The quest for supercarbon

Graphene's dazzling properties promise a technological revolution, but it may take a billion euros to overcome some fundamental problems.

BY MARK PEPLOW

Mr G gazes out from a recruitment poster hanging in an engineering building in Cambridge, UK. His cartoon cape billows out behind him, his sketched-in muscles ripple beneath his costume, his chest is emblazoned with a 'G' inside a hexagon — and his forefinger points straight at the viewer. "I want you for the Graphene Flagship!" declares the cartoon crusader, championing a material as super as he is.

Graphene is the thinnest substance ever made: a single sheet of carbon atoms arranged in a hexagonal honeycomb pattern. It is as stiff as diamond and hundreds of times stronger than steel — yet at the same time is extremely flexible, even stretchable. It conducts electricity faster at room temperature than any other known material, and it can convert light of any wavelength into a current. In the decade since graphene was first isolated, researchers have proposed dozens of potential applications, from faster computer chips and flexible touchscreens to hyper-efficient solar cells and desalination membranes.

But harnessing graphene's qualities for practical use has proved a massive challenge. Graphene is complicated and expensive to make in large sheets, which usually have so many atomic-scale flaws and tears that they fail to match the amazing properties of the tiny flakes studied in the laboratory. And even if its quality were good, there are no well-established industrial methods for handling something so thin, or for integrating it with other materials to create useful products. What's more, graphene has a superweakness. Its electrons may be extremely mobile, but other properties make it fundamentally unsuitable for the sort of on–off switching that lies at the heart of digital electronics.

Hence Mr G's call to arms. The character was created in 2011 to help publicize a multinational push for a Graphene Flagship project: a decade-long, €1-billion (US$1.35-billion), all-European effort to take graphene from the laboratory bench to the factory floor. And not just graphene. The project's proponents also wanted to study more than a dozen other atomically thick materials discovered in graphene's wake — that, when sandwiched together with graphene, might help to overcome its limitations[1].

The campaign worked: the European Commission in Brussels gave its go-ahead to the graphene flagship project in January (see *Nature* **493,** 585–586; 2013). Already the world's largest research effort on the material, encompassing hundreds of scientists across 17 European countries, it will grow even larger after the flagship puts out its first call for additional project proposals on 25 November.

The infusion of funds and energy has galvanized the graphene community, says Andrea Ferrari, director of the Cambridge Graphene Centre and chair of the flagship's executive board. Ferrari, whose office wall sports Mr G's poster, says "Nobody has been involved in anything this big before."

TOO MANY COOKS?

But some question whether the programme is too big. Is an academia–industry collaboration, inevitably fettered by the bureaucracy of such a large venture, the best way to deliver a technological revolution? "This is not the way products are actually developed," says Phaedon Avouris, a graphene and nanotechnology researcher at IBM's Thomas J. Watson Research Center in Yorktown Heights, New York. And some researchers involved in the project are concerned that political forces, rather than scientific priorities, will steer the dispersal of funds over the next few years.

Still, the flagship's prospects for success seem strong enough that national governments and industry partners, such as Nokia and Airbus, will collectively put up half its funding. (The European Commission will provide the rest.) "I hope that after ten years, technologies based on graphene or other layered materials are mainstream," says the flagship's director Jari Kinaret, who is based at Chalmers University of Technology in Gothenburg, Sweden. Just as we now do with polymers, semiconductors and ceramics, he says, "we should take graphene for granted".

