

Interestingly, the nano-selenium material captured five times more mercury than the maximum predicted on the basis of its surface area, indicating significant penetration of mercury into the nano-selenium matrix. This did not occur in the other sorbent materials. Even so, the amount of mercury sequestered was less than 10% of the potential 1:1 molar stoichiometry for Hg:Se. This means that the binding capacity of nano-selenium can be further improved by optimizing its surface area.

The use of elemental selenium to capture elemental mercury to form mercury selenide eliminates the need to first oxidize the mercury into a charged form that can subsequently be sequestered by a partner of opposing charge. The chemistry of mercury and selenium, particularly the readily interactive electron orbitals of elemental selenium (Fig. 1), predisposes its binding to elemental mercury with high affinity.

Capture of uncharged gas-phase elemental mercury onto a solid substrate such as elemental selenium has obvious advantages because the mercury selenide forms directly from the initial collision rather than requiring a sequential two-step process.

The nano-selenium sorbents are intended for use in protective barrier cloths that can stop the release of mercury from carpets contaminated by broken fluorescent lamps. They can also be applied in containment bags designed for safe disposal of the lamps or other mercury-containing wastes. Unstabilized nano-selenium in the form of a dry powder or in an impregnated cloth was successfully used in a proof-of-principle test for *in situ* real-time suppression of mercury vapour escape following the fracture of fluorescent lamps.

Mercury's binding interaction with nano-selenium parallels the interaction that occurs when mercury enters the body. The

mechanism of mercury toxicity appears to involve covalent binding of mercury to selenium at the active sites of selenium-dependent enzymes<sup>4</sup>, such as glutathione peroxidases, as well as other important selenoenzymes including the thioredoxin reductases. Binding of mercury irreversibly inhibits the antioxidant functions of these enzymes and leaves vulnerable tissues such as the brain poorly protected against oxidative damage. Therefore, it is highly appropriate that the small but precious supply of selenium in the body may someday be protected from airborne mercury exposures by using products containing nano-selenium sorbents.

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## GRAPHENE PRODUCTION

# New solutions to a new problem

Two independent teams have shown that it is possible to produce stable suspensions of single-layer graphene from graphite crystals using chemical techniques.

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**G**raphene — a single layer of carbon atoms — stepped out of the textbooks and into reality in 2004 when researchers used 'scotch tape' to peel off micrometre-wide sheets of this novel material from a sample of crystalline graphite<sup>1</sup>. Remarkably, a single layer of graphene resting on a silicon dioxide substrate can be seen by a trained eye with a good optical microscope. Exhibiting unusual physical and electronic properties, as well as excellent charge-carrier mobility, graphene quickly grabbed the attention of physicists and engineers, who hope that it might, one day, compete with silicon to be the material of choice for certain applications in electronics<sup>2</sup>.

Whereas dry mechanical exfoliation (to give the 'scotch tape' method its formal name) produces graphene of the highest quality that is suitable for fundamental studies, and epitaxial growth may provide the shortest path to graphene-based electronic circuits<sup>3</sup>,

chemists are excited about processing graphene in solution. In addition to offering low costs and high throughput, this approach also opens the door to many well-established chemical techniques that could be used to cast graphene sheets into various structures or to integrate graphene with other materials to form nanocomposites. Graphitic materials possess excellent electrical, mechanical, thermal and optical properties (think of graphite, carbon nanotubes and carbon nanofibres), so the technological impact of exploiting these properties at the nanoscale in a cheap and practical material will be enormous.

There are, however, two obstacles that must be overcome: first, achieving complete exfoliation of graphite by chemical means; and second, stabilizing this exfoliated graphene in a suspension. On pages 538 and 563 of this issue Hongjie Dai and co-workers at Stanford University and the CAS Institute of Physics in Beijing<sup>4</sup> and, independently, Jonathan Coleman of Trinity College Dublin and co-workers in Dublin, Oxford and Cambridge<sup>5</sup>, report significant advances in overcoming these obstacles by showing that it is possible to exfoliate graphite down

to individual graphene sheets, and then suspend these sheets stably in solution with the help of carefully chosen intercalants and/or surfactants.

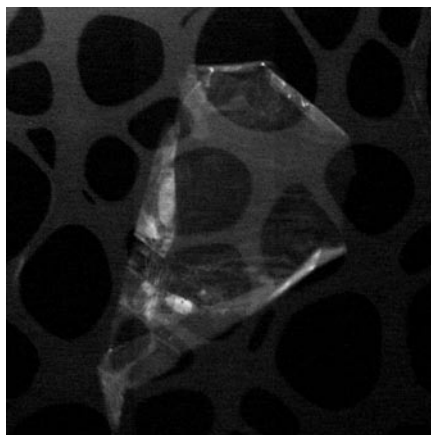
Dai and co-workers start by introducing sulphuric and nitric acid between the graphene layers (a process known as intercalation), and then rapidly heating the sample to 1,000 °C. The explosive evaporation of the intercalants produces thin (~ tens of nm) graphite flakes that contain large numbers of graphene sheets. Improving on earlier methods, which relied solely on the mechanical force of sonication to break these flakes into graphene sheets<sup>6,7</sup>, the Stanford–Beijing team then performs a second intercalation step by inserting two molecules, oleum and tetrabutylammonium hydroxide (TBA), into the spaces between the graphene layers. Assisted by these intercalants, sonication in a surfactant solution produces a suspension of single and few-layer graphene sheets from which the single-layer sheets can be extracted via centrifugation. Dai and co-workers stress that the insertion of TBA is critical to obtaining a high yield of single-layer graphene, presumably because TBA further increases the distance between

