Two Dimensional Soft Material: New Faces of Graphene Oxide

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CONSPECTUS

Graphite oxide sheets, now called graphene oxide (GO), can be made from chemical exfoliation of graphite by reactions that have been known for 150 years. Because GO is a promising solution-processable precursor for the bulk production of graphene, interest in this old material has resurged. The reactions to produce GO add oxygenated functional groups to the graphene sheets on their basal plane and edges, and this derivatization breaks the π-conjugated network, resulting in electrically insulating but highly water-dispersible sheets.

Apart from making graphene, GO itself has many intriguing properties. Like graphene, GO is a two-dimensional (2D) sheet with feature sizes at two abruptly different length scales. The apparent thickness of the functionalized carbon sheet is approximately 1 nm, but the lateral dimensions can range from a few nanometers to hundreds of micrometers. Therefore, researchers can think of GO as either a single molecule or a particle, depending on which length scale is of greater interest. At the same time, GO can be viewed as an unconventional soft material, such as a 2D polymer, highly anisotropic colloid, membrane, liquid crystal, or amphiphile.

In this Account, we highlight the soft material characteristics of GO. GO consists of nanographitic patches surrounded by largely disordered, oxygenated domains. Such structural characteristics effectively make GO a 2D amphiphile with a hydrophilic periphery and largely hydrophobic center. This insight has led to better understanding of the solution properties of GO for making thin films and new applications of GO as a surfactant. Changes in pH and sheet size can tune the amphiphilicity of GO, leading to intriguing interfacial activities. In addition, new all-carbon composites made of only graphitic nanostructures using GO as a dispersing agent have potential applications in photovoltaics and energy storage. On the other hand, GO can function as a 2D random diblock copolymer, one block graphitic and the other heavily hydroxylated. Therefore, GO can guide material assembly through $\pi-\pi$ stacking and hydrogen bonding. Additionally, the selective etching of the more reactive sp^3 blocks produces a porous GO network, which greatly enhances interactions with gas molecules in chemical sensors. With their high aspect ratio, GO colloids can readily align to form liquid crystalline phases at high concentration.

As single-atomic, water-dispersible, soft carbon sheets that can be easily converted to a conductive form, this 2D material should continue to inspire many curiosity-driven discoveries and applications at the interfaces of chemistry, materials science, and other disciplines.
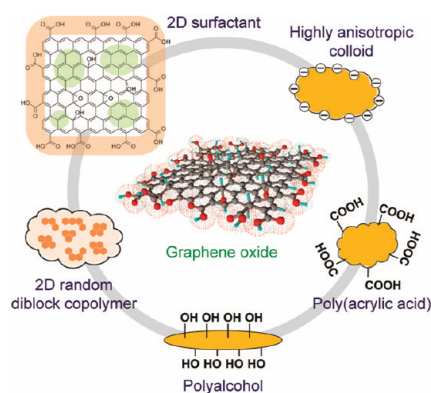
Introduction

Graphite oxide is an old material that has been known for more than 150 years.[1] It is typically synthesized by reacting graphite powder (Figure 1a) with strong oxidizing agents such as KMnO$_4$ in concentrated sulfuric acid.[2] The oxidized graphene sheets, now termed graphene oxide (GO), can readily exfoliate to form stable, light brown colored, single layer suspensions in water and other common polar solvents. As a result of the functionalization, the apparent thickness of GO increases to about 1 nm, as measured by atomic force microscopy (AFM) imaging of single layers (Figure 1b) and X-ray diffraction of the spacing between stacked GO sheets.[3] It has been proposed[4] and recently confirmed by high-resolution transmission electron microscopy (HRTEM) (Figure 1c)[5] that the graphite oxidation reactions break the extended 2D π-conjugation of the
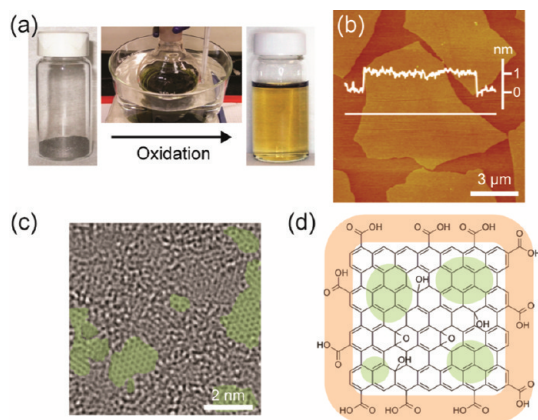
FIGURE 1. Synthesis and structures of GO. (a) GO can be synthesized by oxidizing and exfoliating graphite powders. (b) AFM image and height scan of a GO sheet showing an apparent thickness of around 1 nm. (c) HRTEM image of GO showing discontinuous sp^2 graphitic nanopatches (green) surrounded by heavily oxidized sp^3 carbon domains. (d) A structural model showing ionizable carboxylic acid groups attached at the edges (orange) of GO, epoxy and hydroxyl groups, and graphitic domains (green) on its basal plane. Panel c is reproduced from ref 5. Copyright 2010 WILEY-VCH.