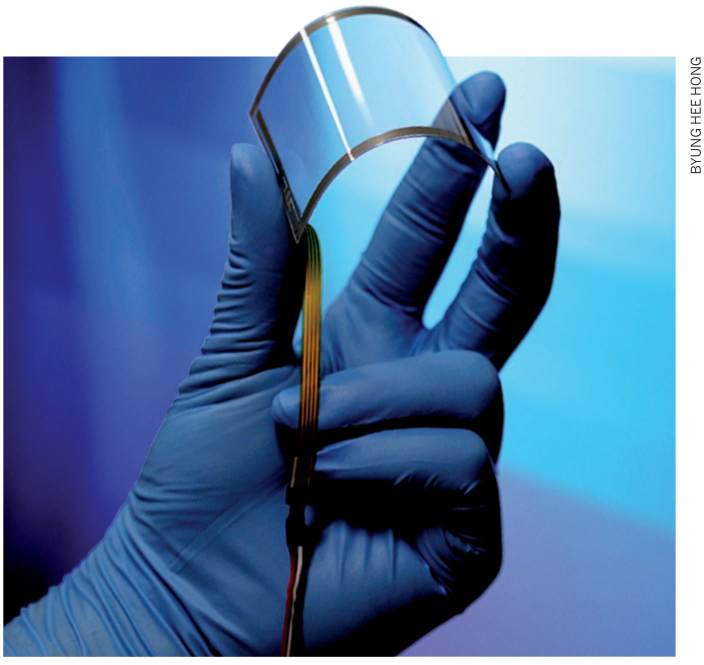
The flagship programme is divided into 16 work packages, most of them targeted at developing applications such as high-frequency electronics, sensors and energy storage. Next week's call for proposals, worth €9 million, comes at the beginning of a €54-million ramp-up phase that is expected to deliver the first wave of prototypes by 2016.

But there will be no graphene computer chips, graphene sensors or graphene solar cells without a steady supply of graphene itself. One of the flagship's first and biggest challenges is to find more economical and reliable ways to produce high-quality sheets of the material.

Most research laboratories still make graphene using the method pioneered in 2004 by Andre Geim and Konstantin Novoselov at the University of Manchester, UK, who went on to win the 2010 Nobel Prize in Physics for their studies. Geim and Novoselov found that they just had to touch a strip of household sticky tape to ordinary graphite — which consists of billions of layers of graphene stacked on top of one another — and they could peel off thin flakes of carbon. By repeatedly splitting those flakes, they were eventually left with graphene[2]. This was a technique that any laboratory could use, and graphene research exploded.

But the method is much too slow and finicky for industrial-scale production. Just one micrometre-sized flake made in this way can cost more than $1,000 — making it, gram for gram, one of the most expensive materials on Earth.

The leading alternative[3] relies on chemical vapour deposition (CVD), whereby methane is piped over a catalytic copper foil heated to about 1,000 °C. As the methane breaks down, small islands of pure carbon begin to grow on the foil, linking together to form a patchwork polycrystalline sheet of graphene. Harsh chemicals are then used to etch away the copper to free a sheet of graphene tens of centimetres wide, which can be transferred to a silica or polymer substrate. That process brings costs below $100,000 per square metre, but the product is often riddled with defects, impairing its electrical properties and making it much weaker than flakes produced by the sticky-tape method.



BYUNG HEE HONG

Graphene offers a way to make flexible and transparent smartphone screens.

INDUSTRIAL ACTION

The flagship programme is tackling this problem in part through its industrial partners, such as Graphenea of San Sebastián, Spain, which already makes about 15 square metres of graphene per year. And it should benefit from a deal signed in September that will see fledgling graphene producer Bluestone Global Tech of Wappingers Falls, New York, open a pre-production facility and offices at the National Graphene Institute in Manchester, the hub of Britain's graphene effort. This year, Bluestone began speeding up production and lowering costs by using bubbles of hydrogen to tease large graphene monolayers away from the copper foil without etching[4,5].

Yet even Bluestone's manufacturing process is "still a very complex way of adding graphene to a substrate", says Tapani Ryhänen, head of sensors and material research for Finish company Nokia, and a member of the flagship's advisory council. The flagship aims to refine the CVD process and to improve on alternative production methods. Also problematic is the tricky process of transferring the freshly made graphene from its catalytic foil to a new substrate. Lay it on top of silicon, for example, and the sheet wrinkles and puckers. One solution would be to grow graphene directly on the substrate, or on top of another sturdy, protective monolayer such as boron nitride, a process demonstrated at small scale earlier this year[6].

"Nobody will ditch silicon unless there's a really compelling reason to do so."

But ultimately, says Rod Ruoff at the University of Texas at Austin who led the development of the CVD production method, the best way to slash costs and propel graphene into the mainstream would be to make high-quality monolayers from bulk graphite — exfoliation on an industrial scale. The flagship will investigate chemical treatments, ultrasonic vibration and more, but a practical, scalable method still seems a long way off. "We need some sort of a breakthrough here," says Ruoff.

