FEATURES

COMING OF AGE

Twenty years after the ballyhooed discovery of graphene, the atom-thin carbon sheets are finding their footing

By **Mark Peplow**, in Manchester, England

On a rare sunny day in northern England, the National Graphene Institute (NGI) here gleams like a five-story block of obsidian. Squeezed into the University of Manchester's sprawling downtown campus, the research center is clad in almost 2000 lustrous black panels with small hexagonal perforations—an architectural nod to the structure of the atom-thin sheet of carbon that gives the building its name.

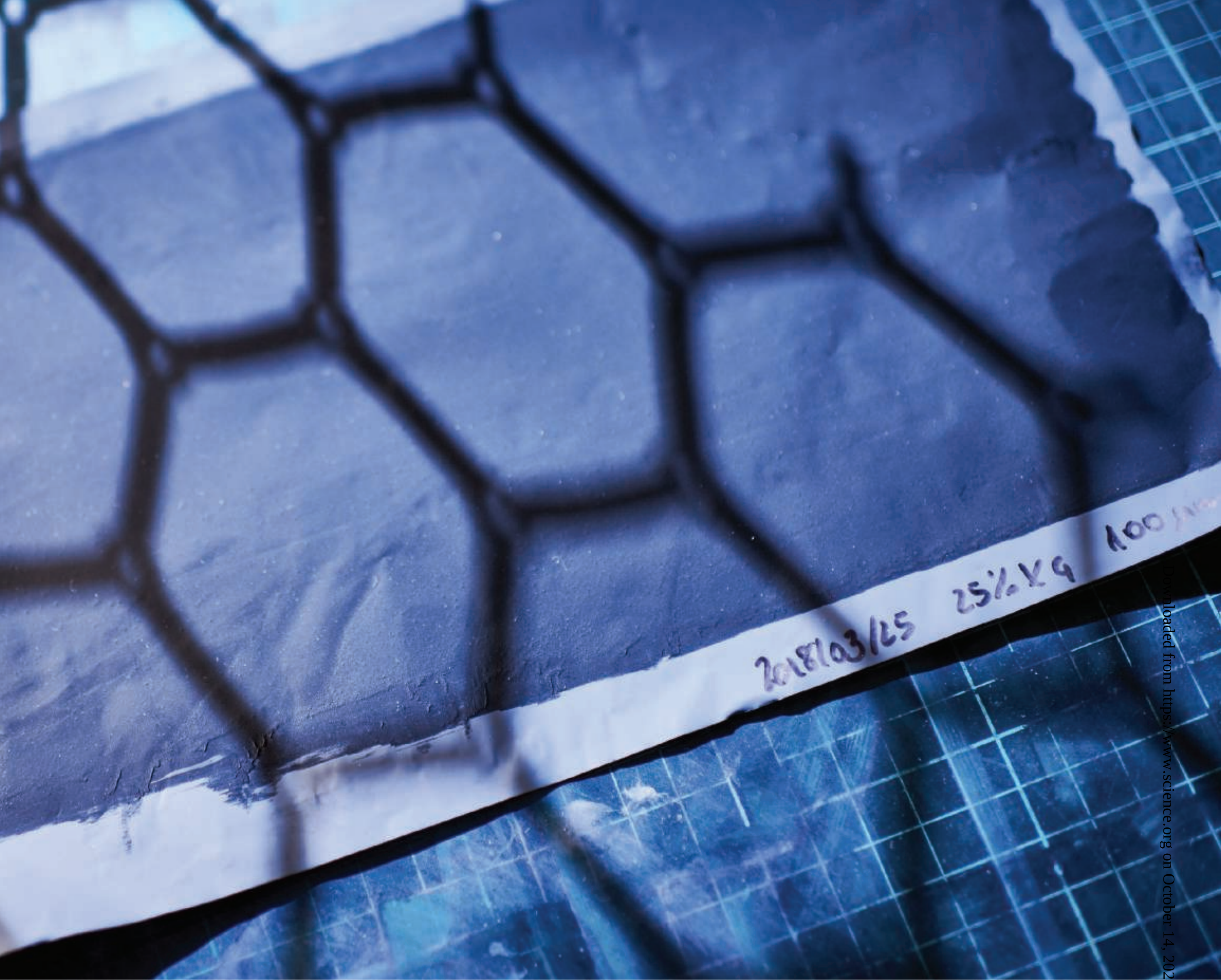
NGI exists because graphene was first isolated a short walk away in a University of Manchester lab. Andre Geim and Konstantin Novoselov presented it to the world 20 years ago this month and later won a Nobel Prize for the work. Since its unveiling, billions of dollars of R&D funding have flowed to graphene, in a global race to exploit its peerless properties. It is better at carrying electricity than any metal, a superb heat conductor, and hundreds of times stronger than steel—selling points trumpeted in the marketing materials of universities and companies alike.

