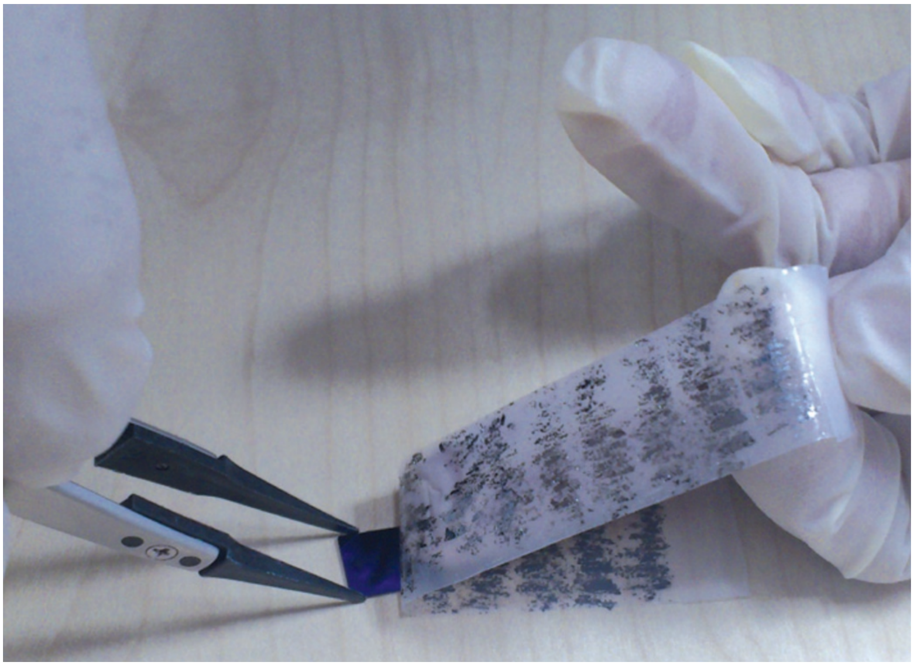

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PRODUCTION

Beyond sticky tape

Flecks of graphene are easy to make. But producing sheets of pristine, electronics-quality material is another matter.

BY RICHARD VAN NOORDEN

Unlike many hi-tech materials, graphene is so simple to make that anyone can produce it at home. First, press adhesive tape onto a chunk of graphite and pull: this peels off a thin flake of grey-black carbon. Then repeatedly stick the carbon-covered tape against itself and peel away: the carbon flake breaks up further into thin, faint fragments, each hundreds of micrometres across. After a few rounds of this, some flakes have been whittled away to single-atom thickness — a fleck of graphene.

All in all, it is a pleasingly artisanal way to make a remarkable material. The graphene is high quality, too: it was on similar products that Manchester University physicists Andre Geim and Kostya Novoselov measured extraordinary electron-transport properties in 2004 — experiments for which they won the 2010 Nobel Prize in Physics. "You can make several square millimetres with a couple of hours' work," says Peter Blake, cofounder of Manchester-based Graphene Industries, which sells such flakes to researchers for £500–1000 (US$780–1550) each.

But one can't mass produce graphene with sticky tape. To do this, researchers use chemicals to split graphite into graphene platelets by the tonne. Unfortunately, with speed and volume comes variable quality: few of these platelets are perfect single sheets. The platelets are typically rough stacks of 5 to 10 carbon layers riddled with defects, and begrimed with other chemicals. Yet they still have the attributes that make graphene so appealing: they're lightweight, strong, have a large surface area and conduct electricity and heat. It's already possible to buy dozens of different grades of graphene made this way as powders or in solution. Developing applications range from conductive inks and fillers in composites, to battery electrodes and electrochemical sensors.

For more demanding electronics, however, researchers need much purer graphene in large sheets — millimetres or centimetres in diameter. The aim is to grow theoretically perfect graphene: a hexagonal, honeycomb carbon lattice with not a single atom out of place. In practice, a real carbon lattice is strained by defects, polluted by 5- or 7-membered rings, its edge is ragged, and it sits on a substrate that interferes with its properties. These imperfections impair conductivity and other electronic properties. Whether that matters in practice depends on the purpose: transparent conducting films in touch screens, for example, need not be as conductive as those in solar cells.

Large carbon sheets and small imperfect carbon platelets are such contrasting forms of graphene that they could almost be considered different materials. In fact, each version has its merits, depending on cost and application. "We don't all buy $5,000 suits. A lot of the time a $300 suit is all you need to wear," says James Tour, an organic chemist who specializes in nanotechnology at Rice University in Houston, Texas. But for materials scientists allured by graphene's extraordinary potential in electronics and optics it is the $5,000 suit — or high-quality graphene – that they strive to produce on a large scale.