Despite its manufacturing challenges, enthusiasts are quick to point out that graphene has already hit the market. Multi-layered graphene, in which many sheets are stacked together, is used to strengthen a tennis racquet made by Head, for example, and forms a conductive circuit in anti-theft packaging produced by Vorbeck Materials in Jessup, Maryland.

But these cheaper forms of graphene include a range of different structures that are essentially nanometre-sized chunks of graphite. The properties of this sooty jumble of fragments are no match for Mr G's superpowers, which reach their zenith only in pristine, one-atom-thick layers in which the atomic arrangement is perfect. Only in this state can electrons flow more quickly than in any other material.

To get current moving through any crystal, electrons must first clear a hurdle called the band gap: the energy required to knock them loose from individual atoms and set them free to roam. Insulating materials have a large band gap, meaning that electrons tend to be tightly bound to the atoms and need a huge kick to start moving (see 'Mind the gap'). Semiconductors such as silicon and germanium have a much smaller band gap, so only a little jolt of energy is required. Metals have no band gap at all; they are great conductors because at least some of their electrons are always free. But graphene sits right on the boundary, blessed with an infinitesimally small band gap that helps current to zip across its interlocking hexagons 100 to 200 times faster than it can move through silicon[7].

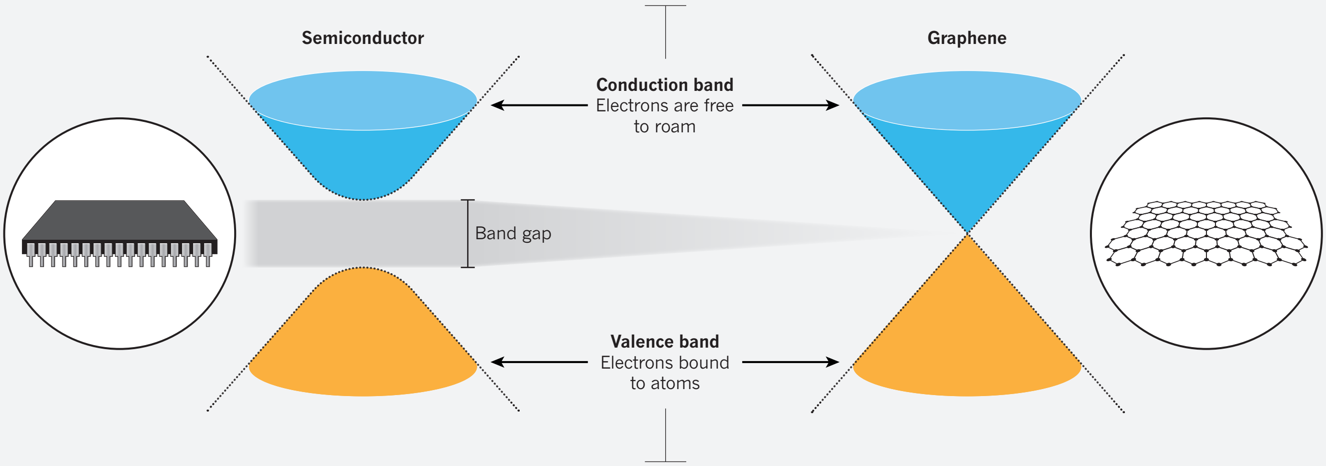
This tiny band gap also makes graphene optically omnivorous. Silicon can only absorb photons with energies greater than its band gap; if weaker photons hit it, they can't free electrons from the parent atoms. Graphene, by contrast, can absorb photons across the visible spectrum and beyond, turning their energy into electrical current. "There's not really another material that has good properties for both optics and electronics," says Daniel Neumaier of the contract research company AMO in Aachen, Germany, who is leading the flagship's high-frequency electronics work package.

This combination of abilities makes graphene a promising candidate for converting photons into electrical signals. Graphene photodetectors could allow computer chips to communicate with light rather than comparatively sluggish, energy-wasting electrons — an advance that would cut power consumption and allow computers to handle data more efficiently. Such photodetectors would be smaller than current devices made of germanium, and could handle a wide range of wavelengths, allowing them to interpret multiple signals bundled together into the same beam (see *Nature* http://doi.org/pz2; 2013).

