

GRAPHENE

What lies between

Opening a gap in graphene is still a considerable challenge on the path towards applications. A clever solution to this problem is to exploit the preferential adsorption of hydrogen in patterns that leave narrow stretches of pure graphene in between.

Jeroen van den Brink

The electronic properties of graphene — a one-atom-thick layer of graphite — are attracting ever-increasing attention. These single sheets of carbon already show electron mobilities comparable to present-day semiconductors. But a significant hurdle to overcome is that graphene intrinsically behaves more like a metal than a semiconductor. In contrast to silicon for instance it lacks a bandgap, which is essential to guarantee controlled and reliable transistor operation.

Writing in *Nature Materials*, Richard Balog and co-workers¹ propose a clever remedy for the absence of a gap in graphene. They demonstrate that if a graphene sheet rests on a carefully chosen template, hydrogen adsorption onto it tends to self-organize. Large-scale superstructures of hydrogenated carbon atoms emerge, turning the sheet into a semiconductor with a bandgap of at least 0.45 eV.

Several schemes have been put forward in the past few years to open and tune a bandgap in graphene, each of which having its own pitfall. In theory a clean gap opens when graphene binds to particular substrates², for instance boron nitride or silicon carbide. However, the experimental realization of this idea has proven to be very difficult and controversial^{3,4}. Another method used to engineer bandgaps is to cut nanoribbons out of graphene, for instance by plasma etching⁵. The confinement of electrons to nanostructures immediately produces a gap. But in this case it is difficult to control the magnitude of the gap as it critically depends on the atomic-scale edge geometry of a nanoribbon. Balog and co-workers managed to steer clear of these pitfalls by building graphene nanostructures in a bottom-up approach, by self-organization, and thus avoiding the roughness of top-down etching techniques.

The self-organization relies on the formation of so-called Moiré patterns. A Moiré pattern appears when two grids with slightly different mesh sizes are overlaid. Consider the example in Fig. 1a: the orange and blue horizontal bars have a spacing that is only slightly different, specifically by 5%. Printing the grid of orange bars on top of the blue results in a motif, a Moiré pattern, with

a much larger periodicity — 20 bars in this case. This interference effect has a famous equivalent in acoustics. When two slightly off-key notes are played simultaneously, acoustical beats — periodic changes in volume — are audible. In this case a small frequency difference also causes a very large period modulation. The absence of such an ‘acoustical Moiré pattern’ signals that two strings, or two musical instruments, are in perfect tune.

Balog and co-workers made use of the Moiré pattern generated by the periodic lattice structure of graphene and an iridium(111) surface. At the (111) surface iridium atoms order into a triangular lattice. The graphene lattice is not triangular, but is made out of carbon atoms packed into a honeycomb

grid. However, the centres of graphene’s honeycombs do form a triangular lattice — often referred to as the dual honeycomb lattice. When graphene binds to an iridium substrate a Moiré pattern appears because the two triangular lattices — the dual graphene lattice and the iridium(111) surface — have spacings that are comparable, but only slightly different. The emerging large-scale Moiré motif, shown in Fig. 1b, is again triangular but with a periodicity of 25.2 Å — over 10 times the lattice constant of graphene⁶. In this Moiré lattice carbon atoms are embedded in a local iridium environment that varies continuously and periodically. This is an important point, because it turns out that the local iridium constellation determines how likely it is for hydrogen to adsorb onto a carbon atom.

