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Conformation Engineering of Two-Dimensional Macromolecules: A Case Study with Graphene Oxide

Yanqiu Jiang,[#] Ya Wang,[#] Zhen Xu,* and Chao Gao*

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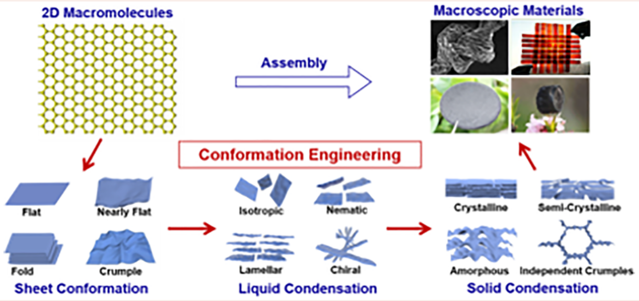

CONSPECTUS: Two-dimensional sheets, a new family of macromolecules with 2D topology, are posed to rapidly extend material technologies and indispensably shape our lives. The great expectations of 2D macromolecules urgently call not only a unified understanding of their macromolecular behavior in the new 2D topology but also a general methodology to guide the precise fabrication to achieve disruptive performances of their macroscopic materials. Motivated by these mutual fundamental problems, we have explored the conformation principle of 2D macromolecules and established a systematic routine for macroscopically assembled materials, in the model of graphene oxide. This Account concludes our recent works in investigating macromolecular conformations and condensed states of 2D graphene oxide and initializes a conceptually new methodology of conformation engineering of 2D macromolecules.

In analogy with classic 1D polymers, we have depicted a systematical conformation map of graphene oxide extending from individual to multiple sheets. The conformation map unifies the theoretic description and experimental observations, establishing the conformation principle of 2D polymers. We have found rich liquid crystalline phases of graphene oxide and uncovered their extremely slow relaxation behavior. We have created a liquid meta-crystal of graphene oxide, a new mesophase state with stable meta-periodicity beyond ordinary molecular order, by the invented shearing microlithography to achieve the free design and control of artificial meta-structures. The proposed conformation engineering concept has underpinned the versatile design and rational control of multiscale structures of graphene macroscopic materials and promoted advanced performances of graphene fibers, films, and aerogels. The conformation principle in the case of graphene oxide can establish a unified theory of 2D polymers after the classic 1D antiquity. The conformation engineering will become a useful concept to depict the systematic "fabrication—structure—properties" loop and guide the scalable fabrication of 2D macromolecular materials.

1. INTRODUCTION

Polymers have achieved tremendous accomplishments in the last "polymer century" and continuously helps us to head the fundamental problems in the present century, such as cheap energy, clean water, and disease curing.[1] After classic linear polymers, such as polyethylene, nylon, and DNA, graphene has uncovered a board family of macromolecules with two-dimensional topology.[2] In the past decade, the 2D polymer family has expanded to include hundreds of members from superconductor and metal to semiconductor and insulator, rapidly exhibiting potential breakthroughs in many applications, such as thermal management, structural materials, nanocomposites, energy harvest, and storage.[3] It is not a utopian envision that 2D polymers will be extensively applied in the modern industry and our daily lives in the near future, as classic linear polymers we gradually depended on.

The emergence of 2D polymers has raised two fundamental questions, which mutually ignite deep deliberations in both 2D nanomaterial area and polymer science. (1) We need to understand the fundamental molecular behaviors of 2D polymers, including the generality with 1D counterpart and the specificity of 2D topology. Although the theoretical description of linear polymer has been generalized to 2D topology,[4] the unification between theoretical predictions and experiments still needs to be verified and characteristic 2D features are waiting to be unveiled. (2) The massive production, processing, and macroscopic materials of 2D sheets should have a general guidance, as the intertwined science and industry of classic polymers.[5,6] Especially, the expected breakthroughs in macroscopic materials of 2D sheets rely on precisely controlling hierarchical structure starting from molecular scale. Without question, classic polymers provide an

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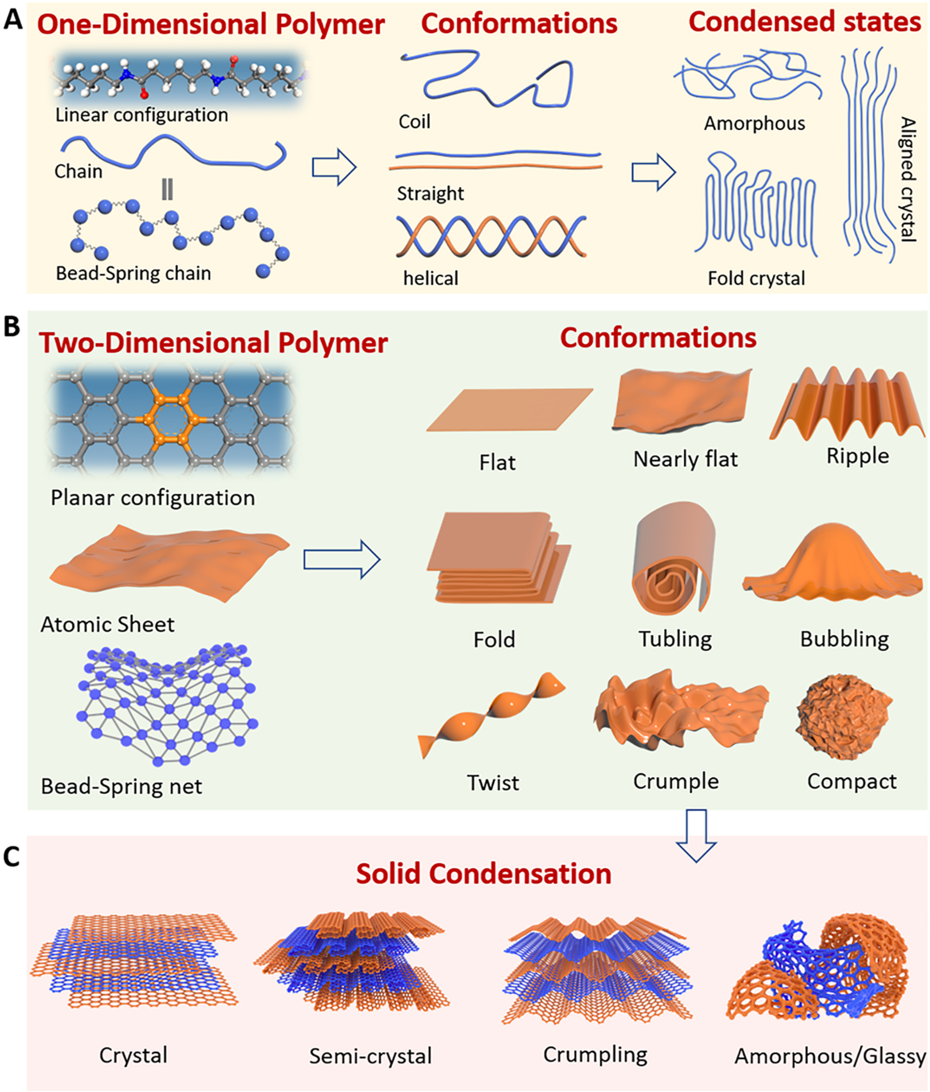

Figure 1. Conformations of 1D and 2D macromolecules. (A) Molecular models (nylon), typical conformations and condensed states of linear polymers. (B) Conformations of 2D macromolecules in analogy with 1D polymer. The graphene example with planar configuration and its coarse-grain bead–spring net model. The rich conformations extend from ideal flat to amorphous compact. (C) Basic condensed solid states of graphene model.

important analogy for the emerged 2D sheets, not only to realize the disruptive performances but also to guide the whole process from laboratory experiments to industrial production. Motivated by these two mutual questions, we have started experimental attempts to address important conformation issues and depicted a conformation engineering framework of 2D macromolecules.