Graphene could also be useful in medical and security scanning that

MIND THE GAP

Electrons in a solid are restricted to certain ranges, or bands, of energy (vertical axis). In an insulator or semiconductor, an electron bound to an atom can break free only if it gets enough energy from heat or a passing photon to jump the 'band gap', but in graphene the gap is infinitesimal. This is the main reason why graphene's electrons can move very easily and very fast.



uses terahertz-frequency radiation. The generation and manipulation of terahertz waves, which lie between the infrared and microwave regions of the spectrum, often requires bulky equipment or cryogenic cooling. Graphene-based devices are compact and can generate or detect the waves at room temperature. This may be graphene's best opportunity for a groundbreaking application, says Avouris, because it could find a role not already occupied by other well-established materials.

Others think that graphene's most obvious optical property — its transparency — may yield its first major application in the electronics industry. Samsung and other Asian companies are developing transparent graphene electrodes to serve as smartphone touchscreens. The indium tin oxide electrodes in use today are brittle, whereas graphene is strong and flexible. And although graphene touchscreens are currently more expensive than the conventional variety, "the cost is falling rapidly as we ramp up the scale of production", says Bluestone's co-founder Yu-Ming Lin.

TURN OFF

When it comes to digital electronics, however, graphene's greatest strength is also its greatest weakness. In principle, its extremely mobile electrons could allow graphene transistors to process data at very high rates, with some devices already clocking in at more than 400 gigahertz — many times faster than comparable silicon devices[8]. But graphene's lack of band gap makes it very hard to turn the current off once it starts flowing, a serious impediment to logic operations, which are all about on–off switching. Doping graphene with other materials or slicing it into narrow ribbons can open up a small band gap, but this also slows the flow of electrons. So researchers are trying to tune its electrical properties by combining graphene with other monolayer materials such as boron nitride or creating transistors from molybdenum disulphide and tungsten diselenide[9–11].

But graphene is still a long way from replacing silicon electronics, says Tim Harper of the technology-development company Cientifica, based in London: "Nobody will just ditch silicon unless there's a really compelling reason to do so." In the near term, a graphene transistor's biggest selling point may be its ability to operate over a range of voltages, rather than any ability to switch on or off. Applications might include sensors for environmental pollutants or blood-oxygen levels, or the transmitters and receivers inside mobile phones. By the end of the programme's 30-month ramp-up phase, Neumaier's goal is to build prototypes that demonstrate graphene's potential in these areas. "Expectations at the moment are very large," he says.

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So are the concerns of some researchers. As one of Europe's highest-profile science projects, the graphene flagship has some treacherous political waters to navigate.

The European Commission wants the flagship to be as inclusive as possible, to ensure that under-represented member states get a piece of the action. One consequence is that next week's call is open only to new partners — existing flagship research groups are barred from bidding for those funds. "That came as a surprise," says Kinaret. The rule excludes all researchers who have signed up en masse through national research networks, including the CNRS in France, the Max Plank Society in Germany and the CSIC in Spain. The networks have lobbied the commission to change that rule, but "we have been less than successful", says Kinaret.

Kinaret expects that restriction to change next year after the European Union's Horizon 2020 research programme comes into force, and other funding streams are available in the meantime. But some researchers have been left with a sense of foreboding. Ferrari worries that there is a risk of losing sight of the original goal: a genuine technological revolution in ten years. By slicing the flagship's money into smaller chunks and spreading it more widely, Europe could keep more member states happy — but might dilute the project's impact. "Excellence must be the criterion," he insists.

Meanwhile, Europe faces stiff competition from Asia in the race to commercialize graphene. Although the European Union leads the world in academic publications on the material, the UK government's Intellectual Property Office in Newport reported in March that 15 of the top 20 global graphene patent-holders are Chinese, Japanese and South Korean companies and universities, with Samsung way out in front. Some Chinese manufacturers say that mobile devices bearing graphene touchscreens will hit the market next year.

Europe has led in academic research on graphene, but it trails in development. "That," says Kinaret, "is what we are hoping to change." ■

Mark Peplow *is a freelance writer based in Cambridge, UK.*

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