EXFOLIATING GRAPHITE

For at least a century, researchers have been producing stacks of thin carbon platelets by pulling graphite apart into its constituent layers. (A description of a suspension of small graphite flakes was published in 1907, for example). But these days manufacturers, alert to graphene's potential, produce consistently thinner platelets. Graphite's layers are very close-knit, so acids are used to oxidise the material to graphite oxide, layers of which are more easily separated to form graphene oxide. Chemical reduction of graphene oxide leaves graphene platelets crumpled in a solution, or as a powder: a process first reported in 1961 by German chemist Hanns-Peter Boehm, who called his product 'thinnest carbon films'. It is this method — with proprietary modifications — that companies such as Vorbeck Materials, in Jessup, Maryland; Angstron Materials in Dayton, Ohio; and XG Sciences in Lansing, Michigan, still use to produce large quantities of graphene. Researchers constantly invent twists in the technique: in 2011, Chao Gao at Zhejiang University in Hangzhou, China, reported spinning a concentrated solution of graphene oxide flakes into fibres several metres in length, which could then be chemically reduced to filaments of pure graphene[1].

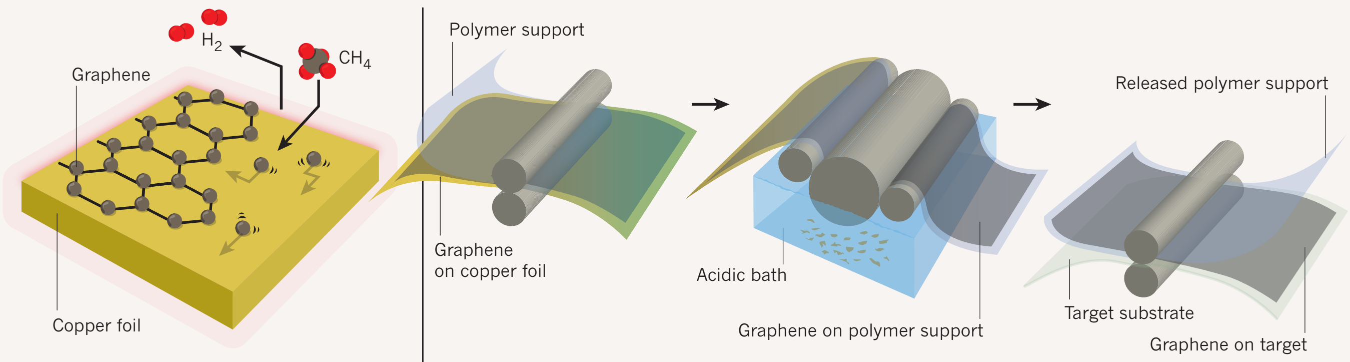
Angstron scientists have found a way to produce graphene without the harsh acid treatment of the graphite oxide route. They disperse pieces of graphite in water and surfactant, and use ultrasound to peel off layers of carbon: a more pristine graphene as fewer chemicals are involved in its production. Andrea Ferrari, professor of nanotechnology at the University of Cambridge, UK, who has worked on solutions of graphene for ink-jet printing, reckons this method might be useful in electronics that do not need the highest quality graphene, such as touch screens, 'smart windows' that can adjust light levels when a voltage is applied, or conductive fabrics that might carry signals from iPods, for example, or heart monitors.

GROWING GRAPHENE

To make larger, higher-quality sheets of graphene, researchers are growing the material as a single-layer carbon film on top of another surface, a technique known as chemical vapour deposition. This isn't new either: 'monolayer graphite films', or graphene, were made this way in the 1970s. Typically, a mixture of methane and hydrogen gas is passed across a sheet of copper in a furnace at 800-1000°C, and a single carbon layer forms atop the copper; chemical processing can remove the copper

GROWING GRAPHENE FILMS

Researchers make large (centimetre-scale) graphene films by depositing carbon atoms from a vapour onto a copper surface. Roll-to-roll processing then transfers the graphene film from copper to another substrate.



Copper foil is heated to 800-1000°C in a furnace, where hydrogen (H_2) and methane gas (CH_4) are piped through. Carbon atoms grow as graphene film on top of the copper.

Adhesive 'thermal release' tape is attached on top of the graphene, by applying pressure between heavy rollers.

The copper is eaten away in a plastic bath filled with etchant (such as ammonium persulfate, a bleaching agent and oxidant).

On heating to 90-120°C, the adhesive tape unsticks, leaving the graphene clinging to a target substrate.

and deposit the graphene on a more useful substrate material, such as silicon dioxide (see 'Growing Graphene Films'). Tour says a laboratory using a US$10,000 setup can make graphene sheets a few square centimetres in size. And while methane is the standard reactant, any carbon source will do: Tour has even put cockroach legs on top of copper and produced a thin graphene film.

