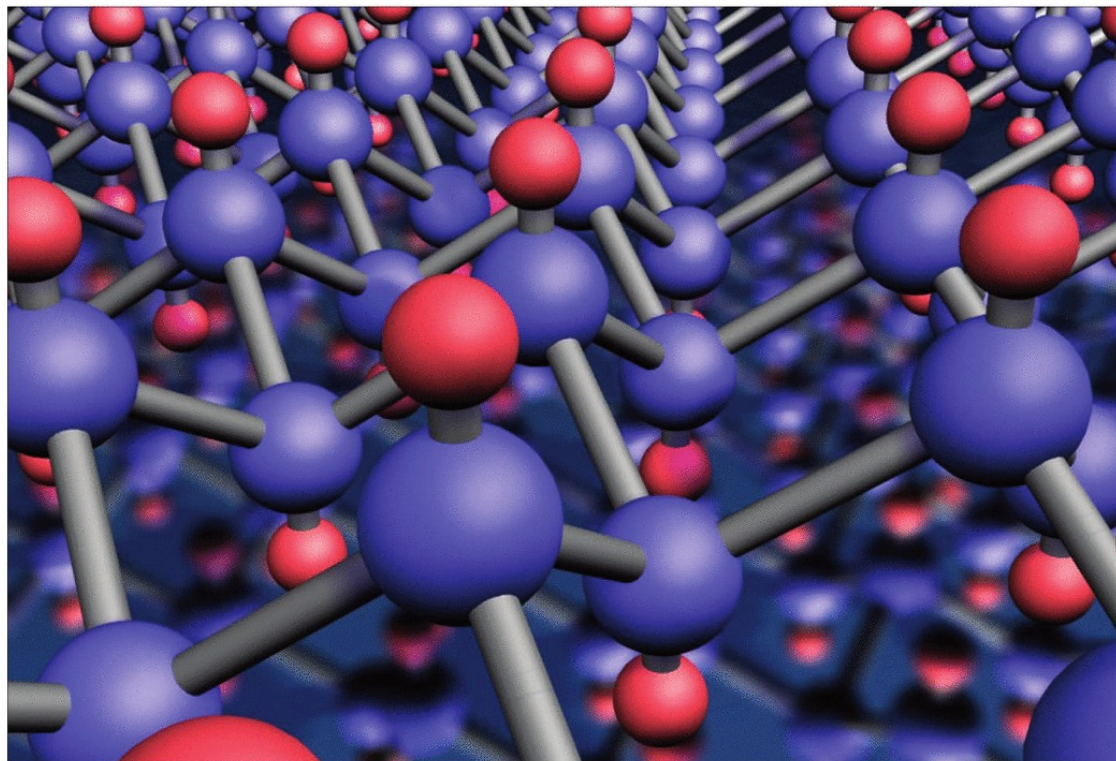


# Beyond the wonder material

The remarkable properties of graphene – a one-atom-thick sheet of carbon that was first isolated in 2004 – have produced a wave of discoveries in fundamental physics. But its new chemical cousin, graphane, may prove more amazing still, as **Kostya Novoselov** explains



Tatiana Luytchenskaya

When nature had to choose an element as the basis for life, it chose carbon. If I had to guess why, I would say the reason was carbon's extraordinary versatility. Bonding between carbon atoms is exceptionally strong; indeed, the strongest materials on Earth are all made of carbon. However, bonding between carbon and other elements, though stable, can easily be changed by chemical reactions. The resulting compounds are often surprisingly different from one another. For example, a pair of carbon atoms bonded together can accept one, two or three hydrogen atoms, forming ethyne, ethene and ethane – chemicals used in welding, anaesthesia and vodka-making, respectively.

