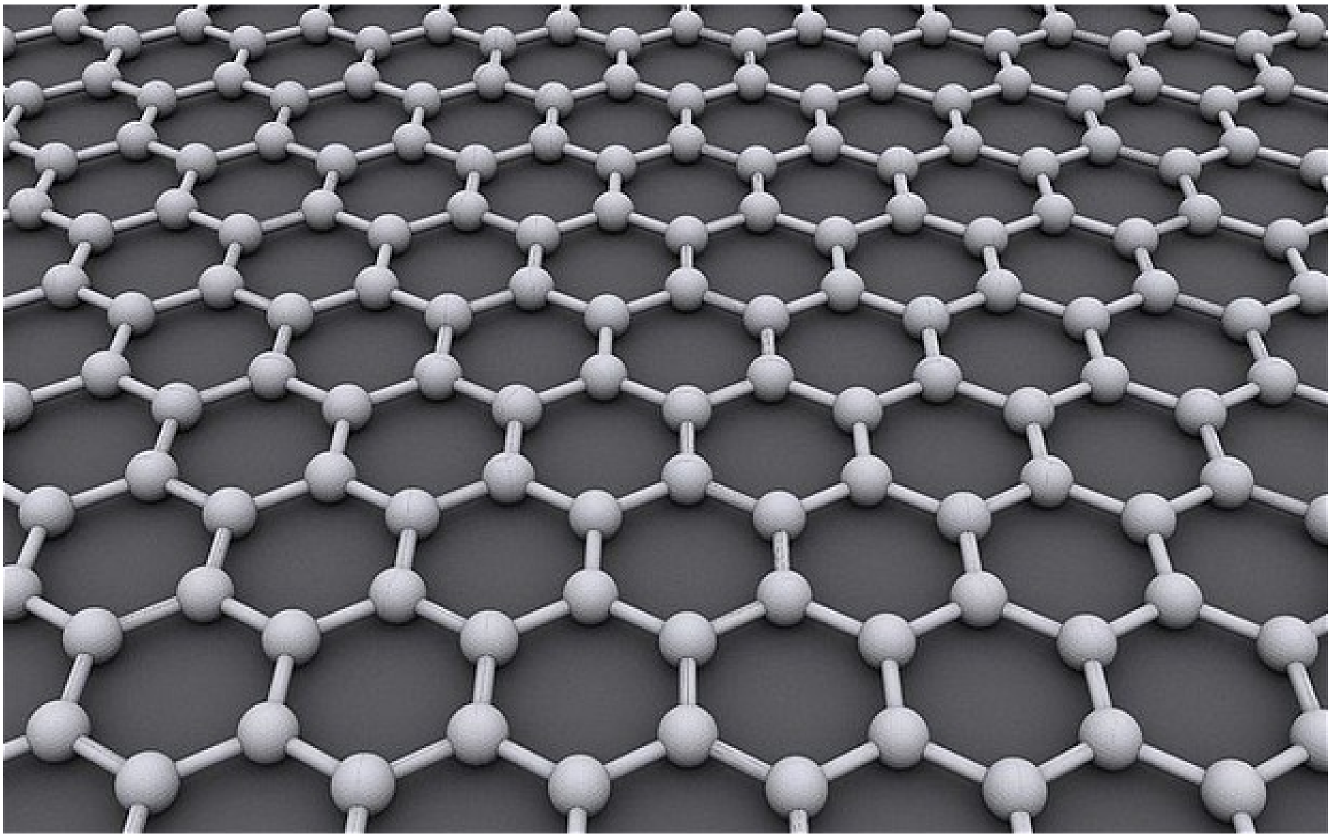
Miracle material: the graphene revolution

The race is on to harness the potential of graphene, a substance that is harder than diamond, yet incredibly flexible, and the world's best conductor of electricity.



The ideal crystalline structure of graphene is a hexagonal grid Photo: Alexander Aius/Wikimedia Commons

By Harry de Quetteville

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Kostya Novoselov tends to wear an air of slight distraction. But when a problem or topic of conversation sparks his curiosity, his gentle, rather doughy features settle and his focus visibly intensifies.

To watch this happen is to watch a great mind at work. Yet Novoselov is also engagingly modest. Too modest to boast about the fact that in 2010, along with Andre Geim, he won the Nobel Prize in Physics for isolating an atom-thick layer of carbon known as graphene – something that has been described as a 'miracle material' that will transform the lives of almost everyone.

