Controlled gelation of graphene towards unprecedented superstructures

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Abstract

Graphene exhibits a range of exceptional physical properties and holds great promise for development of novel bulk materials for widespread applications. Properly engineering of assembled structures of graphene at multiple length scales is essential to realize its full potential in bulk. In this Concept article, we highlight the unique colloidal and gelation behavior of a commonly used precursor for graphene, graphene oxide (GO), and discuss how the colloidal chemistry of GO and reduced GO can enable new scalable and cost-effective approaches to construct graphene-based soft superstructures with excellent properties.

1. Introduction

Graphene is a two-dimensional (2D) carbon allotrope, which possesses a long list of outstanding features such as high thermal conductivity and charge carrier mobility, superior strength and flexibility, and an extremely high aspect ratio.\(^1\) Graphene is not only attractive for electronic and photonic devices based on single or few-layer sheets, but also highly promising as a molecular building block for constructing bulk materials for a wide range of applications, such as catalysis, energy storage, sensors and filtration.\(^2, 3\) Among various precursors for graphene-based bulk materials, graphene oxide (GO), is one of the most studied and holds great potential for mass production and processing using cost-effective solution processing techniques.\(^2, 4\)

In this Concept article, we will first highlight the unique chemical structure of GO and how it is related to its colloidal behavior and gelation properties. We will then demonstrate how the colloidal behavior of GO and chemically reduced GO can enable simple and potentially
scalable techniques for fabrication of graphene-based soft superstructures with unprecedented properties, mainly using the materials developed in our group as example. The key aim of this article is to emphasize the unique enabling role and enormous potential of colloidal chemistry in the development of graphene-based bulk materials.

2. Unique colloidal and gelation behaviors of GO

GO can be considered as a partially oxidized version of graphene, which can be fabricated via chemical oxidation, expansion and exfoliation of graphite.\textsuperscript{[5]} The $\pi$-conjugated plane of graphene is largely disrupted during this oxidation process and the resultant structure of GO consists of highly oxidized domains with epoxides and hydroxyl groups residing at the basal plane, while ketones, lactones and carboxyl groups dominate the edges and defect sites (Figure 1).\textsuperscript{[6]} Although these oxygen-containing groups come at a cost of much lower electronic conductivity, these are what make GO interesting from a materials chemist point of view and are also what enable it as a multifunctional polymer and colloidal particle (Figure 1).\textsuperscript{[6]}
Figure 1. Chemical structure of GO and its multifunctionality.\textsuperscript{[6]} Owing to the unique chemical structure, GO can be viewed as different types of functional molecules. (Figure adapted from [6] with permission)

Due to its hydrophobic crystalline sp\textsuperscript{2}-hybridized domains and hydrophilic amorphous sp\textsuperscript{3}-hybridized domains containing different oxygen functional groups, there are many different ways of describing GO, such as an amphiphile/surfactant, a highly anisotropic colloid, and as a polymer with resemblance to poly(acrylic acid), polyalcohol and 2D random diblock copolymers (Figure 1).\textsuperscript{[6]} As such, GO can be viewed as a multifunctional and highly tunable material for a variety of purposes enabled by its ability to interact with itself or other particles in different ways.

Because of the amphiphilic property, the GO colloid particles can be readily dispersed in a wide variety of organic solvents, especially in water.\textsuperscript{[6-8]} In addition, with elaborate
manipulation of the colloid chemistry during chemical reduction, the reduced GO (rGO) can also maintain good dispersibility.\[7\] Because the dispersibility of the GO/rGO is mainly enabled by the repulsion forces caused by the oxygen functional groups, weakening of the repulsion forces or inducing additional attractions could lead to their assembly of a bulk network.\[9\] For example, reducing a dispersion of GO with a high concentration can lead to its self-gelation, since the high concentration of rGO nanosheets easily forms a percolation network due to their high aspect ratio and their ability to interact through π-π interactions and hydrogen bonding.\[7, 10\] Combining with good dispersibility and controllable gelation, GO/rGO dispersions can be readily processed using cost-effective processing strategies, such as filtration, spinning coating, freeze casting and self-assembly. Various graphene-based bulk materials have been successfully developed, including membranes, foams and fibers.\[11\]

