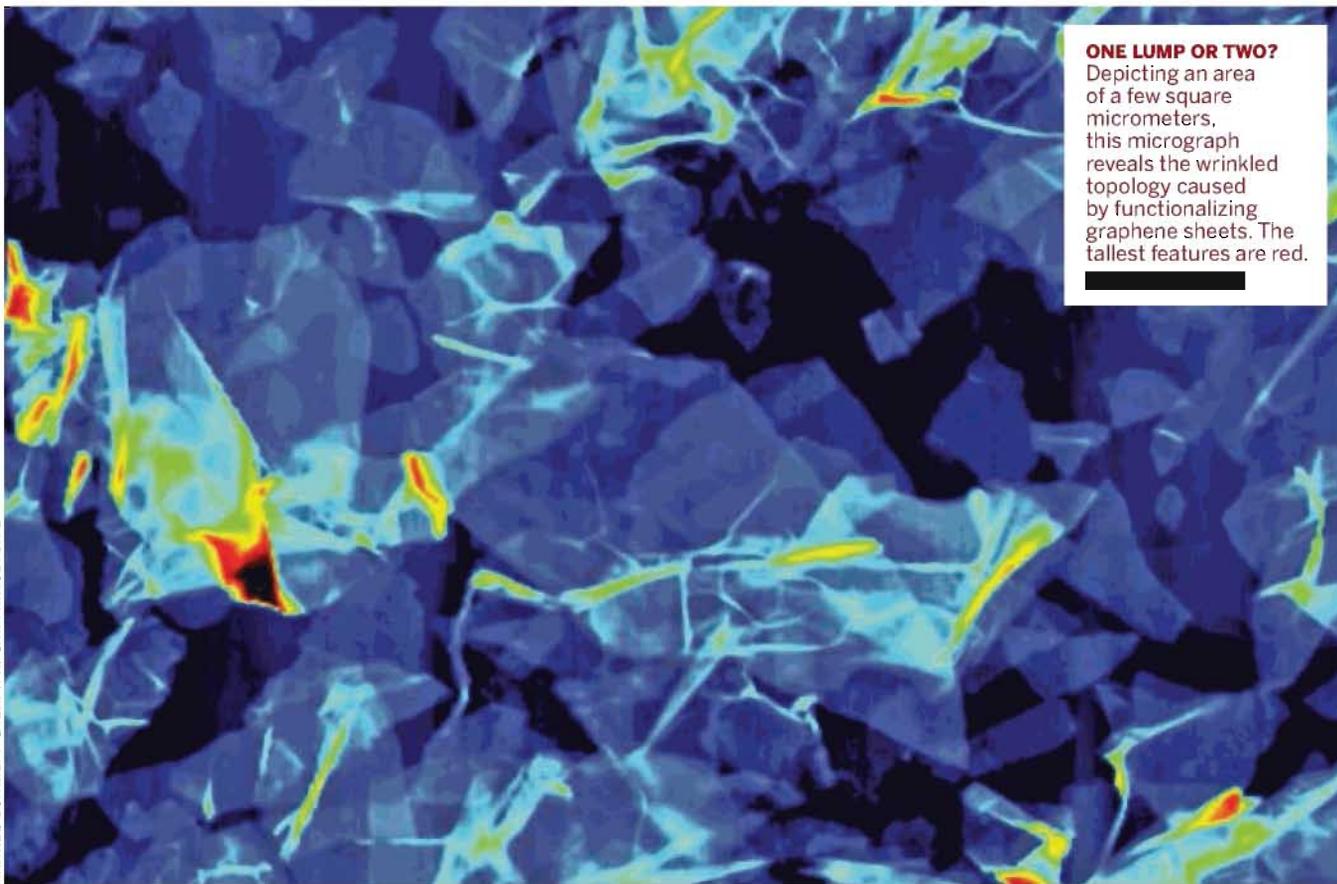


ONE LUMP OR TWO?

Depicting an area of a few square micrometers, this micrograph reveals the wrinkled topology caused by functionalizing graphene sheets. The tallest features are red.