adjacent graphene layers and facilitates their separation via sonication.

Coleman and co-workers, meanwhile, demonstrate that it is possible to effectively exfoliate graphite to produce single- and few-layer graphene without the use of intercalants if the solvents are chosen judiciously (Fig. 1). The trick is to choose solvents for which the solvent–graphene interfacial interaction energy matches that of graphene–graphene<sup>5</sup>.

The success of both experiments relies on finding the right intercalants and/or solvents. Other researchers have tackled the exfoliation challenge from a different direction: converting graphite into graphite oxide<sup>8–10</sup>. These methods take an ‘oxidation–exfoliation–reduction’ approach in which the graphene basal planes in graphite are first decorated with covalently bonded oxygen functional groups. This oxygenated graphite is hydrophilic and can be readily exfoliated into single graphene oxide sheets through sonication and dispersed in aqueous solutions. These functionalized sheets have been processed into films and composites with excellent mechanical and optical characteristics<sup>11</sup>.

However, oxidation damages the electrical conductivity of graphene, and the electrical conductivity of the graphene-like sheets produced by the chemical reduction of the graphene oxide sheets is several orders of magnitude lower than that of pristine graphene<sup>9</sup>, making this route to exfoliation unattractive for electronics applications. The loss of conductivity originates from the disruption of the network of  $sp^2$  carbon–carbon bonds in the graphene sheets caused by the oxidation and reduction reactions,



**Figure 1** Small-angle dark-field transmission electron microscope image of a defect-free graphene monolayer that has been deposited by Coleman and co-workers<sup>5</sup> from a liquid-phase dispersion onto the microscope grid (also made of carbon). The monolayer is approximately 1.5  $\mu\text{m}$  by 2.5  $\mu\text{m}$ . Graphene, in its freestanding form, is unstable against the formation of ripples, as can be seen at the centre of the monolayer.

and neither of these processes is completely understood at this point. Experimental evidence suggests that vacancies and defects generated in the reactions cannot be completely removed by reduction or thermal treatment<sup>8,9</sup>. These imperfections scatter charge carriers in graphene, lowering their mobility.

In this context, the progress made by Dai, Coleman and their co-workers is particularly valuable and timely. In the

Stanford–Beijing experiments, caution was taken to ensure that the intercalants interact with graphene basal planes predominantly through non-covalent bonding, thus preserving the  $sp^2$  network in the graphene. Indeed, electron diffraction, Raman spectroscopy and conductivity measurements indicate that the graphene sheets produced by both groups have fewer structural defects and are more conductive than chemically reduced graphene oxide<sup>4,5</sup>.

Although the graphene samples produced by the two collaborations are of higher quality than those produced by other chemical routes, they are still far from pristine, and unanswered questions remain. What is the nature of the remaining disorder and how can we further improve the conductivity for more demanding electronics applications? What role does the surfactant play in electrical transport? Large-scale production calls for an increase in the yield for single-layer sheets. The ability to control the size and dispersion of graphene sheets in a variety of organic and inorganic solvents will provide chemists with important leverage in shaping the future of this exciting new material.

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## MOLECULAR LOGIC

# Monolayers with an IQ

Thin films of redox-active molecules can be used to construct logic gates, which can then be linked together to create basic circuits.

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**W**hen a molecule is subjected to a stimulus — such as a pulse of light, an electric potential or an encounter with another molecule — it has to make a choice. It can either do nothing or it can undergo a reaction that leads to a new stable

or metastable state with physicochemical properties differing from those of the initial state. In this sense, any chemical reaction, even if carried out on a statistically significant ensemble of molecules rather than on a single entity, can be viewed as a transformation of ‘inputs’ into ‘outputs’, and can thus be used to process information<sup>1–3</sup>. This concept is best illustrated by living organisms, in which information is elaborated, transported and stored using ‘soft’ molecular or ionic substrates. Conventional computers, on

the other hand, operate in a radically different manner: they are made of ‘hard’ semiconductor devices, signals are carried by electric charges, and two states are used to store and process data because such binary or Boolean logic is robust with respect to fluctuations of the physical signals.

The primary motivation behind the search for computing strategies based on molecules is to develop novel paradigms for information processing that, by moving beyond silicon-based technology, could lead