Because the structure of the graphene-based bulk materials obtained through the wet chemistry routes is largely governed by the colloidal interactions, rationally controlling the colloidal behaviors of GO and rGO, such as by controlling their amphiphilic properties, creating liquid crystals, and through shear-thinning, to name a few, can enable new ways for engineering their assembly structure. For example, because of the amphiphilic properties and its 2D structure, GO sheets are able to congregate at the liquid-liquid and liquid-air interfaces to minimize surface tension by forming well-ordered thin films with a layered structure.\[12\] Additionally, the shear thinning behavior of the GO dispersion can improve its ability to flow, which has been used for development of graphene-based inks for 3D printing and blade casting techniques.\[13, 14\] In particular, the colloidal forces plays a very important role in manipulating the nanostructure of graphene-based bulk assemblies. The repulsion forces that are essential to the formation of stable GO/rGO dispersions can also be used to tune the interlayer distance in densely packed
hydrogel membranes.\cite{15, 16} In addition, the unique corrugation behavior that is an intrinsic feature of suspended rGO sheets in solution, can also be employed to prevent restacking in their assembled structure.\cite{17} These unique behaviors have been successfully used to create nanochannels between GO/rGO nanosheets, which allows charge and nutrition transport, crucial for numerous applications for graphene-based bulk materials, ranging from energy storage, biological scaffold to nanofiltration.\cite{18}

Apart from above mentioned examples, the control of colloidal behavior of the GO/rGO has also been widely adapted to engineer the architecture of the graphene-based bulk materials, such as wet-spinning of graphene fibers and emulsion templating of graphene foam.\cite{19, 20} Due to the limited space of this concept article, these examples are not elaborated in detail here. We refer the reader to recent published comprehensive reviews for more detailed discussions on how the microstructure of graphene assemblies can be well controlled by controlling their colloidal interactions (Ref 6, 9 and 12).

### 3. Rational assembly of graphene towards superstructures

Many applications proposed for graphene require assembling of graphene into bulk structures. However, the properties of a bulk assembly is dependent not only on the physical properties of its basic building blocks, but also on how the building blocks are assembled, \textit{i.e.} architecture. Because of ill-engineered architecture, many graphene-based aerogels or hydrogels only show mediocre properties. Properly controlling the architecture of the bulk assemblies from nano- to macro-scale, or superstructures, is the key to harnessing the outstanding properties of individual graphene sheets in a bulk form.

The in-depth understanding of the GO colloidal behavior has enabled various effective techniques to engineer the structure of graphene-based bulk materials. Numerous graphene-
based superstructures have been developed by many research groups in the past years. In this section, we mainly use the superstructures developed by our group to demonstrate how the architecture of graphene assemblies can be rationally controlled by taking advantage of the colloidal forces and its micro-corrugated 2D configuration of GO/rGO.

3.1 Ultralight and superelastic graphene cellular materials

Freeze casting is a commonly used method to fabricate cellular materials with well-defined honeycomb-like structure.[21] However, random GO-based network structure is formed when direct freeze casting of GO dispersion is applied.[22] Our research demonstrated that the well-defined honeycomb-like structures can be fabricated by carefully controlling the intermolecular interactions of GO during the freeze casting process.[22] Given that the intermolecular interaction between GO in the solution largely relies on the surface charge induced by the oxygen functional groups, we have investigated intermolecular interactions by controlling the chemical reduction degree of GO, i.e. the carbon to oxygen (C:O) ratio. The optimal ratio found to be around 1.9. At this ratio, the partially reduced GO sheets contain an optimum surface charge so that they remained mobile during the formation of ice-crystals. Thus, the partially reduced GO sheets are able to congregate at the solid-liquid interfaces, which can be rearranged during further compression from the crystal growth (Figure 2a-d). After removal of the ice via freeze drying, a well-defined graphene-based honeycomb-like cellular structure can be obtained.
Although previous research has suggested that an elastic foam is hard to be fabricated solely based on single-layered graphene, the graphene monolith with a honeycomb-like structure was found to be able to recover from large deformation.\textsuperscript{22, 24} In particular, the graphene foam with density of 5 mg/cm\textsuperscript{3} was able to recover from 80\% compression strain with a speed of >7,000 mm/min, which was much faster than conventional polymer elastomers (Figure 2e).\textsuperscript{16} This is
because the cork-like hierarchical superstructure of the graphene elastomer can maximize the elastic modulus and strength of the bulk structure. Additionally, due to the highly efficient structure, graphene elastomers with a density as low as 0.5 mg/cm$^3$ can be achieved, which is lower than the density of air (1.2 mg/cm$^3$).[22]

The mechanical strength of the graphene elastomer could be further improved via modification of the colloidal behavior of GO by introducing some polymer during the assembly process.[25] The polymer introduced was found to be able to tune the viscoelastic behavior of the GO dispersion, which led to an improved packing structure of the GO sheets in the cell walls.[25] Although very little polymer remained after assembly and dialysis, the resulting graphene-based composite elastomer could be vacuum or air dried while retaining the cork-like structure and elasticity. This is an important feature and different from traditional hydrogels, which are fragile and needs to be either freeze dried or dried under supercritical conditions to avoid collapse of the cell walls due to capillary forces.