original graphene sheets into nanoscale graphitic sp^2 domains surrounded by disordered, highly oxidized sp^3 domains and carbon vacancy defects. It is now generally believed that GO sheets are derivatized by carboxylic acid groups at the edges, and phenol hydroxyl and epoxide groups mainly at the basal plane (Figure 1d). Although fractionating the conjugated network renders GO sheets insulating, their conductivity can be conveniently partially restored by thermal, chemical, or light treatment, producing chemically modified graphene sheets (aka reduced GO, r-GO).[6,7] Therefore, due to the surging interest in graphene-based materials,[8] GO has regained significant attention as a solution-processable precursor for bulk production of graphene for products such as transparent conductors, chemical sensors, biosensors, polymer composites, batteries, and ultracapacitors.[6,7,9−13]

In addition to being a graphene precursor, GO itself is a quite intriguing material. Like graphene, GO sheets are single atomic layers, yet their lateral dimension can readily extend to hundreds of micrometers. GO connects the two abruptly different length scales of typical molecular compounds and particulate materials. Therefore, it shall naturally be a material of interest at the interface of chemistry and materials science. This Account highlights GO as an unconventional soft material. Soft materials, such as plastics, paints, gels, foams, detergents, and liquid crystals used in some modern electronic display devices, are typically characterized by length scales between atoms and macroscopic

objects and held together by weak interactions comparable to thermal fluctuation.[14,15] Therefore, they have rich dynamics and self-assembly behaviors determined by the subtle balance of energy and entropy. As one can find in a textbook, typical categories of soft matter include polymers, colloids, liquid crystals, membranes, and amphiphiles. GO seems to fit the description of each of these categories.[16] For example, GO is naturally a 2D *polymer* and *membrane* made of a covalently tethered, oxygen-derivatized carbon atom network. GO *colloids* are highly anisotropic and can disperse well in water and some other polar solvents. With its extremely high aspect ratio, GO sheets can form *liquid crystals* if they are aligned in concentrated solutions. As shown in Figure 1c,d, a GO sheet has both hydrophilic (e.g., the edge −COOH groups) and hydrophobic (e.g., the graphitic domains in the basal plane) segments; therefore, it could effectively be a 2D *amphiphile*. Based on its molecular structure and morphology, it should be appropriate to call GO a soft material. On the other hand, the "softness" of GO is also apparent based on simple mechanics since even hard and brittle materials can become soft and flexible as their aspect ratio increases.[17] In the following sections, we will highlight some discoveries inspired by this new soft material perspective of GO.

Interfacial Activities of GO

Since GO disperses well in water, it has long been described as hydrophilic in the literature. If GO is indeed amphiphilic, it should be able to adhere to interfaces and lower the interfacial energy. A surface-selective imaging technique, Brewster angle microscopy (BAM), can be used to monitor the surface activity of GO in water. BAM utilizes *p*-polarized light incident on the bare water surface at the Brewster angle (θ_B, 53° for an air−water interface), the angle at which no reflection can occur. Surface active material can alter the local refractive index to allow reflection (Figure 2a), thus producing bright spots against the dark background in a BAM image. The BAM image of a freshly prepared, undisturbed GO dispersion shows little material on the surface (Figure 2b, left). This is due to slow diffusion of GO to surface since they are very large "molecules". Indeed, BAM would start to spot surface GO sheets after a few hours of stirring the dispersion. One way to speed up the surface enrichment of GO is flotation. The sheets are picked up by rising gas bubbles (such as CO_2 or N_2), transported to the surface (Figure 2a), and imaged by BAM (Figure 2b, right), suggesting that GO is indeed surface active.[18,19]

GO can also create highly stable Pickering emulsions of organic solvents.[19] For example, when a toluene−GO water

biphasic system was gently shaken, GO sheets can adhere to the newly created oil–water interfaces and stabilize submillimeter sized oil droplets (Figure 2d–g). Interestingly, the stability of GO-stabilized Pickering emulsions can be tuned by the pH of the aqueous phase (Figure 2c). At high pH (pH = 10), the edge –COOH groups of GO are fully charged, making GO more hydrophilic and causing it to favor the aqueous medium; therefore few emulsion drops are formed (Figure 2d). As pH decreases, however, GO becomes protonated, less charged, and more amphiphilic. Therefore, the volume of Pickering emulsion phase increases (Figure 2e,f). The emulsification is reversed when pH is adjusted to make the solution basic again, thus returning the GO sheets from the interface to the aqueous phase. This suggests that GO can be used as a pH-responsive phase transfer agent. Drop shape analysis of toluene droplets in GO water has confirmed that the interfacial tension can be lowered by GO, and the effect is indeed more pronounced at lower pH.[19]
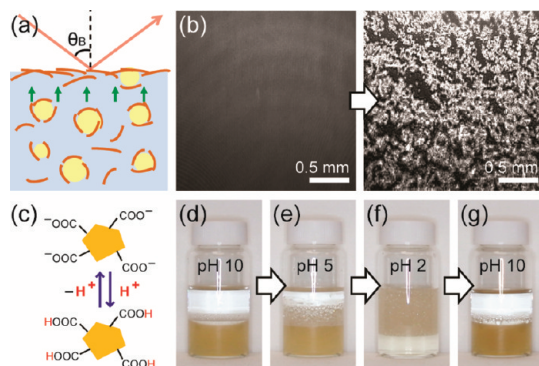

