SURFACE ASSEMBLY

Graphene goes undercover

The formation of robust monolayers of organic molecules on graphene substrates not only sweeps this material's defects under a self-assembled carpet, but may help it achieve its full potential as a building block for molecular electronic devices.

E. Charles H. Sykes

In everyday life, one meets carbon in its three most common forms: the graphite in your pencil, amorphous carbon on your barbeque and maybe a diamond on your finger. This was also the *status quo* in the lab until 1985, when the discovery of C_{60} or 'buckyballs' initiated the search for new forms of carbon that led to the discovery of a host of carbon nanotube varieties. Then, just over four years ago when the initial excitement had died down a little and we thought that carbon couldn't surprise us again, came the discovery of graphene, a single hexagonal atomic layer of carbon atoms with entirely new properties.

Up until 2004, conventional wisdom assumed that it was impossible to synthesize truly two-dimensional materials just one atomic layer thick, as it was thought that they would be unstable and just curl up into particles or decompose unless they were grown on a supporting 3D structure. Then Geim and co-workers, using nothing more complex than sticky tape in a process called mechanical exfoliation, repeatedly peeled layers off graphite islands that had been stuck on photoresist-covered glass[1]. After a quick rinse they examined the remaining layers using atomic force microscopy and their images revealed that the graphite sheets

they had created were just a few nanometres thick, and in some cases just a single atomic layer thick — graphene was born.

Theoretical work over the past 60 years has predicted many exciting properties of graphene, but the community has treated the material as merely an academic model system. One would need a PhD in physics to fully understand graphene's electronic properties, as they arise from a combination of relativistic and quantum mechanical effects. Experiments over the past four years have revealed that graphene is a zero-gap semiconductor and that its electrons can roam freely for hundreds of nanometres before they encounter defects[1,2]. These unique electrical properties coupled with interesting optical interference effects and graphene's incredible sensitivity to individual molecules bound to its surface, give it vast potential as a revolutionary material. As silicon technologies begin to reach their fundamental limitations, companies like IBM and Intel are looking closely at graphene for its potential use in devices such as very-high-frequency transistors.

If graphene is ever to meet its true potential in the electronics world, techniques for patterning, functionalizing, interfacing and making electrical contacts

to it must be developed. The paper by Hersam and Wang on page 206 of this issue, describes the use of self-assembly to coat the surface of graphene with a well-ordered, robust layer of molecules that are stable under ambient conditions[3]. Owing to its potentially useful semiconducting properties, the molecule of choice for their study was 3,4,9,10-perylene tetracarboxylic dianhydride, or PTCDA[4]. PTCDA is a common ingredient in prototype molecular photovoltaic devices[5].

Although mechanical exfoliation with sticky tape is just fine for making graphene samples for study in the lab, commercial production will require a much more controlled approach. Luckily there is a simple method for making graphene-terminated surfaces that involves heating a flat crystalline surface of silicon carbide (a robust material used in high-performance automobile brakes) to temperatures above 1,200 °C (ref. 6). This method produces a mixture of monolayer and bilayer graphene, and is compatible with conventional wafer-scale processing.

Hersam and Wang used scanning tunnelling microscopy (STM) to image how the PTCDA molecules assembled on graphene grown on SiC. Their data revealed (Fig. 1) that the molecules packed in a
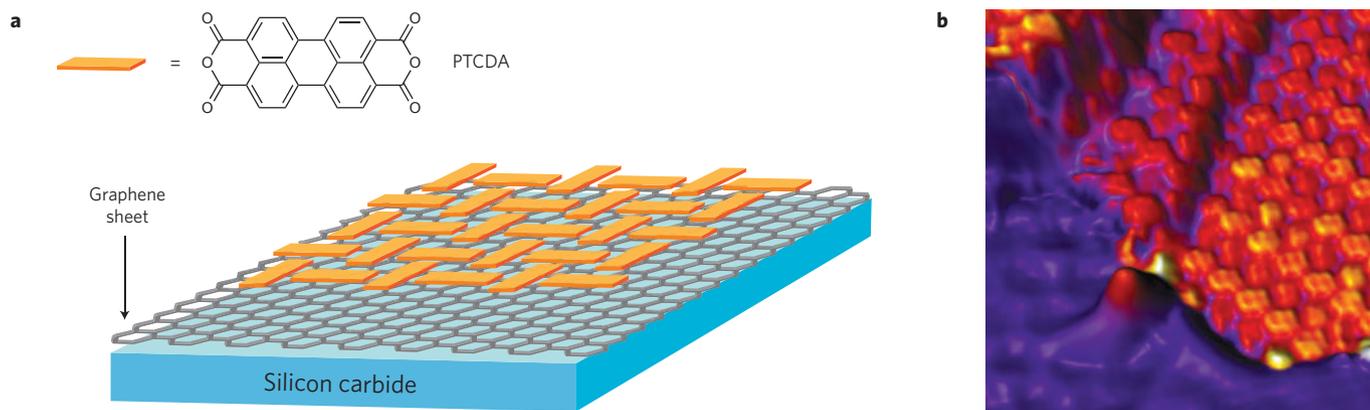
Figure 1 | The self-assembly of organic molecules on graphene. **a**, A schematic showing an ordered PTCDA monolayer formed on epitaxial graphene grown on a SiC(0001) substrate. **b**, A room-temperature STM image[3] of PTCDA molecules (red–orange) assembled on a graphene substrate (blue).

very regular fashion with long-range order. Interestingly, when the self-assembled molecular layer encountered defects in the underlying surface — such as step edges on the SiC crystal or carbon deposits at the interface between the SiC and the graphene layer — they would grow straight over the defects without interruption of their molecular packing. In fact, the PTCDA monolayer had fewer defects than the underlying graphene.