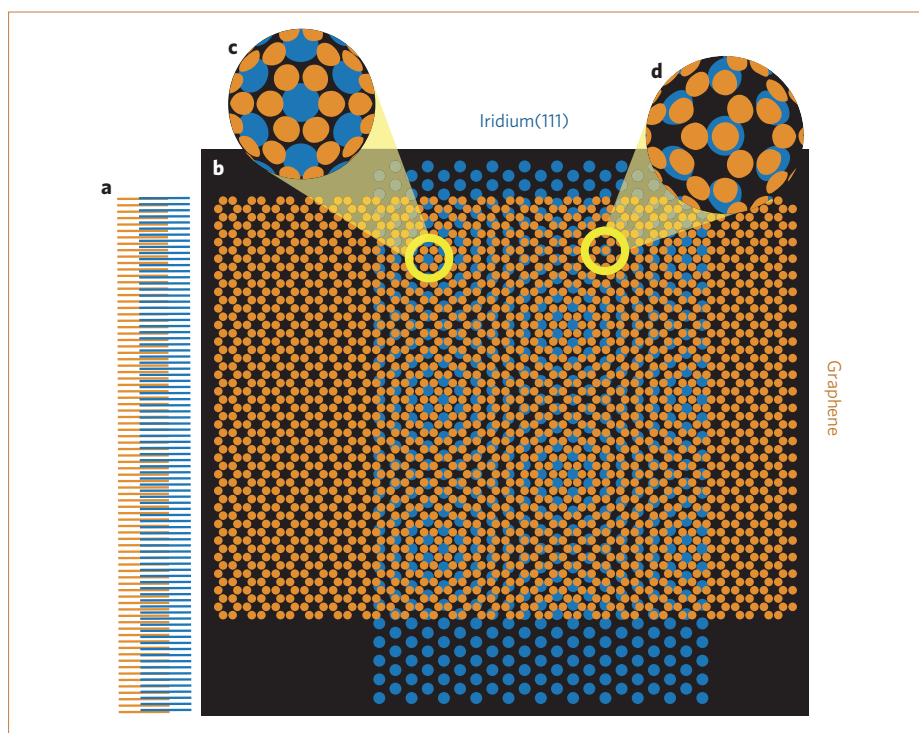


Figure 1 | Moiré motifs. **a**, Moiré pattern formed by a mesh of orange and blue lines with a spacing that is 5% different. **b**, Moiré motif formed by graphene’s honeycomb lattice on top of a triangular iridium(111) surface. **c**, A high-symmetry carbon-iridium configuration, in which a carbon ring is centred above an iridium atom. **d**, In the other high-symmetry configuration, a carbon atom sits on top of iridium, situating its three neighbours in troughs between iridium sites. Hydrogenation preferentially takes place at carbon sites such as this one, closest to peaks in the iridium landscape.

In essence there are two distinct local iridium–carbon configurations with a high symmetry. The first one occurs when a honeycomb carbon ring is centred above an iridium atom (Fig. 1c). In the other configuration a carbon atom sits on top of iridium, situating its three neighbours in troughs between iridium sites (Fig. 1d). Balog and co-workers discovered that in the latter configuration carbon hydrogenation is much easier. Thus when a graphene–iridium sandwich is exposed to hydrogen, spots where carbon atoms are situated closest to the peaks in the iridium landscape are hydrogenated first.

The electronic consequences of graphene hydrogenation are acute^{7,8}. When a C–H bond forms, it localizes a carbon electron. The C–H bond then blocks all other graphene electrons. As a result, hydrogen bonding knocks a carbon atom completely out of the electronic game.

As the graphene–iridium Moiré motif preselects the areas where C–H bonds tend to form, hydrogenation causes a progressive segregation of the carbon sheet into regularly

spaced insulating and conducting patches. Balog and colleagues observe that after prolonged hydrogenation the conducting graphene areas shrink into disconnected islands. Electrons tend to localize onto these hydrogen-free islands, which leads to a well-defined gap.

The basic principle of self-organized graphene patterning is not only interesting *per se*, but can also become important as a tool to craft graphene on the nanoscale. It constitutes another step towards the goal of engineering bandgaps in graphene. Yet in spite of this development, challenges naturally lie ahead. For example, it needs to be established how partial hydrogenation affects electron mobilities. Another open question is whether the principle of uncovered self-organization can be transferred to graphene on other substrates — for electronic devices metallic iridium is not suitable as it short-circuits graphene's electronic gaps.