In this Account, we present the conformation engineering methodology and give a systematic sketch of conformations and condensation state of 2D macromolecules in the model graphene oxide (GO). GO was selected as the research paradigm due to its ideal 2D topology as single layers and good dispersity in multiple common solvents. Our research extends from the conformation transition map of individual and multiple 2D macromolecules to their exotic liquid crystalline behaviors and the condensed structure of their macroscopic assemblies. We conclude with an analogy between 1D and 2D polymers and depict the conformation principle of 2D macromolecules. The introduced conformation notion of GO sheets offers a general descriptive language to qualitatively set up the fundamental relationship of processing-structure–property of graphene materials. A new conformation engineering methodology is proposed to generally guide the precise control and design of macroscopic materials of 2D polymers. We hope that this Account can refresh the understanding of flourishing 2D nanomaterials and extend the topology space of polymers beyond 1D antiquity.

2. CONFORMATION PRINCIPLE OF 2D MACROMOLECULES

2.1. Atomic Origami: Conformation of 2D Macromolecules

The conformation, the spatial structure of macromolecules, is the key to describe and understand molecular behaviors in various states, such as solution, gel, melt, and solid, which is clearly exemplified by classic 1D polymers.[1] The conformation of polymeric chains following scaling laws generally govern the processing and controllable fabrication of materials, such as the standard viscosity method to test molecular weight and highly stretched chains in high performance fibers. Rich properties and bioactivities originate from the tremendous conformations

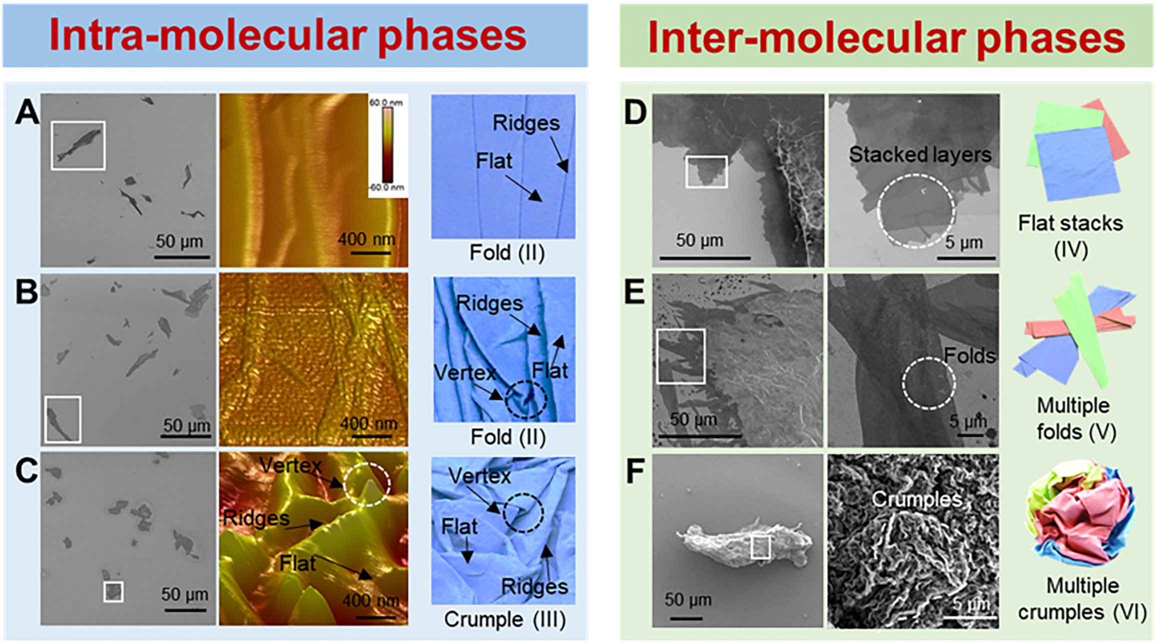

Figure 2. Observed conformations of GO in solution. Intramolecular phases (A)−(C) and intermolecular phases (D)−(F) illustrated by SEM, AFM, and origami models. Reproduced with permission from ref 21. Copyright 2020 Elsevier Inc.

of chain polymers, for example, coils in solution, alignment in crystal, membrane ion channel proteins, and double helix DNA to carry genetic information (Figure 1A).

For 2D macromolecules, their conformations should have the equal significance as their 1D cousins. It is intuitive to imagine their conformations as daily origami crafts but with atomic thickness. The delicate structures of origami imply the great complexity of 2D macromolecules. Starting from the perfect flat conformation, some conformations immediately emerge, for instance, nearly flat with indulgence, loose crumples, compact balls, fan-like folds, rolled tube, and other fascinating shapes (Figure 1B). Beyond these listed conformations, more exotic conformations can be possibly generated by precisely tuning the spatial distribution of chemical composition in the planar direction and shapes. The macroscopic materials consist of 2D sheets with these diverse conformations. In this context, to clarify the underlying mechanism of conformations transitions and to develop effective modulating process methods are of great importance for their materials.

2.2. Theoretic Description of Conformation of Tethered Surface

Since the 1980s, theoretic researchers have tried to sketch the statistical mechanics of membranes with in-plane connections (called tethered surface), mostly driven by motivations to understand cell shapes.[4,7−9] In the basic coarse-grain "bead−spring net" model, the competition between thermal fluctuations and stretching/bending energy determines the equilibrium conformations, as concluded in monographs of Nelson and others.[4] The conformation theory offers some important deductions, including the following: (1) A self-avoided 2D polymer follows a general scaling law between the radius of gyration (R_g) and contour size (L) as $R_g \sim L^{\lambda}$, where λ is 0.8 in ideal solvents as compared with a self-avoided 1D polymer ($R_g \sim L^{0.5}$). This deduction implied that the self-avoided 2D polymers take a nearly flat shape with ripples in good solvents that are caused by thermal fluctuation.[9] λ of the tethered surface varies from 1 to 0.67 under different interfacial interactions and structural anisotropy.[10−13] The scaling law between R_g and L provides a theoretic statistical description of the conformational shape of GO, which qualitatively assesses their conformation evolution in their materials processing under controllable surroundings. For example, aligned lamellar materials can be prepared from dispersed GO with a nearly flat conformation ($\gamma > 0.8$) and porous crumpled solids from GO with a crumpling conformation (for example, γ approaching 0.67). (2) The entropy-favor crumpling transition can be driven by strong thermal fluctuation at a high enough temperature or a low bending rigidity, which is described as a second-order phase transition in Landau's theory.[10] This reasonable crumpling transition is important for the behaviors and properties of 2D polymers at high enough temperatures but still needs to be directly observed by experiments. (3) Some intramolecular conformation phases have been predicted as intrinsic properties and interaction force potential change, such as crumples, compacts, and tubes,[9,14,15] but the intermolecular phases remains unknown in theory.

