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Cite this article as:

Yun Xia-Wei, Tang Bo, Xiong Zhi-Yuan, Wang Xiao-Gong. Understanding Self-assembly, Colloidal Behavior and Rheological Properties of Graphene Derivatives for High-performance Supercapacitor Fabrication[J]. *Chinese J. Polym. Sci.*, 2020, 38(5): 423-434. doi: 10.1007/s10118-020-2411-0

View online: <https://doi.org/10.1007/s10118-020-2411-0>

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Understanding Self-assembly, Colloidal Behavior and Rheological Properties of Graphene Derivatives for High-performance Supercapacitor Fabrication

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Abstract Graphene derivatives, such as graphene oxide (GO) and reduced graphene oxide (RGO), have been widely used as promising two-dimensional nanoscale building blocks due to their fascinating properties, cost-effective production, and good processability. Understanding the intrinsic self-assembling, colloidal, and rheological features of graphene derivatives is of critical importance to establish the formation-structure-property relationship of graphene-based materials. This article reviews recent progresses in our studies of these interesting properties of graphene derivatives for developing high performance supercapacitors. The content is organized to include characteristics of the dispersions of graphene derivatives, self-assembly of nanosheets from liquid medium, colloidal behavior, rheological properties of the dispersions, processing methods based on the properties, and performance of the fabricated supercapacitors. GO and RGO nanosheets are proved to form different types of assembled structures with unique morphologies, such as ultrathin layer-by-layer films, porous aggregates, and nanoscrolls. The unique rheological properties of GO dispersions and hydrogels, feasible for both the traditional wet-processing and newly-developed technology like three-dimensional printing, are highlighted for their potential in structural manipulation and scalable fabrication of graphene-based devices. The research devoted to up-grading the performance of supercapacitors is presented in some details, which could be applicable for fabricating other graphene-based energy storage devices. Some challenges and perspectives in our point of view are given in the last part of this feature article.

Keywords Graphene derivatives; Self-assembly; Colloids; Rheology; Processing; Supercapacitor

Citation: Yun, X. W.; Tang, B.; Xiong, Z. Y.; Wang, X. G. Understanding self-assembly, colloidal behavior and rheological properties of graphene derivatives for high-performance supercapacitor fabrication. *Chinese J. Polym. Sci.* 2020, 38, 423–434.

INTRODUCTION

Graphene, a monolayer of sp^2 -bonded carbon atoms with the honeycomb lattice, has attracted tremendous interest during the last two decades due to its unique mechanical, electrical, and thermal properties.^[1,2] Graphene derivatives, including graphene oxide (GO), reduced graphene oxide (RGO), and others, have been widely explored for diverse applications due to their cost-effective and scalable production.^[3–17] GO is an oxidative derivative of graphene and also a precursor for the preparation of other graphene-based materials such as RGO.^[3] Preparation of GO by exfoliation of graphite through chemical oxidation can be tracked back to the 19th century and several innovative methods have been developed in recent years.^[4] In the preparation, large amounts of oxygen functional groups are incorporated on the surface and edges of the nanosheets, which endows GO with amphiphilic properties. Through reduct-

ion, the conjugated sp^2 -carbon lattice can be partially recovered to form RGO.^[5,6] Thus-prepared graphene, also termed chemically converted graphene (CCG), possesses unique electrical, mechanical, and thermal properties.^[7,8] Different types of functional groups can be introduced in GO and RGO to form various types of graphene derivatives. Distinct from the graphene, which can be hardly dispersed in liquid, graphene derivatives with certain amounts of functional groups show good dispersion capability in water and some organic solvents. This unique advantage makes some traditional wet-processing technologies as well as newly-developed technologies feasible for the scalable fabrication of graphene-based materials for device applications.^[7,9,10] The past two decades have witnessed a lasting research boom of fabricating macroscopic graphene assemblies such as films, fibres, and aerogels, from GO dispersions, which demonstrates huge development potential in practical applications.^[11–17] Explorations of their unique functions and applications in a broad spectrum of fields, such as composite, separation, sensor, actuator, and energy storage/conversion, have been well documented in the literature.^[18–27]

One ultimate goal of these research endeavours is to translate the extraordinary physical properties of nanoscale GO or CCG sheets into performance of macroscopic graphene as-

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Special Issue: Polymers for Energy and Electronic Devices

Received December 20, 2019; Accepted February 24, 2020; Published online March 26, 2020

semblies through judicious control of the assembled structures. For graphene films and fibres, high orientation and strong interactions between the nanosheets are favorable to rendering high mechanical strength and modulus.^[12,28,29] On the other hand, for energy devices, such as supercapacitors, porous structures and well-isolated graphene sheets are desired to facilitate ion transport and absorption.^[30–34] In this regard, the controlled assembly of GO or CCG sheets to form desirable structure is crucial to exploit the full potential of this unique type of material for different applications. Specifically, the dispersion of the two-dimensional (2D) colloids can be well exploited for controlled assembly through different processing methods. The intrinsic rheological properties of GO dispersions and hydrogels, which are beneficial to industrial processing and up-scale applications of graphene materials, are of particular interest.

Although there are many breakthroughs and interesting developments in this area, the limited space of this mini-review could not include them in the full scale. Therefore, this article will only concentrate on recent progresses in our effort to understand the intriguing properties of graphene derivatives for supercapacitor fabrication. The main contents of this article are illustrated in Fig. 1, which include the self-assembly and processing as the two parts. Under the title of self-assembling, several methods developed to obtain macroscopic assemblies from graphene derivatives are presented. One way of the controlled assembly of RGO is through the ionic interaction between the nanosheets and a polymer to

obtain macroscopic assemblies and tune the morphology of the assemblies. Among them, porous GO powders have been prepared through controlled coagulation by using polyethyleneimine with positive charges as a coagulant.^[11] The RGO/polyelectrolyte multilayer films have been fabricated *via* layer-by-layer (LbL) self-assembly.^[35,36] One interesting property of GO sheets is that GO nanoscrolls can be formed in dispersions through the solvent-induced self-assembly.^[37–39] On the other hand, the processing of GO dispersion and hydrogel is based on the rheological features. We found that the GO hydrogels formed from dispersions have unique rheological properties such as strong shear-thinning and ultrafast viscosity recovery.^[40,41] These rheological properties are suitable for both traditional and newly-developed processing technologies to achieve the structural manipulation and scalable fabrication of bulk GO assemblies. Based on the rheological properties of GO hydrogels, mechanically tough porous graphene films have been prepared by blade-casting processing.^[41] The obtained wet porous films were used directly to afford supercapacitor electrodes,^[40] and the freeze-dried ones were found to be suitable for laser-carving to fabricate interdigital micro-supercapacitor electrodes.^[42] Based on these rheological properties, GO dispersions were proved to be an ideal material for printing and spray processing. Two typical cases are demonstrated, *i.e.* three-dimensional (3D) printing with highly concentrated GO hydrogel^[43] and spray printing of GO/polyaniline composite hydrogel.^[44] These contents are presented in the following sections in detail.

