

Personal perspectives on graphene: New graphene-related materials on the horizon

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In this article, I describe my early interest in graphene and contributions that I and my co-authors, in particular, have made to the field, along with a brief history of the experimental discovery of graphene. I then turn to new carbon materials whose experimental syntheses might be on the horizon. One example involves using graphene as a template to generate large-area ultrathin sp^3 -bonded carbon sheets that could also be substitutionally doped with, for example, nitrogen atoms, as one approach to making materials of interest for quantum computing. Such large-area sp^3 -bonded carbon sheets hold tremendous promise for use in thermal management; as a new material for electronics and photonics; and as ultrahigh-strength components in various structures including those used in aerospace, among other applications. Another example is the class of negative-curvature carbons (NCCs) that have atom-thick walls and carbon atoms trivalently bonded to other carbon atoms. Such NCCs have a nanoscale pore structure, atom-thick walls, and exceptionally high specific surface areas, and they fill three-dimensional space in ways that suggest their use as electrode materials for ultracapacitors and batteries, as adsorbents, as support material for catalysts, and for other applications.

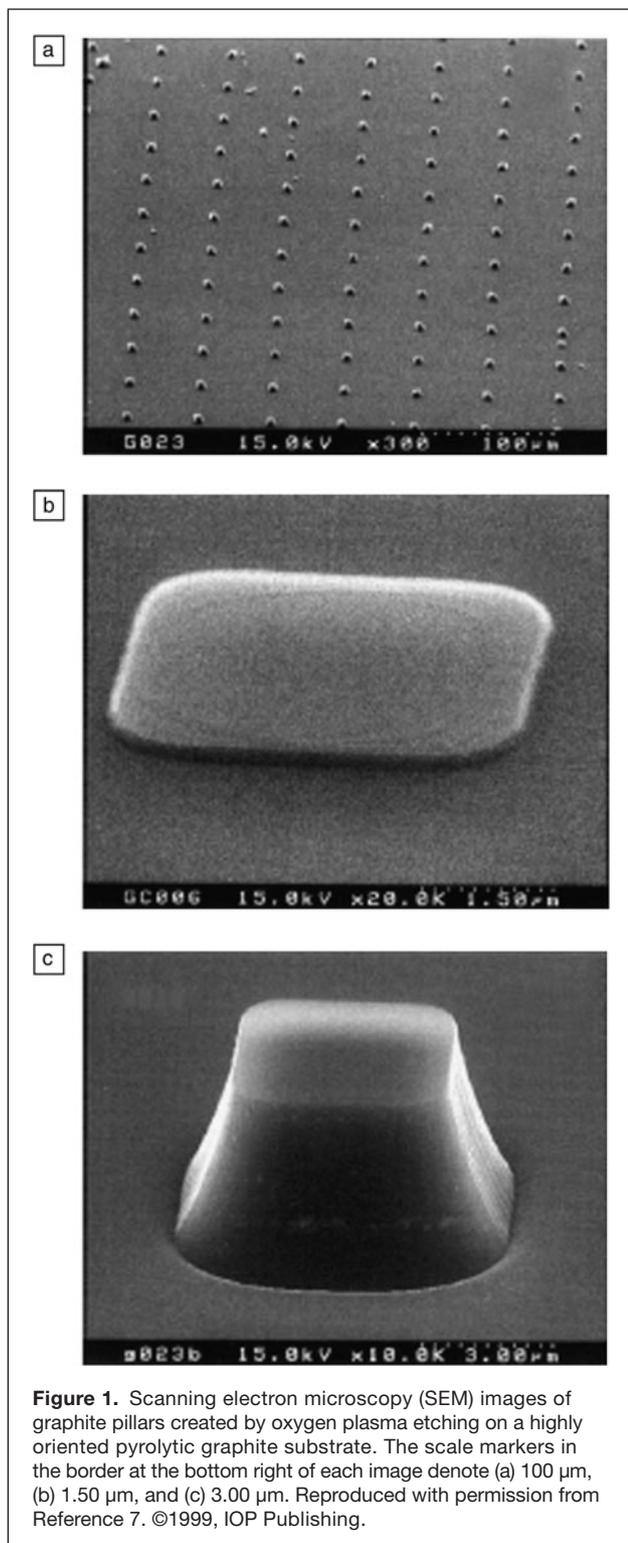
While working at the Molecular Physics Laboratory at SRI International in 1991, I noted an article by Iijima in *Nature* on carbon nanotubes.¹ Considering graphite (three-dimensional) along with this article on carbon nanotubes (one-dimensional), I started thinking: Why not large two-dimensional sheets of sp^2 -bonded carbon (now referred to as graphene)? One could expect such a material to have exceptional mechanical, thermal, and possibly electronic properties, from the well-known in-plane properties of graphite. However, my search of the literature did not find any examples of scalable methods of exfoliating graphite based on liquid-phase processing, although there were some tantalizing discussions of achieving enormous expansion in the interlayer spacing of other layered materials such as vermiculite² and montmorillonite³ in the early literature. Eventually, the expansion can reach a point where the layers are so far apart from each other that crystal integrity is lost and the gentlest agitation of the liquid leads to complete exfoliation. Indeed, vermiculite, a phyllosilicate layered material similar to mica in structure, is exfoliated on a very large scale, and the thin layers obtained are used in many applications, including as an additive to cement.⁴