THANNES SCHNIEPP & ILHAN AKSAY/PRINCETON U



GRAPHENE: CARBON AS THIN AS CAN BE

Surprising mechanical, structural, and electronic properties of **ONE-ATOM-THIN SHEETS** grab widespread attention

MITCH JACOBY, C&EN CHICAGO

WHAT ARE THE KEYS to designing a material that rivets researchers' attention? Rare and precious elements? Previously unknown bonding configurations? How about fascinating molecular and geometric structures?

If those are the elements of a winning formula, then a simple thin sheet made from just one type of atom ought to be a scientific dud. But that's not the way things are shaping up for graphene. First isolated just a few years ago, graphene—a single layer of carbon atoms tightly packed in a honeycomb structure—quickly grabbed center stage in the scientific world. It doesn't seem to be budging from there.

"Graphene is one of the hottest topics in materials science these days," says Jan-nik C. Meyer, a postdoc at the University of Ulm, in Germany, who co-led a groundbreaking electron microscopy study of graphene two years ago. Indeed, a quick peek at the numbers on the preprint server arxiv.org, which captures only a fraction of journal submissions, shows that well over 1,000 papers about graphene have been written since 2007.

The widespread interest in this planar form of carbon stems from fundamental science surprises and a host of potential commercial applications. Intrigued by the material's combination of outstanding me-

chanical, structural, electronic, and other properties, scientists and engineers are eager to get to know graphene in detail. They see bright opportunities to fashion circuit components from graphene for use in computing, digital displays, and other types of electronic technologies. Researchers are also exploring methods for synthesizing graphene in commercial quantities, chemically modifying the material, and using it to prepare advanced composites. These applied studies, as well as ones that focus on graphene's fundamental properties, are taking place in academic and major industrial facilities, as well as in the labs of small start-up companies.

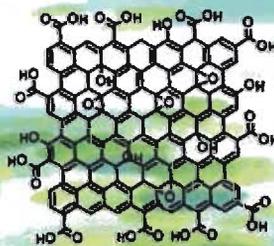
A popular starting point for telling graphene's story is 2004. That's the year Andre K. Geim, a physicist at the University of Manchester, in England, together with Kostya S. Novoselov, a postdoc at the time, figured out how to isolate and image single sheets of graphene. Conceptually, however, the material has been around since long before that date. For years, scientists have discussed and described the properties of many carbon-based materials in terms of sheets of graphene.

Graphite, for example, is described as a three-dimensional crystal built from graphene layers. And fullerenes, including carbon nanotubes and buckyballs, which have been known since the 1980s, are thought of as wrapped or rolled-up forms of graphene sheets.

THE STORY could start even earlier because graphite has been used as pencil "lead" for centuries, which means that graphene actually has been close at hand for a very long time. Every time someone scribes a line with the ubiquitous pencil, the resulting mark contains bits of this hot "new" material, Geim says. But graphene isn't readily available in freestanding, single-sheet form in ordinary pencil markings, so its properties cannot be explored or exploited.

Not surprisingly, scientists have been trying for a long time to split graphite into its constituent parts. For years, their efforts met with little success. Early on, researchers tried a chemical method for thrusting molecules or atoms in between

POND-ER THIS Floating like water lilies, micrometer-sized flakes of functionalized graphite oxide can be corralled successively closer until they coalesce into a centimeter-sized close-packed continuous sheet (bottom).



graphite's layers to pry apart the graphene sheets. This chemical exfoliation technique generally yielded a slurry or sludge of graphitic particles similar to wet soot. The chemical method soon gave way to a mechanical approach to cleaving graphite.

