and keep GO suspension a shear thinning behavior to flow, which provides the

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**Fig. 23** (a) Photograph of as-printed woodpile structure of graphene CAs from a top view. (b) SEM image of the 3D graphene CAs architecture and its gradient porous structure. (c) The rate performance of supercapacitors for 3D GAs with different thicknesses. (Reprinted with permission from Ref. [84]; Copyright (2018) Wiley). (d) The catalytic mechanism of S→O acetyl migration by neat graphene oxide aerogel in a confined cell. (Reprinted with permission from Ref. [231]; Copyright (2015) American Chemical Society). (e) Schematic illustration of the assembly of highly stretchable CAs through 3D ink-printing. (f) A photograph of ultralight CAs with hierarchical buckled structures (5.7 mg/cm$^3$) floating on a flower. (g) In situ SEM tracking on the structural evolution of CAs. (Reprinted with permission from Ref. [78]; Copyright (2018) Nature Publishing Group). (h, i) Micrographs of re-dispersed GO fibers and the wet-fusing process of GO fibers under optical microscopy and POM. (Reprinted with permission from Ref. [235]; Copyright (2016) Nature Publishing Group).

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availability of the DIW method for a neat GO system. The obtained graphene CAs present high gravimetric capacitance of 213 F/g at 0.5 A/g and 183 F/g at 100 A/g while used as the electrode of supercapacitors, and retain over 90% after 5.0×10^5 cycles due to the rich hierarchical pores and high electrical conductivity. Besides, this ion-induced gelation method is also available for preparing GO-based composite inks, such as GO/CNT ink. Moreover, neat GO aerogel can be used as a catalyst in the reaction of S−O acetyl migration for the synthesis of thiol compounds (Fig. 23d). The CA still face stability and performance issues that hinder their wide-spread applications. For example, CAs behave severely brittle under tensile deformation, especially under extreme temperatures due to frozen chains at low temperature and viscous behavior at high temperature. Besides, incorporation with polymer materials may weaken the favorable functionalities of CAs like highly electrical conductivity and low density. To solve these problems, Guo et al. developed a kind of highly stretchable carbon aerogels with a retractable 200% elongation through hierarchical synergistic assembly.[78] The CAs were fabricated by ink-printing homogeneous aqueous mixtures of GO and purified multiwalled carbon nanotubes (MWNsTs) to program-controlled 3D structures, followed by freeze-drying and chemical/thermal reduction treatment (Figs. 23e–23g). The elastic strain energy to conform to large tensile deformations originates from the enhanced van der Waals force between MWNsTs and graphene caused by restored conjugated domains after chemical reduction. Therefore, the multi-order hierarchical structures and synergistic reinforcement between graphene and MWNsTs endowed CAs with highly stretchable behavior and allow applications such as strain sensors for precise logic identification of complex shape conversions.

The intrinsic properties of graphene aerogel films (GAF) such as lightweight, chemically stable and high conductive endow them with high electromagnetic interference (EMI) shielding performance. Xi et al. designed GAF with multilayer structure, showing excellent shielding effectiveness (SE) of ~135 dB in 0.1−3 GHz at GAF thickness of 1.4 mm, and an up trend from 65 dB to 105 dB in 2−18 GHz at thickness of 120 mm.[195] The high EMI shielding performance of GAF is related to the expanded interlayer spacing in a multilayer structure, as proposed as “expansion enhancement effect (EEE)”. The electro-magnetic waves are reflected or transmit at each interface of the layers, and the reflected wave will experience reflection and transmission again on the other interface. As a result, the incident wave would experience infinite reflections between the interfaces, and the effective transmissivity (τ) can be calculated by the equation:

\[
τ = \frac{2Z_1 Z_2}{(Z_1 + Z_2) \cdot \sinh (γ_1 d) + (2Z_1 Z_2) \cdot \cosh (γ_1 d)}
\]

where \(Z_1\) and \(Z_2\) are wave impedance of free space (−377 Ω) and material, respectively, \(γ_1\) (m−1) refers to propagation constant of free space, and \(d\) (m) is the thickness of space layer. Other carbon-based materials for EMI shielding and microwave absorption (MA) have also been reported, such as porous graphene microflowers, graphene micro-porcorns with hollow structure, porous biomass-pyrolyzed carbon (PBPC) based on natural wood, graphene/carbon nanotube composite films, etc.[200,232–234]