Early on, researchers were not shy about promising graphene breakthroughs, with predictions that it would enable superthin rollable TVs and space elevators, and even supplant silicon in computer chips. "Expectations were very, very high," Geim says. "The companies I was involved in were mostly based on hype."

For all its allure, graphene had drawbacks, not least that it is difficult to incorporate into mass-produced devices without sacrificing its much-vaunted properties. Many companies came and went, taking their futuristic graphene dreams with them. Graphene supply has long outstripped demand, and major manufacturing companies still haven't leapt into graphene production, says Conor O'Brien, a technology analyst at IDTechEx, a U.K. market research consultancy that tracks the graphene industry.

Yet today, some graphene businesses seem to finally be finding their footing. That's partly because the name "graphene" is now applied to a plethora of other substances—cheaper forms of carbon stacked in multiple atomic layers or decorated with various chemical appendages. These heterodox forms of graphene can now be found not only in consumer electronics, but also in concrete, pickup trucks, and brain devices. "Graphene is now hundreds, maybe even a thousand different things," says Peter Bøggild, a graphene researcher at the Technical University of Denmark.

PHOTOS: (LEFT TO RIGHT) UNIVERSITY OF MANCHESTER; MATTHEW LLOYD/BLOOMBERG/GETTY IMAGES



The National Graphene Institute (NGI, left) is near the Manchester labs where graphene was discovered. In an NGI lab, graphene ink coats a metal foil (right).

But what of the iconic graphene monolayer itself? Even it may be emerging from its slough of despond. Companies are getting better at making it cheaply and consistently, and they are using atom-thin graphene to build magnetic sensors, optical communication chips, and medical diagnostic devices, for example. “It’s gone through the hype cycle,” says Natasha Conway, research director at U.K. graphene device manufacturer Paragraf. “It’s gone up the hill, down into the big valley—and now it’s coming out as people see that it really does have value.”

GRAPHENE’S ORIGIN was famously humble: Geim and Novoselov’s team used ordinary Scotch tape to peel thin fragments from a chunk of graphite. They then sifted through the flakes to find those that were just 1 atom thick. They soon realized that graphene’s 2D honeycomb structure makes it a seriously weird material.

For instance, it is neither a metal, nor an insulator, nor even a true semiconductor. In conventional semiconductors, electrons are confined to a range of energies (known as the valence band) that prevents them from conducting electricity—until a jolt of energy boosts them into the conduction band, enabling current to flow. Instead, graphene is a semimetal, somewhat like a semiconductor but with zero band gap, so the tiniest of nudges makes it conduct electricity. Indeed, the unusual arrangement of graphene’s energy states makes its electrons behave as if they have no mass, and helps them flow through graphene like greased lightning, experiencing very little electrical resistance.

Other researchers showed how graphene’s flawless array of strong chemical bonds gives it great strength, and how its honeycomb structure allows atomic vibrations to ripple freely through the material, rapidly transporting heat as they go. It also turned out to be keenly sensitive to small magnetic fields, which sweep its mobile electrons to one side in a phenomenon known as the Hall effect.