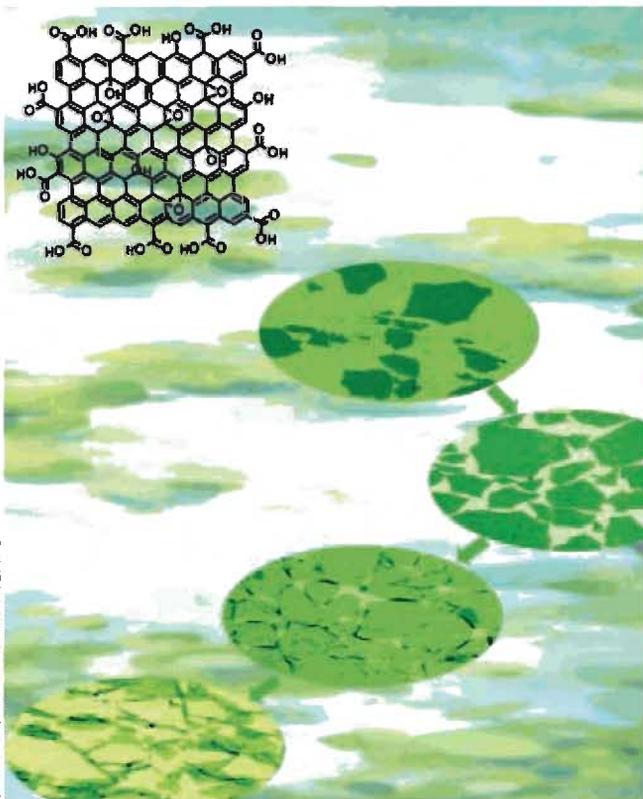
By rubbing or scraping graphite against a surface, researchers managed to peel off microscopic chunks as thin as roughly 100 atomic layers. Referred to as micromechanical cleavage, that method was taken up by scientists in many labs and worked well enough almost 20 years ago to produce graphite slivers that were optically transparent. Yet the slices still weren't atomically thin.

More recently, Philip Kim and coworkers in the physics department at Columbia University sought to develop a more controllable, higher tech mechanical-cleavage process. They attached a graphite crystal to an atomic force microscope (AFM) tip and used the device to make nanometer-sized graphite markings on silicon wafers. Fondly referred to as the "nanopencil," Kim's

AFM "writing" instrument decorated the wafers with very thin graphite crystallites. "It worked pretty well," Kim says. "We were able to get down to 10 or 20 layers," but no thinner.

Looking back to the first few years of this decade, Kim and Geim say that at that time no one really expected that one-atom-thick sheets of graphene could actually exist in a freestanding state. Yet they were determined to see how thin they could go. Geim

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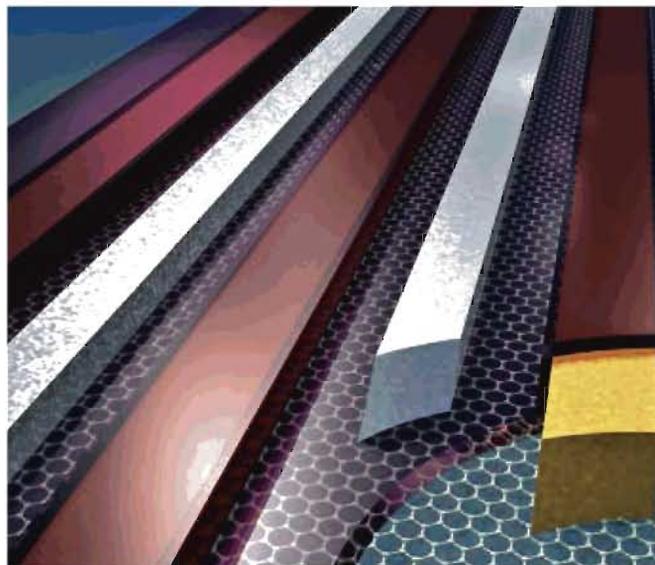
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explains that conventional wisdom based on decades-old thermodynamics arguments held that “freestanding” graphene—meaning a one-atom-thick film that’s somehow suspended or resting on a nonbinding support such as silicon dioxide—would be unstable against the “urge” to roll into a nanotube or other curved structure. “At that time, graphene was considered a hypothetical or academic material,” Geim recalls.

Then in 2004, Geim’s group turned that notion on its head. Starting with flecks of graphite generated by mechanical cleavage, the Manchester team stuck these little specks of carbon onto adhesive tape, folded the sticky sides against the tiny crystals, and pulled the tape apart, cleaving the flakes in two. By repeating this rather rudimentary splitting process a couple of times, they prepared thinner and thinner slices. Indeed, they showed that some of the pieces were one-atom-thick bits of graphene that remain surprisingly stable even at room temperature (*Science* 2004, 306, 666).