FIGURE 2. Interfacial activities of GO. (a) GO can adhere to the surface of rising bubbles (e.g., CO_2 or N_2, yellow circles) and thus accumulate at the air–water interface by flotation as shown in the (b) BAM images taken before (left) and after (right) bubbling the dispersion. (c) The edge carboxylic acid groups of GO can be reversibly protonated and charged, producing pH-dependent amphiphilicity as illustrated in panels d–g, where GO sheets are reversibly shuttled between the aqueous phase and the oil–water interface by tuning pH.

Interfacial Assembly of Soft GO Sheets

The discovery of GO's amphiphilicity has inspired new strategies to assemble GO sheets at interfaces such as through the Langmuir–Blodgett (LB) technique (Figure 3a),[20] a classical tool for molecular surfactant assembly. Droplets of GO dispersion (typically in water/methanol mixture) can be directly spread onto the water surface, generating a monolayer of GO sheets trapped at the air–water interface.[16,18] The packing density of the GO monolayer can be controlled by moving the barriers and monitored by the change in surface pressure using a tensiometer. The tiled monolayer can be transferred to a solid substrate by dip coating. Figure 3b–d shows GO monolayers deposited on SiO_2/Si substrates collected at increasing surface pressures imaged by fluorescence quenching microscopy (FQM).[21,22] The LB technique has several advantages for making GO thin films. For example, one can precisely control the thickness by collecting one monolayer (~1 nm) at a time. When confined in this 2D space, GO sheets only "see" each other in the edge-to-edge geometry,[16] which is dominated by electrostatic repulsion. Therefore, GO sheets tend to be well dispersed on the water surface. Furthermore, the surface tension of water helps GO sheets stay flat until they are squeezed against each other, thus minimizing the undesirable deformation of the sheets often observed in otherwise prepared thin films. LB assembly can prepare GO monolayers over large areas with tunable density and microstructures,[16,23] which can provide a model system for studying graphene-based transparent conductors,[23] ultracapacitors,[24] and transparent windows for environmental photoelectron spectroscopy.[25]

Since GO sheets are amphiphilic, they could form a uniform surface coating capable of blocking solvent evaporation. This effect can significantly delay drying during drop casting GO thin films. However, it has also inspired a facile method to prepare GO windows for environmental scanning electron microscopy (SEM) sample cells.[25] As shown in
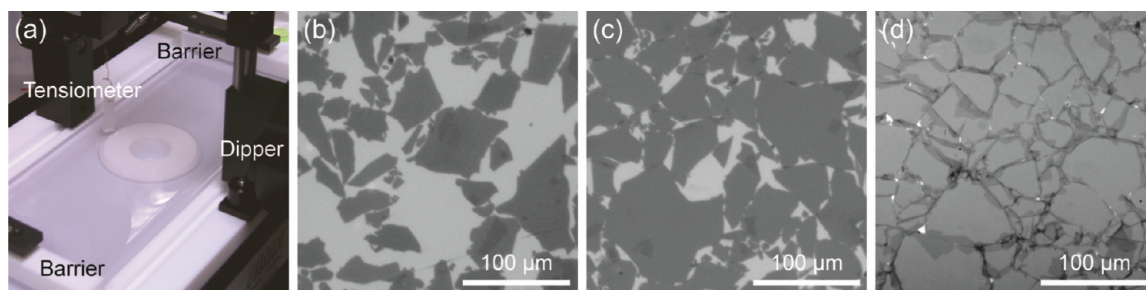

FIGURE 3. Two-dimensional tiling of GO sheets by LB assembly. (a) GO can be directly spread on water surface and controllably tiled using a LB trough. (b–d) FQM images of GO LB monolayers dip coated on SiO_2/Si substrates with increased coverage.
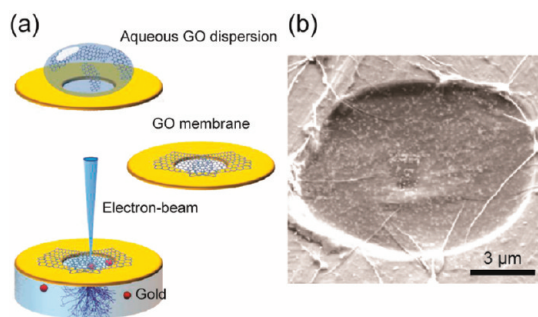
FIGURE 4. Spontaneously assembled GO window for environmental SEM. (a) Since GO sheets are surface active, they can spontaneously migrate to the surface of an evaporating droplet supported on an orifice, eventually forming an electron-transparent but molecularly impenetrable window over the aperture. (b) SEM image of gold nanoparticles (bright dots) suspended in an aqueous medium taken through a GO window. Reproduced with permission from ref 26. Copyright 2011 American Chemical Society.