The phrase 'miracle material' does not spark Novoselov's curiosity. Rather, his eyes glaze over. As a research physicist – born in Russia, but a British citizen – he is just not that interested in the hype. Indeed, it makes him slightly uncomfortable, as does the fact that he and Geim (a Russian-born Dutch-British national) were knighted in the New Year's honours last year for services to science.

Novoselov was working at the University of Manchester as Geim's most brilliant doctoral student when, in 2004, they attempted to build a transistor out of graphite. Transistors control the flow of electrons in a circuit, like a tap, with an 'on' state and an 'off' state. When 'on' and 'off' represent one and zero, the flow of electrons becomes a flow of data. It is on the back of such transistors that much of the modern world is built – from radios to computers to smartphones, they are at the heart of our electronic society. And the material that underpins the transistor is silicon, which is very good at turning the electron flow on and off reliably and cheaply.

The transistor was invented in 1947. But that did not stop Geim and Novoselov messing about with the concept in a rather plain, spare laboratory on the University of Manchester campus, which lies to the south of the city centre, just beyond the Mancunian Way ring road. 'It's never boring working with Andre,' Novoselov says. 'He asks strange questions about obvious systems. Sometimes, interesting things come up.'

The first attempt at a graphite transistor failed, and the researchers were on the point of abandoning their quest when Novoselov had a brainwave. 'I had seen how people clean graphite by cleaving it. Two and two came together and in a couple of hours we had a working device.'

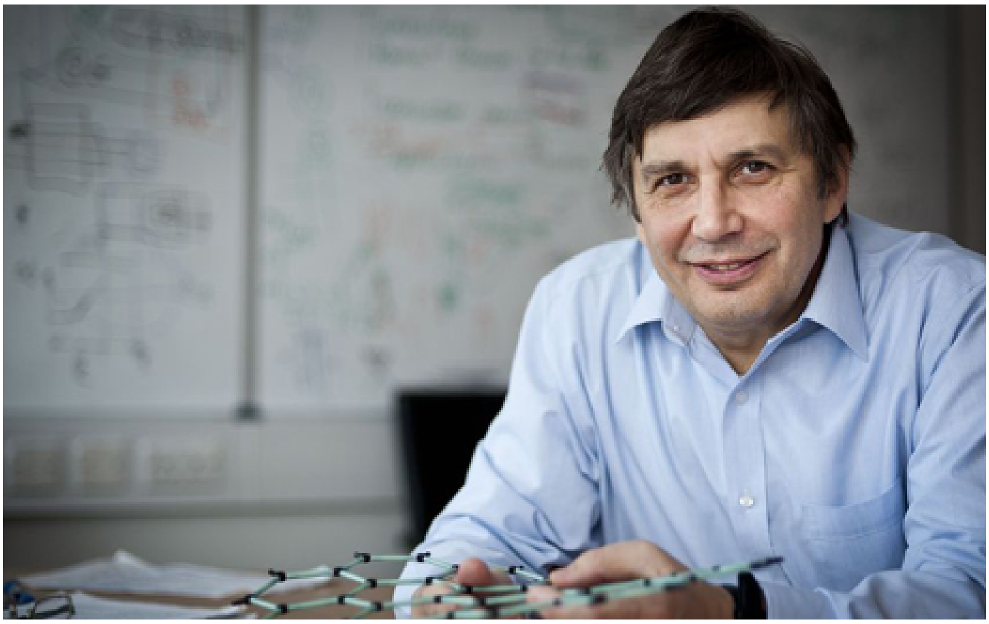
What had happened was that Novoselov and Geim had taken graphite – which is essentially formed of countless flat sheets of carbon atoms, stacked one on top of the other like a deck of cards – and started stripping away card after card, leaving them with an ever-thinner piece of graphite. When these super-thin pieces were introduced into their transistor, it flickered into life. 'It was still a very, very bad transistor,' Novoselov says. 'But we could see the passage forward and, for the next year, we worked very hard to improve it.'

The obvious way to do that was to try to produce ever-thinner sheets of graphite. And the way they managed it was breathtakingly simple. The two men simply stuck a flake of graphite, the same material used in pencils, on to a strip of sticky tape, folded the tape over on the flake, and then pulled it apart. Hey presto! Two improbably thin pieces of graphite. It was science, but hardly rocket science.