Apart from the ice-templated approach, there are many other interesting colloidal techniques have been reported by other groups for synthesis of graphene-based elastomers. For example, when mixing aqueous GO dispersions with oil the amphiphilic GO can self-assemble at the oil-water interface resulting in emulsification. After removal of the liquids by freeze drying, graphene-based cellular elastomer can be fabricated.[19] Barg et al. and Shi et al. have successfully employed this emulsion template strategy to fabricate highly compressible graphene elastomers.[19, 26] Moreover, the graphene elastomer were also fabricated via various techniques to control the colloidal and gelation behavior of GO, such as the 3D printing of GO dispersion with controlled viscoelastic behavior and modified solvothermal reactions of GO in alcohol.[14, 27]
Ultralight graphene elastomers possess a range of fascinating features such as ultralow density, fast recovery rate, high conductivity, and low modulus. Combining these outstanding features, graphene-based elastomers have been explored for widespread applications. For instance, the graphene elastomers showed ultrafast piezoresistive response nearly independent of the frequency, making them useful in applications like soft mechanical sensor systems for artificial skins (Figure 2f). Additionally, because of the ultralow modulus of the graphene elastomer it can respond to very subtle pressures and provide ultrahigh sensitivity. The cellular structure of the graphene elastomer can also be used as a multifunctional scaffold for reinforcing polymers in nanostructured composites. For example, we have demonstrated that N-isopropylacrylamide monomers and cross-linkers can be readily backfilled into the elastomer to induce in-situ polymerization of PNIPAM. Remarkably, this strategy was shown to have neglectable effect on either of the composite components, thus yielding a multifunctional material having both the graphene elastomers electromechanical properties and the PNIPAM stimuli-responsive properties.

3.2 Flow directed gelation of hydrogel membranes

Although graphene-based gel materials are generally fabricated in a form of 3D porous network, graphene-based 2D hydrogel with parallel arranged superstructure can also be prepared by taking advantage of the unique 2D geometry and unique colloidal behavior. Previously, we discovered that rGO sheets can be assembled in a face-to-face manner to form
a layered graphene-based hydrogel membrane by using flow directed assembly (Figure 3a-c). During the vacuum filtration, the 2D rGO sheets are prone to lie down on the filter membrane under a directional flow caused by vacuum suction. Because of the unique colloidal behavior of the rGO, the sol-gel transition occurs only at the liquid-filter interface, which is sharply different from the gelation process in a bulk solution. During this sol-gel
process, the rGO sheets are held together in a nearly parallel manner by means of $\pi-\pi$ stacking of the crystalline hydrophobic regions and hydrogen bonding in the amorphous oxygen rich regions. Nevertheless, the corrugated configuration of the graphene sheets, hydration and electrostatic repulsion forces between hydrated graphene sheets can effectively suppress their restacking. Despite the graphene nanosheets are largely separated, the resultant graphene-based hydrogel exhibited a tensile modulus of several orders of magnitude higher than that of conventional hydrogel materials.\textsuperscript{[15]} This is because the strong graphene sheets are interlocked together in the hydrogel membrane due to its unique corrugated structure and van der Waals forces. Together with the trapped water, the applied load can be effectively distributed throughout the entire structure, leading to excellent mechanical performance.

Our previous research indicated that graphene-based hydrogel membranes can be used as electrodes to fabricate high power density and high gravimetric energy density supercapacitors. This is enabled by the highly open pore structure of the hydrogel membrane, which allows the ease access of the ions to the individual graphene sheet. The resultant hydrogel membrane-based supercapacitor can maintain high capacitance of 156.5 F/g at an ultrahigh charge/discharge rate of 1080 A/g.\textsuperscript{[16]} This result suggests the charging and discharging of the supercapacitor can be done at the millisecond scale.
Figure 3. a) Schematic of the fabrication of graphene-based hydrogel membrane.[16] b) Photograph of graphene-based hydrogel membrane.[26] c) SEM image of the cross-section of a freeze-dried graphene-based hydrogel film.[15] d) Schematic showing the soft chemistry route
to prepared highly dense graphene gel film. e) Photograph of graphene gel film. f) and g) SEM images of the cross-section of the graphene film before and after densification via using soft chemistry route. It can be seen the thickness of the gel film significantly reduced after densification.[29] h) Schematic of the water molecules flowing through a graphene hydrogel film.[29] i) Water fluxes of the graphene hydrogel films prepared at different hydrothermal temperatures.[17] (Figure adapted from [15], [16] [26] and [29] with permission)

