MATERIALS SCIENCE

Transforming Graphene

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Synthesis of a new material by the hydrogenation of graphene offers the opportunity for wider device applications.

Hydrogenation is a process in which an added hydrogen atom bonds to another atom by sharing its only electron with this atom. Organic chemists use hydrogenation to convert unsaturated into saturated fats and to transfer alkenes into alkanes (*1*). On page 610 of this issue, Elias *et al.* (*2*) show that a similar process can also be realized in condensed matter physics. Incorporating hydrogen into graphene—a single layer of carbon atoms arranged in a hexagonal crystal lattice and the thinnest material conducting electricity—transforms it into graphane, a new material whose physical properties are very different from those of graphene.
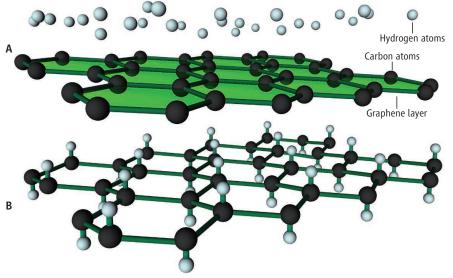
A graphene layer can be separated from a crystal of graphite by a peeling process while preserving its crystal structure and excellent electrical conduction (*3*). Furthermore, its electrical conduction can be tuned—similar to that of a field-effect transistor—by putting it on a substrate and varying the density of mobile particles (electrons and holes) by applying a voltage between the layer and substrate. The unique physical and electrical properties of graphene allow not only the experimental testing of fundamental principles of quantum physics but also the fabrication of new devices

for future carbon-based nanoelectronics (*4*).

Unlike in conventional semiconductors, the conducting electrons and holes in graphene are massless and behave like photons. In addition, there is no gap between the two energy bands in which the electrons and holes are located. Therefore, the electrical conductance of graphene is nonzero, even when the voltage between the layer and sub-

strate is tuned so that there are no free charged particles in the graphene layer (*4*). Some device applications, however, require a gap between the two bands. One way to create such a gap is to cut a narrow ribbon from the graphene sheet with a width of less than 100 nanometers, thereby confining the electrons and holes to a "quantum box" and splitting the energies of the two bands (*5*, *6*). Such cutting

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Graphene hydrogenation. (**A**) A graphene layer, where delocalized electrons are free to move between carbon atoms, is exposed to a beam of hydrogen atoms. (**B**) In nonconductive graphane, the hydrogen atoms bond their electrons with electrons of carbon atoms and pull the atoms out of the plane.

can modify further the properties of graphene, because the dangling electron bonds at the ribbon edges are chemically active and can capture elements from the environment (7).

The surface of graphene is thought to be relatively inert. The electrons that are not part of the bonds between carbon atoms in the plane are shared between all atoms. It is these mobile electrons that are responsible for electrical conduction. In a recent theoretical study, Sofo et al. predicted that hydrogenation of the graphene surface should create a stable material, graphane, with a large energy band (8). In hydrogenated graphene, alternating carbon atoms are pulled out of the plane in opposite directions by the attached hydrogen atoms (see the figure, panel B). This atomic arrangement resembles that in diamond, a nonconductive form of carbon with a large energy gap. In hydrogenated graphene, though, the size of the gap can be controlled by varying the amount of hydrogen on its surface (9).

Elias et al. present the first experimental demonstration that graphane can be synthesized, showing that the surface of graphene is chemically active and that the energy gap can be produced without cutting graphene into a ribbon. The authors also show that the chemical modification of graphene is reversible; the original properties of graphene can be largely restored by annealing the hydrogenated samples at high temperatures.

Adding atomic hydrogen to graphene is not a simple task: Hydrogenation first requires breaking apart the diatomic molecules of hydrogen gas; this is why hydrogenation in chemistry is usually performed with a hot catalyst. Instead, Elias et al. exposed the graphene samples to a hydrogen plasma discharge, in which the hydrogen gas is dissociated into hydrogen ions (see the figure, panel A). The sample has to be placed some distance from the plasma discharge to avoid mechanical damage of graphene by energetic ions.

The emergence of the energy gap manifests itself in the electrical conductance, which becomes strongly temperature dependent. It shows an exponential dependence corresponding to so-called electron "hopping." Such dependence has been seen in thin electron layers confined within semiconductors with an energy gap, such as silicon (10) and gallium arsenide (11). Although in pristine graphene, electrons are free to move across the crystal, the presence of the gap after hydrogenation forces them to "hop" from one site to another, and this conduction mechanism is much more efficient at higher temperatures.

Another direct confirmation of the modification due to hydrogenation is provided by the diffraction image of the new crystal lattice in transmission electron microscopy, where a noticeable decrease of the separation between the carbon atoms caused by the pulling effect of hydrogen atoms is seen. Raman spectroscopy, which is sensitive to the vibrations of the atoms in the crystal lattice (phonons), also shows the evolution of the lattice during hydrogenation.

The demonstration of reversible hydrogenation of graphene is an important step in expanding the device applications for this exciting material. There will be a search for optimal ways of graphene hydrogenation, including chemical methods: Recently there has been a study of graphene hydrogenation using dissociation of a hydrogen-rich material deposited on graphene (12). Future research should aim at using graphene for hydrogen storage in hydrogen-fuel technologies, because graphane has a very high hydrogen density (8). This extremely thin material with an energy gap is also likely to find use in nanoelectronics. But research will probably not be limited to adding only hydrogen to graphene. Elias et al. show that the graphene surface can be used as a base for creating new materials, and it will be interesting to study the effects of incorporating other elements into its structure.

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