To date, liquid-phase processing methods for converting graphite to pristine graphene platelets that are scalable to tens

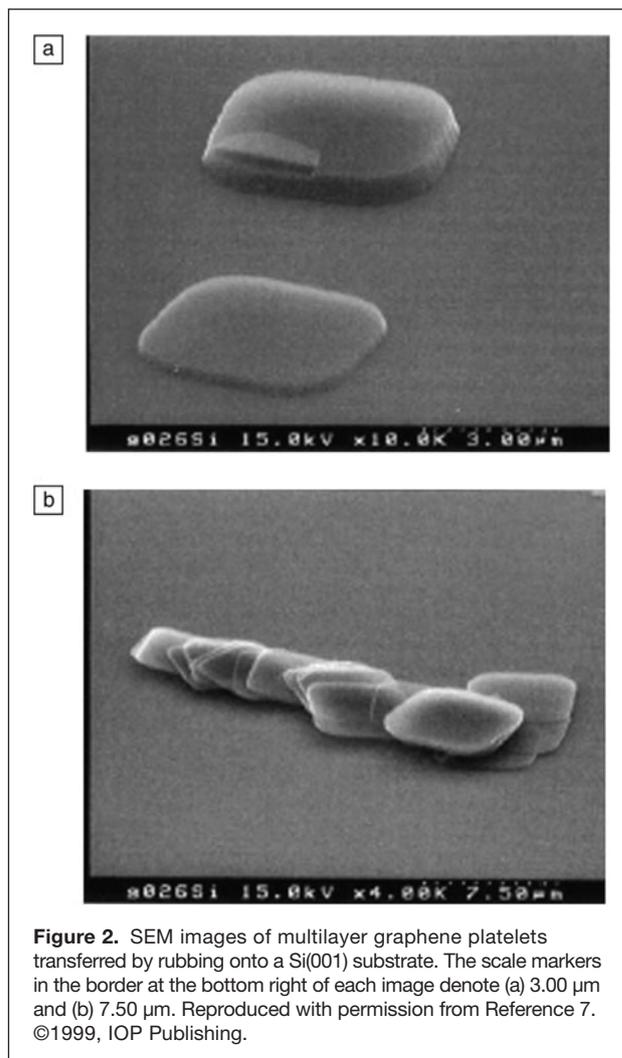
or millions of tons have not been reported. Meeting this challenge would provide such graphene “flake” material for a host of important applications, for example, conductive inks; filler for polymer, rubber, ceramic, and possibly metal composites; electrode material for electrical energy storage in ultracapacitors and batteries; conductive thin films; barrier films; and many others.

After moving to the Physics Department at Washington University in 1996, I conceived of a method to achieve individual layers of graphite (i.e., graphene, as defined by the International Union of Pure and Applied Chemistry in a 1995 publication⁵) of controlled shape and lateral dimensions, through top-down lithographic patterning of graphite, such as from high-quality samples of highly oriented pyrolytic graphite (HOPG).^{6,7} **Figure 1** shows the patterned pillars obtained using this process, and **Figure 2** shows what happened when the pillars were rubbed with a piece of silicon wafer, as observed by scanning electron microscopy. Quoting from Reference 7:

Since graphite can be easily cleaved along the basal plane, the islands can be transferred to flat surfaces of other substrates, such as mica or Si, simply by



rubbing the HOPG surface against the surface of other substrates. Figure 2 shows islands transferred onto a Si(001) substrate. The original islands were 6 μm in height. After being transferred to a Si(001) substrate, all the islands were “fanned out” into smaller-height pieces. Well-separated as well as stacked plates were found on



the surface, as shown in Figure 2. It was noticed that some very thin plates were created by this method of transferring from the patterned HOPG surface onto the Si surface. This implies that more extensive rubbing of the patterned (island) HOPG surface against other flat surfaces might be a way to get multiple or even single atomic layers of graphite plates.