According to Geim, writing in Scientific American in 2008, when they took a closer look at the resulting slivers of graphite, they ‘were astonished to find that some were only one atom thick’. Their astonishment was so acute because the atom-thick layer was stable independent of the graphite from which it had been ripped – something that previously had been considered impossible.

Though graphene research dates from the early 1960s, Geim and Novoselov were the first to succeed in isolating it. When they put graphene under the electron microscope, they saw hexagons, each formed of six carbon atoms, in a perfect two-dimensional lattice resembling chicken wire. While beautifully simple to look at, it turned out that graphene had many extraordinary properties. For as Geim and Novoselov undertook a frantic research effort, each discovery seemed to trump the last. The transistor that had piqued their interest lay neglected.

‘Science usually works with the goal being overtaken by sidetracks which are much more interesting,’ Novoselov says. ‘So it was with us – we still had the transistor to aim for, but the properties of graphene completely overtook our minds. We started to explore its electronic properties. We didn’t know anything about it. The amount of things we learnt over that year was incredible.’



What he and Geim found was that graphene was not simply the thinnest of all materials, it was also fantastically strong. The bonds between its carbon atoms also allowed it to bend and stretch, imbuing a material harder than diamond with enormous flexibility. More important still was the fact that graphene's perfect lattice structure caused electrons, which carry current, to move freakishly fast – at speeds approaching the speed of light. The electrons even resembled light particles, behaving as though they had no mass, unlike electrons in any other system known to man. So graphene was not only supremely tough and flexible, it was also the world's best conductor of electricity.

It was for this period of investigation, for their 'groundbreaking experiments regarding the two-dimensional material graphene' that Geim and Novoselov were awarded the Nobel, whose committee clearly decided that 'for their patience with pencils and sticky tape' was a less impressive citation. Once Novoselov and Geim had opened the door, graphene quickly seized the imagination of researchers and companies across the world. Now, only nine years after it was first isolated, it is being touted as the key to myriad potential applications.

Unbreakable touch screens for mobile phones as bendable as the watch strap on your wrist; a revolution in medical diagnostics, drug delivery and bionic devices; pin-sharp environmental monitoring; protective coatings for everything from food packaging to wind-turbines; a torrent of fresh water through desalination membranes; easy clean-up of radioactive waste; dramatically faster computer chips and broadband; solar panels that could be painted or sprayed on to any surface; revolutionary batteries of infinitely higher capacity than those we currently use – these are only a few of the graphene-led revolutions that researchers worldwide suggest are to come.

Which is why the Engineering and Physical Sciences Research Council (EPSRC) – which has a vast remit and a budget of about £800 million per year – has helped steer £70 million of state funding at graphene research in the past couple of years. Of that, £38 million has gone towards the £61 million total cost of building a National Graphene Institute at the University of Manchester, in sight of the lab where Geim and Novoselov made their breakthrough in 2004. The centre is due to open in spring 2015. Meanwhile, Cambridge University is hurrying to erect its own graphene centre, at a cost of £8-10 million, which it will fund itself and hopes to open by the end of 2014. The university has also received £12 million of EPSRC money for graphene research.

For the moment, however, real-world applications remain rather modest. 'I told EPSRC I could produce a singing Christmas card,' Prof Clare Grey at Cambridge University says. A specialist in energy storage, she prompted a few raised eyebrows at the top table at Pembroke College by demonstrating to me the power of a new supercapacitor midway through lunch.

Though the flying sparks were eye-catching, it was her collection of transparent plastic strips, each no bigger than the drinking-straw wrappers on packed-lunch juice-boxes, that were most captivating. Flexible and see-through, they contained graphene-based batteries and supercapacitors. Currently, batteries use graphite electrodes. But graphite snaps, whereas graphene is flexible and can bend. And graphene can also be mixed with nanoparticles of silicon and metal oxides to make batteries of far greater capacity than those that exist today.

Efficient, bendy, robust, capacious power sources utilising graphene could thus be stitched into almost anything – the heel of shoe, the handle of a handbag, or, as Prof Grey noted, a Christmas card, where it would doubtless power tinny playback of a popular carol.

Such research may sound trivial. But it has the potential to transform the way we use power on the move, in everything from mobile phones to electric cars. It could also power a revolutionary new era of microscopic sensors – sensors that themselves are based on graphene. For graphene's supreme conductivity makes it a supreme sensor, as even single atom changes in the atmosphere around it trigger changes in its electrical properties that can be measured. That could enable graphene sensors to detect changes in the body at the tiniest scale and control drug delivery mechanisms – say, insulin for diabetics.