Because the microstructure of the graphene hydrogel membranes is governed by various colloidal forces, we have demonstrated that tuning the colloidal forces through a capillary compression process can be used to make denser hydrogel membranes for high-energy-density supercapacitors. By first exchanging the solvent and then evaporating the (volatile) water through vacuum evaporation a graphene gel solvated by a non-volatile liquid was obtained (Figure 3d).[29] The capillary pressure arising from the evaporating solvents resulted in an irreversible densification of the gel and by changing the volatile/non-volatile mixing ratios, densities ranging from 0.13 g/cm$^3$ to 1.33 g/cm$^3$ could be obtained, with completely dry membranes having a density of 1.49 g/cm$^3$(Figure 3e-g) Although similar in density, due to the fact that graphene flakes remained solvated by the non-volatile solvent, the pores remained sufficiently open and the graphene gel with a density of 1.33 g/cm$^3$ showed excellent ion transport property. As such, the supercapacitor based on the resulting gel film exhibited high volumetric energy density of 60 Wh/L, which was far higher than commercially commercialized supercapacitors (5~8 Wh/L) and comparable to that of lead-acid batteries (50~90 Wh/L).[27]

Apart from the supercapacitor, the graphene hydrogel membranes with highly ordered nanochannels are promising for nanofiltration application. Given the graphene sheets are arranged in a highly ordered manner and yet largely separated, the resultant graphene hydrogel
membrane contains a large amount of interconnected nanochannels with tunable pore sizes (Figure 3h). Thus, the graphene hydrogel film can be used as nanofiltration membrane to separate nanoparticles with different sizes. Note that the controllable pore size is particular important for nanofiltration application. We thus have developed a simple hydrothermal method to control of the corrugation degree of graphene-based building block and the nanochannel size of the assembled graphene-based hydrogel membrane.[17] Through control of the hydrothermal temperature from 90 to 180 °C, we successfully fabricated graphene-based hydrogel membrane with pore size range from 3~15 nm (Figure 3i).[19] The development of graphene-based nanofiltration via control of the corrugation has successfully enabled a new promising application for graphene-based bulk materials.

To further enable controllable nanochannel size and chemistry in graphene-based hydrogel membranes, graphene is co-filtrated with functional polymer to form a smart hydrogel membrane.[30] Here the rGO functions as the gelator and pore forming agent and dependent on the polymer used, different functionalities can be introduced to the membrane. For example, we used the widely-studied thermally-responsive polymer poly-(N-isopropylacrylamide) or PNIPAM, to introduce a thermal stimuli-response, which resulted in tunable pore-size of the hybrid membrane, dependent on the reversible globule to coil configuration of the PNIPAM.[30] Here, rGO’s unique ability to interact with polymers, as well as its 2D structure to form a coherent agglomeration network, was used to enable an efficient and even polymer distribution through-out the gel. This is a very fast an easy way of screening composite gels with limited loss of functionality from neither the graphene nor the polymer. As such, it was used to fabricate many different stimuli-responsive smart membranes capable of pH-, glucose- and biomolecule (DNA) sensing.[30]
Taking advantage of the dense structure, the extremely high surface area provided by the corrugated sheets and the tunable stacking distance, these unique membranes were shown to be suitable for a diverse range of applications including supercapacitors with high power and energy density, molecular sensor applications, nanofiltration, bone regeneration, and can be used as a unique platform for nanoionics research. These examples illustrate nicely how the unique materials properties of GO/rGO and its colloidal/gelation behavior can be used to tune the gel structure for many different applications.

**Perspective**

In the past few years, we have witnessed fast progress in development of graphene-based superstructures through control of the gelation/colloidal behavior of GO and its derivatives. Apart from the examples mentioned in the above sections, a large number of superstructures have been successfully developed, such as controlling the liquid crystal behavior of the GO to enable ultrastrong graphene fibers, and controlled colloidal behavior of GO to enable 3D printing. These examples have demonstrated that structural control and mastering of the colloidal behavior plays a key role in achieving superstructured gels with outstanding properties.

There is no doubt that control of colloidal/gelation behavior of the GO has become a very effective method to synthesize graphene-based bulk materials. With further in-depth understanding of the colloidal behavior of GO and its composite materials, it is safe to predict the more exciting graphene-based superstructures are to be discovered. Because these fabrications are based on scalable wet chemistry processes, these materials hold great potential for large-scale and cost-effective industrial production. We expect that some of these graphene-
based superstructures will lay the foundation for commercially available graphene based products and that they will be available in the near future.

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References