In contrast to theoretical advances, the experiment lagged, possibly for the lack of neat 2D macromolecules (with atomic thickness) and the complexity of available biomembranes (for example, plasma membrane with attached spectrin and actin dynamic network). Despite all these hindrances, some experiments have been tried to unveil the fundamental attributes of 2D macromolecules.[14−20] For example, to verify the fundamental scaling law, Wen, Hwa, and co-workers investigated the scaling relation using graphite oxide colloids with an ambiguous distribution in thickness but not as a single layer.[14,15] The wide distribution of thickness in partially exfoliated graphite oxide crystals gave great errors of the calculated bending rigidity and brought a high ambiguity of experimental results. The static laser scattering results implied that graphite oxide in solution follows the predicted scaling relation. By contrast, the ambiguity in thickness and the inaccuracy of the scattering technique were doubted by freeze-

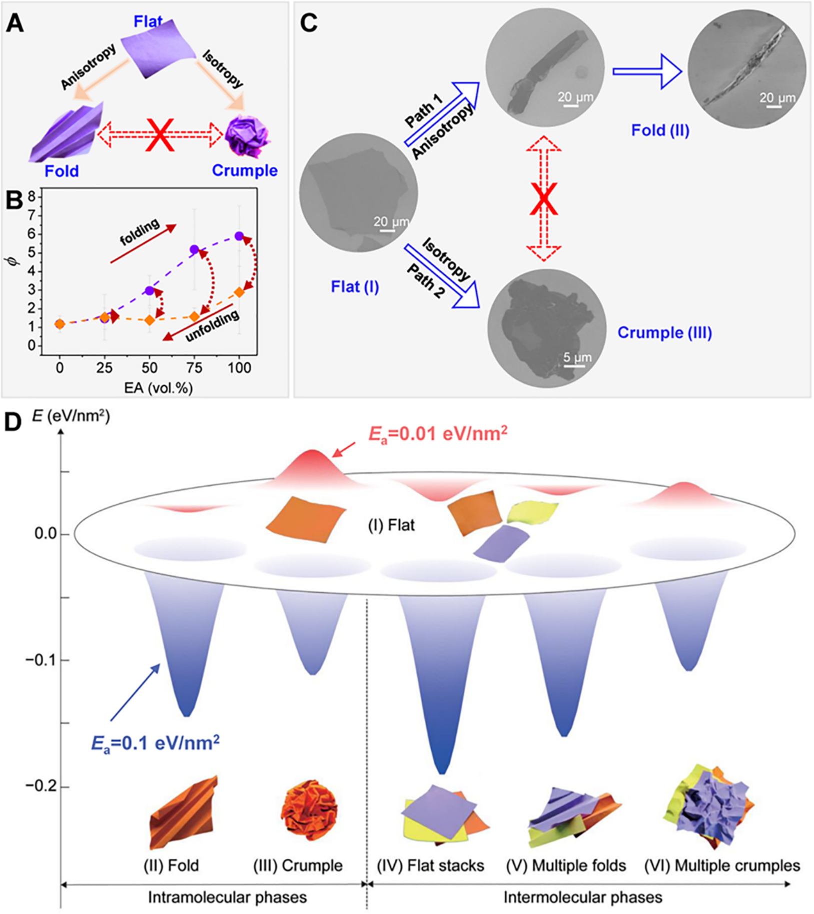

Figure 3. Conformation phase map of GO in solution. (A, B) Path-dependence and reversibility of conformation transition. (C) Symmetry selective transition. (D) Calculated energy landscape of the phase map, dominated by the surface energy (E_a). Reproduced with permission from ref 21. Copyright 2020 Elsevier Inc.

fracture electron microscopy observations and recent optical inspections, especially on the scaling law and crumpling transition.[19] The conformation theory of 2D macromolecules has to be reliably verified or possibly rectified by experiments.[20]

2.3. Conformation Atlas of Graphene Oxide

By an improved synthetic method, GO can be well-dispersed as single layers (thickness smaller than 1 nm) in common solvents for its abundant oxygen containing groups (e.g., hydroxyl, carboxyl, and epoxy group).[5] GO also partly keeps the crystalline order of graphene and can be taken as a 2D macromolecule consisting of mixed isogenous monomers. Monolayer GO is a possibly ideal experimental model to investigate the conformations of 2D macromolecules. To revisit the fundamental conformation issue in the case of GO, we established a conformation atlas of 2D macromolecules in solution, including both intra- and intermolecular conformations.[21]

Given the identical bending rigidity, we designed three molecular interaction modes in GO solutions to investigate its conformation behaviors: (1) the self-avoidance mode tuned by poor solvent; (2) the short-range attraction by short-range cross-linking between trace metal ions and oxygen functional groups of GO; (3) the long-range attraction under hydrophobic interaction by mild chemical reducing GO to increase its hydrophobicity. We also extended the researches from the dilute to concentrated range, in order to investigate the intra- and intermolecular behaviors.

Intramolecular Conformation Phases. In the extreme dilute range with a GO concentration (~0.005 mg/mL), two major conformation trends evolved from the nearly flat conformation (phase I) in good solvents (Figure 2). The folded phase (II) with unsymmetrical creases (like a Chinese paper fan) emerges in the self-avoided and short-range attractive modes. The other crumpled phase (III) as paper ball emerges in long-range attractive mode. In comparison with folded phase, the crumpled conformation possesses random vertexes and ridges caused by a global shrinkage.

Intermolecular Conformation Phases. In the concentrated range (1−10 mg/mL), we found three intermolecular phases: (IV) a flat stack phase in self-avoidance mode, in which GO sheets stack with each other; (V) a multiple folded phase in short-range attractive mode in which GO sheets fold first and stagger together; (IV) a multiple crumpled phase with many sheets crumpling together in the long-range attractive mode.

Through these observations, we experimentally sketched a systematic phase map of 2D macromolecules including both intra- and intermolecular phases and concluded two basic categories of conformations with different structural symmetries. The intramolecular phases from I to III have verified the theoretic predictions. But for the intermolecular phases, our phase map preceded theoretic advances and revealed the

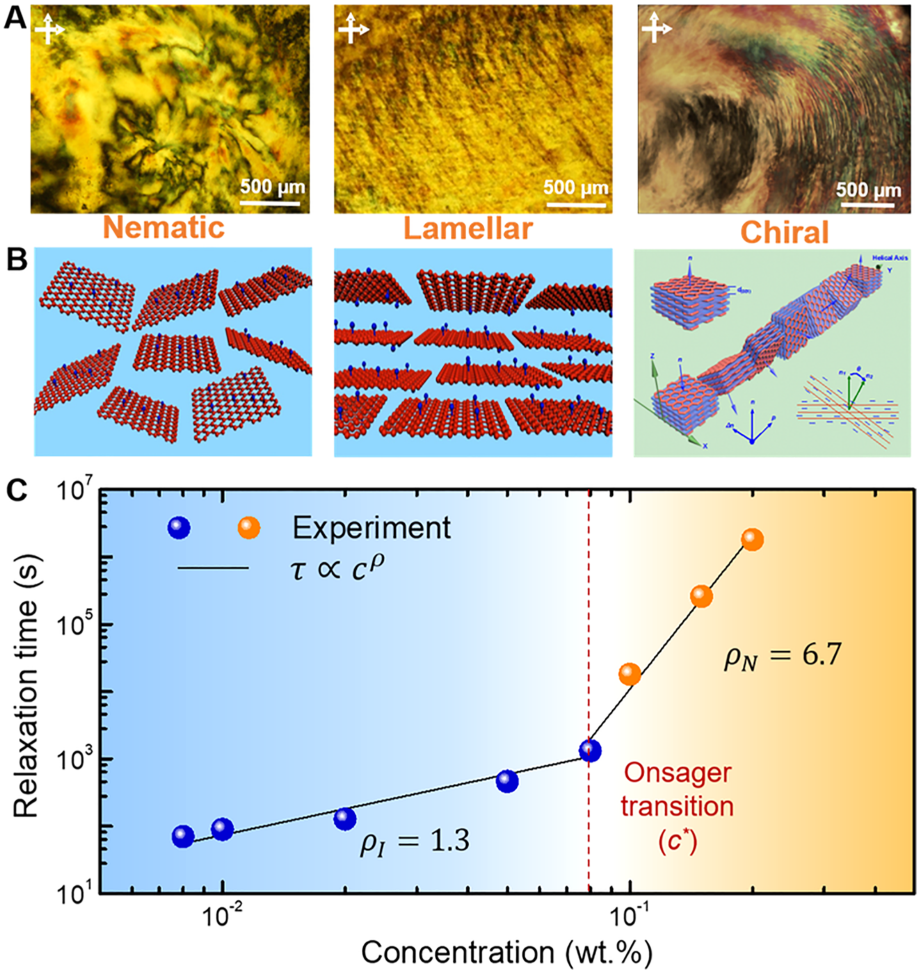

Figure 4. Rich phases and relaxation dynamic of GO LCs. Optical textures (A) and schematic structures (B) of GO LCs. Reproduced with permission from refs 24 and 28. Copyrights 2011 American Chemical Society and 2011 Springer Nature. (C) Relaxation time diagram with concentrations. Reproduced with permission from ref 34. Copyright 2019 Springer Nature.