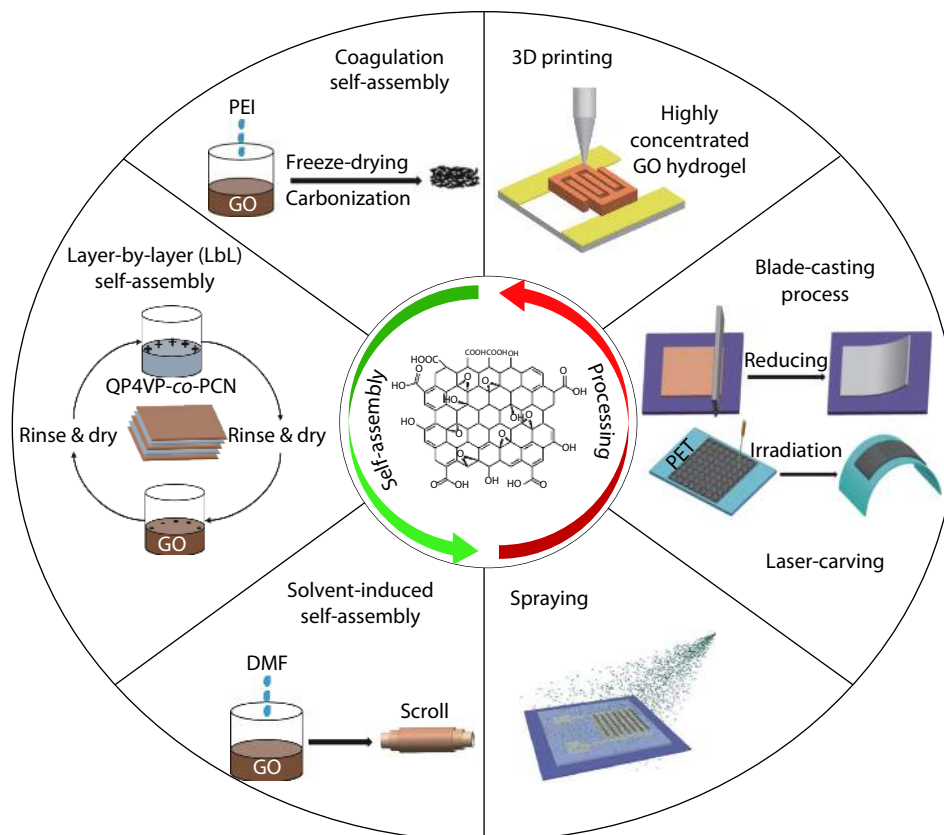


Fig. 1 Illustration of the strategy and methodologies used to fabricate high-performance supercapacitors from graphene derivatives.

DISPERSION OF GRAPHENE DERIVATIVES

Graphene derivatives possess complex chemical structures and different compositions depending on the preparation methods and conditions. According to the well-accepted Lerf-Klinowski model,^[45] GO nanosheets consist of both non-polar aromatic domains and oxygenated polar domains, such as epoxy groups and hydroxyl groups on the basal plane, and carboxyl groups at the edge. The aromatic domains preserved from pristine graphite bring the attractive van der Waals interaction as well as π - π stacking between GO sheets.^[46] When GO nanosheets are dispersed in a liquid medium, other kinds of interactions exist in the colloidal system, such as solvation, electrostatic interaction, hydrogen bonding, and lyophilic effect.^[46–48] The nature of the solvation depends on the polarity match between GO and solvent.^[49,50] The electrostatic interaction is primarily ascribed to ionized groups such as carboxyl groups. After reduction reaction, the conjugated sp^2 -carbon lattice can be partially recovered to form RGO, where the π - π interaction and hydrophobicity are enhanced. Various functional groups can be introduced through chemical reactions to form other types of graphene derivatives. On the other hand, the oxygen functional groups on the basal plane and at the edge are not thermodynamically stable and could change during thermal or chemical treatment.^[7] The complex interplay between these interactions and the variations of chemical compositions with conditions determine the morphology of a single nanosheet in dispersion, the stability of a dispersion, and its rheological properties, and consequently control the structure of the bulk assemblies formed from the dispersion.^[7,47,49]

Such structural complexity and variability would certainly bring difficulty in understanding their colloidal behavior, while in turn give rise to great opportunity to tune the colloidal interactions for controlled assembly and processing. Previous works have revealed many intriguing facets of GO as a typical graphene derivative, such as nanoparticle, surfactant, amphiphilic substance, and polyelectrolyte, which are unique and exploitable with regard to the advancement of controlled assembly.^[50] As will be presented in the following sections, a piece of GO nanosheet can behave as a 2D polyelectrolyte and the electrostatic attraction can guide the assembly of GO with traditional 1D polyelectrolyte. The obtained assemblies show the face-to-edge packing, which facilitates the formation of the macroporous structures.^[11] GO also can be regarded as a 2D amphiphilic substance. A piece of GO nanosheet could adjust its morphology when exposed to different types of dispersion medium. GO nanosheets then transform into GO nanoscrolls induced by a suitable dispersion medium.^[37–39] Due to the ultrahigh aspect ratio of 2D GO nanosheets and the strong interaction with the dispersion medium, GO dispersions can show unique rheological properties distinct from other conventional colloidal dispersions.^[40,41] These unique features of GO and other graphene derivatives result in diverse self-assembling, colloidal, and rheological properties, which can be exploited to achieve controlled assembly and processing for real-world applications. To reach this goal, it is extremely important to understand how the 2D morphology and composition of the nanosheets can affect these unique properties of their dispersions and the structures of assemblies.

SELF-ASSEMBLY OF NANOSHEETS

Layer-by-layer (LbL) Assembly

The multilayer films of RGO and an azo polyelectrolyte have been obtained via electrostatic LbL self-assembly and tested for the application as a supercapacitor electrode.^[35] The azo polyelectrolyte (QP4VP-co-PCN) with the chemical structure shown in Fig. 2(a) was synthesized by radical polymerization, post-polymerization azo coupling reaction, and quaternization. QP4VP-co-PCN was used as the cationic component, and the LbL films were prepared through alternately dipping a substrate in the solutions of cationic azo polyelectrolyte and the dispersion of negatively-charged RGO nanosheets. The linear build-up of LbL bilayers with dipping cycles was confirmed by UV-Vis spectroscopy. With increasing numbers of the bilayers, the optical transparent multilayer films become darker due to the absorption of azo chromophores and graphene nanosheets (Fig. 2b). The LbL multilayer films of graphene/QP4VP-co-PCN were used as supercapacitor electrodes. Their electrochemical properties were characterized by cyclic voltammetry (CV) curves (Figs. 2c–2e). The gravimetric specific capacitance (C_g) in Na_2SO_4 solution was measured to be 71 F/g under the scan rate of 10 mV/s. The C_g reached 173 F/g for LbL film with 9 bilayers as measured in 1.0 mol/L H_2SO_4 under the scan rate of 50 mV/s, compared with 49 F/g in 1.0 mol/L Na_2SO_4 under the same conditions. This work proves that the film of RGO/polyelectrolyte can be feasibly fabricated by LbL deposition and the film shows the potential for applications in supercapacitors.