Figure 4a, an electron-transparent but molecularly impermeable GO window (tens of nanometers thick) can be conveniently made over an open orifice by just drying a droplet of GO solution on the aperture. It can then be used to seal wet or dense gaseous samples, such as gold nanoparticles suspended in water in an environmental cell for *in situ* SEM observation (Figure 4b).[26] The GO window was found to be sufficiently robust to survive the pressure differential during SEM imaging.

GO as a Functional Dispersing Agent

Perhaps the most notable application of surfactant is as detergents or dispersing agents to solubilize materials. The amphiphilic behaviors of GO suggest that it may also act as a dispersing agent. As a proof-of-concept, we chose some graphitic materials to disperse, graphite powders, unfunctionalized multi-walled carbon nanotubes (MWCNTs), and single-walled carbon nanotubes (SWCNTs), all of which are very difficult to process in water.[19] As shown in Figure 5, GO is capable of dispersing all the graphitic materials in water after sonication. For example, while graphite powders in water rapidly settle down almost immediately after sonication, the dispersion in GO water can remain stable for days. An SEM image of the complex (Figure 5d) shows that graphite particles are broken into much smaller pieces, adhering to GO sheets. For carbon nanotubes (CNTs), microscopy analysis of both GO:MWCNTs (Figure 5e, SEM) and GO:SWCNTs (Figure 5f, AFM) spin-coated samples reveals that the nanotubes are disentangled and adhered to GO, which again reflects the $\pi-\pi$ interactions between CNTs and GO. Unlike other dispersing agents, such as molecular surfactants and polymeric wrapping agents, GO does not completely cover
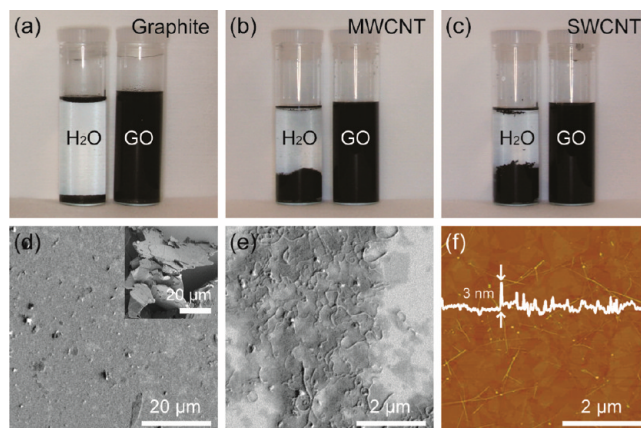

FIGURE 5. GO as a dispersing agent for insoluble materials such as (a) graphite, (b) MWCNTs, and (c) SWCNTs. Panels d−f are SEM (d, e) and AFM (f) images of samples cast from their GO dispersions shown in panels a−c, respectively. Reproduced with permission from ref 19. Copyright 2010 American Chemical Society.

the surface of the CNTs and can be readily reduced to conduct electricity. Thus, GO surfactant can also contribute to the electrical conductivity of the final complex. Furthermore, the soft GO sheets can help to planarize the solution-processed films.[27] For example, the height profile across the spin-coated GO:SWCNTs film in Figure 5f suggests surface roughness of just a few nanometers, which would have been a few hundred nanometers if the SWCNTs were processed without GO or even with common molecular surfactants. It has been found that GO can also disperse other π-conjugated materials, such as organic semiconductors and conducting polymers.[19]

Size-Dependent Amphiphilicity of GO

The unique edge-to-center arrangement of hydrophilic and hydrophobic components suggests that GO's amphiphilicity should be size-dependent.[19] Smaller GO sheets have a higher edge-to-area ratio and should be more hydrophilic. Indeed, we have discovered spontaneous size separation when GO sheets are spread at the water surface: the smaller ones (<1 μm) sink (Figure 6a, right), while the larger ones (>5 μm) stay afloat (Figure 6a, left). The water surface itself is acting as a size-separation filter for GO sheets! Size separation is also observed at oil−water interface.[28] Figure 6b illustrates that Pickering emulsions can selectively extract large GO (>5 μm) sheets from their aqueous dispersion (Figure 6b, left). After repeated extraction steps, no Pickering emulsions can form (Figure 6b, middle) due to the depletion of large sheets (Figure 6b, right).