Pure carbon also occurs in several different forms, including diamond, graphite, buckminsterfullerene and the newest member of the family, graphene – a sheet of crystalline carbon just one atom thick that was first produced only five years ago. In diamond, each carbon atom is bonded to four others, and all four electrons in its outer shell are involved in joining the atoms

together. This means that diamonds are insulators, and thus rather boring (at least in physics terms). In contrast, graphene has one communal electron left over when each carbon atom bonds with three others, thus making it an excellent electrical conductor (see figure on page 28).

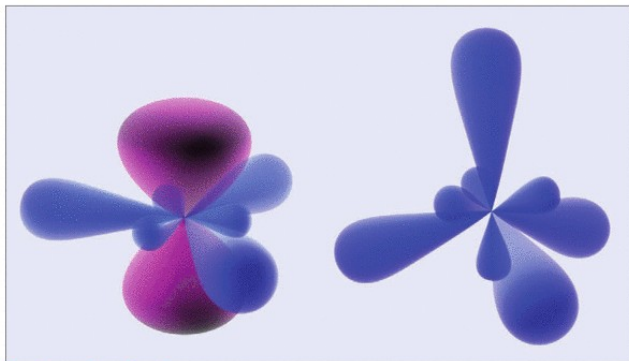
This conductivity is far from the only remarkable thing about graphene, however. Its single-layered honeycomb structure also makes it a building block for other forms of carbon. For example, the graphite in pencils is just a stack of graphene layers, while buckminsterfullerene molecules are nanometre-sized spheres of rolled-up graphene. But perhaps the most amazing thing about graphene is its very existence. For years, researchers assumed that this 2D atomic crystal could not exist in a free state. Yet in 2004 a group of researchers led by Andre Geim and me found a surprisingly simple method of producing graphene by cleaving a sample of graphite with sticky tape (*Science* 306 666–669).

## Building blocks

Experiments on graphane (above) and other graphane-based compounds may lead to novel electronic devices.

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**New dimensions for carbon** Changing the configuration of electronic orbitals in carbon atoms produces strikingly different forms of pure carbon. In diamond (right), all four electrons in the carbon atoms' outer shells are involved in strong  $\sigma$ -bonds ( $sp^3$  hybridization). The angle between these bonds is approximately  $109^\circ$ , and hence diamond forms 3D crystals. For carbon atoms in graphene (left), only three electrons form  $\sigma$ -bonds ( $sp^2$  hybridization), and these bonds lie in a plane at  $120^\circ$  angles to each other, thus producing a flat structure. The fourth electron is in communal use, forming weaker  $\pi$ -bonds and making graphene an excellent conductor. Here, the blue clouds represent  $\sigma$ -orbitals, while purple represents  $\pi$ -orbitals.

That breakthrough enabled a huge number of scientists around the world to start studying graphene, the properties of which have continued to amaze. Generally defect-free and highly ordered, crystals of graphene are the thinnest objects possible and, simultaneously, 100 times stronger than structural steel – making them the strongest material in nature. Graphene is also optically transparent and chemically inert, as well as being highly conductive. Such an unusual combination of extreme properties makes this 2D crystal attractive for a wide variety of applications. It can be used for transmission electron microscopy, which requires very thin, conductive and strong materials to support delicate biomolecules under study; for high-frequency transistors, which need highly mobile charge carriers to operate; and for transparent conductive electrodes for liquid-crystal displays and solar cells.

However, in terms of electronic applications, sometimes graphene is a little *too* conductive. Although the electronic band structure of graphene produces many effects of great importance and novelty to condensed-matter physics (see *Physics World* November 2006 pp33–37), it also makes graphene so highly conductive that it is hard to create graphene-based transistors suitable for applications in integrated circuits. Electrons in graphene cannot be stopped; they penetrate through any potential barriers, making transistors “leaky” even in the off state. To improve the efficiency of graphene transistors, and to have extra flexibility when building graphene nanostructures, we need to find a way to reduce the conductivity of this “wonder material”.

