Graphene Patchwork

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ABSTRACT Graphene oxide (GO) holds tremendous potential for large-area electronics, high strength and conducting fillers in composites, and high-surface-area electrodes for energy storage. Graphene oxide for such applications will require manufacturing methods that are industrially compatible but also preserve its unique properties. Recent work by Korkut *et al.* describes a promising new scheme for continuous processing of colloidal suspension of GO into tapes that are meters long and tens of micrometers thick. Tapes of restacked graphene sheets exhibit graphite-like mechanical robustness and electrical conductivity but retain the high surface area and flexibility of graphene.

The unusual properties of graphene have led to demonstrations of novel, fundamental condensed-matter phenomena as well as proof-of-concept devices. Graphene is unusual in many aspects, but the fact that it is a robust and stable two-dimensional crystal with single-atom thickness may be its most intriguing quality. The combination of this stability with the well-known superlatives of graphene—highest current density, thermal conductivity, strength, stiffness, and specific surface area—makes it an exciting material for exploration of new fundamental phenomena and their exploitation for many applications. The rapid development of the field has proven that graphene holds tremendous promise in a wide variety of applications ranging from ultracapacitors to solar cells. The question now is, "how can the technological potential of graphene be realized?" Capitalizing on the exciting properties of graphene for applications will require technologically feasible methods of manufacturing and shaping graphene that retain the unique characteristics of the material. Compatibility with industrial processes will require scalability at a reasonable cost, which typically means making tons of material and processing it in a continuous manner to yield large volumes of products.

There is tremendous progress being made in the large-scale synthesis of graphene. There are several options for synthesizing graphene depending on the desired applications. Chemical vapor deposition (CVD) of single-layer graphene on large-area copper and subsequent transfer onto insulating substrates is a simple and inexpensive way to access high-quality material for nanoelectronics. However, for bulk applications, CVD graphene is unlikely to satisfy the material requirements. Instead, platelets of graphene in large quantities that readily suspend in common solvents are desirable. Exfoliation of graphite *via* oxidation is a scalable and potentially cost-effective route toward mass production of chemically modified graphene-like atomically thin platelets. Graphene oxide is a chemically heterogeneous, atomically thin layer composed of graphene that is decorated with hydroxyl and epoxy groups on the basal plane[1] and a host of functional groups along the edge, as shown in Figure 1. Typical lateral dimensions range from a few to tens of micrometers, depending on the exfoliation chemistry. The oxygen coverage on the graphene basal plane is not uniform, leaving pristine sp^2 clusters within the basal plane, which can facilitate carrier transport and photoluminescence in GO.[1] The presence of oxygen groups serves several technologically important functions: First, they allow GO to be readily soluble in most solvents, creating stable colloidal suspensions; second, they allow unique hydroxyl and/or epoxy chemistry to be performed so that specific molecules can be attached to the GO basal plane; third, they facilitate binding to polymer, ceramic, or metal matrices for composites.

Tremendous effort has been put into exfoliating chemically modified or intercalated graphite in solution phase to achieve colloidal suspensions of graphene. Mass production of graphene-like platelets has seen some success.[2] The next challenge is the large-scale assembly of the exfoliated graphene sheets into a desired format, such

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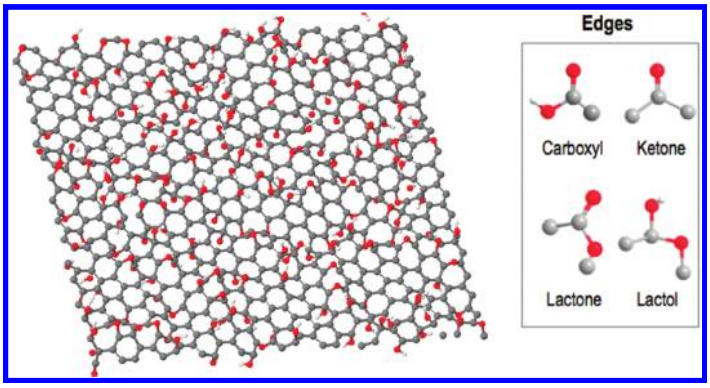

Figure 1. Simulated image of the graphene oxide (GO) atomic structure showing that the basal plane is functionalized with epoxy and hydroxyl groups while the edge can be functionalized with a number of different groups.

as thin films and papers. Uniform deposition of GO thin films over large areas on a variety of substrates has been successfully demonstrated using methods that are compatible with organic or large-area electronics.[1] Additional improvements of the electrical properties will facilitate implementation into production. In contrast, thick films with optimized properties from chemically derived graphene solutions require new developments in techniques and better understanding of their rheological properties. In particular, maintaining microstructural order over large length scales to achieve consistent material properties is a key challenge. Filtration and Langmuir–Blodgett techniques that have been reported in the literature are useful for laboratory-scale demonstrations but do not meet practical throughput, yield, size, and shape requirements of potential bulk products. A reliable technique to achieve meter-scale assembly of graphene is therefore necessary to allow implementation into technology as well as exploration of new applications.