This approach was subsequently used in other attempts at micromechanical exfoliation, including “rubbing” the pillars with a truncated atomic force microscope tip to cleave multilayer platelets⁸ and in the now-famous “Scotch-tape” approach that generated monolayer graphene flakes.⁹

To further explore the idea of exfoliation of controlled-geometry graphene, I formed a collaboration with electrochemist/inorganic chemist Michael Lerner of Oregon State University in 1998–1999. Specifically, we used large intercalants [such as bis(trifluoromethanesulfonyl)imide and other anions with perfluoroalkanesulfonyl substituents] that he and his group had already found could intercalate into large graphite pieces,^{10–13} greatly expanding the adjacent layers. I thought that the large

interlayer separations that his team had achieved in larger graphite pieces would make obtaining individual layers from smaller areas in patterned pillars “straightforward.” Our team was surprised to find that the pillars did not intercalate, and we also did not understand why they did not. (For this reason and also because intercalation is, in principle, a promising approach, I consider this technique to be worth revisiting for pillars created by such types of lithographic patterning or by methods such as direct cutting.¹⁴)

Of the more than 130 articles that I have co-authored on graphene, I next mention a few other ways in which our group (sometimes in collaboration with other groups) has made and studied graphene. In addition to our aforementioned investigations of top-down lithography to create and micromechanically exfoliate layers of graphite,^{6,7} our work has included chemically modifying graphene platelets and performing large-area growth of monolayer graphene by chemical vapor deposition (CVD),^{15–36} as discussed next.

Pioneering studies in the use of chemically modified graphene platelets included using them as a conductive filler to make electrically conductive polymer composites,¹⁵ overlaying them and thereby forming thin films and mechanically strong “paperlike” films,¹⁶ embedding them in silica to make optically transparent electrically conductive films,¹⁷ developing simple optical methods for imaging them at high contrast,¹⁸ and synthesizing ¹³C-labeled graphite and thus ¹³C-labeled graphite oxide and studying its structure with solid-state nuclear magnetic resonance spectroscopy.¹⁹ In addition, we tuned the electrical conductivity of individual platelets of graphene oxide by thermal reduction,²⁰ mapped their solubility behavior using solubility parameters,²¹ and used them as the electrode material in supercapacitor (ultracapacitor) devices.²² We also discovered a graphene-derived material called activated microwave-expanded graphite oxide (a-MEGO), achieving significantly improved performance in terms of energy density²³ and high-frequency response²⁴ for electric double-layer (EDL) capacitors, as well as excellent performance with a-MEGO used as the cathode in a lithium hybrid battery/supercapacitor device.²⁵

Regarding the electrical energy storage possibilities of graphene,^{22–25} note that porous carbons such as activated carbons are used commercially as electrode materials for supercapacitors because of their high specific surface area (on a gravimetric or volumetric basis). This large area translates into a larger stored charge per unit weight or volume, because of more extensive EDL formation over that larger surface. The double layer is formed by the charged carbon attracting oppositely charged ions that are present in the electrolyte, in each half-cell. The high electrical conductivity and surface area of graphene made it a natural choice to test as an electrode material.²²

We also found that, by activating an expanded graphite oxide material, it is possible to generate a new type of carbon (a-MEGO) having atom-thick walls and surface areas exceeding the theoretical limit of graphene itself (which is 2630 m²/g), namely, as high as 3100 m²/g.²³ Use of chemically modified graphene as a precursor allowed this almost-pure-carbon a-MEGO

product to be made (thus, a “graphene-derived” material) that exhibits exceptional performance as a new electrode material.

In another research direction, we discovered a scalable method for the large-area CVD growth of monolayer graphene,²⁶ used Raman mapping of isotopically labeled graphene films to understand growth mechanisms,²⁷ studied CVD-grown graphene for transparent conductive film applications,²⁸ enormously increased the grain size from micrometers to millimeters of monolayer graphene,^{29,30} studied the thermal transport of isotopically labeled graphene,³¹ showed that graphene acts as an excellent barrier protecting bare metals from oxidation,³² discovered that graphene and lightly oxidized graphene are superb supports for transmission electron microscopy imaging of biological molecules,^{33,34} and explained how chemical functionalization in selected regions could be used to make new devices.³⁵ Other studies are listed on the publications page of our research group web site.³⁶

In one of these discoveries, the thermal conductivity of 99.99% ¹²C-pure graphene was found to be significantly higher than that of normal graphene (that is, 98.9% ¹²C and 1.1% ¹³C) at room temperature: about 4700 W m⁻¹ K⁻¹ versus about 2800 W m⁻¹ K⁻¹.³¹ This dramatic difference is due to phonon–isotope scattering, and it is likely that the difference at lower temperatures will be much larger. Could isotopically pure graphene be used for thermal management? If the answer depends only on cost (because it looks favorable in all other aspects), then cost is, perhaps surprisingly, not a strong factor, as ¹²C-pure graphene can be made in square-meter (or larger) sizes for relatively low cost.