A new concept of non-woven graphene fiber fabrics (GFFs) was raised by Gao’s group.[235] These non-woven GFFs consist of randomly oriented graphene fibers with strong interfer interaction. In other words, GFFs present macroscopically paper-like structure with randomly cross-linked graphene fibers at the microscopic scale. The synthesis of GFFs is shown as follows: firstly, GO staple fibers were prepared by the continuous spinning of GO/DMF solution into an ethyl acetate coagulation bath; then the collected GO fibers were re-dispersed in the mixture of water and ethanol, and subsequently filtrated and dried to make interused GO fiber fabrics; finally, GFFs were obtained after chemical reduction and high-temperature thermal treatment of GO fiber fabrics. Particularly, the mechanism of cross-linking of the graphene fibers was explained as wet-fusing assembly. The dried GO fibers got wetted immediately during the re-dispersion in aqueous solvents, and they gradually swelled and then turned into gel fibers by solution. Strong interfer interaction could be realized among the gel state of fibers, and the gel fiber was able to fuse at the contact part, connect with each other and become one crossing fiber in the subsequent drying process (Figs. 23h and 23i). We ascribe this wet-fusing assembly to the swelling of fibers and hydrogen bonding between GO sheets at the interface. Benefitting from the well-connected framework and link transmission routes for electrons and phonons, the obtained binder-free GFFs possess record-breaking-specific electrical (2.8×10^4 S/m) and thermal conductivities (301.5 W/(m·K)), as well as low density (0.22 g/cm^3). GFFs can be used in applications such as electrothermal heaters, organic adsorption, separator membranes, catalyst supports, and conductive electrode. While using as textile electrodes of supercapacitors, hydrothermally activated GFFs can achieve an areal capacitance of 1060 mF/cm^2 at a thickness of 150 μm and 7398 mF/cm^2 by overlaying several layers of GFFs.[236]

In conclusion, Gao and coworkers have established a common method for the assembly of GO molecules from liquid crystals to macroscopic materials, including aerogel ball, aerogel fiber, non-woven fabric, short/long fiber, film, ribbon and their composite materials (Fig. 24). The properties of these graphene-based materials can be tuned by the successful controlling of GO liquid crystal precursors.

7. GO-BASED COMPOSITES

Hybridization of the materials can bring more degrees of freedom to combine physical/chemical properties and achieve multi-functional applications. The synergistic effects of the individual materials allow intriguing properties on optical, electrical, thermal, mechanical and electrochemical fields. In general, the interaction between GO and the target materials could be maintained by n-n interaction, electrostatic attraction, van der Waals force, covalent bonding, hydrogen bonding, and coordinate bonding. It is important to demonstrate that the manufacturing of graphene-based composites should meet the following requirements, to harness the individual and synergistic properties to applications. First, graphene sheets should be produced on a sufficient scale via a relatively simple, low-cost and energy-saving method. Secondly, graphene is proposed to incorporate into the target materials successfully.

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Thirdly, these materials should be distributed homogeneously. GO has proved its advantages over pristine graphene in the compositing progress due to its scalable production and good dispersion in organic/inorganic solvents. Moreover, based on the rich groups on GO sheets, the hybridization of GO and other organic/inorganic materials gives new opportunities to produce desirable-performance materials in target applications.

### 7.1 Incorporation with Organics

Compositing graphene/graphene oxide with polymers is an important area which can usually improve the electrical, mechanical or barrier properties. In this part, we would like to summarize the interactions between graphene and target materials and demonstrate how these interactions work for designed applications. According to Kinloch’s opinion,[237] four different chemical interactions were demonstrated for graphene incorporated with polymer matrix, including chemical bonding (e.g., covalent bonding, hydrogen bonding and coordinate bonding), $n$-$n$ interaction, electrostatic attraction, and van der Waals force.

