

PERSPECTIVE



A means to an end

Exploring graphene's chemical properties reveals a world of potential away from the purely two-dimensional, says **Rodney Ruoff**.

Much of graphene's appeal comes from its extraordinary electronic properties that might one day make super-high-speed devices a reality, but graphene has more to offer than just its high electron mobility. It has other attributes deserving of attention — in particular, taking advantage of its chemistry to make new materials.

We recently made an activated microwave-expanded graphite oxide (a-MEGO) by activating a graphene-like precursor with potassium hydroxide¹. This porous material is composed of atom-thick walls of trivalently bonded carbon and pores 0.6–5.0 nanometres in diameter. It has a remarkably high surface area — 3,100 metres squared per gram — some 17% higher than anything possible with graphene itself. And it came as a complete surprise to us; its carbon lattice includes heptagons and octagons that form regions of so-called negative curvature — or the familiar saddle shape. We expected to get separate perforated thin sheets with many atoms along the sheet edges.

Saddle-shaped 'carbon nanofoams' have never been made in bulk and have mostly remained a theory; if they could be made in a continuous sheet form tens of micrometres thick, they would likely be the ultimate electrode material for very high energy density and ultrafast supercapacitors (thus having extremely high power density as well), which store electric charge. Until recently, supercapacitors have had much lower stored charge per unit weight or volume than batteries. But carbon a-MEGO gives supercapacitors energy densities comparable to that of conventional lead-acid batteries — but they are able to deliver electricity much faster. Supercapacitors with such high-performing carbons could find use in the electric grid, consumer electronics, power tools, and to replace the lead-acid batteries in cars, but with a much longer cycle life into the hundreds of thousands (thus surpassing the lifetime of most cars).

Treating graphene as a reactant rather than a product opens up other possibilities for novel and unexpected things. Graphene could be transformed into diamond without the conditions of the Earth's core. For example, stacks of graphene layers could be converted to a product that has a mixture of trivalently and tetravalently bonded carbon atoms — or perhaps only tetravalently bonded, like diamond. Such a material might have a tensile strength far exceeding the 5.6 gigapascals achieved by the carbon fibres that hold the world record in strength. There is rapid progress towards making metre-size sheets of graphene; on the research front, there is intense interest in improving reel-to-reel production to make, say, kilometre lengths of graphene

foils. It is time to consider clever ways to convert such graphene-based foils to nanometres-thick diamond foils. This can probably be done using low-energy chemistry, either by building up from monolayer graphene or by stitching adjacent layers together². This route might provide a form of diamond that would be ultrastrong over lengths of metres or longer, while keeping diamond's alluring properties intact. Doping very large-area diamond foils with nitrogen or other elements could render it electrically conductive for nanoelectronics — a product that might use nitrogen-doped graphene as the precursor.

Another interesting phenomenon with graphene is how its physical deformation affects its chemical activity. When crumpled, the carbon atoms along a fold are more reactive³. One can — at least in principle — tune the reaction barrier and reaction energetics by manipulating physical form. Very well-defined ripples or edges with curves of a few nanometres and spaced apart by, say, tens of nanometres would activate select rows of carbon atoms to achieve chemical patterns. That type of control over reactive sites could be important in nanoelectronics and nanoelectromechanical systems.

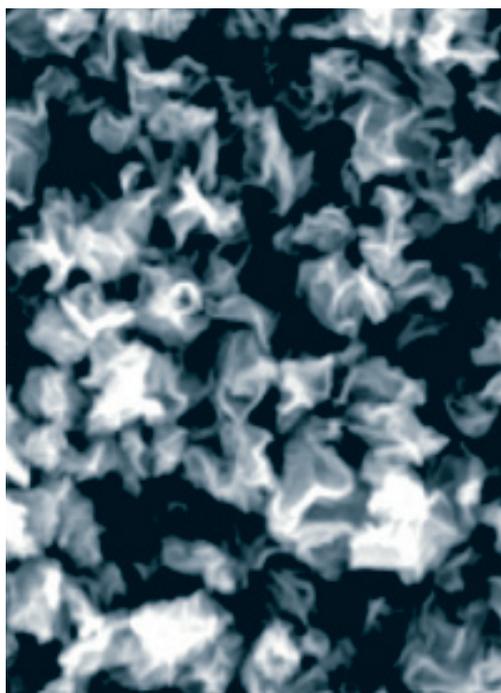
Depositing graphene on substrates patterned by nanoimprint lithography to create rows of highly curved regions would thereby allow a particular chemical function in certain regions. One could, for example, create insulating zones that border highly conductive pristine graphene zones to produce graphene nanoribbons. Alternatively, highly curved regions could be patterned by deposition onto arrays of tiny dimples, and then etched away to render an array of very small holes to make a nanomesh for filters and other applications.

Graphene platelets also deform naturally. Noteworthy forms of crumpled graphene are the reduced graphene oxide (rG-O) sheets embedded in a polymer⁴ and more recently

made⁵ by drying aerosol droplets. If this crumpling leads to localized highly reactive regions, we might find that its durability is influenced by certain chemical environments — and also that it would work well for certain applications when mangled. ■

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1. Zhu, Y. *et al.* *Science* **332**, 1537 (2011).
2. Dikin, D. A. *et al.* *Nature* **448**, 457–460 (2007).
3. Srivastava, D. *et al.* *J. Phys. Chem. B* **103**, 4330–4337 (1999).
4. Stankovich, S. *et al.* *Nature* **442**, 282–286 (2006).
5. Luo, J. *et al.* *ACS Nano* **5**, 8943–8949 (2011).



Particles of crumpled graphene sheets created by capillary compression in evaporating aerosol droplets⁵.

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