Kim remembers well the day he first read about the Geim group’s results. “I was shocked,” he recalls, “and kind of depressed.” He had submitted a paper detailing his group’s work with the nanopencil just days earlier and was surprised to discover that he had been beaten to the atomically thin finish line by a team using such a simple method. Kim quickly decided to abandon the AFM approach and began experimenting the next day with the “Scotch-tape method,” as the technique was soon to be called. “It’s a simple brute-force method,” Kim says. “But the beautiful thing is, it works.” As Kim recalls, within one week, his group reproduced the Manchester results.



PHAEON AVOURIS/IBM

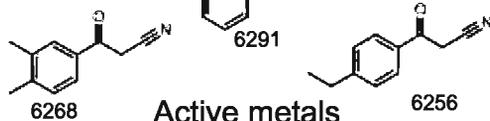
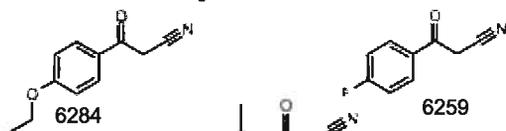
With the benefit of hindsight, the existence of one-atom-thick 2-D crystals can be reconciled with theory. A key piece of that reconciliation came from a transmission electron microscopy (TEM) study in which Meyer teamed up with Geim and others to probe graphene’s structure.

TEM samples are typically prepared on a mesh or other holey support so that electrons can pass through the sample and reach the detector. By using lithography and other procedures, Meyer came up with a way to drape graphene flakes across a scaffold made from microscopic wires, thereby leaving relatively large sections of graphene (tens of millions of atoms) hanging freely over the holes. The group found that the one-atom-thick films were highly ordered yet slightly warped or corrugated—a structural feature that they argued was key to the 2-D crystal’s existence and surprising stability (*Nature* 2007, 446, 60).

THE FINDINGS quickly drew other scientists to make their own samples and study graphene’s properties. The material was found to be extremely strong and stiff and a faster room-temperature conductor of electrons than any other material. Physicists were especially enthralled because graphene appeared to be endowed with some quirky relativistic properties. As a result of the speedy and unimpeded way in which electrons travel through graphene, the electrons behave more like massless relativistic particles, such as photons, than ordinary electrons. The upshot, according to Kim, is that this easily obtained form of carbon provides a simple and relatively low-cost lab system for testing the predictions of relativistic quantum mechanics—the kinds of predictions that previously were thought to be observable strictly in particle accelerators and black holes.

It’s no surprise that graphene’s unusual properties and promise for electronic applications grabbed attention and generated “a bit of hype,” according to Geim. The way he sees it though, the basic science is fascinating in its own right. “From a chemistry perspective, graphene is quite unique,” he says. “It can be thought of as a giant flat macroscopic molecule of infinite size.” He adds that graphene may turn out to be the first example of a

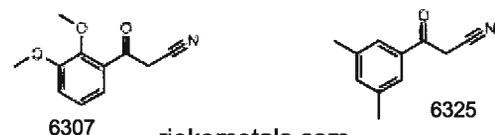
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whole class of one-atom-thick materials. Time will tell. Meanwhile, researchers are focusing on developing synthesis methods and applications.

The Scotch-tape “synthesis” method, though popular and fun to discuss, isn’t likely to produce large quantities of graphene. Experts say the trick isn’t making the super-thin flakes, but finding them. After transferring the peeled or exfoliated bits of graphite from the tape onto an oxidized silicon wafer, the user needs an optical microscope and a trained eye to help spot the rare graphene “needle” hiding in a haystack of thick graphite chunks. Some of the members of the Manchester group who have that expertise recently formed Graphene Industries, a start-up company that sells individual microscopic graphene flakes for research.