Smaller GO sheets also form more stable colloidal dispersions because they have higher charge density.[29] While the
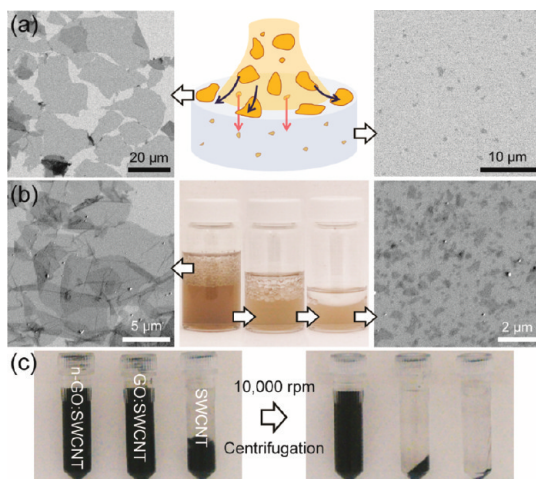
FIGURE 6. Size-dependent amphiphilicity of GO. Smaller GO sheets (<1 μm) have higher edge-to-area ratio and therefore are more hydrophilic than large sheets (>5 μm). Spontaneous size separation is observed at both (a) air−water and (b) oil−water interfaces, where smaller GO sheets tend to stay in water. In panel b, large GO sheets can be selectively extracted by removing the Pickering emulsions. (c) Nano GO (n-GO) sheets (<100 nm) can better disperse SWCNTs, forming a more stable colloidal dispersion as shown in the high-speed centrifugation test.

size of common GO samples can range from hundreds of nanometers to micrometers, smaller and more uniform sheets can be obtained from nanostructured graphite. For example, graphite nanofibers with coin-stacked graphene sheets can be exfoliated to produce GO nanocolloids with uniform sizes tunable between 20 and 50 nm.[29] These GO nanocolloids have greatly enhanced colloidal stability over regular GO and produce more stable dispersions of SWCNTs (Figure 6c).[29]

All-Carbon Composites Created Using GO as a Surfactant

Unlike molecular surfactants or polymeric wrapping agents, GO does not contaminate the functional surface of the materials, such as CNTs. It can also be easily converted to conductive r-GO. Therefore, in contrast to direct growth of one carbon material onto another,[30] a new group of all-carbon composites can be made, in which the graphitic components are brought together using GO as the processing agent. For example, water-processed GO:SWCNTs thin films have been made for the interfacial layers in polymer solar cells.[31,32] Converting GO to r-GO generates a nanotube/graphene composite,[28,33] in which SWCNTs prevent the stacking of graphene sheets and enhance the electric conductivity, resulting in higher specific capacitance and power density of graphene-based ultracapacitors.

Although neither fullerene nor pristine SWCNT is water dispersible, we have noted that they can be directly blended in water by sonication. This suggests that SWCNTs:fullerene heterojunctions may be created by direct mixing under sonication, even though the resulting composite is not water-processable. With GO as a dispersing agent, fullerenes and pristine SWCNTs can be conveniently codispersed in water (Figure 7a).[27] A solid-state Raman spectrum of the ternary hybrid (Figure 7b) shows characteristic signatures of all three constituents. The overall spectrum is red-shifted compared with those of individual components, suggesting strong $\pi-\pi$ interactions between GO, SWCNT, and C_{60}. After thermal reduction of GO, a hybrid of fullerene−nanotube−graphene can be obtained, which was found to be photoconductive with an on−off ratio of nearly 6 orders of magnitude. Figure 7c shows schematic illustration of the device architecture and a corresponding energy level diagram of solar cells using the annealed all-carbon composite as the active layer. An early stage device showed an open-circuit voltage (V_{OC}) of 0.59 V and a power conversion efficiency of 0.21% (Figure 7d).[27] Replacing C_{60} with the more light-absorbing C_{70} can increase the efficiency to 0.85%.[34] Since graphitic materials are highly stable in ambient conditions, it is expected that these all-carbon composites should have greater long-term stability compared with organic active layer materials.

