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Controlling Graphene Properties Through Chemistry

Carbon is a fascinating element because of its ability to form sp , sp^2 , and sp^3 hybridization of electronic orbitals, which leads to a large variety of compounds and structures with a very wide array of properties. Carbon is the basis for organic life, but it also forms a number of inorganic allotropes and forms, which have been extensively studied by material scientists, physicists, and chemists. Graphite, diamond, fullerenes, and nanotubes have received much attention because of their diverse properties that find numerous applications in virtually every area of human activities.¹ Naturally, carbon chemistry, especially the chemistry of graphitic carbon, is one of the most studied subjects,¹ and we know a lot about it. So, why the excitement? It is because chemists can now play with not just the surfaces of bulk graphite samples, they can handle single layers of carbon built of a hexagonal lattice with a 0.142 nm bond length, which we call graphene.² With the interest of researchers shifting from other carbon materials and nanostructures toward graphene, it is not surprising that the number of papers on graphene has been increasing exponentially in the past 5–6 years (from 30 papers having “graphene” in the title in 2005 to more than 2600 in 2010, according to ISI).

This issue of *JPC Letters* includes two Perspectives that are concerned with graphene chemistry. The Perspective by Sun, James, and Tour³ describes synthesis strategies and ways to manipulate the structure in addition to specific electrical and optical properties of graphene. The methods for producing structure-doped graphene-based materials, such as nitrogen-doped graphene and hexagonal BNC, and their properties are discussed. The authors also cover covalent functionalization of surfaces and edges via hydrogenation and azide reactions.

The Perspective by Niyogi, Bekyarova, Hong, Khirzoev, Berger, DeHeer, and Haddon⁴ is concerned with the use of covalent chemistry for graphene electronics. It describes how bond-forming chemical reactions can be applied to engineer the electronic properties of graphene circuitry. The authors discuss covalent functionalization of the surface producing dielectric regions in a graphene wafer, the use of Raman spectroscopy and scanning tunneling microscopy for characterization of surface moieties, and correlation between the surface chemistry and electronic and magnetic properties of graphene. When one of the coauthors of this article, Walt deHeer, delivered an award lecture after receiving the Utz–Hellmuth Felcht Award for the invention of graphene-based electronics (sponsored by SGL Carbon) at the world conference on CARBON in Shanghai in July 2011, he talked about physics of graphene. I asked him after his lecture about the role of chemistry in making graphene electronics a reality, and he answered that chemistry will play a major role in tailoring the electronic structure of graphene for future devices and circuitry. It is great to see a Perspective on graphene chemistry coauthored by deHeer to be published so soon after this meeting.

The Nobel Prize in Physics was awarded for graphene in 2010 because the isolation of stable sheets of graphene revitalized and inspired the physics community. While the initial excitement was in the physics community, graphene provided plenty of work for

chemists who developed large-area and large-volume synthesis methods as peeling graphene layer-by-layer using scotch tape was not practical. Second, covalent functionalization of the surface and edge chemistry of graphite can be used to pattern graphene and modulate its band gap, electron scattering, and other physical properties.⁴ However, modification of graphene is not easy because high energy barriers need to be overcome due to interlayer conjugation and van der Waals forces between single layers in multilayer graphene. Also, unlike conventional crystals, graphite and graphene have a tendency of forming folded (arched) edges⁵ that are difficult to functionalize.

It is important to note that covalent functionalization of graphene is of great importance for many applications beyond electronics. Transparency of conductive graphene films for touch screens, smart windows, and other optical applications, as well as adhesion of those films to glass or polymer can be improved by controlling the surface chemistry of graphene. Surface chemistry determines the capacitance and cyclic lifetime of supercapacitor electrodes. Biocompatibility and cytotoxicity of graphene will be controlled by the surface functional groups. Bonding to the polymer matrix through covalent bonds will be required to maximize thermal and mechanical properties of nanocomposites.

Both Perspectives^{3,4} focus on chemical modification for electronic applications, but we also need to produce bulk quantities of graphene for composites⁶ and electrical energy storage devices (supercapacitors and batteries).⁷ Those applications can use tons of graphene annually but will only become commercially viable if the price of graphene approaches that of clay (the most widely used nanofiller in composites) or exfoliated graphite (material of Li ion battery anodes). Multilayer graphene is the candidate for those large-volume applications.⁶ Moreover, we need this graphene to show hydrophilic or hydrophobic properties on demand, have excellent electrical conductivity (to replace carbon black as a conducting additive), and be able to form covalent bonds with polymer matrixes. Functionalization and exfoliation techniques that will not degrade the lattice structure, electrical conductivity, and mechanical properties of graphene are required for these applications. Chemical functionalization is also important for stabilizing colloidal solutions of graphene sheets.⁸

Synthesis methods for graphene range from oxidation and exfoliation of graphite (graphene oxide synthesis and reduction) to vacuum decomposition of SiC, hydrothermal synthesis, chemical vapor deposition, unzipping of nanotubes, and dehydrogenation of polyaromatic compounds.^{3,9} The first one is the best for large-volume manufacturing of multilayer graphene, while the latter two are the most compatible with electronic device fabrication. However, what we need is an ability to produce a monolayer of graphene (preferably, a predesigned pattern) on any surface, under mild conditions, on a large area, and at low cost.¹⁰ Developing such a technique will require a major effort from chemists.

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Finally, chemically modified graphene-based structures such as graphene oxide (oxidized graphene), graphane (hydrogenated graphene), or h-BCN (boron- and nitrogen-substituted graphene) may offer new exciting properties that differ from that of pure graphene sheets and enable new applications of 2-D materials.³ Chemical bonding of metal and oxide nanoparticles to graphene is important for electrochemical energy generation (fuel cells) and storage (batteries and pseudocapacitors).¹¹

The ability of scientists to chemically modify 2-D single- and multilayer graphene is already a triumph of chemistry. However, local functionalization is currently achieved using scanning probe tips, which is not a scalable process. Selective functionalization and patterning of graphene with nanometer accuracy is of extreme importance for electronic device manufacturing. The effect of the underlying substrate on chemical interaction of graphene must be better understood because graphene is usually used on a substrate, whether it is silica, silicon, SiC, or graphite (multilayer graphene). The understanding of the effects of heterogeneity and defects on chemical interactions and properties of graphene requires further study. Understanding transport in multilayer graphene is complicated by the presence of multiple conducting graphene layers, whereas covalent functionalization typically changes the surface layer only. Further research on graphene chemistry should enable any surface functionality “on demand” as well as achieve the atom-by-atom functionalization of graphene with a high precision and on large-area graphene wafers.

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