Working on a larger scale, Vorbeck Materials, based in Jessup, Md., is gearing up to supply graphene in ton quantities. The company has licensed core technology to make graphene by chemical exfoliation developed by İlhan A. Aksay, Robert K. Prud’homme, and coworkers at Princeton University,

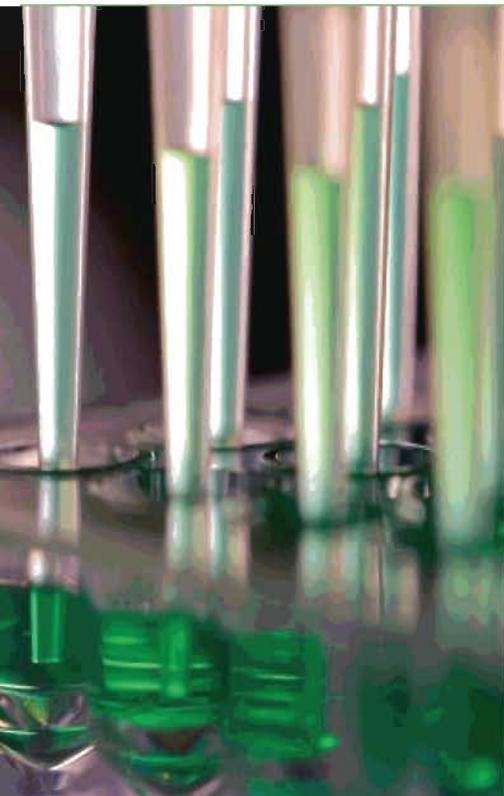
and it recently announced a joint research program with BASF to develop graphene formulations for use in the electronics industry. According to John Crain, vice president of strategy and business development, Vorbeck plans to launch its first product—graphene dispersions for making electrically conductive coatings—later this year.

THE PRINCETON method for making graphene is based on science first reported in the 1800s. According to Aksay, researchers discovered back then that treating graphite with strong acids forms graphite oxide and that heating the oxidized material causes it to expand dramatically. The “expanded graphite” materials have surface areas of 20–100 m²/g. The Princeton group modified that more than a century-old process in way that oxidizes graphite more completely and coats its layers with hydroxyl and epoxy groups. That process leads to highly exfoliated materials with surface areas exceeding 1,700 m²/g.

Aksay explains that heating the graphite oxide to some 1,100 °C decomposes its functional groups, triggering the release

of CO₂. As a result, gas pressure builds up quickly inside the solid until it exceeds the van der Waals forces holding the graphene sheets together (*Chem. Mater.* 2007, 19, 4396). Similar to the pressure buildup that pops popcorn, the evolving CO₂ exfoliates the crystal forcefully, yielding mainly single-layer sheets. Aksay notes that his team’s process induces defects and leaves some functional groups intact. The imperfections cause the sheets to wrinkle, but that feature turns out to be helpful in preventing the sheets from restacking.

Other groups have taken related approaches to preparing graphene by exfoliating graphite chemically. For example, Hongjie Dai and coworkers at Stanford University expose graphite to acid and heat but then treat the product, which includes multilayer graphite crystals, with oleum (fuming sulfuric acid) and tetrabutylammonium hydroxide (TBA). That step further nudges the graphene sheets apart by inserting (intercalating) oleum and TBA molecules between the atomic planes, leading to single- and few-layer graphene samples (*Nat. Nanotechnol.* 2008, 3, 538).



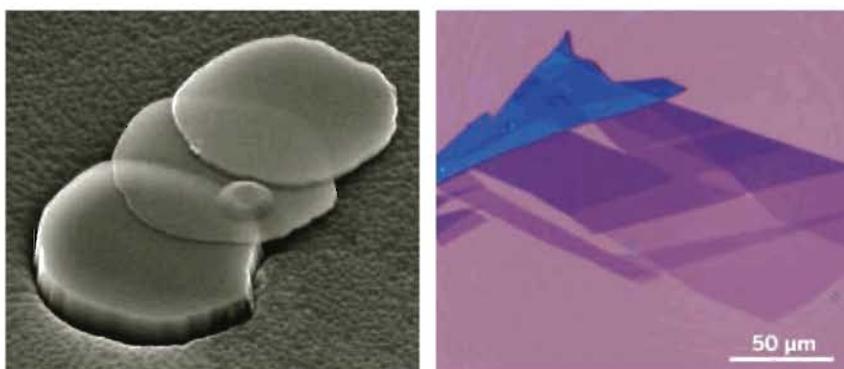
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THICK AND THIN Multilayer graphite crystallites (gray, 2 μm in diameter; thinnest is 30 atomic layers) can be thinned by successive peeling until they are reduced to a few, two, or just one (ranging from dark purple to nearly transparent regions) layer of graphene.