In this issue of *ACS Nano*, Korkut *et al.* report a potentially promising scheme to this end.[3] The authors demonstrate continuous fabrication of a tape-cast network of rGO into paper-like substrates that exhibit exceptional properties. Tape casting, a method traditionally used to produce thin ceramic films, allows fabrication of indefinitely long tapes, limited only by the material supply. In their work, the authors utilized an aqueous colloidal suspension of surfactant-stabilized reduced GO sheets with surfactant and polymer binding agent, which was then fed under a blade onto a supporting surface (see Figure 2). The evaporation of water from the cast film leaves behind a tape of graphene–polymer composite. The thick composite film (tens of micrometers) is easily removed from the substrate, and the polymer is subsequently removed by thermolysis to yield a self-supporting flexible graphene tape. The resulting tape can, in principle, be meters long with a thickness of tens of micrometers and can be handled easily. Restacked graphene sheets exhibit graphite-like mechanical robustness and electrical conductivity but also retain high surface area and flexibility of graphene. The authors find that graphene tapes exhibit 1 order of magnitude higher specific strength and modulus compared to Grafoil, a structurally similar graphitic analogue made from rolling of graphite particles. This suggests that removal of oxygen at high temperatures could facilitate strong interactions, perhaps even covalent bonding, among at least some of the sheets. This could be a route for further improving the strength of graphene-based membranes and papers.

Graphene Rheology. The report by Korkut *et al.* highlights the importance of understanding the rheology of graphene suspensions and applying well-established techniques from the colloidal chemistry and ceramic processing fields. Graphitic nanostructures suspended in solvents come in a variety of forms (single *versus* multilayers of varying lateral dimensions, functionalized *versus* nonfunctionalized) and can be assembled or deposited in many different ways. The properties of the ensemble are often dominated by the interactions between the individual constituents. Thus, controlling the ordering and orientation (*i.e.*, microstructure) along with interactions between the graphene sheets during deposition from the liquid phase is one key parameter for achieving the desired properties. Graphene is a giant, two-dimensional molecule with no immediate analogue, and its behavior in liquids is not well understood. One-dimensional molecules such as linear polymers exhibit different conformations depending on the interactions with the surrounding medium due to their ability to adjust torsional angles of individual bonds. Polymer chains typically form into hydrodynamic spheres in solvents. These polymer chains can entangle with each other above a critical concentration, giving rise to viscous or viscoelastic behavior in liquids. On the other hand, bond rotation is not permitted in graphene and the two-dimensional sheets do not entangle with one other. Instead, graphene sheets may crumple and lock onto each other or present large frictional forces upon sliding. These fundamental differences open up

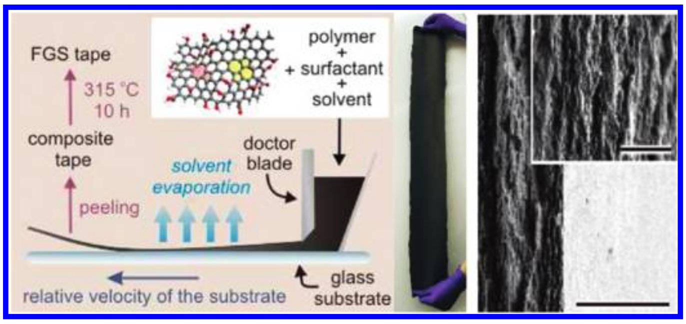

Figure 2. Schematic of the tape-casting method used by Korkut *et al.* to produce macroscopic GO tapes is shown on the left panel. A photograph of the meter-long tape is shown in the middle panel. The SEM image showing aligned GO platelets is shown on the right. Reproduced from ref 3. Copyright 2011 American Chemical Society.

new questions about the rheological properties of graphene-based solutions. Specifically, a number of factors including size, shape, topology, and the chemistry of graphene are expected to play important roles. Understanding the influence of such parameters will be critically important in assembling graphene into complex hierarchical structures for energy and structural devices. Once this fundamental understanding is achieved, then the role of graphene in the rheology of polymer solutions can be tackled.

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Orientation of GO Sheets. Because the properties of graphene are highly anisotropic, orientation of the sheets in an ensemble structure plays a dominant role in determining the macroscopic properties. A number of different approaches have been proposed to achieve uniform orientation of graphene sheets. A simple method for controlling the orientation dependence of graphene-based composite thin films for electronic applications is spin coating at different speeds. The rate of solvent evaporation and shear rate experienced by the chemically derived graphene platelets can be controlled by the spin coating speeds so that sheets are oriented perfectly parallel to the substrate or randomly oriented at some angle to the substrate.[4] Controlling the orientation of the flakes is more challenging in bulk samples. Korkut *et al.* found that their graphene oxide sheets can be oriented parallel to the substrate surface when their rotational motion is constrained during deposition. This gives rise to the large electrical conductivity and mechanical strength of the graphene tapes along their axis.