Continuous neat graphene fibers have been achieved by wet-spinning due to the liquid crystal behavior of GO. Therefore, if the LCs of polymer-grafted GO could be stabilized in solvents, it would show great potential for the synthesis of polymer-functionalized graphene fibers. Liu et al. reported that PAN grafted GO was highly dispersible in polar organic solvents such as DMF and dimethyl sulfoxide (DMSO), and it was introduced to the continuous wet-spinning of nacre-like materials. In contrast, the approach starting from GO aqueous solution and PANI solution in N-methyl-2-pyrrolidinone (NMP) leads to uniform incorporation of GO into PANI at molecular level. Because of the $n$-$n$ interaction between PANI and GO, the PANI on GO sheets are stable in the GO reduction process after the PANI/GO sheets lose their dispersibility when the oxygen-containing groups of GO are removed by the reductant ascorbic acid, and a uniform 3D network is finally assembled (Figs. 25a and 25b). The supercapacitor using PANI/rGO composite as the electrode shows a high specific capacitance of 808 F/g (5717 mF/cm$^2$) at a current density of 53.33 A/g. Boland et al. reported viscoelastic graphene-silicone polymer nanocomposites with electromechanical properties.[242] The electrical conductivity of the composites increases strongly with graphene content, and the stiffness of the composite also increases. These special properties make the obtained graphene-grafted silicon polymer high-performance sensing materials which can monitor deformation and pressure with high sensitivity (Figs. 25c and 25d). The $n$-$n$ stacking of rGO and commercially poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is crucial to the self-assembly of composites. The rGO/PEDOT:PSS composites work as high-performance flexible electrodes for electrochemical capacitors with high volumetric and areal specific capacitance performance. PEDOT:PSS works as a binder to bridge graphene sheets together and provides highly conductive networks for electron/ion transport. Firstly, the one-dimensional PEDOT:PSS chains crosslinked with rGO particles to form a hierarchical architecture, and then PSS was protonated and partially removed after the adding of H$_2$SO$_4$, resulting in the enhancement of $n$-$n$ stacking of rGO and PEDOT (Figs. 25g–25i). Hence, the inherited hierarchical architecture ensures the 3D interlinked network with sufficient ion transport, delivering ultrahigh areal (5365 mF/cm$^2$) and volumetric (203 F/cm$^3$) specific capacitances at 1 A/g.[243]

However, in situ polymerization of aniline on rGO matrix yields a non-uniform PANI coating, and it will cause undesired concentration polarization in the composite electrode.[240] Consequently, the approach starting from GO aqueous solution and PANI solution in N-methyl-2-pyrrolidinone (NMP) leads to uniform incorporation of GO into PANI at molecular level. Because of the $n$-$n$ interaction between PANI and GO, the PANI on GO sheets are stable in the GO reduction process after the PANI/GO sheets lose their dispersibility when the oxygen-containing groups of GO are removed by the reductant ascorbic acid, and a uniform 3D network is finally assembled (Figs. 25a and 25b). The supercapacitor using PANI/rGO composite as the electrode shows a high specific capacitance of 808 F/g (5717 mF/cm$^2$) at a current density of 53.33 A/g. Boland et al. reported viscoelastic graphene-silicone polymer nanocomposites with electromechanical properties.[242] The electrical conductivity of the composites increases strongly with graphene content, and the stiffness of the composite also increases. These special properties make the obtained graphene-grafted silicon polymer high-performance sensing materials which can monitor deformation and pressure with high sensitivity (Figs. 25c and 25d). The $n$-$n$ stacking of rGO and commercially poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is crucial to the self-assembly of composites. The rGO/PEDOT:PSS composites work as high-performance flexible electrodes for electrochemical capacitors with high volumetric and areal specific capacitance performance. PEDOT:PSS works as a binder to bridge graphene sheets together and provides highly conductive networks for electron/ion transport. Firstly, the one-dimensional PEDOT:PSS chains crosslinked with rGO particles to form a hierarchical architecture, and then PSS was protonated and partially removed after the adding of H$_2$SO$_4$, resulting in the enhancement of $n$-$n$ stacking of rGO and PEDOT (Figs. 25g–25i). Hence, the inherited hierarchical architecture ensures the 3D interlinked network with sufficient ion transport, delivering ultrahigh areal (5365 mF/cm$^2$) and volumetric (203 F/cm$^3$) specific capacitances at 1 A/g.[243]