GO-Based Liquid Crystals

Liquid crystal (LC) is another important category of soft materials. It is usually made from molecules or colloids with elongated shapes, which line up yielding orientational ordering even in the liquid state. Since GO has an extremely high aspect ratio, it should be able to form a LC phase. Figure 8a shows a vial of concentrated GO dispersion with parallel sets of "swirling lines" due to anisotropic light reflection/scattering, suggesting local alignment of GO sheets.[35] The liquid crystallinity is confirmed by a prominent optical birefringence when the solution is viewed between two crossed polarizers (Figure 8a, right). Since Kim et al. first reported GO LCs,[35] several groups including us have confirmed the observation and made some additional interesting discoveries. For example, a fiber can be directly drawn by hand from an aqueous LC gel of GO/poly(acrylic acid) composite. The fiber also shows brilliant optical birefringence between crossed polarizers due to well-aligned GO sheets along the pulling direction (Figure 8b).[35] It is also possible to create GO only fibers by wet spinning of the liquid crystalline GO gels.[36] Another work revealed a "shape memory" effect
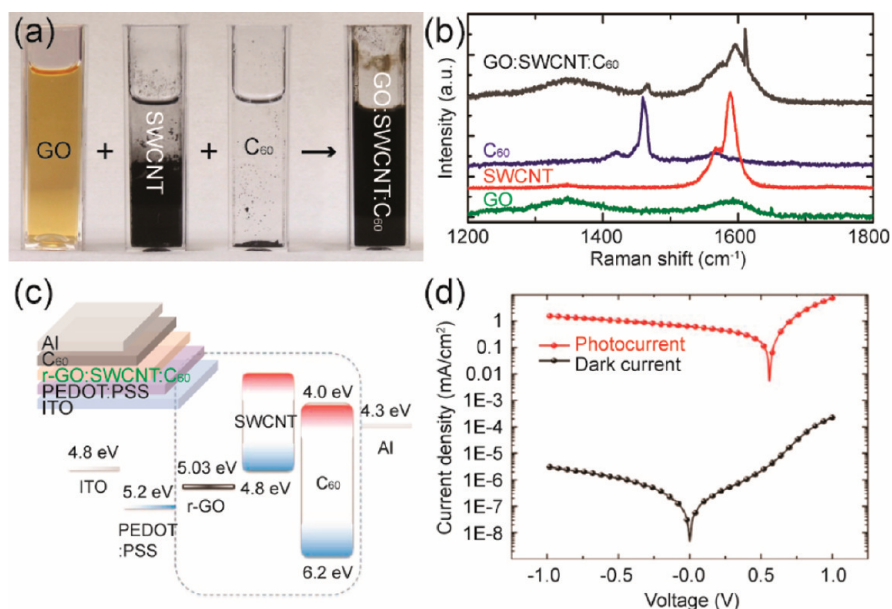
FIGURE 7. Water-processable photovoltaic all-carbon composite. (a) A stable dispersion can be created by sonicating C_{60}, SWCNTs, and GO in water. (b) Raman spectrum of the dried all-carbon composite showing characteristic bands of each element, all of which red-shifted, suggesting intimate contacts between them due to $\pi-\pi$ interactions. (c) Device structure (top left) of a solar cell using the annealed all-carbon composite as the active layer. The corresponding energy level diagram is shown. (d) Current density–voltage ($J-V$) plot of the device clearly showing photovoltaic response. Adapted from ref 27. Copyright 2011 American Chemical Society.
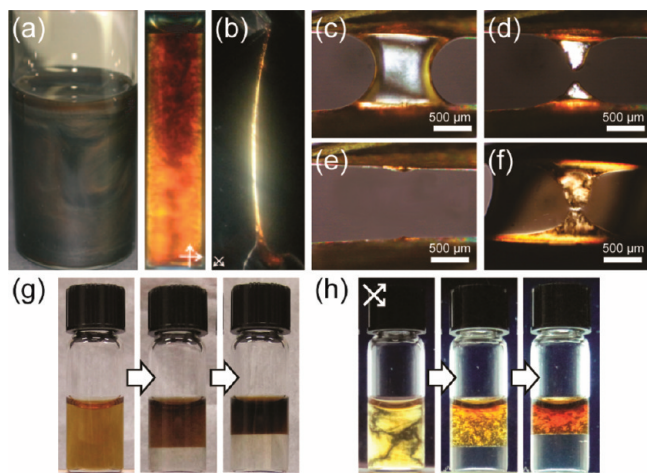

FIGURE 8. GO based liquid crystals. (a) A concentrated GO dispersion showing the "swirl" lines (left), reflecting the ordering of GO sheets, which is confirmed by the optical birefringence seen through crossed polarizers (right). (b) A GO/polymer fiber hand drawn from the liquid crystalline phase, showing strong birefringence. Panels c–f are snapshots showing that dried GO liquid crystalline gel can restore its wet shape upon hydration. (g,h) Depletion-induced phase separation in a binary colloidal mixture of GO and silica (diameter = 30 nm), in which GO forms the liquid crystalline phase on the top layer. Panel a, b, and c–f are reproduced from refs 35 and 37, respectively. Copyright 2011 WILEY-VCH and 2011 American Chemical Society.

of GO LC gel.[37] Figure 8c–f are snapshots taken through crossed polarizers showing the drying and rehydration process of a droplet of GO LC gel confined in a slit. The gel

first shrank (Figure 8c) and deformed into an hourglass shape (Figure 8d), eventually broke apart upon complete drying (Figure 8e), leaving a GO film on both sides of the slit. Upon rehydration, the dried GO pieces expanded and reconnected, recovering its original "wet" hourglass shape (Figure 8f). This behavior is attributed to a hydration-responsive buckling and unbuckling transition of GO stacks.[37]

We also discovered that GO LCs can form through depletion-induced phase separation.[38] When GO is mixed with another aqueous colloid, such as SiO_2 nanoparticles (diameter = 30 nm), which are also negatively charged, the binary mixture can undergo spontaneous phase separation at high silica concentrations (>2 wt %). Figure 8g,h presents images showing the GO/SiO_2 mixture undergoing phase separation over the course of a few days, taken under normal illumination and through crossed polarizers, respectively. Due to the large anisotropy of the GO sheets and great size mismatch between GO and silica, GO sheets tend to align and stack so that silica nanoparticles can be depleted from between the sheets.[38] This entropy-driven depletion process effectively creates a concentration gradient of the charged silica particles, which builds up an osmotic pressure to further push the GO sheets together to form LCs. The rate of phase separation is faster if the silica concentration is higher. For example, with 4.5 wt % of silica, phase separation can be observed after just 1 day. Depletion-driven phase separation is more

pronounced if the size mismatch between the two colloids is greater. Since it is quite typical to obtain GO sheets of a few micrometers in size, phase separation should also occur when GO is mixed with other water-dispersible, noninteracting nanoparticles. Note that direct mixing is commonly used to prepare GO or graphene/nanoparticle composites. Therefore, the phase separation and the tendency of GO to form LCs should be borne in mind as they could affect the uniformity of the final composites.