It is reasoned by Hersam and Wang that PTCDA's ability to pack in ordered arrays and its insensitivity to defects arises from the relative strengths of the molecule–surface and molecule–molecule interactions. PTCDA molecules bind fairly weakly to the underlying graphene through π–π interactions, but strongly to each other through hydrogen bonding and quadrupolar interactions. This fairly weak bonding of the molecular overlayer to the graphene substrate is shown by the lack of any registry between rows of carbon atoms of the graphene and the molecular rows of the PTCDA layer, and allows the robust

molecular layer to traverse defects without disruption of its own packing structure.

In addition to the self-assembly work, the spectroscopic capabilities of the STM were used to characterize the electronic properties of the PTCDA layer and compare them with the bare graphene surface. The results revealed that the electronic properties of the PTCDA monolayer are distinct from those of the underlying graphene substrate, and seem to be largely unperturbed by the electronic properties of the epitaxial graphene. These observations support the idea that the PTCDA layer interacts weakly with the graphene surface and therefore maintains its own electronic properties.

Although graphene-based electronics are still a distant prospect, potential applications in the short term include conductive additives to plastics, battery parts and field emitters[7]. The demonstration that the same principles of molecular self-assembly — which are well understood on substrates such as graphite — can be transferred to graphene opens the possibility of using the existing bank of information

about molecular assembly to functionalize graphene for a myriad of applications. Such well-ordered, stable and nearly defect-free molecular monolayers present many opportunities for exploring self-assembly chemistry on graphene, tailoring its chemical functionality, and templating the growth and deposition of other materials. In turn, these opportunities will offer potential routes towards realizing graphene-based molecular electronic and sensing devices. ❑

E. Charles H. Sykes is in the Department of Chemistry, Tufts University, Medford, Massachusetts 02155, USA.
e-mail: charles.sykes@tufts.edu

References
1. Novoselov, K. S. *et al. Science* **306,** 666–669 (2004).
2. Novoselov, K. S. *et al. Nature* **438,** 197–200 (2005).
3. Wang, Q. H. & Hersam, M. C. *Nature Chem.* **1,** 206–211 (2009).
4. Lauffer, P. *et al. J. Phys. Stat. Sol. B* **245,** 2064–2067 (2008).
5. Forrest, S. R. *J. Phys. Condens. Matter* **15,** S2599–S2610 (2003).
6. Berger, C. *et al. J. Phys. Chem. B* **108,** 19912–19916 (2004).
7. Geim, A. K. & Novoselov, K. S. *Nature Mater.* **6,** 183–191 (2007).

Chemistry awakens a silent giant

Progress in NMR spectroscopy has been held back by sensitivity issues inherent to the way the measurements are taken. Now, two separate studies show how simple chemical processes can be used to unveil NMR's sensitive side

Lucio Frydman

Nuclear magnetic resonance (NMR) has a number of unique roles in science, such as characterizing molecular structures and contributing to the *in vivo* identification and localization of disease through magnetic resonance imaging (MRI). Further progress in the uses of NMR and MRI are hampered by sensitivity problems, and incremental 'bigger machine' approaches have reached a stage of diminishing returns. Writing in *Science*, Duckett and co-workers[1] and Warren and co-workers[2] deal with these sensitivity issues by relying on highly original propositions that result in NMR 'super-signals' that surpass those normally afforded by state-of-the-art spectrometers by factors of ~10^2–10^3. Uncharacteristically, these studies share a call for synthetic chemistry to come to the aid of NMR spectroscopy, rather than the other — and more common — way around.

The key to NMR/MRI is the alignment that nuclear spins from stable isotopes (^{1}H, ^{13}C, ^{19}F, ^{31}P) undergo, when samples are
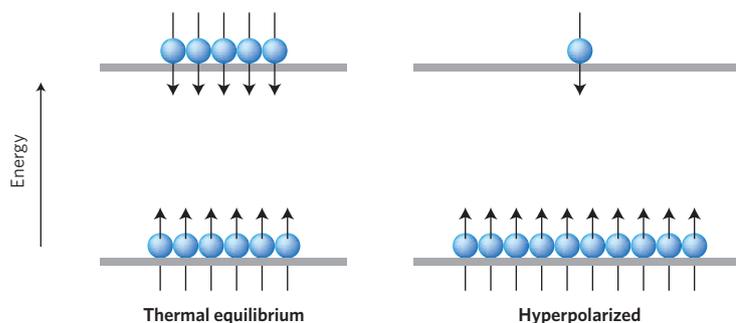

Figure 1 | Population differences between equilibrium and hyperpolarized states. Duckett and colleagues[1] and Warren *et al.*[2] propose new routes to defeat Boltzmann's frustratingly low degree of equilibrium spin alignment (left), through nuclear hyperpolarization methods capable of yielding correspondingly stronger NMR/MRI signals (right).

placed within the powerful magnetic fields in which these experiments take place. Once aligned, the spins can be excited away from equilibrium with a radiofrequency pulse, making them emit characteristic electromagnetic 'sounds' specific to either

chemical locations (in NMR) or to spatial positions (in MRI). This nuclear symphony then affords accurate information about the structures of molecules and of objects, as well as unique information about their atomic-level dynamics.