Chemical bonding interactions between GO and polymers
can be realized by choosing proper pairing materials, e.g., gelatin. Gelatin is a natural protein with both hydrophobic and hydrophilic amino acid side chains, while GO possesses an amphiphilic structure with hydrophobic carbon backbone and hydrophilic functionalized groups on the basal plane and edges, thus facilitating the formation of multiple interactions between GO and this polymer. The ultrafiltration hybrid membrane fabricated by layer-by-layer (LbL) self-assembly of the composites of GO, gelatin and hydrolyzed polyacrylonitrile (H-PAN) possesses multiple interactions: electrostatic attraction, hydrogen bond, and hydrophobic interaction (Fig. 26a). Stankovich et al. chose 1,4-phenylenediamine-2-sulfonic acid (PDASA) as a crosslinker for coating GO films onto a Nafion support, because the double primary amine groups can react with the epoxy groups of GO during thermal treatment. Stankovich et al. fabricated the graphene-polymer composites via the molecular-level dispersion of individual GO sheets with poly(ethylene oxide). An isocyanate treatment of the surface of GO sheets promotes the formation of amide and carbamate ester bonds to the carbonyl and hydroxyl groups, making GO stable dispersions in polar aprotic solvents such as DMF. Subsequently, the isocyanate-derivitized GO flakes can be easily solution-phase mixed with other organic polymers, which is favorable for the synthesis of graphene-polymer composites.

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Fig. 26  (a) Schematic illustration of multiple interfacial interactions between gelatin and GO, including electrostatic attraction, hydrogen bond and hydrophobic interaction. (Reprinted with permission from Ref. [244]; Copyright (2015) Elsevier). (b) TEM image showing the binding of SWNTs with rGO fibers and (c) the schematic diagram of hydrogen bonding interactions between them. (Reprinted with permission from Ref. [156]; Copyright (2012) Nature Publishing Group). (d), (e) SEM images of PSS-G-coated PAH-functionalized polystyrene beads and the sample after the treatment of toluene. (f) Longitudinal section and (g) cross-section of PSS-G/PVA freeze-dried monolith. (Reprinted with permission from Ref. [250]; Copyright (2009) Wiley). (h) Schematic illustration of the steps used to prepare the rGO/Nylon-6 yarns. SEM image of (i) knotted rGO/Nylon-6 yarns and (j) two-ply rGO/Nylon-6 yarns. (Reprinted with permission from Ref. [251]; Copyright (2013) Wiley-VCH). (k) Schematic illustrations of the conformal and nonconformal morphologies of GO coatings on microfiltration (MF) and reverse osmosis (RO) membranes, to explain the factors determining the adhesion of graphene films and the substrate. (Reprinted with permission from Ref. [252]; Copyright (2018) American Chemical Society).

At the same time, the presence of polymer in the solution prevents the agglomeration of GO sheets, facilitating its coating on GO sheets and individual dispersion in solvents.

Apart from the chemical bonding interaction, electrostatic attraction is one of the main interactions between GO and polymers. GO/rGO sheets can be integrated with other functional polymer materials at a molecular scale to create multifunctional graphene-based composites. The formation of electrostatic attraction arises from the negatively charged carboxyl groups on GO and a positively charged polycation solution, such as poly(allylamine hydrochloride) (PAH), PAN, PEI, PSS, etc. For example, higher-order 3D architectures such as hollow micrometer-size spheres (Fig. 26d and 26e) or sponge-like macroporous scaffolds (Figs. 26f and 26g) can be designed for graphene-polymer nanocomposites using the stable aqueous suspension of GO/PSS. Besides, Yun et al. wrapped GO on nylon-6 via electrostatic self-assembly with bovine serum albumin (BSA). BSA molecules were grafted via a dipping process which induced positive charges on the surface of the nylon-6 yarn, facilitating the subsequent GO coating via electrostatic self-assembly (Figs. 26h–26j). Therefore, BSA serves as a universal adhesive for enhancing the adsorption of GO sheets onto the textile, thus leading to GO easily attached to textiles which provides a very promising platform for wearable electronic devices applications.