GO as a 2D Random Diblock Copolymer

GO can also be viewed as a 2D random diblock copolymer with one graphitic block and another highly oxidized block, both of which are about a few nanometers in size (Figure 1c,d). Therefore, GO should be able to guide molecular assembly through both $\pi-\pi$ stacking and hydrogen bonding. We recently discovered that GO strongly interacts with a water-soluble conducting polymer, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) and induces gelation upon mixing (Figure 9a).[39] Interestingly, the addition of insulating GO to PEDOT:PSS actually enhances the conductivity of the resulting GO/PEDOT:PSS film by over an order of magnitude. Based on Raman spectroscopy and AFM studies, this enhancement was attributed to the changes in polymer chain conformation and morphology. The Raman band of the thiophene unit of the polymer was red-shifted upon mixing with GO (Figure 9b,c, insets), suggesting a benzoid—quinoid transition of the PEDOT unit for higher conductivity. Since the quinoid configuration is more rigid, the morphology of PEDOT changes from granular (Figure 9b) to nanofibrillar (Figure 9c) upon interacting with GO.

With greatly enhanced viscosity and electric conductivity, the GO/PEDOT:PSS gel can be used as a conductive adhesive to establish electrical and mechanical connections in optoelectronic devices. For example, a double layer tandem polymer solar cell was fabricated by directly gluing two subcells together (Figure 9d).[39] The subcells used the poly-(3-hexylthiophene):[6,6]-phenyl C_{61} butyric acid methyl ester (P3HT:PCBM) bulk heterojunction system as the model system since it has been developed to a relatively mature stage. The two subcells were first separately fabricated on indium tin oxide (ITO) electrodes and a poly(dimethylsiloxane) (PDMS) stamp, respectively, and then stacked by stamping. Here the GO/PEDOT:PSS glue not only acts as a sticky layer to facilitate the transfer of the PDMS-supported subcell but also acts as an interconnect that physically separates but electrically connects the two neighboring subcells (Figure 9d, SEM) as supported by the nearly doubled V_{OC} of the tandem device.
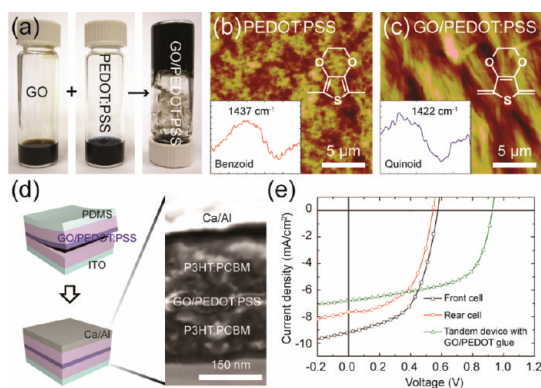

FIGURE 9. GO guided reconfiguration of polymer chains. (a) Mixing GO with conducting polymer PEDOT:PSS solution results in dramatic increase in viscosity. AFM images (b,c) and Raman spectra (insets, bottom left) reveal that adding GO changes the microstructure of PEDOT:PSS thin films from (b) particulate to (c) nanofibril and induces the benzoid—quinoid transition of the thiophene units. (d) The GO/PEDOT:PSS gel can be used as a sticky interconnect to fabricate polymer tandem solar cells by directly gluing two subcells together, yielding much higher V_{OC} as shown in the $J-V$ measurement (e).

This conductive glue enabled, direct lamination approach can turn the conventional layer-by-layer serial mode of device fabrication, which becomes extremely challenging as the number of sequential solution-processed steps increases, to a much more manageable parallel mode. Therefore, it could greatly facilitate the fabrication of organic tandem architectures.

In reminiscence of block copolymer lithography, viewing GO as a diblock copolymer also inspires the creation of nanoporous r-GO.[40] The sp[2]-rich and sp[3]-rich blocks in GO have distinctly different chemical reactivity. Therefore, when treated with an etchant, heterogeneous carbon loss should occur in the basal plane. For instance, hydrothermal "steaming" of GO sheets at 200 °C was found to partially reduce GO and preferentially etch its highly oxidized block (Figure 10a), turning a continuous GO sheet (Figure 10b) into nanoporous r-GO (Figure 10c). When used for gas sensing, this nanoporous r-GO has greatly enhanced sensitivity over the regular nonporous r-GO (Figure 10d) due to much more abundant edge sites.