One way of doing this is to use carbon's innate versatility. By binding the conductive electrons to another chemical species, we can produce a graphene-like carbon compound that acts as an insulator. The simplest and most straightforward candidate to form the extra bond to carbon is hydrogen. Just like the conversion of ethene to ethane, exposing graphene to atomic hydrogen produces a material dubbed graphane, which was first synthesized less than a year ago by the group at the

University of Manchester in the UK (*Science* 323 610). This simple change may open up a whole new world of graphene-based chemistry, leading to novel 2D crystals with predefined properties, and an ability to tune the electronic, optical, mechanical and other properties of a material according to one's needs.

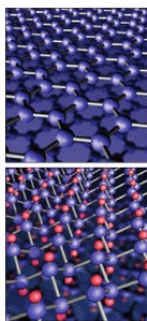
### Building a better molecule

The key to understanding why graphene conducts electricity so well – and why graphene does not – lies in their electronic band structures. In general, all materials can be divided into insulators, metals and semimetals, depending on whether their highest occupied electronic band is full and separated from the next (empty) band by an energy gap; only partially occupied; or fully occupied but with an overlap with the next electronic band. The electrons that bind together carbon atoms in graphene (known as  $\sigma$ -electrons) produce an insulating-type band structure, with a gap of several electron-volts between the last-occupied and empty bands (see figure opposite). However, the remaining “delocalized” electrons (termed  $\pi$ -electrons) are not involved in this bonding, and they give rise to a very different phenomenon: the so-called zero-overlap semimetallic band structure. In this case, fully occupied and fully empty bands are touching each other. The conductivity properties of such zero-overlap semimetals are non-trivial, and have puzzled both theorists and experimentalists since graphene was first observed. But in graphene, the  $\pi$ -electrons are strongly bound to hydrogen atoms, so the  $\pi$ -bands are absent altogether. This creates a huge gap separating the highest occupied band from the lowest unoccupied band – just as in insulators.

Of course, adding hydrogen to graphene is not the only way of opening up a band gap to create an insulator. One could also create a gap by making nanoscale graphene structures like quantum dots and nanoribbons. If these structures are smaller than the electron wavelength, then the low-energy electrons (which have large wavelengths) simply do not fit inside, and so the material becomes an insulator. However, at the moment, it is extremely difficult to control the shape of such structures in the lab.

In contrast, making graphane is comparatively easy. In the first experiments, researchers in the Manchester group exposed pristine graphene to a stream of atomic hydrogen, and found that a number of its physical properties underwent rather radical changes. First, the metallic graphene became an insulator, with resistance in the giga-ohm region at 4 K, the temperature of liquid helium. Electron-diffraction studies showed that the new material's in-plane lattice constant – the distance between carbon atoms in the crystal, projected onto the sample's plane – shrank by a few per cent compared with that of graphene. Encouragingly, the same studies demonstrated that the crystallographic structure of the new material preserved the hexagonal symmetry of graphene. Hence, this simple procedure did indeed result in a new, crystalline form of hydrocarbon.

There are still a number of problems with interpreting these experimental results, however. Most of the experiments have been performed using graphene resting on a silica ( $SiO_2$ ) substrate, and making one side inaccessible for hydrogenation, whereas the predicted



**Carbon cousins**  
The structure of graphene (top) and graphane (bottom).

most stable configuration of hydrogen on a graphene surface requires the hydrogen to be placed on both sides (see figure on page 27). Although the electron-diffraction study was performed using free-standing graphene with both sides accessible, even in this case the lattice constant varied between different regions of crystal surface (although the spacings were always smaller than in graphene). This might indicate that more complicated arrangements of hydrogen on the surface are present in practice. The challenge now is to extend our experiments to study properties like electron transport and optics in free-standing hydrogenated graphene. In time, I expect that we will see even better insulating behaviour with much less disorder in such samples.