Inevitably, there are significant applications for the military, where developers are constantly striving to reduce what they call 'the soldier's burden'. On today's battlefield batteries driving electronics add considerably to that burden. In the armed forces of the future it is hoped that infantry will be able to wear ever more sensors, powered by ever more tiny batteries, at a fraction of the weight they carry now.

The combination of sensors, batteries and transistors, all dotted with graphene's strength, capacity and flexibility, bodes well for the development of what Prof Andrea Ferrari, the head of Cambridge's graphene centre, calls 'an internet of things', where electronics 'can be implanted in devices and materials that do not have them, materials that can be worn, for example. Or on posters or plastic bottles. Currently electronics are too expensive, too inflexible for these applications,' he says. 'Yet already we can produce graphene inks that can be used in the same way as conventional inks, from inkjet printers to screen prints.' The difference, of course, is that graphene inks conduct electricity, and so circuits can simply be sprayed on to almost anything.

Just as Geim and Novoselov pursued atom-thin sheets of graphite armed only with sticky tape, so a spirit of playfulness seems to overtake many of those who work with graphene. 'Working with graphene at this stage is like being a kid in a toy shop,' Ferrari says. 'When we demonstrated graphene inkjet printing, I didn't have to pick up the phone. Companies immediately started calling me.'

Unsurprisingly, big business has been quick to pick up on the potential of graphene, and there are currently few bigger businesses than consumer electronics. Samsung is widely considered the global leader in graphene research. According to Quentin Tannock, a tech sector analyst, Samsung has a unique advantage over all its competitors. Its sheer size means that it can bring every aspect of graphene, from production to commercialisation, under one roof. 'They can manufacture graphene, purify it, put it into a bigger system, put that into a product, and sell the product.'

What those products might be is now a billion-dollar question. Though Samsung is pouring hundreds of millions of pounds into graphene research and has already taken out hundreds of graphene-related patents, it has so far remained secretive about its precise plans. 'For Samsung graphene is all about miniaturisation and flexible electronics, futuristic stuff that might in fact be coming soon,' Tannock says. 'A watch turning into a phone and then back into a wrist device, that kind of thing.'

But not all of graphene's potential uses are on a miniature scale. It has huge potential in the automotive and aerospace industries. 'Aircraft wings need to be stiff so that the engines don't drag along the runway,' Ian Kinloch, a professor of materials science at Manchester, says. 'Graphene is three to four times stiffer than the carbon fibre used in the latest Airbus.'

It would be equally useful in cars. Carbon fibre, though also strong and light, is not used in cars for a simple reason – it can't be used in cheap injection moulding production techniques typical of most car factory floors. Graphene can. 'But we need tons of the stuff,' Kinloch says. 'And that comes down to price.'

Mass production of a material that is famous for being a single atom thick has not proved easy. There are currently a host of different ways of producing graphene, but the best quality stuff is still produced in tiny quantities in what remains known as 'the Scotch tape method'. Nothing yet comes close to being able to meet the demands of the production line. Which is why no one is making money from graphene just yet.

The mass-production process with most hopes invested in it is currently chemical vapour deposition, in which carbon is vaporised and encouraged to form a film on another material, usually copper. The problem is that the copper substrate is expensive, and it is hard to get the resultant graphene film off without ruining the metal. The process also runs at very high temperatures, so requires a great deal of energy. To replace silicon in the electronics industry, someone is going to have to work out how to produce high-quality graphene in industrial quantities at an affordable price.

'The entire industry is built on silicon,' Dr Aravind Vijayaraghavan, who works with Geim and

Novoselov at Manchester, says. 'Not because other materials can't do it better, but because silicon does it well enough for the price you are willing to pay. Companies like Intel have spent billions of pounds on facilities optimised for silicon. So if you want them to switch to graphene you are going to have to drag them kicking and screaming. They are not going to give silicon up easily.'

Graphene also still has to demonstrate that it can be 100 per cent reliable. 'With batteries, testing performance over 10,000 cycles is what counts, not just observing improved performance once,' Prof Rob Dryfe, at Manchester, says. 'You need to know why it's performing better, and if that will last.' It is for this reason that, at IBM, Supratik Guha, the head of physical sciences research, admits that though his team is working hard on graphene, the material 'still has to prove itself'.

The gulf between a production run of 10 at a university lab, and 10 million on a factory floor can prove tricky to bridge for emerging technologies. So much so, in fact, that it is known as a 'death valley' for potential products, where neither academia nor industry takes an interest and they wither and die.