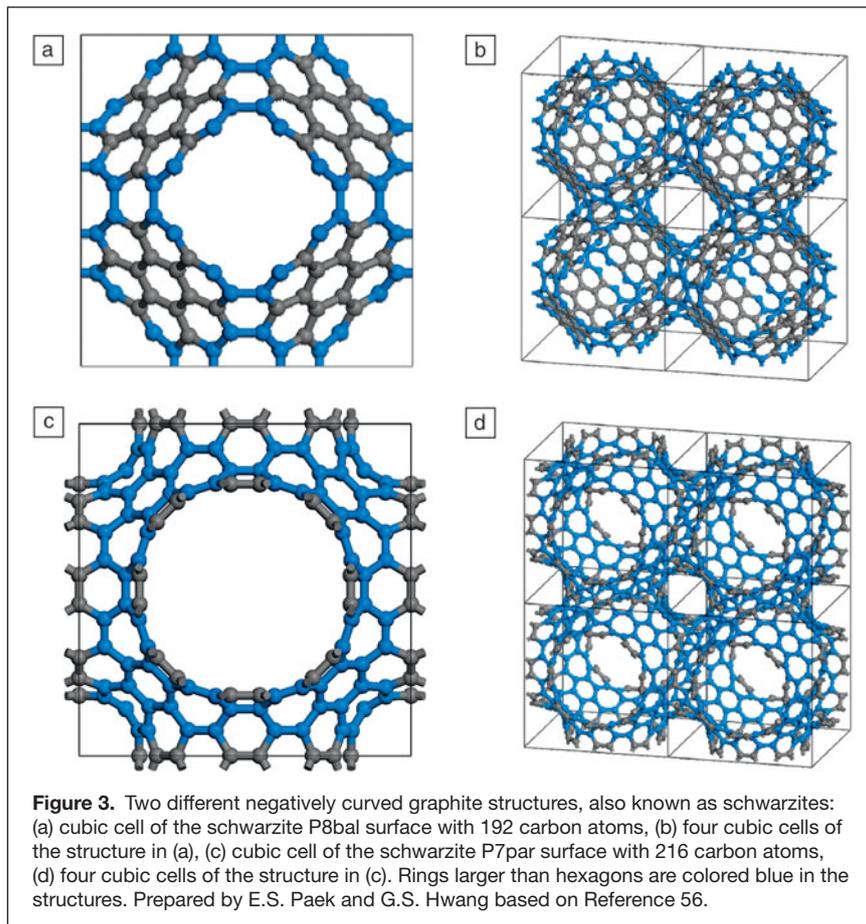
We now turn to an earlier history of experimental work on graphene. It seems that the (experimental) discovery of graphene is (ironically) due to a theoretician, namely, John May,³⁷ who published in 1969 a complete analysis of unassigned low-energy electron diffraction (LEED) data published by the Somorjai group in 1965–1968.^{38–41} These LEED data had been obtained by exposing single-crystal metal substrates to hydrocarbons at elevated temperatures, experiments undertaken because poisoning of such metals in industrial catalyst beds by hydrocarbons was a problem and the mechanism of poisoning was not understood. May assigned those published^{38–41} LEED patterns to “monolayer graphite” attached to the single-crystal substrate surface, and he also assigned other sets of published LEED patterns to stacked layers, including with neighboring graphene layers misoriented with respect to AB (Bernal-type) stacking.

Given the current intense interest in achieving control of the stacking orientation of multiple layers, May’s solving of the structure of misoriented multilayer graphene samples in 1969³⁷ is a sort of “back to the future” success. Controlling interlayer registry is a challenge whose successful achievement will probably also influence the realization of *sp*³ and *sp*²–*sp*³ hybrid materials that might be derived from graphene, as discussed next. (Electronic transport measurements of AB- and non-AB-stacked CVD-grown bilayer graphene have recently been presented and described.⁴²)