The multilayer films with the significantly improved stability were fabricated by electrostatic LbL deposition of a polystyrene-based diazonium salt (PSDAS) with sulfonated reduced graphene oxide (SRGO), and UV light irradiation after the assembly (Fig. 3a).^[36] The films were also explored to be applied in electric double layer capacitors (EDLCs). Herein, polystyrene with the narrow molecular weight distribution was synthesized by atom transfer radical polymerization. PSDAS was prepared through nitration, reduction, and diazotization reactions and used as the cationic polyelectrolyte. Negatively charged SRGO was obtained from GO through a three-step procedure, *i.e.*, pre-reduced with $NaBH_4$, modified with diazonium salt of sulfanilic acid, and further reduced with hydrazine. As shown in Fig. 3(a), the diazonium salt groups on PSDAS can undergo the cross-linking reaction with sulfonate groups on the graphene surface. The multilayer films with the different numbers of bilayers were obtained as verified by UV-Vis spectra (Fig. 3b). C_g of the cross-linked films with 9 bilayers was measured to be 150.4 F/g in 1.0 mol/L Na_2SO_4 under the scan rate of 10 mV/s. With the scan rate increased to 1000 mV/s, C_g decreased to 75 F/g. Due to the cross-linked structure, this electrode exhibited superior cyclic stability with a 97% capacitance retention even after 1.0×10^4 charge-discharge cycles. The photo-cross-linkable multilayer films prepared from the electrostatic LbL self-assembly can be used as promising materials for supercapacitor electrodes.

Coagulation Assembly for Macroporous Network

According to the classic Deryagin-Landau-Verwey-Overbeek (DLVO) theory, ion strength, pH, and other factors can affect the colloidal stability.^[48] Under a typical condition, GO dispersion is a stable colloidal system with negative charges from a large number of ionizable groups on the nanosheets and the electric

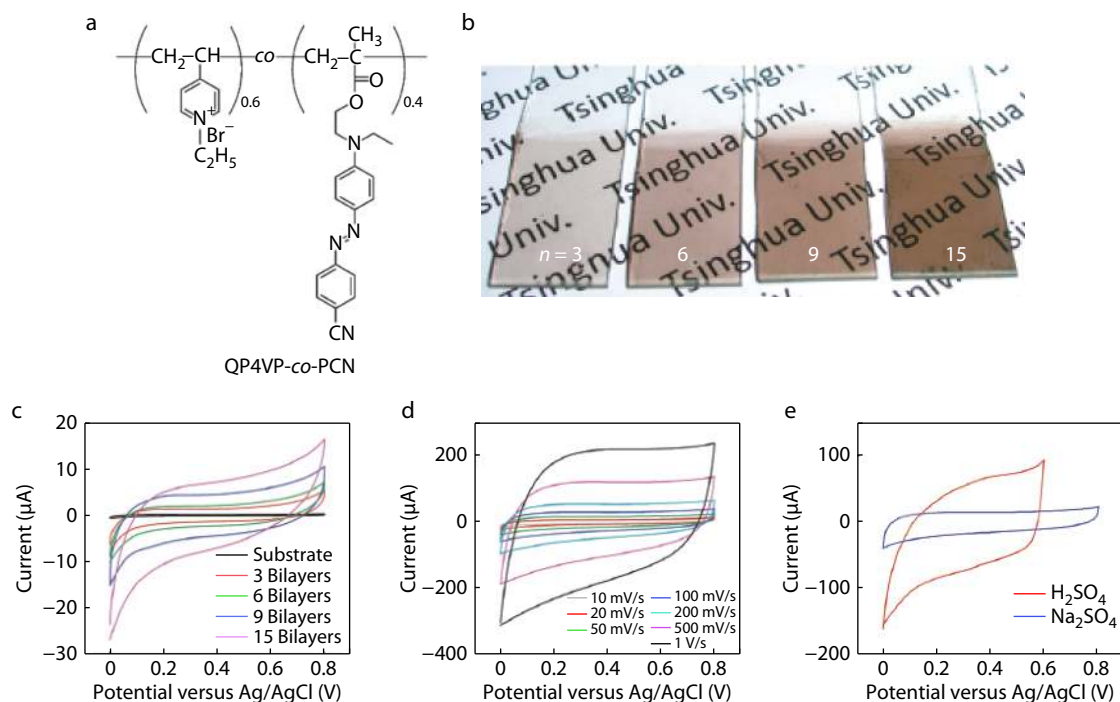


Fig. 2 (a) The structure of the cationic azopolyelectrolyte (QP4VP-co-PCN); (b) Photographic image of the LbL thin films with 3, 6, 9, and 15 bilayers; (c) CV curves of graphene/QP4VP-co-PCN LbL multilayer films with the different numbers of bilayers; (d) CV curves of graphene/QP4VP-co-PCN LbL films with 9 layers at different scan rates; (e) CV curves of graphene/QP4VP-co-PCN LbL films with 9 layers in H₂SO₄ (1.0 mol/L) and Na₂SO₄ (1.0 mol/L) solutions, respectively. (Reprinted with permission from Ref. [35]; Copyright (2011) American Chemical Society).

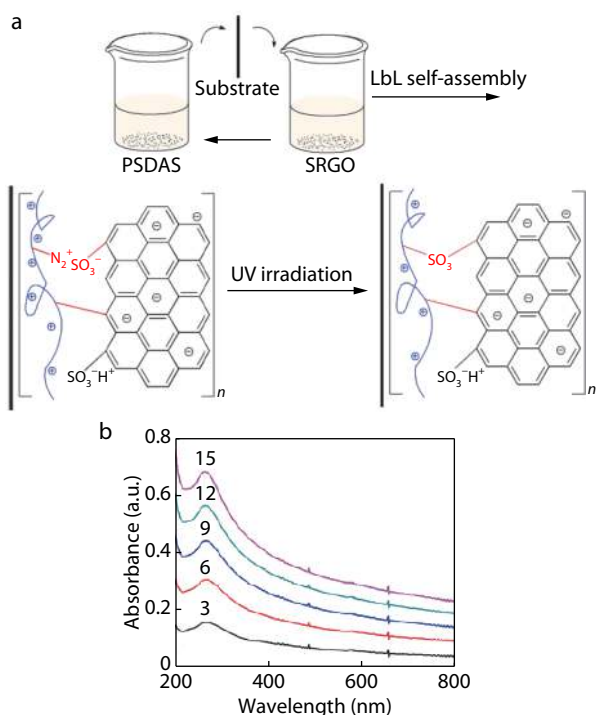


Fig. 3 (a) Multilayer films fabricated via layer-by-layer deposition and post-preparation cross-linking under UV irradiation; (b) UV-Vis spectra of SRGO/PSDAS multilayer films with different numbers of bilayers. (Reprinted with permission from Ref. [36]; Copyright (2014) American Chemical Society).

double layers. The introduction of electrolytes can disrupt the stable state of a GO colloidal dispersion and result in agglomeration of GO nanosheets to form precipitate.^[7] In general, graphene mainly adopts a face-to-face stacking way in the flocs caused by small electrolyte ions.^[7] We found that when a polyelectrolyte (polyethyleneimine, PEI) was used as the coagulant, the stacked manner of the nanosheets could be adjusted to achieve the face-to-edge style to form the 3D macroporous graphene network.^[11] The obtained 3D macroporous graphene network is suitable to be applied in supercapacitors because 3D interconnected macropores facilitate the transport of electrolyte ions to the surface of graphene nanosheets.