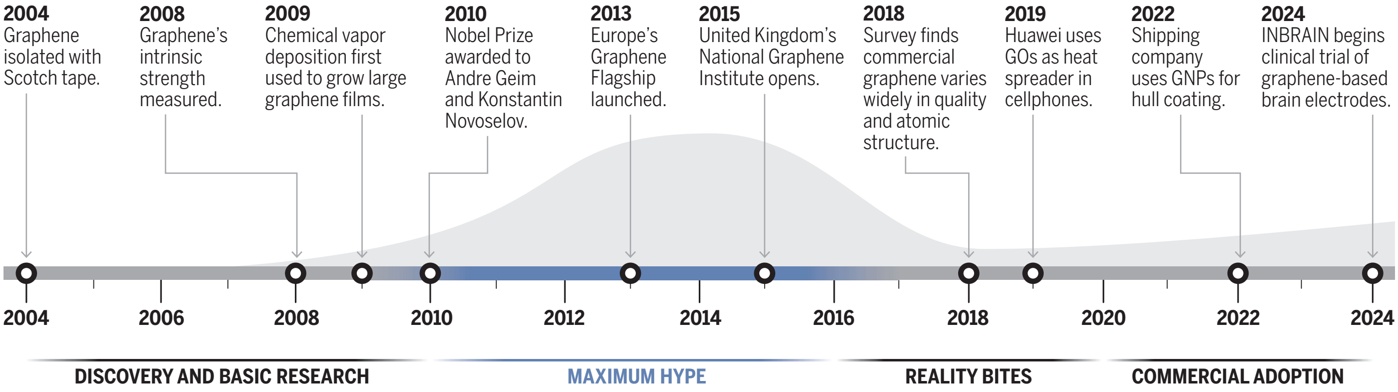
Within a few years of its isolation, researchers had largely explored the fundamental science of graphene. “Essentially, graphene was done and dusted by 2007,” says Geim, who co-authored a review that year. “I wanted to call it ‘Graphene is dead,’ but I was not allowed,” he recalls with a wry smile.

Hand-peeled microscopic flakes of graphene were perfect for laboratory studies, but hardly suitable for commercial products. The "black gold" rush really accelerated after 2009, when researchers in Texas found that a common industrial process called chemical vapor deposition (CVD) could be used to grow strong yet flexible graphene monolayers on copper foil. The copper acts as a catalyst, liberating carbon atoms from a feedstock of methane at about 1000°C to build up the graphene.

Companies quickly scaled up this production method. In 2013, for example, Bluestone Global Tech in New York state claimed it could make at least 20 square meters of CVD graphene per day, and announced it would open a new production plant at the University of Manchester. Bluestone and other companies promised that graphene's conductivity, flexibility, and transparency would make it an ideal material for the touchscreens of electronic devices, for example.

A roller coaster ride

Graphene's discovery 20 years ago led to a wave of hype that saw billions of dollars in R&D funding go to universities and startups attempting to commercialize the atom-thin layers of carbon. More recently, markets for the so-called wonder material seem to be growing, not just for graphene monolayers, but also for graphene oxides (GOs) and graphene nanoplatelets (GNPs).



GRAPHIC: A. FISHER/*SCIENCE*

In the same year, the European Union launched the Graphene Flagship, a 10-year, €1.4 billion research program to put the bloc at the forefront of graphene commercialization.

The United Kingdom doubled down on graphene when it opened the £61 million NGI in 2015. The institute was such a source of national pride that when Chinese President Xi Jinping visited the U.K. that year, his itinerary included a tour of NGI, hosted by Geim, Novoselov, and other dignitaries. A photograph of Xi's visit still hangs in the exact spot where the image was snapped, right outside the facility's enormous clean room. Windows allow passersby on the street to peer inside at scientists clad in bunny suits operating multimillion-dollar instruments.

As graphene reached peak hoopla, it also hit some snags. CVD graphene is actually a jigsaw of graphene monolayer crystals, and companies soon found that the seams in between dramatically affect the material's properties, usually for the worse. "I think they all expected they were going to get the same performance as the tiny little Scotch tape flakes of graphene that people published in research articles," Conway says. It's also notoriously difficult to displace incumbent materials in multibillion-dollar industries. (Spoiler alert: Most touchscreens are still made from that reliable workhorse, indium tin oxide.)

And growing graphene is only the first step—getting it off the copper foil and into a device can be a huge headache. One common method uses a polymer film to transfer it, but this can cause tears and wrinkles, and it leaves residues that act like kryptonite on graphene's superpowers. In those early days, the quality of CVD graphene varied wildly from batch to batch, making it impossible to get consistent results.

Bøggild says surprisingly few of the reported procedures for handling, transferring, and applying CVD graphene can be reliably repeated. He attributes this "reproducibility gap" to the lack of detail about these procedures in many academic papers, and is now working with a consortium of researchers, companies, funders, and publishers to develop more rigorous standards for verifying such results.

The challenges posed by graphene built up atom by atom by CVD prompted some researchers to take a top-down approach, starting with bulk graphite. One method, known as liquid exfoliation, involves shredding it into tiny pieces. (A kitchen blender will do.) Another uses strong oxidants to chew graphite into thinner fragments.