Meanwhile, Jonathan N. Coleman of Trinity College Dublin, in Ireland, and coworkers have shown that graphite could be peeled apart without the use of any intercalating agents if a solvent such as *N*-methyl-pyrrolidone is used (*Nat. Nanotechnol.* 2008, 3, 563). As the team explains,

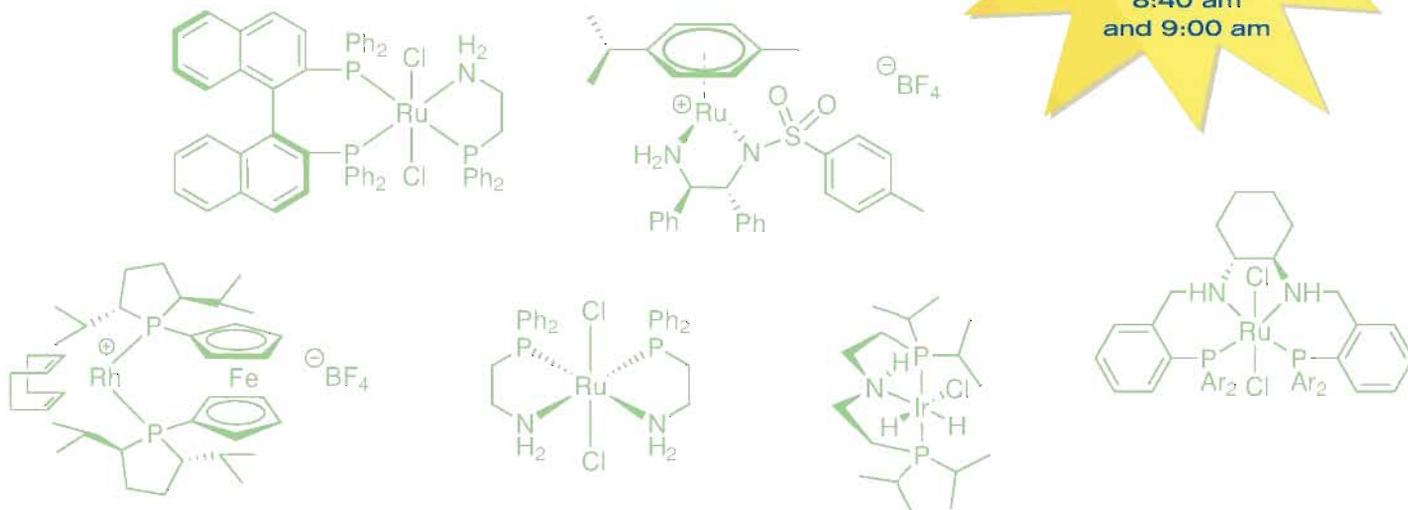
the key to success is selecting a solvent for which the solvent-graphene interaction energy matches the graphene-graphene interaction energy, thereby removing the sheets' "incentive" to remain stacked. By using that method, the group obtained 1 wt % monolayer graphene (isolated by

centrifugation); they say the process could be improved to yield 12 wt %.

Coleman's group followed up recently with another study based on the same principle. This time they demonstrated that water-surfactant solutions can be used to disperse and exfoliate graphite. The group reports that 40% of the graphene flakes obtained in that study consist of fewer than five layers and 3% of flakes are single-layer sheets (*J. Am. Chem. Soc.*, DOI: 10.1021/ja807449u).

One common thrust of recent studies, including those of Dai and Coleman, is to develop graphene synthesis methods that sidestep the use of graphite oxide. Studies have shown that sheets isolated from graphite oxide—graphene oxide sheets—are poorer electrical conductors, even after being reduced, than pristine graphene. Because reduced graphene oxide samples retain some oxygen-based functional groups, they are less attractive than Scotch-tape-cleaved graphene flakes to researchers studying certain types of applications, such as transistors and other nanoelectronic devices. In contrast, scientists pursuing