Fig. 4(a) shows the way of obtaining the 3D macroporous graphene network through a self-assembled coagulation using PEI as the coagulant. For the obtained carbonized GO coagulation assemblies (CGCA), its nitrogen adsorption-desorption isotherm indicates that almost no micropores and small mesopores exist in CGCA but plenty of large mesopores and macropores. The scanning electron microscopy (SEM) images further verify the 3D closely packed and interconnected macroporous morphology, and the pore sizes range from hundreds of nanometers to several micrometers. The electrochemical performance of the CGCA electrode is shown in Figs. 4(b) and 4(c). The CGCA electrode shows a long cyclic life of 98% capacitance retention after 1000 cycles at 10 A/g. The galvanostatic charge-discharge (GCD) curves of the CGCA electrode exhibit a nonlinear and asymmetric profile (Fig. 4b), which could be attributed to the pseudo-faradaic processes involving the surface nitrogen and oxygen-containing functional groups. The surface areal specific capacitance of the

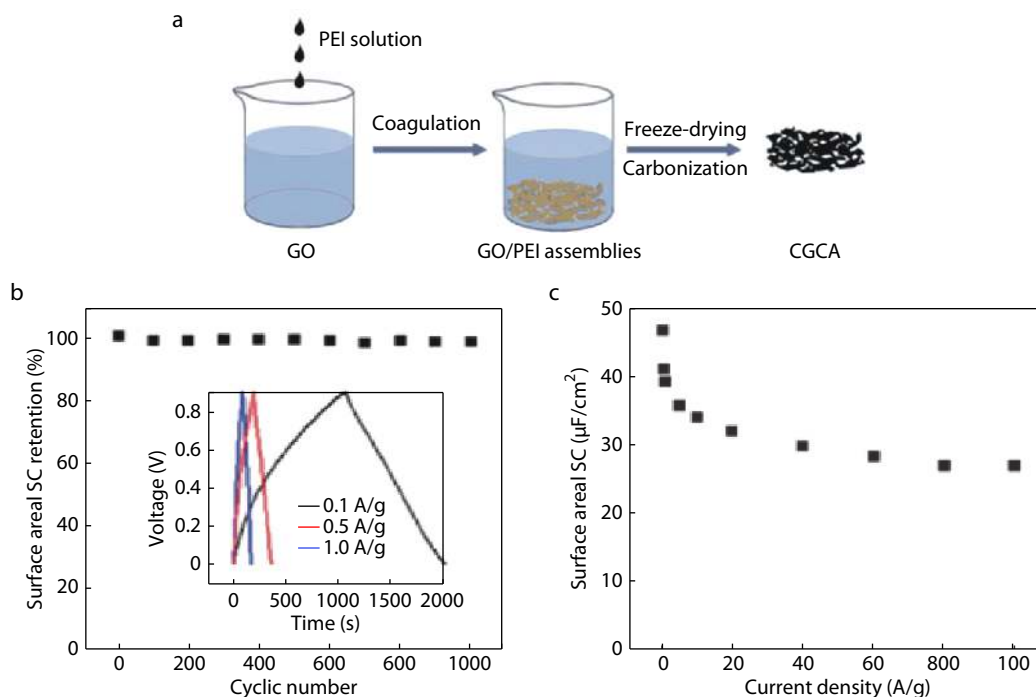


Fig. 4 (a) Schematic diagram of preparation of CGCA by coagulation self-assembly; (b) Cyclic performance and GCD curves; (c) Rate performance for the CGCA-based supercapacitor. (Reprinted with permission from Ref. [11]; Copyright (2014) The Royal Society of Chemistry).

CGCA electrode is $46.3 \text{ mF}/\text{cm}^2$ at $0.1 \text{ A}/\text{g}$, and this high capacitance is still maintained for about 57.8% even the current density reaches $100 \text{ A}/\text{g}$ (Fig. 4c). The excellent performance of the CGCA electrode is attributed to the face-to-edge aggregation of exfoliated single-layer graphene nanosheets.

Nanoscrolls from Solvent-induced Self-assembly

The morphology and existing state of 2D sheets in dispersions have aroused considerable interest in both experimental and theoretical aspects.^[51,52] GO sheets typically show crumpled morphologies when separated from a dispersion^[53], due to the thermodynamic perturbation and structural defects of the atom-thick 2D layer. Our recent studies show that under proper conditions, GO sheets can roll up to form nanoscrolls. The conditions to cause the formation of GO nanoscrolls from nanosheets through a self-assembling process have been studied as presented below.^[37–39]

To investigate the relationship between the scroll formation and solvent properties, monolayer GO obtained from porous GO powder was dispersed in different organic solvents *via* sonication.^[37] As shown in Fig. 5(a), GO was readily dispersed in the organic solvents after sonication. However, it was observed with interest that there were sediments in most of the organic solvents in the 12 h duration after sonication. Only for cases of *N*-methylpyrrolidinone (NMP) and ethylene glycol, the dispersions of GO in the media were stable. As indicated by transmission electron microscopy (TEM) observations, the sediments separated from dimethyl formamide (DMF), pyridine, methanol, ethanol, isopropyl alcohol, acetic acid, and isobutyric acid were nanoscrolls instead of nanosheets. The investigation of the correlation between the scroll structures and the solvent properties reveals the follow-

ing rules. For the polar aprotic or protic solvents, the average lengths of the GO scrolls show a close correlation with the properties of organic solvents, which decrease with the increase of dipole moments of the organic solvents. The diameter of the scrolls relies on both the size of GO sheets and the number of GO sheets contained in each scroll, which is closely related to the Hansen solubility parameters. The results indicate that the solvent-induced rolling of GO sheets is closely related to the interaction of GO sheets with solvents and their dispersion stability, which is influenced by dipole moment, Zeta potential, and Hansen solubility parameter of solvents.

Inspired by the observation on scroll formation in the organic solvents, we further investigated the fabrication of GO scrolls *via* dropwise adding a selective solvent (such as DMF and ethanol) into an aqueous dispersion of GO. As shown in Fig. 5(b), the cylinder-like scrolls and the spindle-shaped scrolls were formed during adding DMF for GO sheets with different sizes and oxidation degrees.^[38] Observation by the high-resolution TEM confirmed the lamellar morphology and the interlayer spacing between adjacent layers was estimated to be about 0.58 nm for the GO nanoscrolls, which proved that the scrolls formed from GO sheets *via* tightly rolling-up. Fig. 5(c) shows the formation mechanism of the scrolls from single-layer GO sheets.^[39] The morphological transition from nanosheets to nanoscroll is controlled by the surface negative charges on GO sheets in the dispersions, which is mediated by the DMF content. The electrostatic potential barrier in the nucleation of a scroll and the electrostatic repulsion in the overlapping regions hinder the morphological transition from planar GO sheets to scrolls. To proceed to the formation of GO nanoscrolls, two criteria have to be