hidden richness of conformations of 2D macromolecules. The rich conformations of GO unveil a hidden possibility of precise control of structure from single layers, which reminds us that the assembly is not a simple pilling step. We need to rethink the ordinary states of GO, such as dispersion and gels, to consider the conformations in more details. For example, we need to know that GO sheets in gels are flat or crumpled, which will greatly affect the final structures in solids.

2.4. Conformation Transitions

Beyond the finding of rich phases, we found some interesting attributes of their transitions. Two basic features in conformation transitions of GO have been detected: restricted reversibility and strong path dependence (Figure 3A−C). It is a general rule that the deformation energy cost determines the energy barrier to activate the conformation change. For 1D polymers, the thermal fluctuation at mild temperatures (for example, −50 to +200 °C) can agitate the mobility of chain segments. In the GO model, the reversibility is restricted by the surface interaction and transition extent. In the attractive mode, the folded and crumpled phases cannot return to the flat phase. In the self-avoided mode, the fold can return to flat under a minor degree of shrinkage and only partly recover at a high degree of shrinkage. This irreversibility attribute mainly originates from the insurmountable energy barrier to open large folds for the overwhelming interlayer attraction of a large contact area.

The 2D topology of GO also generates a strong path dependence of conformational transitions: the symmetric crumple and asymmetric fold cannot mutually transit. This path dependence can be intuitionally understood by our daily experience:[22] regular folding of the paper fan is easier than squeezing a paper into a compact ball (Figure 3). Theoretic simulations revealed a bifurcation in energy cost of folding and crumpling processes. Once the folding occurs, the mechanical anisotropy emerges and aggravates the asymmetric deformation to reject global crumpling.

We concluded a more realistic theoretic description of 2D macromolecules in which the surface interaction dominates, which is reasonable because these atomically thick 2D macromolecules are “ultimate surface materials”.[23] Including the surface interaction potential, the experiment results of model GO were reliably predicted in the energy landscape by coarse grain modeling (Figure 3D). This deduction offers a versatile strategy to control or even design the conformation of 2D macromolecules by tuning surface interaction in strength and spatial distribution, possibly achieving delicate atomic origami crafts.

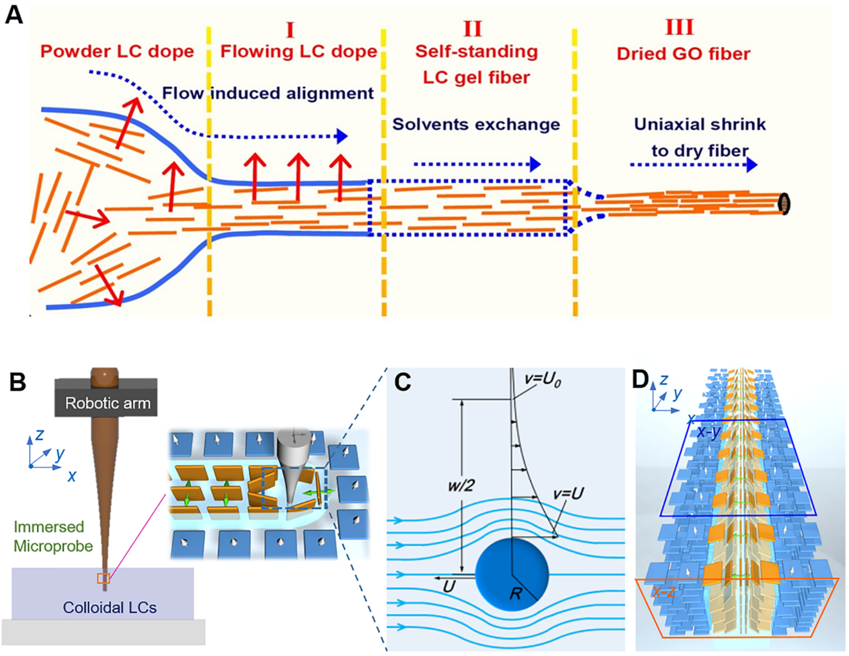

Figure 5. Shear-modulating GO LCs. (A) Uniaxial flow homogenizes GO LCs during wet-spinning. Reproduced with permission from ref 5. Copyright 2014 American Chemical Society. (B, C) SML process to modulate GO LC directors following a hydrodynamic model (C). (D) Basic domain with vertical orientation by SML. Reproduced with permission from ref 34. Copyright 2019 Springer Nature.

3. CONDENSED MESOPHASES OF 2D MACROMOLECULES

Following the thought thread from molecules to organizations, the liquid crystal (LC) of anisotropic 2D polymers is a significant condensed state. In the frame of Onsager's LC theory:[8] for disklike particles, a phase transition from the isotropic state (where particles are randomly orientated) to the nematic state (where particles share a common preferred orientation direction dubbed director) is expected at a volume fraction of $\Phi \approx 4h/D$, where h and D are the thickness and lateral size of the particle, respectively.[24] Due to the high anisotropic nature of 2D macromolecules, GO and other 2D sheets have been confirmed to form lyotropic LC.[8,24−30]

3.1. Rich Phases of GO Liquid Crystals

The LCs of 2D polymers extend the old 2D colloidal LCs and the basic unit evolves from colloids to molecular sheets with atomic thickness. In retrospect, the phenomenon of flow birefringence of 2D colloids has been usually observed in their dispersions[31,32] and was proven as a flow-induced LC relevant behavior, including for clay[32] and graphite oxide.[33] As early as 1948, Heinrich Thiele observed the flow-birefringence of graphite acid (the old name of graphite oxide),[33] which might be the first observation of LC of graphite oxide in the colloidal LC area.[31] In 2009, Kim reported the first stable LC formation of GO in the thesis.[25] In 2011, the nematic LC of GO was reported and demonstrated in details in peer-reviewed journals by Kim et al.,[26] Xu et al.[24] and Dan et al.[27] independently. In the same year, Xu and Gao found lamellar mesophase[24] and a very interesting chiral mesophase.[28] Recently, we created a new state of GO LCs with stable meta-periodicity, which is called a liquid meta-crystal (LMC), extending GO LCs to artificial meta-phases.[34]

The formation of rich phases of GO lyotropic LCs is usually dominated by its concentration. Compared with traditional discotic LCs, GO sheets with an ultralarge aspect ratio can spontaneously form a nematic phase with an orientation order at a volume concentration down to 0.02%.[24] After the nematic phase, a lamellar phase forms as the concentration increases to exhibit a quasi-long-range translation order.[28] Apart from these two ordinary phases, a nontrivial chiral mesophase was also found in the narrowly size distributed GO (Figure 4A,B), which is the first chiral LC of 2D colloid. This chiral helical phase displayed three exotic features: (1) fingerprint-like textures with aligned bands, (2) strong optical activity, and (3) quasi-long-range lamellar order. We proposed the twist-lamellar model where lamellar structures are regularly twisted to form continuous helical structure. We deduced the origin of chiral structure as that negatively charged lamellar blocks would repel each other, forming a rotated helical structure, due to the long-range electrostatic repulsive interaction. The deduced helical-lamellar structure was directly observed under cryo facture SEM.[28] The rich LC behaviors of GO encourage us to explore exotic LC behaviors of 2D sheets.