A more sophisticated version of this approach yields graphene on an impressive scale. In 2010, researchers at Sungkyunkwan University in Suwon, South Korea, made transparent graphene films up to 76 cm across by depositing carbon atoms onto copper and etching the copper away[2]. Electronics giant Samsung wants to use a reel-to-reel version of this technique to produce graphene film on a continuous roll — although Seungmin Cho, principal research engineer at subsidiary Samsung Techwin in Gyeongnam, South Korea, says for now the company is concentrating on making high-quality single sheets.

Materials scientists are working on ways to lift the graphene off the copper plate and onto insulating substrates — which won't interfere with electronic properties — without wrinkling the film or otherwise compromising its quality. Top of their list is silicon dioxide, the ubiquitous insulator used in silicon chips. In 2011, Tour showed that when nickel is placed atop silicon oxide, a layer of carbon film grows at each surface of the interface between the two; etching away the nickel leaves a bilayer of graphene coated directly on silicon oxide[3]. But the growth process takes place at 1000°C: temperatures high enough to wreck any dopants or pre-structured devices (such as transistors) in the underlying silicon. Tour is confident that graphene can be grown easily on insulating substrates. "I'm reviewing papers all the time that promise improvements," he says. One paper this year, by Soon-Yong Kwon and colleagues at the Ulsan National Institute of Science and Technology in South Korea, promises a similar process that works at just above room temperature[4].

Even a graphene film grown on a surface is far from perfect. The film forms when micrometre-sized patches of hexagonally-arrayed carbon atoms — each cluster a tiny fragment of graphene — sprout simultaneously from various points on the substrate. The clusters never stitch together perfectly, so the final graphene sheet looks like a patchwork quilt of carbon, with kinks of 5- and 7-membered rings where each patch joins with the next. The largest single perfect graphene patch ever created is reported by nanotechnologist Rodney Ruoff at The University of Texas at Austin, together with scientists at Texas Instruments in Dallas, who grew individual clusters up to 0.5 millimetres on a side[5].

FROM SHEETS TO RIBBONS

Graphene film conducts electrons so well, it is hard to block their flow — a problem if one wants to use graphene in a transistor to control electrical current. But thin ribbons of graphene can be semiconducting, because the narrow channels alter the energy states of electrons. The problem is in how to make such a ribbon. Using lithography to slice up large sheets into graphene strips is, says Tour, "like using a chainsaw to do the finishing work in your home" — the ribbon's edges produced by this crude approach lack the uniformity required for electronic control.

One approach is to start with carbon nanotubes, which are essentially rolled up graphene. Researchers have variously unzipped them into flat sheets using metal catalysts, or etched 10–20 nm wide ribbons from them using ionized argon gas. But control of the edges remains a problem: only one particular geometry of the ribbon's edge will produce semiconducting graphene.

Physicist Walter de Heer at the Georgia Institute of Technology in Atlanta takes a different tack: growing graphene ribbons directly in place on a substrate. He heats silicon carbide — a compound of silicon and carbon that has been mass-produced for over a century — to 1,600°C, and the silicon atoms on top escape, leaving carbon behind. To grow graphene ribbons exactly as required, de Heer notches a step into the silicon carbide; the graphene grows preferentially on the sidewall[6].

The best graphene ribbons developed so far are those grown molecule by molecule. Chemist Klaus Müllen's team at the Max-Planck Institute for Polymer Research in Mainz, Germany, make flawless ribbons via chemical reactions between molecules based on hexagonal rings — each molecule chosen to produce an atomically precise graphene lattice when they fuse in long chains[7]. Müllen says his team can now make perfect graphene ribbons. The catch: they are only a few hundred nanometres long. De Heer envisages using similar chemistry to grow thin semi-conducting electronic interconnects between larger metallic areas of graphene — although such architectures and their applications are decades from fruition.

From the heights of molecular perfection, to the large, imperfect platelets on the graphene market: there's space for all production methods — though they seem worlds apart. ■

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1. Xu, Z. & Gao, C. *Nature Communications* **2**, 571 (2011).
2. Bae, S. *et al. Nature Nanotech.* **5**, 574–578 (2010).
3. Zhiwei Peng *et al. ACS Nano* **5**, 8241–8247 (2011).
4. Kwak, J. *et al. Nature Comms* **3**, 645 (2012).
5. Li, X. *et al. J. Am. Chem. Soc.* **133**, 2816–2819 (2011).
6. Sprinkle, M. *et al. Nature Nanotech.* **5**, 727–731(2010).
7. Cai, J. *et al. Nature* **466**, 470–473 (2010).