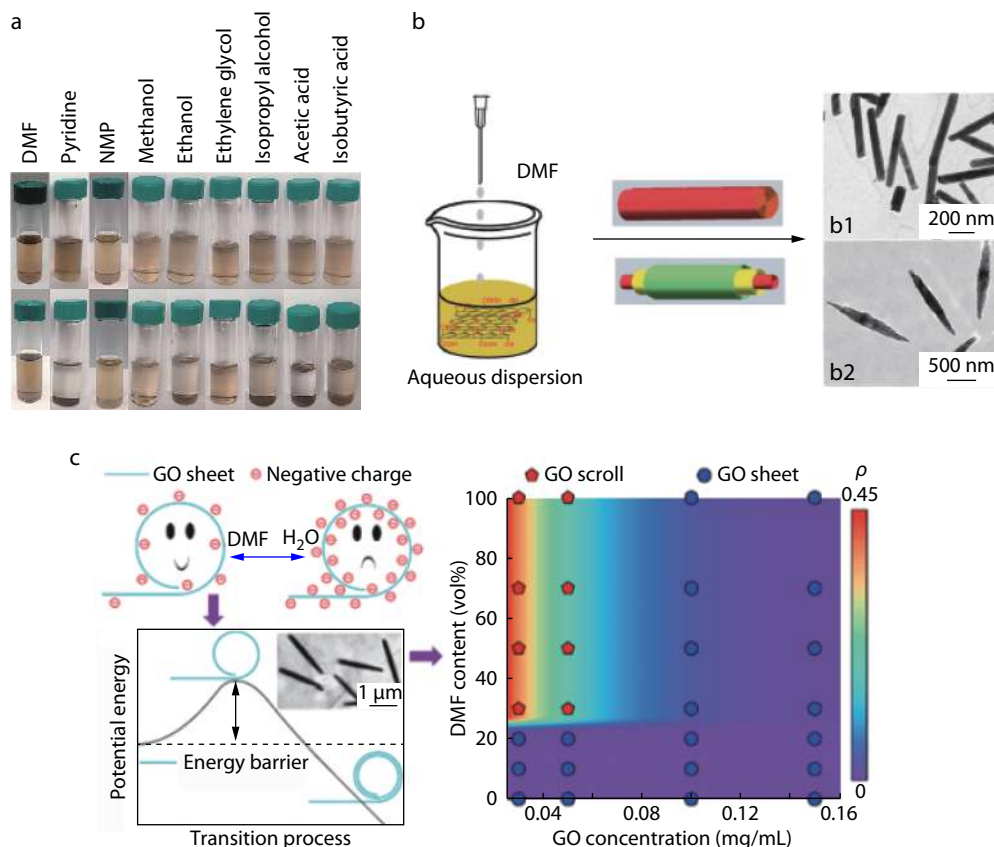


Fig. 5 (a) GO in organic solvents: top, just after sonication; bottom, 12 h after sonication. (Reprinted with permission from Ref. [37]; Copyright (2018) American Chemical Society); (b) Scheme of the self-assembly of GO sheets to form cylinder-like scrolls and the spindle-shaped scrolls. (Reprinted with permission from Ref. [38]; Copyright (2018) The Royal Society of Chemistry); (c) The cartoon of nanoscroll nucleation from GO sheet, the energy barrier for the scrolling of GO, and the morphological phase diagram of GO. (Reprinted with permission from Ref. [39]; Copyright (2018) American Chemical Society).

met: (1) the energy barrier of electrostatic potential barrier and bending energy barrier must be overcome in the nucleation process; (2) the van der Waals interaction between GO sheets in the overlapping regions must overcome the electrostatic repulsion energy and bending energy. These conditions ensure that the final states of nanoscrolls have the lower energy compared to that of planar sheets. Further, GO concentration also influences the scroll formation. The morphological phase diagram of GO, obtained *via* COMSOL simulation, the model of First-Passage-Time and theoretical calculation of the probability of isolated GO sheets, proves the particular importance of the concentration for forming the scrolls (Fig. 5c). The understanding obtained from the above studies are valuable for fabricating GO nanoscrolls in a scalable manner, and the scrolls can be used as promising materials for energy storage.

RHEOLOGICAL PROPERTIES

As aforementioned, one unique characteristic of GO nanosheet, distinct from other colloidal nanoparticles, is their 2D morphology with ultrahigh aspect ratio of 10^3 – 10^5 . Such high anisotropy makes it easy for GO nanosheets to contact with each other in the dispersion medium, affording GO colloids with diverse phase states within low range of mass fraction. Several

colloidal phases of GO nanosheets, such as viscoelastic liquid, liquid crystal, soft glass, and gel, have been discovered, which largely facilitate the fabrication of bulk graphene materials from GO colloids.^[54] The GO dispersion can be processed *via* traditional wet-processing technologies, such as filtering, spraying, spinning, dip coating, bar coating, and spin coating as well as some newly-developed technologies such as 3D printing.^[55] At the current stage, a big scientific research gap still lies between understanding the rheological properties of the GO colloids and applying the properties in various wet-processing technologies. To address this issue, we used GO hydrogel as a typical state of the colloidal phase to reveal the unique viscoelastic characteristics and processing advantages of 2D colloids. Two typical rheological properties, namely shear response and relaxation, of GO hydrogels and GO-based hydrogels have been investigated, which reveal unique rheological features related with the 2D morphology of GO nanosheets.^[40,41,43,44]

One unique rheological property of GO hydrogel is the strong shear-thinning. This property is common for GO hydrogels and GO-based hydrogels. As shown in Fig. 6(a), within the shearing window of traditional wet-processing technologies (10^{-2} – 10^4 s⁻¹), a GO and polyaniline (GO/PANI) hydrogel typically shows a viscosity decrease by 4–6 orders of mag-

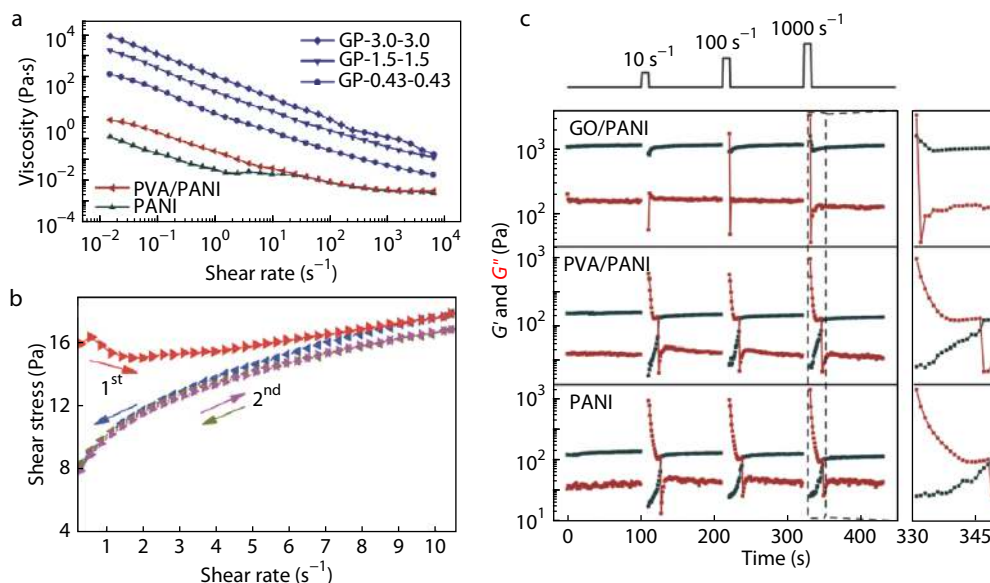


Fig. 6 (a) The viscosity curves of GO/PANI gels. (Reprinted with permission from Ref. [44]; Copyright (2019) Wiley-VCH); (b) Cyclic shear tests of the GO hydrogels. (Reprinted with permission from Ref. [40]; Copyright (2015) Wiley-VCH); (c) Modulus recovery of GO/PANI gels, compared with PVA/PANI and PANI colloids under the different shear rates. (Reprinted with permission from Ref. [44]; Copyright (2019) Wiley-VCH).

nitude, which is at least two orders higher than the one of other nanoparticles or polymers-based colloids. Such strong shear-thinning effect is related to the flow orientation of 2D nanosheets upon shearing, affording GO hydrogels with broad applicability to various wet-processing technologies, spanning from spraying to 3D printing.