The finding of GO LCs has ignited the burst of research interests not only in the fluid physics but also in the ordered assembly. Since 2010, we have drawn the mainstream applications of GO LCs in macroscopically ordered materials, exemplified by graphene fibers (GF),[28,35−37] films,[38] and aerogels.[39] The newly created LMC can fully exploit the potential of GO LC in structural design and offer a new concept to concisely design and control multiscale macroscopic structures.[40]

3.2. Dynamic Behavior of GO Liquid Crystals

GO LC offers a useful strategy to fashion GO sheets into orientated structures by modulating their orientations. Flow, electrical and magnetic fields have been used to achieve uniform alignment of GO LCs, generating high-performance GFs, films, gels,[6,28,41] and electrooptic switching devices.[42] In principle, artificial alignment of LC orders is nonequilibrium and tends to spontaneously relax to random distribution. The

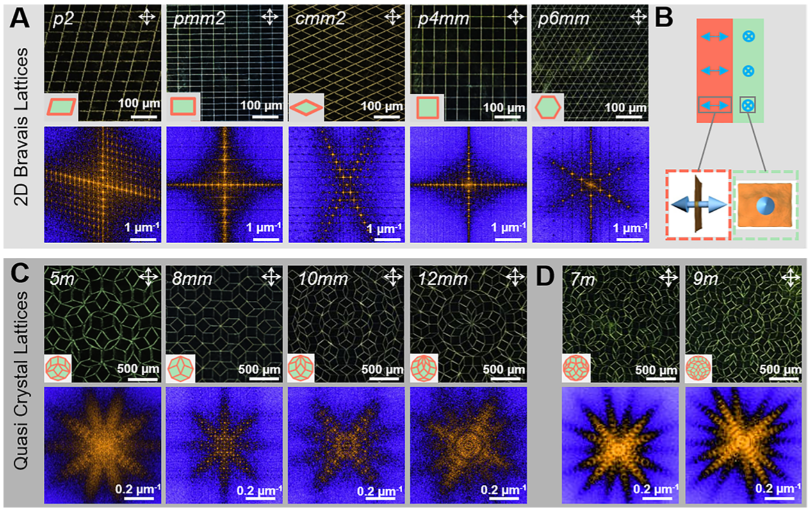

Figure 6. GO liquid meta-crystals. (A) LMCs with 2D Bravais lattices. (B) Illustration of the orientation of GO sheets in different domains. (C, D) LMCs with quasi-crystalline lattices. Reproduced with permission from ref 34. Copyright 2019 Springer Nature.

relaxation properties of GO LCs determine the stability of generated structures, which is crucial for the LC manipulation to final structures and materials.

We investigated the fundamental relaxation dynamics of GO LC and revealed their extremely slow relaxation behavior (Figure 4C).[34] We depicted a power law correlation between relaxation time (τ) and GO concentration (c), that is, $\tau \propto c^{\rho}$. The index ρ takes a great leap from 1.3 to 6.7 at the isotropic−nematic phase transition concentration (~0.066 wt %). This transition is caused by the highly overlapped excluded volume of GO, which dramatically enlarges the rotation energy barrier, leading to the long slow relaxation. The slow relaxation attribute of GO LCs increases the stability of artificial alignment generated by external fields.

3.3. Uniaxial Flow for Uniform Orientations

Uniaxial flow has been widely used to generate uniform orientation of GO sheets along the flow direction.[6,43] More importantly, the uniaxial flow intrinsically meets the continuous fabrication with high efficiency (Figure 5). We developed the LC wet-spinning to fabricate continuous graphene fibers and films. The uniaxial flow in the spinning tube generates the good alignment of GO sheets along flow direction and fiber axis, which mainly contributes their high mechanical strength and high electrical/thermal conductivities. GF is the first fiber model of 2D macromolecules[28] and the LC wet-spinning has been extended to fibers of other 2D sheets, such as MoS_2,[44] oxides[45] and MXene.[46] Resembling GF, all these fibers feature the uniform orientation of 2D sheets. The uniaxial flow can also be generated by stable shearing in blade coating processes and guides the alignment of 2D macromolecules on substrates, which is much more efficient than the vacuum filtration method.

3.4. Shearing Microlithography for Spatial Orientation Regulation

Inspired by flow-in-tube strategy of wet-spinning, we switched to the flow-around-pole concept and introduced shearing field into LCs by moving immersed microprobe. It generates a shearing microlithography (SML) to freely modulate LCs through introducing localized programmable shearing fields (Figure 5B−D).[34] The shearing force guides the local alignment of GO sheets along moving direction and the shearing program was mapped into the spatial distribution of local LC orders, typically as a lithography to freely program LCs. The basic structure achieved by SML is a typical "π wall" structure, where the orientation of GO sheets undergoes a 180° rotation across the shearing domain. SML enables freely regulated spatial distribution of "π walls", thus making it possible to construct arbitrary orientation structures. Compared with previous electromagnetic methods, our SML exhibits some advantages, such as high accuracy (~10 μm), high efficiency, and low cost. SML has also been extended to manipulate LC orders of other 2D and 1D colloids.[34,40]

3.5. Liquid Meta-crystals

GO LC behaves as a new dynamically stable state, beyond conventional LCs of small molecules and 1D polymers featuring with fast relaxation. This slow relaxation of GO LCs enables the stable existence of meta-structures, which is hard to maintain in mesophase fluids without external fields like electromagnetic fields and surface anchoring. Correspondingly, we utilized SML to design meta-structures by digitally organizing two domains (π wall with vertical alignment and planar part with lying GO sheets). Through this procedure, we can obtain GO LCs with periodic meta-structure, called liquid meta-crystals (LMCs) beyond conventional LC phases. The designed LMCs can completely cover the translation (classic Bravais lattices) and rotational (quasi-crystalline lattices) symmetry in the 2D group (Figure 6). Moreover, the SML also allowed the design of 3D meta-structures, such as moiré patterns and tetrahedrons.