In addition, van der Waals force should not be ignored especially in the physically adhesive GO coating materials, for it makes the interaction between GO and substrate much stronger due to the large contact area of the interface induced at a nanoscale regime. For monolayer graphene, the adhesion energy is measured to be ~0.45 J/m² while coating on a silicon oxide substrate. Therefore, it is predicted that large contact areas between GO and the substrate benefit the strong adhesion of these two individual components. Hu et al. explained the interfacial behavior as the competition between the binding energy of GO and adhesion energy of GO-substrate, which determines the equilibrium morphology of the membranes (Fig. 26k). High deposition pressure was employed to make conformal morphology, which facilitates the strong adhesion because of the strong van der Waals interaction resulting from the large contact areas.

Simply coating or wrapping of GO/rGO on the second component is a facial, scalable and economic approach for pre-
paring the composites. Numerous graphene-based composite materials such as reduced graphene oxide wrapped plant fiber sponges (PFS@rGO),
Nafion/GO film,
cotton fabric,
goat and GO/acrylic yarns have been reported. GO/rGO provides the conductive pathway for the incorporated composite materials. Conventional preparation of PANI/graphene composite used for electrode materials focuses on the uniform structure of the composites, and great attention has been paid to enhancing the electrical transport. However, a uniform structure cannot guarantee the diffusion of the electrolyte which is the key factor determining the high rate performance. Wu et al. deposited PANI outside the graphene monolith, forming a phase-separated PANI/graphene structure. It is distinct from the uniform-dispersion or LbL structure reported. In this structure, PANI was electrochemically deposited onto the graphene matrix using cyclic voltammetry (CV) technique. The phase-separated structure avoids blocking of channels for electrolyte diffusion, thus facilitating the diffusion of electrolyte and improving the performance of PANI/graphene composite at large current density.

7.2 Growth of Metal, Metal Oxide/Hydroxide

The composite materials show enhanced electrochemical or catalytic performance compared to the original system by taking advantage of the additional properties of graphene. A variety of graphene-metal, metal oxide or hydroxide materials have been employed for preparing GO-based composites, such as Au,
ZnO,
TiO$_2$,
g-C$_3$N$_4$,
γ-Fe$_2$O$_3$, Fe$_3$O$_4$, CuS (Fig. 27h), etc. Tuning the surface chemistry of GO or rGO sheets offers a way to control the growth and morphology of metal or metal oxides. GO sheets are able to capture the functional nanomaterials with multiple adhesion sites by various interactions due to their abundant surface chemistry, such as physisorption, van der Waals, hydrophobic and π-π interactions.

A universal strategy was developed to incorporate functional nanomaterials into porous graphene structures to form 3D porous graphene hybrid architectures, such as Au-NPs, TiO$_2$-NPs, MnO$_2$ nanowires (MnO$_2$-NWs), InN-NWs, Zn$_2$SnO$_4$-NWs, polyaniline nanofibers and CNTs (Fig. 27a). The functional porous GHAs were fabricated by solution-based approaches based on mixing assisted with ultrasonication, hydrothermal, and freeze-drying process. All these nanomaterials can be well dispersed in GO suspensions and form stable mixed suspensions after ultrasonication treatment because the hydrophobic basal plane and hydrophilic edges of GO sheets make it act as a surfactant. The hydrothermal process initiates the reduction of GO sheets, as well as embeds the additive nanomaterials in hydrogels. SEM images suggest the efficient embedding of Au-NPs in the rGO walls of its continuously cross-linked 3D network, as well as other functional nanomaterials (Figs. 27b–27e). In addition, electrochemical treatment is an efficient approach to the reduction of GO, as well as incorporation of noble metal nanoparticles and metal oxide. Chen et al. fabricated 3D porous graphene-based composite materials by electrochemical reduction of GO dispersion, followed by electrochemical treatment again to
deposit the second component (Pt and ZnO nanoparticles, Figs. 27f and 27g).\textsuperscript{[258]}