But advances in the field of graphene can come stunningly fast. Six years ago when Geim, Novoselov and co-workers discovered how to isolate and pinpoint individual

graphene flakes⁹, fabrication of high-quality, large-area graphene was still a wild dream. Nowadays, chemical vapour deposition makes large-scale production feasible, including the possibility of transferring graphene from one substrate to another¹⁰. Even if knowledge gained often dampens expectations, graphene continues to be the exception. □

Jeroen van den Brink is at Institute for Theoretical Solid State Physics, IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany. e-mail: j.van.den.brink@ifw-dresden.de

References

1. Balog, R. *et al.* *Nature Mater.* **9**, 315–319 (2010).
2. Giovannetti, G., Khomyakov, P. A., Brocks, G., Kelly, P. & van den Brink, J. *Phys. Rev B* **76**, 073103 (2007).
3. Rotenberg, E. *et al.* *Nature Mater.* **7**, 258–259 (2008).
4. Zhou, S. Y. *et al.* *Nature Mater.* **7**, 259–260 (2008).
5. Berger, C. *et al.* *Science* **312**, 1191–1196 (2006).
6. N'Diaye, A. T., Coraux, J., Plasa, T. N., Busse, C. & Michely, T. *New J. Phys.* **10**, 043033 (2008).
7. Boukhvalov, D. W., Katsnelson, M. I. & Lichtenstein, A. I. *Phys. Rev B* **77**, 035427 (2008).
8. Elias, D. C. *et al.* *Science* **323**, 610–613 (2009).
9. Novoselov, K. S. *et al.* *Science* **306**, 666–669 (2004).
10. Kim, K. S. *et al.* *Nature* **457**, 706–710 (2009).

THIN FILMS

Particles release

By using drug-encapsulating nanoparticles as the basis for electrostatic assembly, it is possible to generate highly functional films that do double duty. These adaptable thin films can be used both for releasing the drug in a controlled fashion and for biological imaging.

Paula T. Hammond

Much work has been carried out on well-known degradable polymers in their bulk state; yet the delivery of drugs from functional, and in some cases load-bearing, implants made from these materials has been limited to a few standard systems and a small set of drugs. One way to achieve highly controlled thin-film release coatings is through electrostatic layer-by-layer (LbL) assembly, a mild and water-based assembly method that involves the simple alternation of positively and negatively charged species¹. Writing in *Advanced Materials*, Thomas Soike and colleagues² introduce a twist to the standard approach of alternating charged polymers and macromolecular or molecular drugs: they encapsulate the model drug molecule in a charged biodegradable nanoparticle, and build up layers consisting of these nanoparticles with biopolymers (Fig. 1). In doing so, they demonstrate that drugs can be compartmentalized within the films' layers. The layers then release the drugs at variable

rates depending on the degradation rate of the nanoparticle, the diffusivity of the drug and even the positioning of the nanoparticles within the multilayered thin film.

In the promising area of electrostatically-assembled-delivery thin films, a number of researchers have demonstrated the release

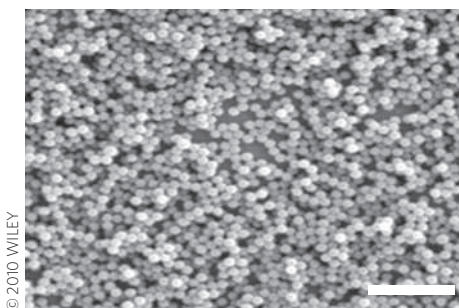


Figure 1 | Scanning electron microscope image of an LbL assembly of polystyrene nanoparticles bearing sulphonate groups on a stainless-steel surface. Scale bar: 3 μ m.

of several drugs after directly incorporating them into multilayers using biologically derived polyions such as polylysine, chitosan and hyaluronic acid³. Controlled release has also been observed using surface-erodible, hydrolytically degradable multilayer thin films containing a range of constituents, from proteins⁴ to DNA⁵. These films have been engineered to release single or multiple drugs through control of the alternating charge deposition of the relevant drug or protein within the film. Although this approach has produced favourable results in many cases, it would be enormously advantageous if it was possible to independently tune the films' release behaviour regardless of the drug's characteristics such as size or charge. Towards this end, there has been some success in incorporating drug-loaded versions of micelles^{6,7} and liposomes⁸ within multilayers. However, problems can arise in retaining the stability of a colloidal system during LbL adsorption, while maintaining high drug loading.