In the fluid state, LMC exhibited anisotropic mechanical properties as-designed and displayed an anisotropic melting behavior like classic crystals under external vibration with varying frequencies. On the basis of LMCs, the spatial organization of alignment of 2D polymers can weave anisotropic microscale domains into designed maps and determine the properties of networks. As preliminary attempts, we used SML to realize the digital programing of GO LC-based films and hydrogel elastomers, achieving facile controlling responses from planar to complex Euclidean and non-Euclidean geometric shapes.[40] Beyond liquid state, the meta-structure of LMCs can guide the formation of solid state materials with designed spatial organization and enrich their

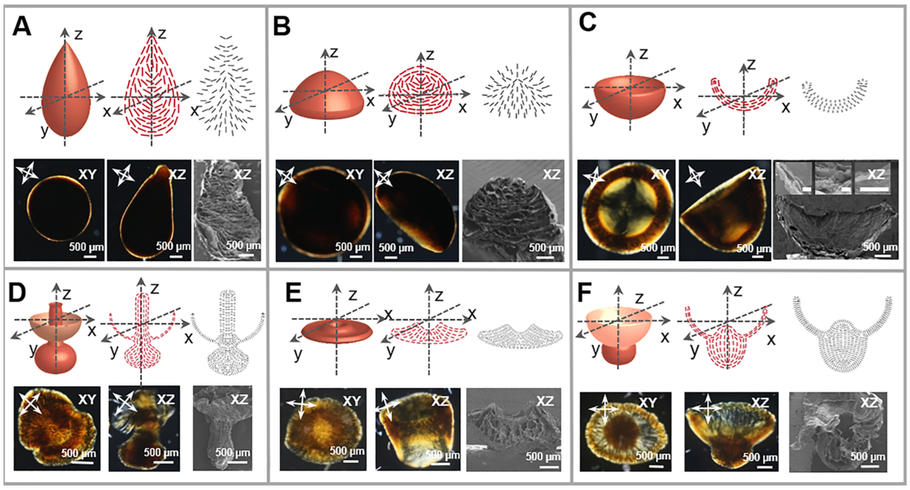

Figure 7. Morphologic GO LCs. Inner organization of GO LCs confined in droplets with different morphology. Top row: schematic illustration. Bottom row: POM and SEM images. Reproduced with permission from ref 47. Copyright 2019 American Chemical Society.

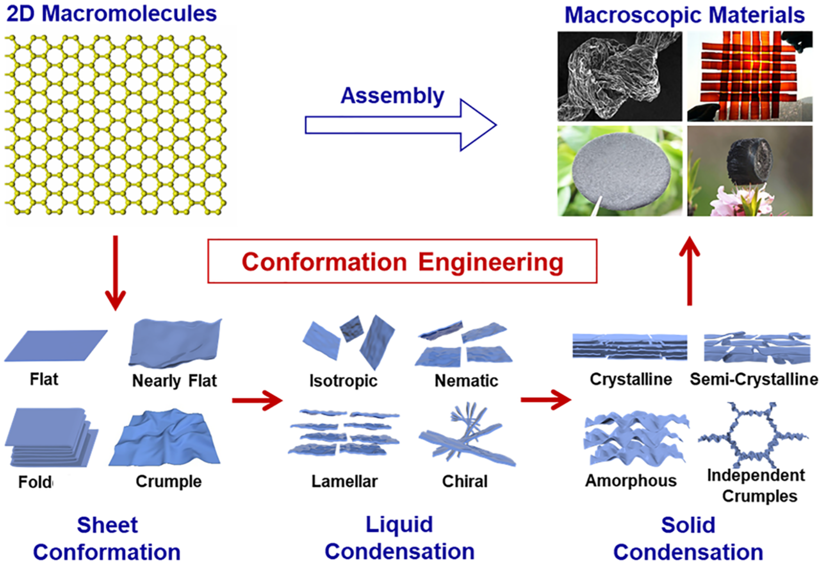

Figure 8. Conformation engineering system of 2D macromolecules. The conformation concept underpins the synthesis, solution properties, liquid crystalline modulation, and consolidation processes to rationally design macroscopic materials with interruptive performances. The SEM image of graphene fiber (top, left) in macroscopic materials are reproduced with permission from ref 28. Copyright 2011 Springer Nature. The image of GO films (top, right) in macroscopic materials is reproduced with permission from ref 38. Copyright 2014 American Chemical Society. The photo of graphene fiber fabrics (bottom, left) in macroscopic materials is reproduced with permission from ref 61. Copyright 2017 American Chemical Society. The photo of graphene aerogels (bottom, right) in macroscopic materials is reproduced with permission from ref 64. Copyright 2011 Wiley.

structural hierarchy, which usually brings anisotropic electrical/thermal conductivities and high fracture tolerance.[34] Starting from our first try, LMC possibly provides the opportunity to find exotic behaviors of colloidal LCs and extend the structural design ability of solid materials to meet more broad applications, such as strong and tough materials, thermal management, and electromagnetic meta-materials.

3.6. Morphologic Liquid Crystals of GO

The geometry of the confined space can guide the organization of LC orders. A drop impact assembly method was presented to fabricate GO LC droplets with multiple morphologies (Figure 7).[47] GO LCs have general features in drop confinement: (1) Near the outer surface, hydrophilic GO sheets tend to be tangent to surface and this tangent alignment extends into the droplet core, resulting in various topological LC defects near core. (2) The topological defect in turn induces surrounding GO sheets to orientate in specific manners like a concentric or radial conformation. The diversified inner organizations in droplets originate from the subtle balance between the surface anchoring energy and the elastic distortion energy, implying a geometric confinement method to prepare diverse particles.

4. CONFORMATION ENGINEERING OF MACROSCOPIC MATERIALS

As we revealed for the rich conformations of 2D polymers in the case of GO, multiscale wrinkles of 3D conformations tend to form in the condensing process, including ripples, folds, creases, and crumples across multiple scales,[48] which is aggravated by the atomic thickness and considerably high

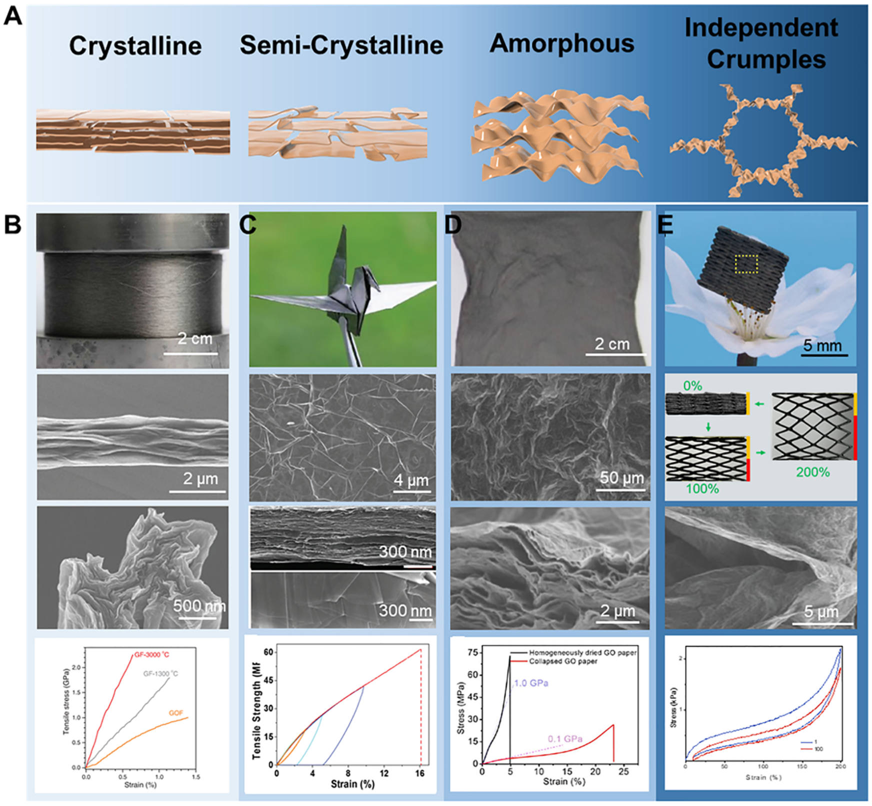

Figure 9. Conformation engineering for graphene macroscopic materials. (A) Typical conformations in the condensed solid state. (B) Crystalline GF with high strength and stiffness. Reproduced with permission from ref 36. Copyright 2016 Wiley. (C) Semicrystalline GPs with massive microfolds and super flexibility. Reproduced with permission from ref 50. Copyright 2017 Wiley. (D) Amorphous rubber-like GPs with random crumples. Reproduced with permission from ref 51. Copyright 2017 American Chemical Society. (E) Highly stretchable GAs with isolated crumples. Reproduced with permission from ref 52. Copyright 2018 Springer Nature.

flexibility. As a conceptual analogy with 1D polymers, we proposed the conformation engineering methodology of 2D polymers to generally govern their description, processing, fabrication, and understanding of the relationship between the structure and properties (Figure 8).[28,36] Recently, we applied this concept to guide the structural design and large-scale production of macroscopic graphene materials (Figure 9).[35−38,49−52] Importantly, the overall performances of graphene macroscopic materials have been greatly promoted by the conformation engineering method.