I recently presented a Perspective in *Nature* on graphene as a precursor for new materials.⁴³ Here, I expand on this topic to discuss, for example, one possible (but unproven) pathway to revolutionize quantum computing. As mentioned in my Perspective,⁴³ one can consider monolayer graphene as a template from which to build, through clever chemistry, ultrathin “diamond” sheets. (These might be better called something like “ultrathin sp^3 -bonded sheets,” as their electronic, optical, and perhaps thermal properties might strongly differ from those of bulk diamond.) In addition to building such sheets from monolayer graphene, computational studies have suggested that bilayer graphene, when functionalized in certain ways on its top and bottom surfaces, could “collapse” into an sp^3 -bonded layer and reported some of the calculated physical properties of such ultrathin sp^3 -bonded layers.^{44–48} Therefore, graphene should be considered as a precursor to yield new sp^2 – sp^3 hybrid or pure sp^3 materials with exceptional properties and applications.

As our team is now using CVD on copper foils to grow graphene with 3–4-mm grain sizes, graphene with centimeter or larger grain sizes might soon be available. With such a material as a template, sp^3 -bonded sheets with nanometer thicknesses and large grain sizes could conceivably be made. The bandgap of such thin sp^3 -bonded sheets has been calculated to be significantly smaller than that of bulk diamond^{44–48} and could perhaps be shifted by surface functionalization and/or adsorbates, as has been done with graphene. The ability to control thickness down to about the nanometer scale through fine control over the spatial distribution of certain sorts of dopant atoms would yield a variety of doped “ultrathin diamond” films having exceptional mechanical, thermal, and electrical properties. One example would be the incorporation of nitrogen–vacancy (N–V) centers in such sp^3 -bonded sheets through substitution of nitrogen atoms in the carbon lattice. Indeed, N–V centers can be used to configure qubits for use in a quantum computer, and it seems to me that this class of thin sp^3 -bonded sheets of material could advance that technology. The N–V center in diamond and its potential for quantum computing is reviewed in Reference 49.

Another class of carbon materials that are reminiscent of graphene but have not yet been made are “negative-curvature” carbons (NCCs), which, when periodic, are beautiful crystal structures with atom-thick walls composed of trivalently bonded carbon. The presence of n -gons larger than hexagons (heptagons, octagons, etc.) introduces Gaussian curvature equal to -1 , and to date, these types of carbons have been studied primarily by theory.^{50–56} Several examples are shown in **Figure 3**. If such structures can be made in large sheets such that the entire sheet is a continuous covalently connected solid, they could serve



as an almost ideal electrode material for EDL capacitors with exceptionally fast time responses and energy density values rivaling or exceeding those of lead acid batteries.

To understand this claim, the reader should consider reading Reference 23 in detail, which describes a form of carbon with an exceptionally high specific surface area (3100 m²/g) and with atom-thick walls of sp^2 -bonded carbon. Note that this new carbon material is not a continuously bonded sheet of material; rather, it is a powder made up of many particles. Particle–particle resistance is a problem in electrode materials in current ultracapacitors, and elimination of interparticle resistance by having a “totally connected” network of trivalently bonded carbon in large-area sheet form is thus an important goal. NCCs in the form of such large sheets might also be excellent electrode materials for lithium-ion and other types of batteries.

These NCC materials have other interesting calculated attributes, including unusual mechanics;⁵³ the possibility of an all-carbon ferromagnet;⁵⁴ and bandgaps that vary from essentially zero (i.e., metallic) to insulating, depending on the particular NCC modeled.⁵⁵ An infinite variety of these NCC structures are, in principle, available as crystals, and they can also be aperiodic⁵⁰ and ought to perform well in many applications in addition to electrical energy storage, for example, as absorbent materials and as catalyst supports with very high surface areas.

Conclusions

Graphene is now the center of worldwide research efforts. This article presented a brief perspective on the history of the discovery of graphene, including efforts by the author and his team (and collaborators) to make and study graphene and chemically modified graphenes by various methods. Several types of carbon materials that have not yet been realized experimentally were also discussed, including large-area ultrathin sp^3 -bonded carbon sheets and negative-curvature carbons, as well as some reasons why these materials seem exceptionally promising.

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It has been my pleasure to collaborate with a number of talented senior scientists and engineers (and in many cases also with their group members) on chemically modified graphene or CVD-grown graphene and of course to have collaborated with the many graduate and undergraduate students and postdoctoral fellows in my group. Specifically for this article, I appreciate Kevin McCarty for pointing out the work of John May and A.L. Ruoff and L. Colombo for critically reading the manuscript. Funding support from NSF, ONR, SWAN-NRI, DOE, DARPA, ARO, AFOSR DURIP, Goodyear, ARPA-E, and the W.M. Keck Foundation has been and is appreciated.

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