The interaction between GO and nanoparticles can be further enhanced by adding a surfactant in the solution. It is reported that glucose is able to serve as the linker, promoting the \textit{in situ} growth of TiO\textsubscript{2} nanocrystals on the surface of graphene aerogel owing to its rich hydroxyl groups.\textsuperscript{[259]} TiO\textsubscript{2} nanocrystals are highly dispersed on the graphene aerogel surface, affording the high surface area for active sites and frameworks for efficient carrier transport pathways. At the same time, glucose molecules facilitate the growth of nanosize TiO\textsubscript{2} seeds with exposed (001) facets, imparting these composite materials excellent photocatalytic activities and outstanding Li-storage performance. Apart from TiO\textsubscript{2}, two-dimensional g-C\textsubscript{3}N\textsubscript{4} is proven to be an efficient photocatalyst. GO sheets can inhibit the aggregation or stacking of subunits, thus exposing more active sites for catalytic reactions. Moreover, the electron-hole recombination of g-C\textsubscript{3}N\textsubscript{4} is inhibited by the good electrical conductivity of GO, and the visible-light utilization is improved via the light multi-reflection across the 3D-connected porous open-framework.\textsuperscript{[261]}

Moreover, the cationic polymers connected with GO sheets could promote the growth of inorganic nanoparticles such as metal and metal oxide particles on the surface or in the bulk of the composites without aggregation. For example, polyethyleneimine (PEI) is a kind of cationic polymer with high amine density, which can be easily physically adsorbed onto the GO surface (hydrogen bonding, electrostatic interaction) and chemically bonded with the functional oxygen-containing groups of GO sheets. These physical and chemical interactions play key roles in controlling the assembly of GO with polymer, as is mentioned above. Besides, the free amine groups of PEI cationic polymer act as mineralization inducers, offering a way to catalyze the nucleation and growth of a variety of inorganic nanoparticles such as metal and metal oxide nanoparticles.\textsuperscript{[249]} The obtained inorganic nanoparticles can be well distributed on the surface of the composites. Therefore, the cationic groups of polymers have played the following critical roles during the synthesis of the composites: (1) assembling GO via physical and chemical interactions, (2) initiating chemical reduction of GO sheets, and (3) inducing the mineralization of nanoparticles.

8. CONCLUSIONS AND OUTLOOK

In recent years, huge progress was registered in terms of the study of GO 2D macromolecules, including experimental observation and theoretical description of the chemical structure and physical properties of GO. The relative molecular mass of GO macromolecules is several orders of magnitude higher than that of 1D polymers. For instance, the relative molecular mass of GO single-layer sheet with a size of 100 μm can reach \textit{10}^{13}, while that of a 1D polymer usually located at \textit{10}^{13}–\textit{10}^{16}. The conformation of 1D polymers includes stretching, fold, random and spiral chains due to its linear intrinsic property, while the conformation of 2D GO polymer varies from anisotropic 1D folding to isotropic 3D crumpling phases (Table 1). Both 1D polymers and 2D GO macromolecules can be used for the assembly of macroscopic materials, such as fibers, films, foams, fabrics and aerogels. However, 1D polymer materials are usually assembled by entanglement of polymer chains, which is different from the assembly process of 2D GO macromolecules via the stacking of GO layers.

The easy dispersion of GO in polar solvents makes it possible for its macro-assembly and modification. The amphiphilicity of GO can be tuned by domain size, pH, and cation introduction. The formation of a uniform nematic phase of GO molecule clusters enlightens the exploitation of the macroscopic ordering graphene materials. Probing and quantifying the rheology behavior of GO sheets is also crucial to guiding their assembly. In terms of GO molecular functionalization, heteroatom chemical doping and surface modification with small molecules and polymer branches are promoted by reconstructing the sp\textsuperscript{2}-bonded carbon atoms and tailoring the surface chemistry interaction, respectively.