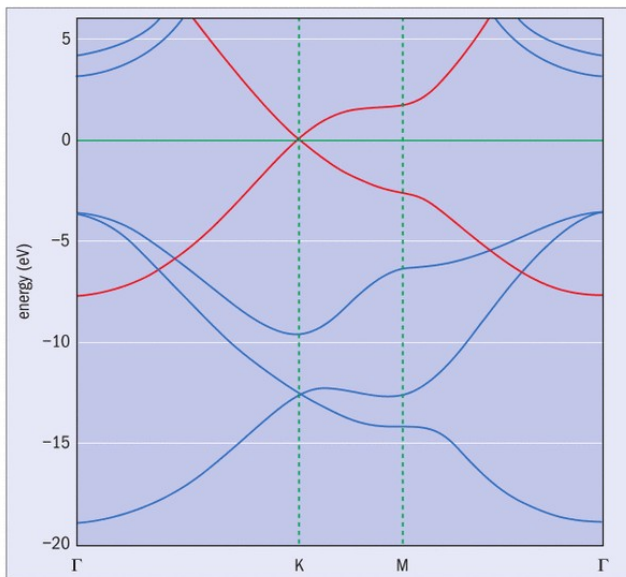
### Making the switch

One important feature of graphane is that it can be easily converted back to pure graphene: simple annealing causes the hydrogen to disperse, leaving the pristine graphene backbone intact. The 2009 *Science* paper that first reported graphane showed that all the properties of graphene can be recovered by this simple operation. This paves the way for *reversible* (or *erasable*) electronic-band engineering. Both the observation of graphane and its “reversibility” are extremely important for the whole field, and although more research still needs to be done, I believe the impact of this finding will be triple-fold.

First, it may change the way various graphene nanostructures – like nanoribbons, quantum point contacts and quantum dots – are formed. In the past, such structures were rather crudely etched using reactive plasma to burn away parts of the graphene. This process is akin to using scissors to cut out shapes in a piece of paper. But now we should instead be able to make these structures by covering graphene with hydrogen, except for those areas that require (for example) high conductivity (see figure on page 30). “Painting” with hydrogen is much easier, and is also expected to produce a “softer” potential – one that changes less abruptly compared with one produced by the crude burning method. Experiments on the new method are on the way and encouraging results have already been achieved by researchers in several labs, including Yu Ting’s group at Nanyang Technological University in Singapore as well as at Manchester.

Furthermore, with hydrogen possibly arranging itself along certain crystallographic directions, one can create crystallographically oriented graphene nanostructures. For example, theorists predict that nanoribbons with perfect zigzag edges will always be metallic. Those with perfect “armchair edges” – oriented perpendicularly to the zigzag type – could be insulating. However, the key word here is “perfect” – if the edge shape deviates even slightly from a certain crystallographic direction, then this changes the electronic properties dramatically. Such perfection is basically impossible to achieve using current lithographic (“top-down”) techniques. But reacting graphene with hydrogen presents a very different, self-organizing, approach, which hopefully will prove more effective.

Another implication of graphene-graphane reversibility is that by varying the concentration of hydrogen