But this graphene is very different from Geim's gossamer flakes. It often contains multiple graphene layers stuck together, a form known as graphene nanoplatelets (GNPs). Other forms, called graphene oxides (GOs), are peppered with oxygen atoms introduced by the chemicals used to break down graphite. Further chemical treatment to remove the oxygen atoms produces reduced graphene oxides (rGOs), which are similar to graphene but have more defects in their hexagonal structure. "All these things are basically different materials," Bøggild says. As graphene layers stack up, their superpowers decline—and some properties of 10-layer stacks become indistinguishable from those of graphite.

Yet these materials are still useful. Whereas CVD-grown graphene is prized as an electrical conductor, GNPs can lend strength to other materials, and GO films can draw heat from sensitive electronics (see graphic, p. 142). The challenge is to find the best kind of graphene for a particular application.

THE UNIVERSITY OF MANCHESTER'S answer to that question lies a short walk from NGI: the £60 million Graphene Engineering Innovation Centre (GEIC), an industrial incubator that opened in 2018. Its stern grayscale décor and large pilot-scale production hall, complete with overhead crane to move heavy equipment around, signal that this place means business. Sitting at a heavy boardroom table in a meeting room with a glossy, corporate sheen, James Baker—CEO of Graphene@Manchester, which oversees the university's business-related graphene activities—explains how GEIC works.

Companies pay GEIC to rent laboratory space and work with the center's in-house experts. "Our business model is quite simple: You pay to come here, and if you succeed in exploiting the project developed at the GEIC, we take a royalty based on net sales," Baker says. That income is reinvested in the facility, and further research. Sixty startups have worked at NGI and GEIC over the past decade, and GEIC currently hosts roughly 230 people from about 30 partner companies.

Canadian company HydroGraph Clean Power opened a lab here in January, in part to develop applications for GNPs that it makes by exploding acetylene and oxygen in a steel chamber. Chief Science Officer Ranjith Divigalpitiya says the United States has been relatively slow to commercialize graphene applications, compared with Europe and Asia. "The biggest challenge is connecting the technology with the customer," he says. "And that's where the GEIC comes in, because they have a lot of credibility, and better connectivity to customers. I think it has just opened so many doors for us."

GEIC also helps companies reliably produce graphene and blend it with other substances, giving them tools and expertise to precisely characterize their materials. "What industry really wants is reproducibility and confidence in the data," Baker says. "Getting that consistency is key."

That's a big improvement on the Wild West environment of the early graphene market, when companies often sold "graphene" without being clear about the material's true identity. In 2017, the International Organization for Standardization decided the word graphene should only refer to monolayers, whereas "few-layer graphene" could contain three to 10 layers. The thinnest GNPs overlap with this second category, although many GNPs are thicker and contain dozens of layers. But many companies did not take the hint. In 2018, a survey of 60 companies found a large variation in the size of flakes and number of layers in materials sold simply as "graphene," which was holding back the development of applications.

Graphene's split personality also sowed confusion. Baker says some of the companies working at GEIC initially expected to get monolayer properties from GNPs, only to be disappointed when they were not 200 times stronger than steel (see sidebar, p. 143). Even today, it's all too common for companies or researchers working with GNPs to proclaim the amazing properties of monolayer graphene in their papers or websites. "That bugs me, it's overselling," Bøggild says. "I think it's bad because it's taken seriously by people who don't understand it."


Slurries of graphene and polymer binders could help boost the performance of batteries (top). The Graphene Engineering Innovation Centre hosts industrial partners commercializing graphene products (bottom).

PHOTOS: (TOP TO BOTTOM) MATTHEW LLOYD/BLOOMBERG/GETTY IMAGES; WILL PRYCE

Despite these tribulations, some of these graphene-ish materials are showing promise. For example, Spain's INBRAIN Neuroelectronics makes biocompatible rGO electrode arrays to measure brain activity, which could help clinicians distinguish healthy and diseased tissue when removing a tumor, for example. The rGO films have tiny pores and a high conductivity, which makes them very responsive to tiny electrical changes. That means these flexible implants, thinner than a human hair, can be smaller than conventional devices and offer a much sharper map of neural activity, says company co-founder Jose Garrido of the Catalan Institute of Nanoscience and Nanotechnology. INBRAIN is now running a clinical trial of the device in Manchester, with the first patient receiving an implant in late September.

The company has also won "breakthrough device" designation from the U.S. Food & Drug Administration for similar rGO electrode arrays that can stimulate the brain as well as recording it, to alleviate symptoms of Parkinson's disease. Garrido hopes the designation will speed the device into clinical trials in the next 4 years.