Furthermore, graphene-based materials have exhibited outstanding mechanical, optical, thermal, magnetic and electronic properties, harvesting great interest of scientific community and huge potential for wide-spread industrial applications. The fundamental parameters between the assembly and mechanical/transport properties have been proposed, including crystalline graphitic domain size, defect-free engineering, alignment of graphene sheet and compactness of graphene layers, to further improve mechanical, electrical and thermal transport properties of graphene-based materials.

Table 1 The properties of 2D GO macromolecule and 1D polymer.

| 2D GO macromolecule | 1D polymer |
|---------------------|------------|
| **Structure**       |            |
|                     |            |
| **Relative Molecular Mass** |          |
| \textit{10}^{6}–\textit{10}^{11} (Size: 1–100 μm) | \textit{10}^{6}–\textit{10}^{9} |
| **Conformation**    |            |
| Flat, fold, crumple, flat stack, multiple folds, multiple crumples | Stretch, fold, random, spiral |
| **Assembly**        |            |
| Stacking            | Entanglement |

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such as covalent bonding, hydrogen bonding, coordinate bonding, n-n interaction, electrostatic attraction, and van der Waals force.

Generally, we still need a deeper understanding of GO macro-molecules, from single-molecule behavior, cluster interactions, macro-assembly to their applications. Despite that huge achievement on GO has been made, there are still numerous challenges on GO macro-molecules, as well as graphene-based materials.

(1) The precise synthesis of graphene oxide with designed properties remains a challenge, including tuning its structure, domain size, C/O ratio, holes and defects, designing the blocks, and multi-level control over morphology from micro to macro.

(2) The study of GO single-molecule behavior in solvent (conformation, stretching, phase separation, dissolution kinetics, thermodynamics, and the interface between liquid and other mediums) is still limited, and efficient observation approaches are waiting to be developed. Subsequently, the system of GO two-dimensional macro-molecular physics remains to be established.

(3) Controllable and designable doping, intercalation, and functionalization have not been realized. For example, covalent functionalization generally compromises the integrity of the sp² network of graphene layers, resulting in defects and loss of the electronic properties. Besides, only specified elements or compounds can be intercalated into graphene layers, such as Au, Co, Na⁺, Li⁺, Ca²⁺, FeCl₂, MoCl₆, AlCl₃, etc. Other intercalation compounds of graphene remain to be explored.

(4) The out-of-plane thermal transport of graphene films limits the practical applications related to a high-efficiency heat dissipation mobile phone. More researches should focus on the out-of-plane thermal transport of graphene films in the future, rather than the in-plane thermal transport.

Up to now, graphene-based materials have gained huge achievements since its discovery in 2004, and shown specific properties and superior performance. They have already shown promising applications in catalysis, energy storage, mechanical devices, chemical sensors, gas/ion/dye/wave absorption, solar-thermal energy conversion, solar-electron energy conversion, electronics, photonics, etc. In the light of the huge progress we have registered, there is still a long way to graphene-dominated “carbon age”. Therefore, disruptive and irreplaceable applications based on graphene materials should be fully explored. A predictable direction is constructing graphene fibers with super-strong, stiff, tough, lightweight, flexible and electrical transport performance. Since carbon fibers have already been widely used in industry, the industrialization of graphene fibers should be promoted to meet the demands in practical applications. Another direction is developing carbon-based nano-electronics with dominant advantages compared with the current semiconductors in “silicon age”. We expect that graphene-based electronics and photonics will usher in a wave of a new round of development very soon, once the interface between graphene and target materials reaches atomic level, based on CVD-graphene membrane with uniform thickness by new technology or controllable macro-assembled graphene nano-films.

We believe carbon materials represented by graphene are unveiling the dawn of a new era in the 21st century.

**BIOGRAPHY**

Chao Gao received his Ph.D. degree from Shanghai Jiao Tong University (SJTU) in 2001. He was appointed as an Associate Professor at SJTU in 2002. He did postdoctoral research at the University of Sussex with Prof. Sir Harry Kroto and AvH research at the Bayreuth University with Prof. Axel H. E. Müller. He joined the Department of Polymer Science and Engineering, Zhejiang University, in 2008 and was promoted as a Qiushi Distinguished Professor in 2014. He leads a Nanopolymer group working on graphene chemistry, macroscopic assembly, and energy storage.

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