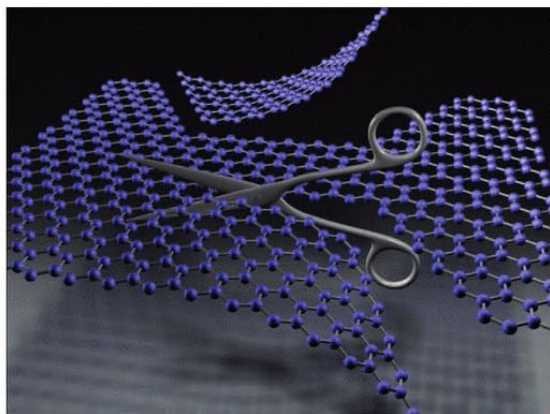


**Electronic band structure of graphane** The blue lines originate from the bound electrons in  $\sigma$ -orbitals, which produce an insulating-type band structure with a gap of about 5 eV between the highest fully occupied level (below the Fermi level denoted by the green line at zero energy) and the next available empty level (above the Fermi level). In contrast, the  $\pi$ -electrons are delocalized, producing a band structure (red lines) in which fully occupied and fully empty bands touch each other. However, in graphane, which consists of graphene with hydrogen added, the  $\pi$ -electrons are strongly bonded to the hydrogen atoms. The  $\pi$ -bands are therefore absent, which means that graphane acts as an insulator. Here, the letters on the x-axis represent the points of high symmetry in the primitive cell in the reciprocal space, known as the Brillouin zone (which has a hexagonal shape for graphene):  $\Gamma$  is the centre of the zone, while K is at a vertex and M is at the centre of an edge.

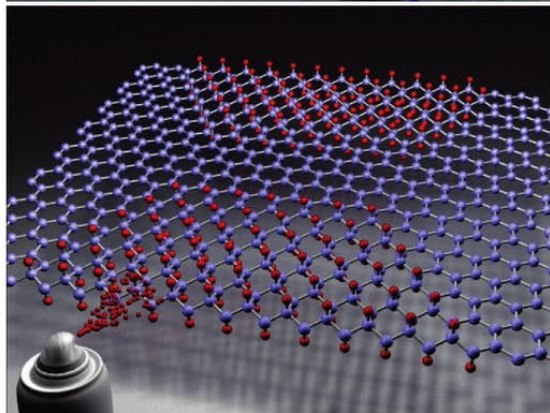
adsorbed on graphene, one can drive this system through a metal-insulator transition. Graphene presents a very peculiar case: unlike all other known 2D systems, the quasiparticles that carry charge through it are not localized. The explanation of this effect may be traced back to the Klein paradox, a deep and long-standing puzzle in relativistic physics that relates to electrons scattering from or tunnelling through a potential barrier. By gradually adding hydrogen to graphene, we should be able to drive the system from a non-localized to a localized state, and investigate what happens during the transition.

The final – and probably the most important – consequence of the emergence of graphane is that it opens the floodgates to chemical modification of graphene, and to the appearance of novel 2D atomic crystals with predetermined properties. Two ends of the spectrum already exist: metallic graphene at one end and insulating graphane at the other. Can we fill in the divide between them with, say, graphene-based semiconductors and other novel materials? This should certainly be possible to some degree. For example, fluorinating graphene – that is, substituting fluorine atoms for hydrogen in graphane – ought to be straightforward, thanks to the high reactivity of fluorine. Experiments to explore this are just starting, but even the first results demonstrate a huge electronic gap opening and mechanical properties that change dramatically.

The emergence of graphane opens the floodgates to chemical modification of graphane



Tatiana Luyten/istockphoto



**Shape-shifting** The traditional method of forming nanostructures from graphene is reactive plasma etching, which is analogous to cutting the structures out of paper (top): the unwanted pieces are simply burned away by oxygen. An alternative method is to sprinkle atomic hydrogen on areas that need to be non-conducting (bottom), leaving a graphene ribbon surrounded by graphane.

And while the conductive properties of graphene and graphane are important, in principle it should also be possible to modify the optical and mechanical properties of graphene-based compounds as well. Imagine a traditional integrated circuit, which contains almost half of the elements in the periodic table. Would it not be great if we could create such a circuit with one single material like graphene, locally modified to gain whatever specific properties were needed? We could, for example, use pure graphene for interconnects; graphane (or something else that has a band gap) for transistors; and magnetic graphane (if we can make it) for spin injection or controlling the electron's spin orientation.

Beyond electronics, the possible range of applications is even wider. Being able to control the resistivity, optical transmittance and a material's work function would all be important for photonic devices like solar cells and liquid-crystal displays, for example, and altering mechanical properties and surface potential is at the heart of designing composite materials. Chemical modification of graphene – with graphane as its first example – uncovers a whole new dimension of research. The capabilities are practically endless. ■