GO hydrogel also shows obvious thixotropy under shearing conditions. Upon cyclic shearing test, the hysteresis loops of stress-strain curves of GO hydrogels disappear from the second cycle, even for concentrated hydrogels and under the low shear rate (Fig. 6b). The rheological memory effect means that GO hydrogels with shearing history would be easier to yield, deform, or flow. Such obvious thixotropy could benefit the spreading and pattern formation of GO hydrogels on substrate through pre-shearing treatment.

Another interesting property of GO hydrogel is the fast structural recovery through relaxation. After cessation of shearing, GO-based hydrogels are found to quickly recover from the viscoelastic liquid to gel state with an immediate reversal of storage and loss modulus (Fig. 6c). The high-speed camera visualizes the ultrafast shape-recovery process of GO-based hydrogels with a strain recovery rate comparable to that of elastic solids. The combined rheological and optical measurements confirm the existence of a fast relaxation process within the time scale of second followed by a slow re-orientation stage of GO nanosheets within several tens or hundreds of seconds.^[44] The structural recovery seems to mainly happen in the fast-relaxation stage considering the small variance of modulus and optical transmission during the subsequent slow fast-relaxation stage. The fast structural recovery could maintain the shape of GO hydrogels after shearing, which is highly desirable for many processing technologies, such as producing the bulk structure through 3D printing.

MULTIPLE PROCESSING METHODS

Based on the rheological properties of the GO dispersion and hydrogel, multiple processing methods can be developed to obtain the required structures and forms for supercapacitor fabrication. Some of the methods explored and developed in our group are presented below.

Blade-casting of GO Hydrogels

The rheological properties of GO hydrogel are suitable for blade-casting, *i.e.*, a simple and widely used industrial processing technology. Blade-casting followed by post-reduction method was proved to be an effective strategy to construct the flexible porous graphene films (Fig. 7a).^[41] GO hydrogel was prepared by adjusting pH of GO dispersion (Fig. 7b) and taking advantages of the carboxylic groups on the GO sheets and amphiphilic characteristics. The viscous GO hydrogel could be easily processed into porous films with designed sizes and shapes. The graphene films with unique cellular structure were fabricated through three processes, shearing-induced alignment of GO sheets, formation of interlinked bridges after shear cessation and relaxation, and solidification of porous structures through chemical reduction. As shown in Fig. 7(c), most of RGO sheets are arranged almost in parallel, caused by shear-induced orientation. A fraction of the nanosheets act as interlinking bridges between the parallel sheets, which is related to the relaxation after shearing. The existence of highly wrinkled graphene sheets not only prevents them from tightly face-to-face packing, but also facilitates the formation of interlayer connections (Fig. 7d). This cellular film exhibits high tensile strength (2.38 ± 0.15 MPa) and high modulus (66.5 ± 2.1 MPa), as well as high toughness (0.102 ± 0.012 MJ/m³) and long fatigue life ($\sim 10^4$). Its specific strength (30.1 ± 2.2 MPa/(Mg·m⁻³)) and specific modulus (842.9 ± 43.7 MPa/(Mg·m⁻³)) are even comparable to the tough cancellous bone.

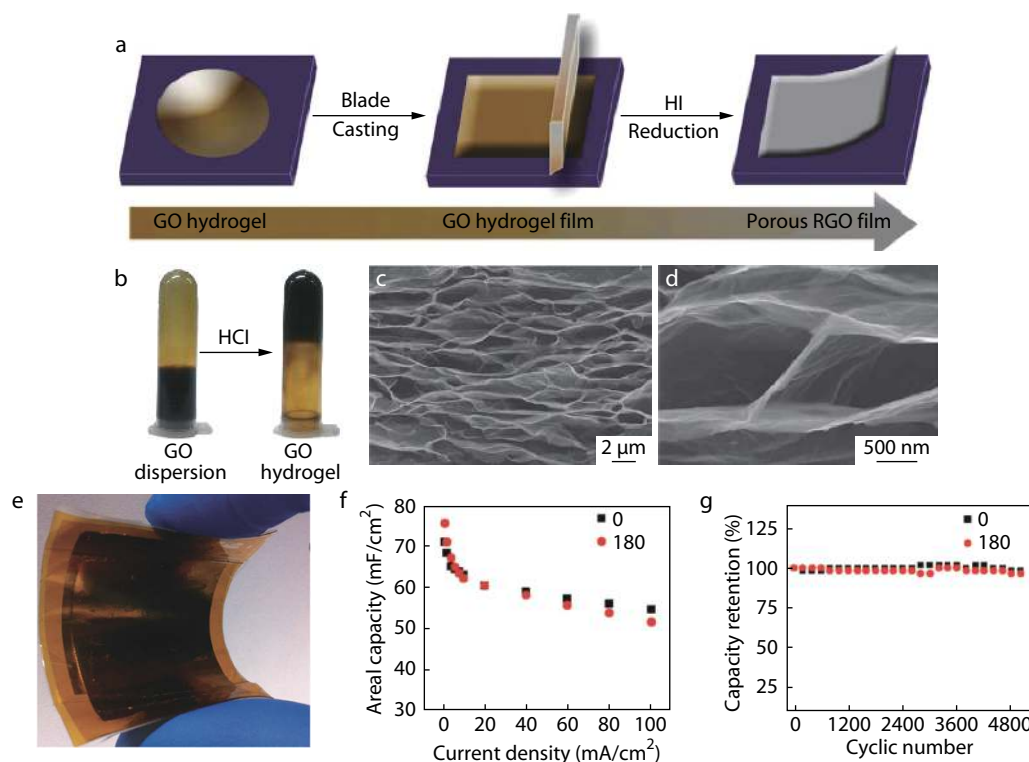


Fig. 7 (a) Schematic illustration of the preparation of the porous RGO film; (b) GO hydrogel formed from the GO dispersion; (c, d) SEM cross-sectional images of the freeze-dried RGO films prepared from GO hydrogel. (Reprinted with permission from Ref. [41]; Copyright (2016) Elsevier); (e) Photograph of flexible supercapacitor based on the porous RGO film; (f) Areal specific capacitance and (g) cyclic life at the normal and 180° bending states. (Reprinted with permission from Ref. [40]; Copyright (2015) Wiley-VCH).

The mechanically tough graphene film shows good flexibility and can be used in the flexible supercapacitor (Fig. 7e).^[40] The prepared wet RGO films show good mechanical properties, compared with those ones with similar oriented structure.^[56,57] When the current density increased from 10 mA/cm² to 100 mA/cm², the capacitance only slightly decreased from 63.0 mF/cm² to 54.7 mF/cm² (Fig. 7f). This suggests that there are efficient electric double layers in porous structures, which are hardly affected even at the high rates. In addition, the supercapacitor shows a long cycle life with 98.3% capacitance retention after 5000 charge/discharge cycles for a current density of 10 mA/cm² (Fig. 7g). The obtained supercapacitors do not show obvious capacitance loss at the 180° bending, which can meet the requirements of flexible energy storage devices.