Although conformation engineering has a broad connotation, we temporarily concluded four major conformation categories based on our recent advances, as referred to the condensed state of graphene: (1) Crystalline packing favors high mechanical strength and outstanding transport properties. (2) Semicrystalline folding can achieve good transport properties and favorable flexibility. (3) Amorphous or glassy wrinkles engender high porosity and flexibility. (4) Intracrumples enable the high stretchability of frameworks. Through designing the conformation, graphene macroscopic materials have exhibited a broad property spectrum as classic polymers, extending from highly stiff structural fibers and films to highly stretchable rubbers (Figure 1C).

4.1. Crystalline State with Flat Conformation

2D sheets intrinsically have extremely anisotropic properties, as exemplified by graphene with extraordinary strength (1.1 TPa of modulus and 130 GPa of strength) and transport properties (∼5000 W/mK of thermal conductivity, *K*) along the planar direction. These properties intuitively triggered the great expectations to fabricate macroscopic materials with interruptive performances.[5,6] To translate these anisotropic properties of graphene to the utmost extent needs the good alignment of 2D sheets with less random wrinkles, approaching the crystalline and even the single crystalline state. In the past five years, improving the packing crystallinity of GO and graphene sheets has become a leading method to upgrade the mechanical and conducting properties of macroscopic materials. To date, GF and graphene papers (GP) have begun to exhibit some expected properties that greatly exceed conventional carbonaceous materials,[35,49−51] such as higher thermal conductivity of GF than carbon fibers and higher strength of GPs over graphite foils, justifying the advantage of 2D macromolecules and their macroscopic materials.

GF is a newly emerged fiber species with regularly aligned graphene sheets along fiber axis, usually featuring with regular wrinkles and folds.[35,37,53−56] LC wet-spinning has been invented to continuously fabricate GFs from the GO precursor and becomes the most valuable method because of its continuity and reliability for potential industrial production. In the first report of GF,[28] uniaxial flow of GO LCs was used to homogenize GO powder LCs to achieve uniform alignment in the solid fibers. Following this work, we used GO with giant size to decrease the boundary defects and a shearing stretching by rotating coagulation bath to increase the regularity of GO alignment and to decrease the random wrinkles along fiber axis. These strategies improved the mechanical strength of chemical reduced GO fibers to 0.5 GPa, together with an electrical conductivity of 4.1 × 10^4 S/m.[35]

To further enhance the crystallinity of GF, we developed a full-scale synergetic defect engineering method that contains graphitization, finning, and gel stretching techniques.[36] Graphitization eliminates the atomic lattice defects, and finning and gel stretching techniques reduce random wrinkles along the fiber axis and compacting voids, meanwhile improving the compactness of graphene sheets (Figure 9B). X-ray scattering revealed that the orientation degree of graphene sheets was improved to 87%, approaching a good crystallinity along the fiber axis. Through these conformation engineering techniques, GF exhibited a high mechanical strength (1.45 GPa in average and 2.2 GPa of the best) and modulus (282 GPa in average and 400 GPa of the best). Meanwhile, the high crystalline order facilitated the transport of electrons and brought a high electrical conductivity of 0.8×10^6 S/m. Apart from our attempts, the alternative microfluidic technique has been proposed by Xin et al. to improve the LC order by narrowing and flattening channels. The resultant graphene ribbons exhibited a strength of 1.9 GPa and thermal conductivity of ~1500 W/mK.[53,54]

In fluid processing GO sheets, an intrinsic challenge exists: the high flexibility of atomically thick GO aggravates the trend to form random wrinkles during drying for solid fibers and papers, which impairs their packing order and crystallinity. To conquer this limitation, we initialized an intercalation modulated plasticization stretching method to diminish the random wrinkles and flatten GO sheets.[49,57] This is a useful processing state of GO to allow the conformation engineering close to solid state. As solvent molecules intercalate into GO solids, the interlayer interaction weakens and brittle GO solids turn plastic, achieving a highly plastic state of GO at high solid content (up to 50%). Through stretching in this near-solid plastic state, we recently promoted the crystallinity of GF and achieved superior overall performances, including mechanical strength (3.4 GPa), electrical conductivity (1.19 MS/m), and thermal conductivity (1480 W/mK).[57] These performances imply that GF can be competitive as compared with the benchmark carbon fibers and exhibit advantages in the functionalities.

We also extended the fiber spinning technique to modulate the conformation and condensed crystallinity of GO papers.[38,49] The random wrinkles of GO papers formed in drying dilute GO dispersions (less than 2% concentration) was flattened by a continuous stretching after solvent plasticization. The flat conformation of GO renders papers with highly ordered lamellar structure, achieving a Herman's order parameter of 0.93 and stacking density of 1.82 g/cm^3. By this facile method, we turned ordinary GO cast papers with inevitable chaotic wrinkles to highly crystalline reduced GO papers with a high σ (1.1 GPa) and functionalities (K of 109.11 W/mK, 1.09×10^5 S/m of electrical conductivity). The crystallinity of GPs can also be improved by the centrifugation repeating coating[58] and the surface spreading shear-flow-induced alignment strategy.[59]

4.2. Semicrystalline State with Folding Conformation

The folding conformation of graphene sheets should bring high flexibility to their macroscopic structures. Meanwhile, giant GO can generate extremely large graphene crystalline grains and guarantee the ultrahigh K of assembled materials. We proposed a microfolding strategy to fabricate graphene semicrystalline films to simultaneously achieve high K and flexibility (Figure 9C).[50] This method solves the conflict between K and flexibility of thermal conductive materials.

The massive microfold conformation was introduced by flattening microgasbags that formed by gas exhaust during thermal reducing GO films. The semicrystalline graphene film is constituted by dense packed graphene sheets with folded conformation. As the lateral size of GO stock increased from 5 to 110 μm, the K increased to reach a peak up to 1940 W/mK, which approaches that (2000 W/mK) of benchmark HOPG and half of that (5300 W/mK) of single layer graphene. The microfolding conformation endows the film considerable flexibility. The fracture elongation reached 16%, higher than that of copper foils and (3−5%) commercial pyrolyzed graphite film. We deduced that a periodic folding conformation structure could relieve the conflict between strength and toughness of graphitic materials. This deduction has been tentatively applied in drying spinning for strong and tough graphene fibers[52] and the twisting technique to generate helical folds and wrinkles around fiber axis.[60]

4.3. Amorphous State with Wrinkles

GO can condense into amorphous or glassy state dominated by wrinkles, crumples, and folds. In principle, this amorphous structure has two distinctive features: (1) loose packing with high porosity, decreasing their mechanical strength yet increasing mass transport for energy storage applications, and (2) large internal space between constituent sheets to allow their movement to deform, enabling high flexibility, which is in contrast to the high stiffness of well-aligned planar sheets (crystalline state).