One of the biggest producers of GOs and rGOs is the China-based Sixth Element (Changzhou) Materials Technology Co., which has a capacity of about 1000 tons per year. In 2019, electronics company Huawei started to use Sixth Element's GO to draw heat from the circuits in its smartphones, enabling them to be thinner. Other brands followed suit, and Bernhard Münzing, the company's European sales director, estimates that its GO is now inside millions of electronic devices. "I think it's the largest application [of a graphene material] you can find on the market at the moment," he says.

Other bulk applications are on the rise. Canada's GIT Coatings uses GNPs to make a tough coating that keeps barnacles and other residue off ship hulls. It avoids some of the toxic compounds in conventional coatings and reduces friction to save on fuel. Finnish shipping company Finnlines started using the hull coating in 2022, and several other ship operators have joined in since then.

One early GEIC project with the automaker Ford led to an injection-molded foam engine component that included GNPs to improve heat protection. The GNPs also act as nucleating agents to create little air bubbles in the foam that reduce engine noise. "That's already gone into production in over 5 million vehicles in the U.S.," says John Whittaker, engineering director at GEIC. Another product, which an undisclosed GEIC partner company is due to launch soon, blends an elastic polymer with 0.1% GNPs to produce a strong, lightweight, and stretchy material suitable for personal protective equipment.

Meanwhile, some startups are exploiting graphene's inert and impermeable honeycomb in anticorrosion coatings and air-tight packaging. Others are puncturing their graphene, or stacking flakes to leave gaps between layers, to create porous membranes for separating gases or desalinating seawater.

There are also high hopes that mixing graphene materials into concrete could reduce the amount of cement needed to make it. Cement production accounts for up to 8% of global carbon dioxide emissions. "I think the largest market, long term, will be the concrete market," Münzing says. For example, GEIC partner company Concretene can reduce cement content by 30% with a mixture that includes just 0.1% GNPs and GO nanoplatelets. "It allows us to take cement out of the concrete without any impact on strength," says Craig Dawson, Concretene's chief scientific officer. Three trial construction projects already used the additive, and the company hopes precast concrete parts with it will be commercially available next year. "We believe we are the first to do this, and we are well ahead of the game," Dawson says.

INBRAIN Neuroelectronics's implants contain reduced graphene oxides (top). Graphenea uses monolayer graphene in its field effect transistors (bottom).

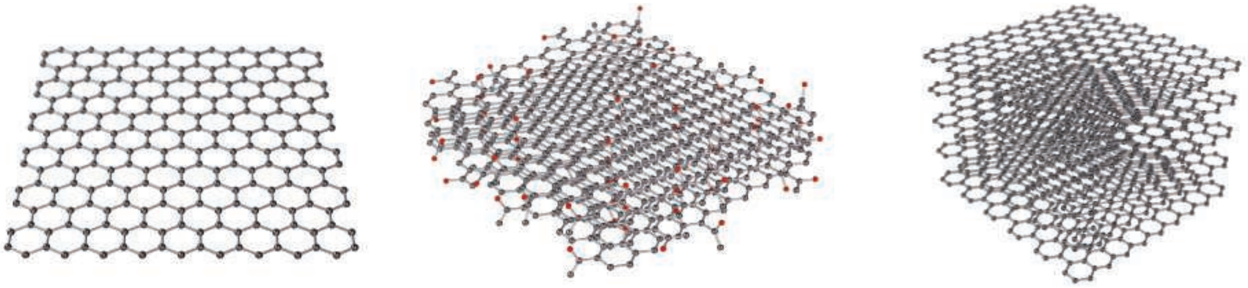
IDTECHEX ESTIMATES the market for all types of graphene is currently worth about \$150 million per year, mostly from bulk graphene applications, and could rise to \$1.6 billion by 2034. But the company reckons monolayer graphene is poised to grow its share of that market, because some companies are finally overcoming the problems of transferring CVD-grown graphene.

Spain's Graphenea, for example, can now use polymer films to transfer CVD graphene from its copper foil to 200-millimeter-diameter wafers of silicon or other substrates, large enough to use in full-scale semiconductor fabrication lines. "I think transfer is not the main bottleneck anymore," says Graphenea's Chief Scientific Officer Amaia Zurutuza. Engineers are also learning exactly how good CVD graphene needs to be for specific applications.