The porous graphene film prepared by the above method is an ideal material for laser-carving due to the hierarchical porous structure.^[42] This property has been exploited to fabricate microelectrodes through laser scribing. Fig. 8(a) shows the way to fabricate flexible RGO-based microsupercapacitors (MSCs) from hierarchical porous RGO films through the laser-carving approach without any post-processing. The laser-carving process was conducted to obtain the designed electrode pattern, controlled by a computer program. This facile processing procedure can afford the good scalability for high-throughput fabrication. The interdigitated electrodes of MSCs obtained from the RGO film by the laser-carving show smooth surfaces (Fig. 8b) and smaller thickness dilation dur-

ing laser-carving. It can be attributed to the macro/mesoporous structures of the RGO films, which can easily expel the volatile gases in the laser-carving process. The hierarchical porous structures remain in the electrodes after laser-carving (Fig. 8c), which is desirable for the high-performance MSCs. The maximal areal specific capacitance is 37.95 mF/cm² at a current density of 0.6 mA/cm², which is higher than the most reported values of all-solid-state MSCs using carbon-based materials, especially compared with those obtained by the laser irradiation assisted methods.^[58–62] Meanwhile, the MSCs also possess superior rate capability, good mechanical stability, excellent flexibility, and long cycle life. For applications, the MSCs can be easily connected in series, parallel, or combined series and parallel to output high voltage and energy.

3D Printing of GO Hydrogels

Scalable and cost-effective printing techniques have been widely used to develop energy storage devices, particularly for the fabrication of portable and wearable electronics with a variety of available printing inks.^[63,64] For each printing technique, it is crucial to adjust the composition and especially rheological properties of the ink to an appropriate range to ensure its printability. The inks range from dilute dispersions for spray or ink-jet printing, to relatively viscous ones for screen printing, and to extremely viscous gels for 3D printing.^[55,63,64]

A highly concentrated GO dispersion without any additive can be used as an ink to fabricate MSC electrodes by direct 3D printing (Fig. 9a). The highly concentrated GO dispersion pos-

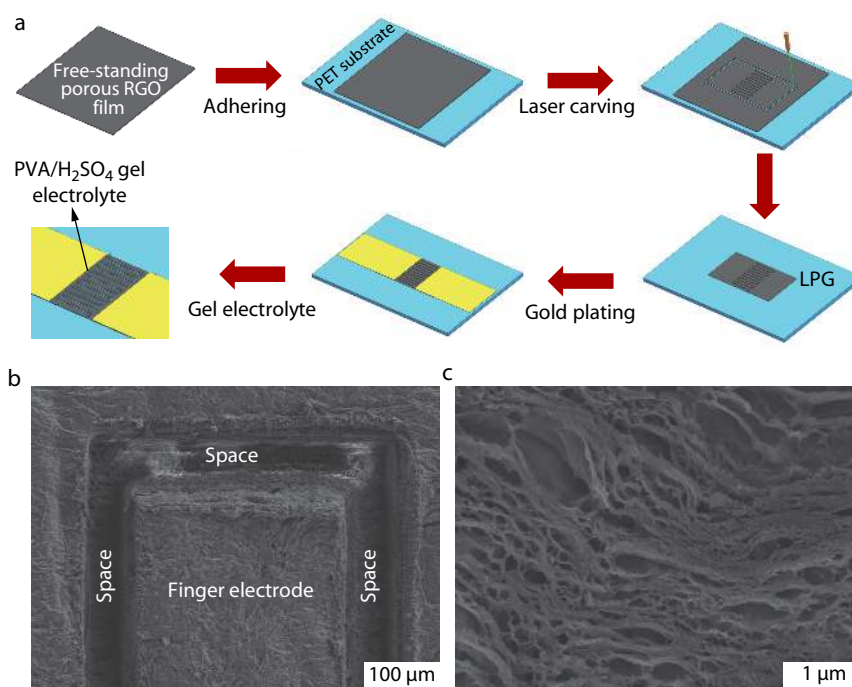


Fig. 8 (a) Schematic illustration of the fabrication process of the MSCs; (b, c) SEM images of the MSCs electrode obtained by the laser-carving: (b) a top view and (c) a cross-section view. (Reprinted with permission from Ref. [42]; Copyright (2017) Elsevier).

sesses unique rheological properties, such as high storage modulus, shear-thinning, and rapid viscosity recovery, which are suitable inks for 3D printing (Figs. 9b–9d). The GO inks show both gel and viscous liquid properties, where the gel-liquid transition depends on the shear strain amplitude and shear rate. In the extrusion process, the ink showed obvious shear-thinning and fast viscosity recovery, which are desirable for 3D printing. The higher storage modulus ensures the stability of the printed structure for multi-layer printing to load more active materials in the footprint area. Based on comprehensive study of the impact of 3D printing feasibility, printing accuracy, and stability, the optimal concentration range of the GO dispersion and appropriate needle type were determined. In addition, to achieve the extrusion stability and precision controllability in the actual printing process, the suitable extrusion speed and scanning speed region were determined and the precise 3D structure was then constructed. The five-layered MSCs with 3D interdigitated architecture exhibited a high areal specific capacitance of 111 mF/cm² at a scan rate of 10 mV/s, which is ascribed to more effective materials loading per unit area and the hierarchically porous structures of the 3D printed RGO electrodes.

Spray Printing of GO-based Hydrogels

The inks used for spray printing is usually a dilute dispersion with low viscosity and low solid content.^[61,65,66] Very recently, we found that GO-based hydrogels can be even applicable to spray printing due to their strong shear-thinning effect and fast structural recovery.^[44] When mixing the negatively charged GO and positively charged PANI nanofibers in water with pH of 2, GO/PANI dispersion was observed to spontaneously transform into gel when the mass fraction of GO exceeded 0.25 wt% (Figs. 10a and 10b). The colloidal gels containing a dynamic net-

work of GO nanosheets exhibit rheological behavior of ultrafast modulus recovery after the high-rate shearing. This remarkable rapid structure recovery feature is conducive to the preparation of high-throughput and high-fidelity patterns by spraying GO/PANI gels on a substrate. The spray-printed MSCs exhibit an areal capacitance of 35–57 mF/cm² at the current density of 0.1 mA/cm², which is 4–6 times higher than that of traditionally spray-printed ones. The spray-printed MSCs are further demonstrated to integrate with and power a resistive sensor.