Outlook

Viewing GO as a 2D soft material has already led to some exciting discoveries such as their use as colloidal surfactants, their 2D assembly, and size-dependent amphiphilicity. Although not necessarily graphene-motivated, these new "soft" insights can certainly help better understand the solution processing and the design of graphene-based materials. We hope the new faces of GO highlighted here can help
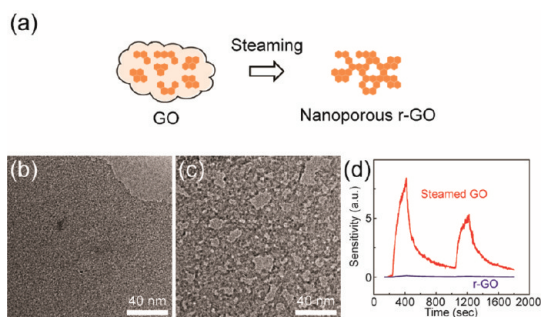
FIGURE 10. Steam-etched nanoporous GO network. (a) The graphitic domains (dark orange) on GO or r-GO sheets are more stable against oxidation than the sp^3-rich areas (light orange). Thus steaming (e.g., at 200 °C) induces pitting and results in a nanoporous sheet. (b,c) TEM images of GO before and after steaming, respectively, showing the development of nanoscale pores. (d) Nanoporous sheet shows greatly increased sensitivity to NO$_2$ vapor (100 ppm) compared with regular r-GO.

inspire more exciting new ideas beyond its current focus as a graphene precursor. Even with seemingly superficial analogies, one could already start to ask many questions along diverse directions. For example, since GO has abundant hydroxyl groups attached to its basal plane, will it have any interesting property and chemical reaction as a poly-alcohol? In fact, the GO/PEDOT:PSS gel shown in Figure 9 was already partially inspired by this thought, because it echoes some earlier reports showing that the conductivity of PEDOT:PSS can be enhanced by polyalcohol compounds such as sorbitol.[41] And if one only focuses on the carboxylic acid groups, which are believed to decorate the edges of GO sheets, both along the periphery and at the carbon vacancy sites (e.g., holes), one would see rings of poly(acrylic acid)!

Thinking deeper in the paradigm of soft materials, there are even more intriguing questions. For example, what would GO sheets look like at the air−water and oil−water interfaces? Since its edge is more hydrophilic than the center, will they be able to bend outward away from the aqueous phase and bulge the interfaces? We would probably need new tools and ideas to answer this question. And as a surfactant, will GO have any micelle structure? Molecular surfactants can assemble into ordered micelle structures in solution after reaching a threshold concentration. In essence, the two signatures of micelles are "aggregate" and "ordering" due to thermodynamics and the "monodisperse" identical molecular building blocks, respectively. Since the size of common GO sheets is extremely polydisperse, the only ordered aggregate structure one can envision is the nematic LC. Therefore, from this angle, the LCs are probably the first known "micelle" structure for GO. On the other hand,

as a 2D polymer, will GO really change its conformation under different solvent conditions?[42,43] And if so, will the driving force be sufficient and controllable to achieve folding or even GO origami? Would the size and shape of GO affect this conformational change because they could alter the flexural modulus and the symmetry of the GO−solvent boundaries, respectively? And how would folding affects properties (e.g., rheology) of the dispersion and solid in the dried state?[44]

GO uniquely links nearly all the categories of soft materials together. As single atomic, water-dispersible, soft carbon sheets that can be easily converted to a conductive form, this century-old material, now with greatly advanced knowledge of its synthesis, processing, and characterization, should continue to inspire many curiosity-driven discoveries and even applications at the interfaces of chemistry, materials science, and other disciplines.

BIOGRAPHICAL INFORMATION

Jaemyung Kim is a Ph.D. candidate in the Department of Materials Science and Engineering at Northwestern University. His current research in 2D materials focuses on high-throughput optical imaging, interfacial activities, and their applications in organic solar cells, for which he has received a Materials Research Society (MRS) Graduate Student Silver Award.

Laura Cote is a Ph.D. candidate in the Department of Materials Science and Engineering at Northwestern University. Her graduate work is focused on controlling the assembly of graphene-based sheets to better understand the materials' structure−property relationships. Her work has been recognized with a MRS Graduate Student Silver Award, P.E.O. Scholar Award, and Josephine de Karman Fellowship.

Jiaxing Huang is an Assistant Professor of Materials Science and Engineering and the Morris E. Fine Junior Professor in Materials and Manufacturing at Northwestern University. He received a Ph.D. in chemistry from the University of California, Los Angeles, in 2004 and was a Miller Research Fellow at the University of California, Berkeley, before joining Northwestern in 2007. His main research

interest is in the general area of material chemistry and processing. Some of the examples include 2D soft materials, organic nanocrystals, and metal nanostructures. He is a recipient of an Alfred P. Sloan Research Fellowship and the NSF CAREER Award.

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