Such is the promise of graphene, however, that it is inconceivable that it will perish in such a manner. No one wants to be on the wrong side of the next commercial revolution. Not again. 'In Britain there is a tradition of coming up with ideas, then losing them,' Ferrari says. 'Think of the cathode ray tube.'

At EPSRC its chief executive Dave Delpy does not believe that British graphene funding, though dwarfed by outlays being made in America and Asia, will prove a stumbling block. 'We're not so good at turning ideas into billion-dollar products. But that's not the fault of the universities or the funding councils,' he says.

The clear implication is that the fault lies with British businesses, slow to seize on graphene's potential and run with it. 'Obviously there is a need to grow new industries,' Delpy says.

That's why EPSRC has insisted that both the Cambridge and Manchester graphene centres have businesses working alongside academics. The idea is that companies will pay the equivalent of yearly 'green fees' to sit in with researchers and design their products from there. In Cambridge Ferrari says that 'we're going to sign up 20-30 companies'.

Commercial partners that the Cambridge centre lists on its website currently include Du Pont, Dyson, Johnson Matthey, Nokia, Plastic Logic and Philips, among others. Harnessing the potential of graphene will require collaboration, which is why the European Union recently announced a €1 billion funding package for graphene research across the continent over the next 10 years.

For Quentin Tannock it is not the amount of money, though large, that is important, but the fact that it will force cooperation and coordination between research institutions and business across Europe – and that the funding will be spread over a decade. ‘A lot of graphene research areas are likely to prove more of a marathon than a sprint, so that is the time frame needed.’

It is a note of caution that Delpy echoes. ‘If we don’t get involved now we will lose an opportunity for the UK. Historically it is a long time between lab and really good product. It will be a longer haul than people expect with graphene, too.’

That is only natural. After all, it is not every five minutes that such revolutionary materials come along. ‘Roughly every 20-30 years a material comes about that has the ability to change everything,’ Supratik Guha at IBM says. ‘Silicon arrived in the 1940s, which paved the way for information technology. Then in the 1970s came gallium arsenide, making lasers ubiquitous in DVDs and CDs and telecommunications, without which our modern world would not exist. In the 1990s came gallium nitrite, which revolutionised solid state lighting. We are in the middle of that revolution.’ He has, he says, a ‘gut-feeling’ that graphene will be at the heart of the next revolution.

And yet, even if it is, it is possible that graphene will not be the most exciting result of Geim and Novoselov’s afternoon effort with the Scotch tape. For it turns out that graphene is not just a potential wonder material; rather it is one of a host of potential wonder materials. Almost as soon as they realised that the reduction of graphite to layers of graphene produced a new material of extraordinary capabilities, Geim and Novoselov began looking to reduce other substances to single-atom layers, and in doing so unlocked a whole new library of materials, known as ‘two-dimensional crystals’.

And it is this discovery that makes Kostya Novoselov’s eyes light up. These new materials come with exotic names – tungsten disulphide; boron nitrite; molybdenum disulphide; niobium selenide – and each has different properties. The excitement is that these super-thin layers can be stacked up, in combination with graphene, back into a deck of cards structure like graphite. Except that each layer can be manipulated by man.

‘We can artificially set one layer to be conductive, one to insulate, one layer to be photosensitive and so on,’ Novoselov says. ‘You could create structures only a few atomic layers thick which would have many functionalities embedded in them. And we can control those structures with atomic precision. That is very new and very exciting.’

Novoselov is certain that this new library of two-dimensional materials could remake everything around us. ‘Our world is determined by only a handful of materials,’ he says. ‘Our buildings are determined by the strength of steel. Silicon determines how our computers work. Aluminium determines what our planes look like. Now composite materials are enhancing our lives significantly, things that, for example, have the strength of carbon fibre but the plasticity of plastic. What we are talking about with two-dimensional materials is the ultimate reincarnation of the composite material, where we can recombine them into a 3D material that doesn't exist in nature, a material whose properties we can control on an atomic level.'

This microscopic revolution, graphene's enthusiasts insist, will affect everyone. All that is up for debate is whether it will reshape our whole lives, or just specific parts of them. But the change is already under way. 'We are starting with transistors and solar cells,' Novoselov says. 'Two-dimensional crystals that you can paint on a wall and that function like a solar cell. It might sound like science-fiction. But we are doing this.'