This discovery of the fast recovery of GO-containing colloidal gels under high-rate shearing are promising for processing graphene derivatives and other nanomaterials for industrial applications. Graphene-related nanomaterials have been extensively exploited as nanoscale additives to enhance the mechanical, electrical, electrochemical, and other functional properties of traditional materials for a wide range of applications. The above work suggests that the addition of GO into other colloidal nanoparticles could also endow colloidal dispersions with new rheological properties to allow for developing more efficient processing techniques. Compared to the dispersion-based inks previously used in spray printing that generally have a solid content lower than 0.5 wt%, the GO/PANI colloidal gel-based inks have a much higher solid content up to 6 wt%. This high throughput, along with the simultaneously achieved high fidelity, is highly desirable to reach the challenging goal of large-scale industrial printing and processing of nanomaterials-based devices, as demonstrated by the successful fabrication of high-performance micro-supercapacitor array through spray printing of GO/PANI colloidal gels. GO shows the great potential as an extremely efficient and multifunctional rheological modifier for traditional materials. Owing to the 2D nature and high aspect ra-

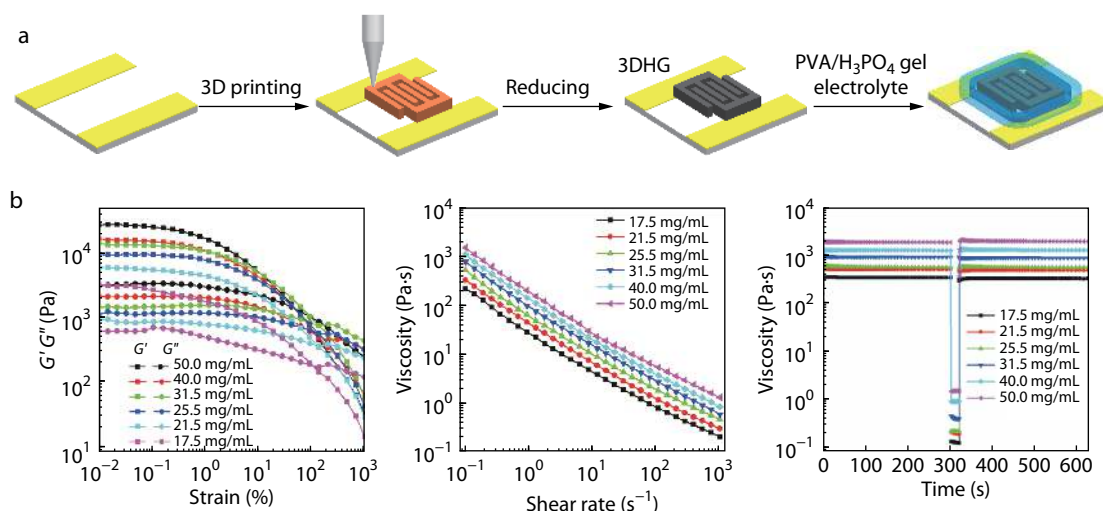


Fig. 9 (a) Schematic illustration of the fabrication process of 3D printed MSCs; (b–d) Rheological properties of GO suspensions with the concentrations of 17.5, 21.5, 25.5, 31.5, 40.0, 50.0 mg/mL: (b) oscillatory shear measurements at a constant frequency of 1 s⁻¹ with the increasing strain amplitude, (c) the viscosity curves, and (d) viscosity recovery after shearing. (Reprinted with permission from Ref. [43]; Copyright (2019) The Royal Society of Chemistry).

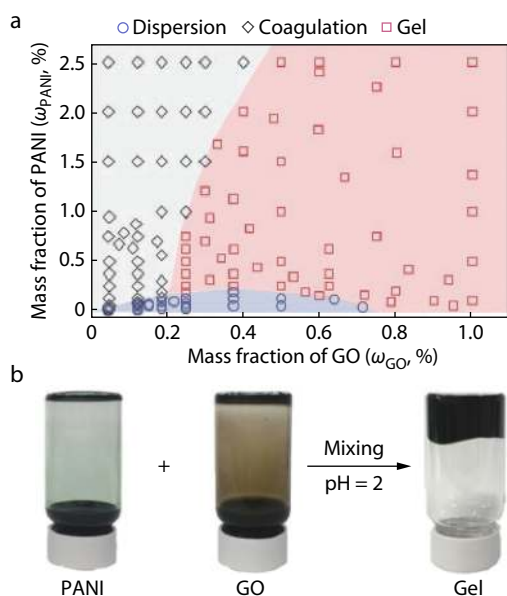


Fig. 10 (a) Phase behavior of GO/PANI colloids under pH = 2; (b) GO/PANI gels formed through mixing the GO and PANI dispersions under pH = 2. (Reprinted with permission from Ref. [44]; Copyright (2019) Wiley-VCH).

tion of GO, a continuous jammed GO network can be easily formed at a low mass fraction of 0.25 wt% to generate a drastic effect on the viscoelastic properties, which is nearly a magnitude lower than the cases for traditional colloidal gels based on polymer or clay. This unique feature, together with the ability of converting GO to electro-conductive RGO, can open up new opportunities to add value to traditional paints. This work gives us a perspective to consider graphene derivatives and other 2D substances as a functional rheological enhancer, which can facilitate industrial processing and accelerate the commercialization of nanomaterials.

CONCLUSIONS AND PERSPECTIVE

This article reviews our recent works on the self-assembly, colloidal behavior, rheological properties of graphene derivatives, and their potential applications in supercapacitors. The fascinating properties of graphene derivatives originate from the unique chemical compositions and 2D architecture of the nanosheets. The derivatives show characteristics similar to electrolytes, amphiphiles, and colloidal particles as well as π - π stacking of aromatic molecules, depending on the preparation conditions and post-preparation modifications. Based on these unique features, macroscopic assemblies of the graphene derivatives can be obtained through different self-assembling approaches. The unique rheological properties of GO dispersion and hydrogel are suitable for both the traditional wet-processing technologies and some newly-developed technologies like 3D printing. All these properties can be utilized for structural manipulation and scalable fabrication of graphene-based devices. Given the controllable and scalable processing advantages of graphene derivatives, more efforts should be devoted to understanding the formation-structure-property relationship and eventually realizing the real-world application of the materials. In the last part of this article, we would like to share our vision in the aspects of characterization, modelling, processing, and applications of graphene derivatives as colloids.

Due to the low light transmission of the colloids of graphene derivatives especially at high concentration, the classic colloidal characterization techniques, such as light scattering, are largely limited. Advanced synchrotron characterization through X-ray or neutron scattering is needed to *in situ* monitor the structures of the colloids at different scales and under different processing conditions. Moreover, the structural complexity and broad size distribution of graphene nanosheets bring much uncertainty over explaining their diverse colloidal and rheological behavior. In this regard, theoretical modelling should be incorporated. The modelling of the above-mentioned scrolling of GO nanosheets provides a

good example, while the underlying mechanistic origins of the most observed colloidal phenomena, such as the soft glassy states and the fast structural recovery, are still unclear and call for the synergistic combination of theoretical modelling and experiments.

Hydrogels of graphene derivatives are expected to serve as a functional soft-matter platform with the high tuning ability of rheological and mechanical properties. By adjusting the colloidal interactions among the nanosheets, it is feasible to tune the modulus of the hydrogels within six orders of magnitude from Pa to MPa, which covers the modulus range of soft biological tissues. This broad mechanical tunability, along with the multi-functionality supplied by graphene framework and various types of functional groups, could stimulate applications of the hydrogels in multiple fields, including mechanical sensors, flow electrodes to bioelectronics.

Elaborately modulating colloidal processing of graphene derivatives could further spawn many new applications along this line. It has been proved in our work that the shear processing can affect the electrode structure and electrochemical performance of supercapacitors. Very recently, it is reported that graphene films prepared through pre-shearing show more ordered structure, which can suppress the transport of specific metal ion through battery separator or enable homogeneous deposition of metal ion on battery electrodes, leading to optimized performance for batteries.^[67,68] Furthermore, extending the study of 2D colloids from the pioneering graphene derivatives to other 2D materials is envisaged to result in many new colloidal phenomena and more functional applications.

ACKNOWLEDGMENTS

This work was financially supported by the National Basic Research Program of China (973 Program, No. 2012CB933402).

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