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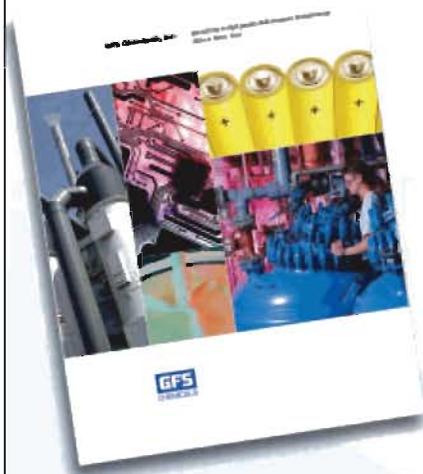
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“Graphene can be thought of as a giant flat macroscopic molecule of infinite size.”

graphene-polymer composites look for ways to capitalize chemically on graphene oxide's functionality.

Another common thrust is to develop methods for making centimeter-sized samples of graphene that could accommodate large numbers of circuit components. Several strategies have been proposed recently. In one study, Jiaying Huang and coworkers at Northwestern University used a stepwise procedure to corral many small waterborne flakes of graphite oxide into successively tighter confines. In that way, the group caused the flakes to coalesce into a high-quality, close-packed, continuous, single-atom-thick sheet, which they reduced chemically (*J. Am. Chem. Soc.* 2009, 131, 1043).

Meanwhile, Byung Hee Hong of Sungkyunkwan University, in Suwon, South Korea, grew centimeter-sized patterned sheets of graphene by using chemical vapor deposition to react methane and hydrogen on a nickel catalyst. The group etched away the nickel, transferred the graphene sheets to other substrates, and showed that even upon bending and stretching, the sheets retain their useful properties. That flexibility may play a key role in portable, foldable electronic applications (*Nature* 2009, 457, 706).

FUTURE FLEXIBLE DISPLAYS and other devices may be made from billions of nanoscale transistors—logic and switching devices, in which graphene serves as the conductive channel instead of silicon, as in today's devices. Graphene's knack for transporting electrons at top speed with little scattering is enabling electronics researchers to fabricate and test fast devices today.

For example, at IBM's T. J. Watson Research Center, in Yorktown Heights, N.Y., Phaedon Avouris' team prepared graphene field-effect transistors with nanometer-scale electrodes and demonstrated an operation frequency in the gigahertz range—a record for a graphene device. The team also determined that the operation frequency increases with decreasing device dimensions, a finding that bodes well for the ongoing trend to shrink circuitry. The

group predicted that optimized graphene transistors would work even faster—in the terahertz range (*Nano Lett.*, 2009, 9, 422).

Considered a hypothetical curiosity just a few years ago, one-atom-thick graphene has stormed the world of scientific research. Much of the enthusiasm resides in the physics community, but chemistry is also playing a prominent role. Witness that of the 374 graphene papers scheduled to be delivered at next month's American Physical Society meeting in Pittsburgh, many of those titles include words like “chemical doping,” “chemical derivatives,” and “chemically modified.”

One of the researchers looking into chemically modified graphene is Rodney S. Ruoff, a physical chemist and professor of mechanical engineering at the University of Texas, Austin. Ruoff and team members have customized the hydrophilicity of graphene oxide sheets by treating graphite oxide with organic isocyanates. That procedure forms amide and carbamate ester bonds to carboxyl and hydroxyl groups on graphite oxide, thereby causing the functionalized material to form stable dispersions in polar aprotic solvents. The dispersions' stability enables the graphene oxide sheets to mix intimately with numerous organic polymers—a key step to forming composites. As a result of these kinds of chemical modifications, Ruoff and coworkers prepared polystyrene-graphene and other electrically conducting polymer composites (*Nature* 2006, 442, 282).

In related work, Ruoff, Yoshitaka Ishii at the University of Illinois, Chicago, and coworkers prepared functionalized ¹³C-labeled graphite oxide and developed a method for probing the material via solid-state nuclear magnetic resonance spectroscopy (*Science* 2008, 321, 1815). They propose that the method will be a powerful probe of chemical bonding networks in chemically modified graphenes.

“The chemistry part of the graphene story has only just begun,” Ruoff says. “And because of the extraordinary number of levers that chemistry affords, there is sure to be a growing dialogue between chemists and researchers in other fields.” ■

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