Poor solvents can drive the collapsing of GO sheets from flatness to folds and crumples, as depicted in the conformation phase map.[21] We designed a sheet-collapse method to soak GO coated dispersions into poor solvent to trigger the collapse and gelation, and the following air-drying resulted amorphous GO and chemical reduced graphene films (Figure 9D).[51] The amorphous films featured rich hierarchical wrinkles and folds across multiple scales and exhibited astonishingly large breakage elongation up to 23% and a rubber-like mechanical behavior, caused by the stretchability of wrinkles. The sheet-collapse method can design the mechanical behavior of assembled papers in a large range, from high stiffness with a high modulus of 1 GPa to considerable softness with a low modulus of 100 MPa, switching from stiff materials to soft rubbers.

Another common strategy to induce crumpled sheet conformation in GO dispersion is hydrothermal treatment. Hydrothermal treatment triggered the gelation to form interconnected 3D framework and the capillary force drove the formation of fine crumpled structures with glassy characteristics.[61] We also used a hydrothermal activation strategy to fabricate highly porous GF fabrics.[61,62] The fine porosity rendered GF fabrics a high areal capacitance of 1060 mF/cm^2 in a thickness of 150 μm. Achieving the glassy state of graphene is a general rule to design compact but porous energy storage materials, making high weight and volumetric energy density compatible for more realistic applications.[63]

4.4. Intra-Crumples

Distinct from the 1D polymer, 2D macromolecules with high bending rigidity can stably exist in the self-standing state to form interconnected molecular frameworks, also known as an aerogel.[64] Graphene aerogel (GA) has been designed to become the lightest solid material with a density of 0.16 mg/

cm^3.[64] GA provides a versatile platform to harness its interface properties of completely exposed surface. GAs usually composed of dilute connection of nearly flat GO sheets, exhibiting considerable compressive elasticity yet little stretchability.[65] Guided by the conformation design, we induced crumpled conformations in the joint of framework by a prebuckled reduction process, aiming to improve its stretchability. The obtained GAs exhibit high stretchability up to 200% elongation at a low density of 5.7 mg/cm^3 (Figure 9E).[52] We revealed that the crumpled conformation can be reversibly stretched and acts as coiled polymer chains of rubber, which is the key mechanism of high stretchability. Besides, the neat carbon rubber exhibited minor plastic deformation (~1%), low energy dissipation (~0.1) and excellent fatigue resistance (up to ~10^6 cycles). Different from the entropy elasticity of polymeric rubber, the elasticity of GA is energetic and has a neglectable influence by temperature and frequency invariance. GAs exhibited a stable stretching elasticity in a wide temperature spectrum from 93 to 773 K. The high stretchability and high thermal conductivity of GA make it a proper candidate as a power grid and thermal transmit network for shape change memory polymeric composites. The high stretching elasticity kept the favorably large deformation strains of polymers to outperform alloys.[66] Extending from our works, further fulfillment of mechanical robustness of GAs still depends on the conformation design of self-standing graphene sheets, for example, periodic crumples and 3D non-Euclidean curvature with saddle shape.

2D macromolecules can be deposited on substrates and used as functional surfaces for wide applications from electronics, optoelectronics to transparent electrodes and sensors, through rich processing methods, such as wet or dry transfer, spinning/blade coating, ink-print, and adsorption.[4] In these processes, the conformation of 2D macromolecules is compulsively determined by complicated interactions. For example, matching the substrate lattice with a graphene lattice can generate an ultraflat conformation to guarantee the extraordinarily high carrier mobility.[67] The prestretching method produced multiscale crumples of graphene to enable the large stretchability for actuators and strain sensors.[68] Albeit considerable research in this broad realm, the philosophy of conformation control can act a self-consistent guidance to precisely describe, design, and fabricate 2D materials with fulfilled performances.

5. CONCLUSIONS AND OUTLOOK

We have started to get the systematic understanding of conformation of 2D macromolecules. The conformation map of GO in solution has glimpsed tremendous conformations of 2D macromolecules. Many fundamental questions emerge for both theory and experiment, such as the validation of theoretic thermal crumpling, quantitative description of conformations, and general mechanism of path dependence and symmetry selection of conformation transition. Beyond these questions, how to design the conformation of 2D macromolecules by tuning interfacial interactions in both time and spatial sequence is a grand challenge. Meanwhile, the conformation diagram needs to expand to other 2D macromolecules with chemical complex and variant configurations.

A 2D polymer expands the polymer category and supplements the topology space of polymer science. To explore the generality and discrepancy between 1D and 2D topologies could be the next central task. On the one hand, the conformation scaling law possibly rules molecular behaviors of 1D and 2D polymers. We can borrow the established theory frame of a 1D polymer to sketch the basic thermodynamic and kinetical behaviors of 2D polymers, such as solubility, conformation, phase separation, and rheology. On the other hand, 2D topology adds extra strong binding in other directions and reduces the free degree as compared with 1D topology. We can foresee that the symmetry breakage in a 2D polymer brings slower dynamic responses, weaker entropy effect, stronger path dependence of conformation transition, the absent entanglement, and so on. The forthcoming research may possibly find more unforeseeable questions. Both the generality and discrepancy between 1D and 2D polymers can help us to establish a unified theory of polymer to include molecular topologies.

The important LCs of GO have been found to include ordinary nematic, lamellar phases, untrivial chiral phase, and meta-periodic states, enabling the macroscopic assembly of ordered structures and materials. Dynamic behaviors of GO LCs are waiting to be deeply understood to extend the processing ability. Along with the whole condensation process for solid materials, conformation evolution also needs to be clearly investigated to form quantitative descriptions. Aside the uniform order, artificial LMC and SML allow precisely control spatial distributions of structural orders in both transient fluid and permanent solid states.

The conformation engineering methodology has been utilized to guide the structural design and greatly promoted overall performances of graphene macroscopic materials. Realizing the extreme properties of graphene materials greatly relies on the precise control of multiscale conformations. For the best, the conformation engineering concept could develop systematic protocols from the molecular conformation and to macroscopic condensed structures. This methodology will not only lead to the near advances of graphene macroscopic materials with interruptive performances but also lay the foundation for basic science, industrial processing, and rationally designed applications in a forthcoming era of 2D macromolecules.

■ AUTHOR INFORMATION

Corresponding Authors

Zhen Xu − *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China;* orcid.org/0000-0001-9282-9753; Email: zhenxu@zju.edu.cn

Chao Gao − *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China; Graphene Industry and Engineering Research Institute, Xiamen University, Xiamen 361005, P. R. China;* orcid.org/0000-0002-3893-7224; Email: chaogao@zju.edu.cn

Authors

Yanqiu Jiang − *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China*

Ya Wang − *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer*

Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China

Complete contact information is available at:
https://pubs.acs.org/10.1021/accountsmr.0c00027

Author Contributions

[#]Y.J. and Y.W. contributed equally.

Notes

The authors declare no competing financial interest.

Biographies

Yanqiu Jiang received his Ph.D. (2020) degree from Zhejiang University under the supervision of professor Gao. He focuses on graphene oxide liquid crystals and graphene-based nanocomposites.

Ya Wang is a graduate student at Zhejiang University under the supervision of professor Xu. Her main research interest is the conformation of 2D macromolecules.

Zhen Xu obtained his Ph.D. degree from Zhejiang University in 2013. He joined the Department of Polymer Science and Engineering, Zhejiang University, as a research professor in 2016. His research covers molecular behaviors and condensed materials of 2D polymers.

Chao Gao obtained his Ph.D. degree from Shanghai Jiao Tong University (SJTU) in 2001. He was appointed as an Associate Professor at SJTU in 2002. In 2008, he joined the Department of Polymer Science and Engineering, Zhejiang University, and was promoted to a full Professor. His research interests focus on graphene chemistry, macroscopic assembly, and energy storage.

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