Graphene Oxide Liquid Crystals. An elegant way to align the graphene oxide sheets controllably in solution into self-assembled structures is to utilize their recently discovered liquid crystalline properties above critical concentrations.[5,6] At the appropriate GO concentrations, typical nematic Schlieren texture consisting of bright and dark regions indicating liquid crystal phases as reported by Xu and Gao[5] are shown in Figure 3. The nematic phase is attributed to interactions between strongly negatively charged GO sheets. The critical parameters influencing the stability of the liquid crystal phase were found to be the ionic strength and pH of the suspension, which can be monitored by measuring the zeta potential of the suspensions. Critically, the liquid crystal phase of the graphene oxide can be maintained even after decoration of sheets by nanoparticles or dissolution of a polymeric phase in the solvent.[6] Indeed, proof-of-concept fabrication of composites with very well-oriented graphene oxide platelets has already been demonstrated by utilizing the nematic characteristics of GO suspensions.[5] Thus, utilization of the liquid crystalline properties of graphene oxide holds tremendous promise for designing self-assembled nanocomposites and structures for energy storage devices.

OUTLOOK AND CONCLUSIONS

There is now recognition within the graphene community that not all "graphenes" are the same and that specific applications will require graphene in various forms. For example, although pristine graphene with minimal disorder is necessary for analog, high-frequency nanoelectronics applications and fundamental studies, it is not desirable for composites where the chemical inertness of the material prevents intimate contact between the matrix and the filler. Instead, defective graphene with readily available functional groups that can be used to perform unique chemistry are desirable for composite and energy storage applications. Other important considerations for these sorts of applications are that large-scale, cost-effective, and sustainable manufacturing, handling, and shaping are required if graphene-based fillers are to displace the existing graphite-based components.

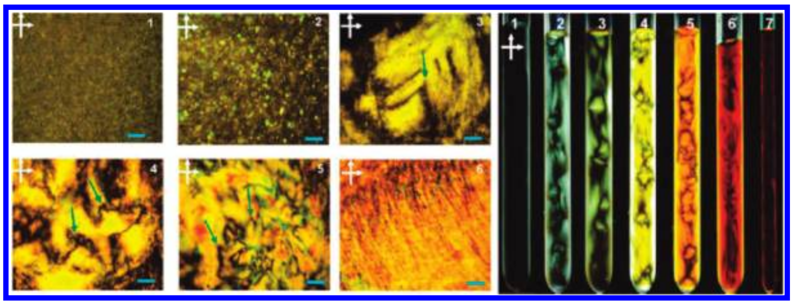

Figure 3. Polarized optical microscopy planar images of various GO suspensions showing distinct Schlieren textures. The arrows point to singularities and biphasic regions. The right panel shows crossed polarizers of GO suspensions of different concentrations in test tubes. Reproduced from ref 5. Copyright 2011 American Chemical Society.

This is a key challenge that must be addressed to go beyond proof-of-concept devices. The work of Korkut *et al.*, therefore, is an exciting new development toward that goal.

Graphene oxide has tremendous potential for large-area electronics, composites, energy storage, and sensing applications. Its heterogeneous chemistry and electronic structure that can be chemically tuned offer opportunities for fundamental as well as technologically relevant research. However, until now, a relatively small amount of work has focused on rheological properties of GO suspensions. Recent work on liquid crystalline behavior of GO suspensions is exciting and should trigger new studies on how to take advantage of these properties. The ability to self-assemble GO platelets in suspensions in a desired manner and integrate them in a wide variety of matrices may lead to new functional composite materials that combine the unique mechanical and electrical properties of GO within metallic, ceramic, or polymeric host materials. For example, combining liquid crystalline properties of GO suspensions with freeze casting to create nacre-like composites with well-aligned GO sheets within a ceramic matrix could substantially enhance the toughness of the composites. Thus, integrating knowledge from colloidal chemistry along with well-established ceramic processing techniques, as well as developing new methodologies for manipulating GO suspensions, will begin to fulfill the promise of graphene-based materials for bulk applications.

Note Added after ASAP Publication: Two reference citations and a typo were corrected in the "Graphene Oxide Liquid Crystals" section. The original version published June 10, 2011. The correct version reposted June 14, 2011.

REFERENCES AND NOTES

1. Loh, K. P.; Bao, Q. L.; Eda, G.; Chhowalla, M. Graphene Oxide as a Tunable Platform for Optical Applications. *Nat. Chem.* **2010**, *2*, 1015–1024.
2. Segal, M. Selling Graphene by the Ton. *Nat. Nanotechnol.* **2009**, *4*, 611–613.
3. Korkut, S.; Roy-Mayhew, J. D.; Dabbs, D. M.; Milius, D. L.; Aksay, I. A. *ACS Nano* **2011**, 10.1021/nn2013723.
4. Eda, G.; Unalan, H. E.; Rupesinghe, N.; Amaratunga, G. A. J.; Chhowalla, M. Field Emission from Graphene Based Composite Thin Films. *Appl. Phys. Lett.* **2008**, *93*, 233502.
5. Xu, Z.; Gao, C. Aqueous Liquid Crystals of Graphene Oxide. *ACS Nano* **2011**, *4*, 2908–2915.
6. Kim, J. E.; Han, T. H.; Lee, S. H.; Kim, J. Y.; Ahn, C. W.; Yun, J. E.; Kim, S. O. *Angew. Chem., Int. Ed.* **2011**, *50*, 3043–3047.