Graphene biosensors, for instance, are often based on field effect transistors (FETs), which can sense tiny changes in electric fields. In a typical FET biosensor, the graphene is decorated with receptor molecules that bind to a target biomolecule, and this

How graphene stacks up

Graphene products may incorporate monolayers, but they might also use graphene oxides or graphene nanoplatelets, which have radically different properties.



	Monolayer graphene	Graphene oxides	Graphene nanoplatelets
Layers	1	1–10	5–10 (or more)
Applications	Magnetic/biochemical sensors; electronics; photonics	Heat management; water treatment; filtration membranes; composites	Strong clothing, composites, and concrete; anticorrosion coatings
Production	Scotch tape; chemical vapor deposition	Chemical oxidation of graphite; controlled gas combustion	Mechanical or chemical breakdown of graphite; controlled gas combustion
Electrical conductivity	High (2x copper)	Low—effectively an insulator	Good, depends on number of layers
Other properties	High thermal conductivity (10x copper); high strength (>100x atom-thin steel)	Mixes well with water; easy to chemically modify	High strength and toughness

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interaction changes the electrical current flowing through the graphene. For this application, the graphene's electron mobility needs to be impressive—but nowhere near as high as that of a Scotch taped flake.

INBRAIN is working on graphene FETs that would be even more sensitive than its rGO electrode arrays, capable of detecting the electric activity of individual neurons firing inside the brain. Experiments in mice show that, unlike electrode arrays, the graphene FETs can record low frequency changes in electrical activity that are related to epilepsy.

Garrido says these developments would not have been possible without the long-term investment provided by the EU's Graphene Flagship program, not least because the company needed to spend years testing and optimizing hundreds of the devices in animal models. "This continuity in the funding has been key for us, definitely," Garrido says. "I think that's why Europe, at least from the point of view of graphene medical devices, has done so much more compared to the U.S."

Monolayer graphene is also being deployed in optoelectronic devices, which rapidly convert light into electrical current and vice versa. Germany's Black Semiconductor, a Graphene Flagship partner, is adding graphene to silicon microchips to speed up optical communication between chips. Ultimately that means faster data processing, and in June the company secured more than €250 million in public and private funding to develop its devices.

But CVD growth and transfer will likely need to improve further before major chipmakers adopt the material. "For the semiconductor industry, you really need to go to the next level," says Inge Asselberghs, director of the Graphene Flagship's €20 million 2D Experimental Pilot Line. The project is teaming with Graphenea and other partners to transfer high-quality CVD graphene using rigid glass substrates. That causes less damage than flexible polymers, although researchers still inspect the material under a microscope to weed out any bad bits.

Meanwhile, Bøggild co-founded a Danish Graphene Flagship spinoff called 2D that is taking a different approach to the transfer problem. His research team realized it could cleanly transfer monolayer graphene from copper foil to a polymer sheet using nothing more than an office laminator. This polymer can then be applied to another surface, and peeled off to leave the graphene behind, with less contamination than other methods. 2D has now commercialized that method in a roll-to-roll process that produces meter-long stretches of polymer-backed single-layer graphene.

Strong stuff

Press releases rarely miss an opportunity to trumpet graphene's strength. But where does the claim that it is "200 times stronger than steel" come from? Back in 2008, a team led by James Hone at Columbia University came up with a clever way to measure graphene's strength. Researchers draped monolayer graphene flakes extracted with Scotch tape over tiny holes in silicon, and then pressed down with the tip of an atomic force microscope until the graphene ruptured.

This was the first time anyone had directly measured the "intrinsic strength" of a material—the strength that comes from a flawless array of chemical bonds, unmarred by defects or cracks. The measurement took advantage of graphene's atomic perfection. But what did the strength of a 2D sheet mean for a 3D object made of graphene? "In any bulk material, the actual practical breaking strength is much lower than the intrinsic strength," Hone says.

To get an idea, the researchers imagined stacking billions of these perfect graphene sheets together to make a beam 1 meter high, and multiplied their intrinsic strength of 42 newtons per meter accordingly to give a 3D answer of roughly 130 gigapascals. That's more than 200 times as strong as structural steel.

Hone acknowledges that creating this theoretical block of graphite from perfectly aligned graphene sheets would be impossible. "It's really just a way to compare what we see in this two-dimensional world to the three-dimensional world," he says. *–M.P.*

ONE U.K. COMPANY has found a way to circumvent the transfer step entirely. Paragraf instead uses a semiconductor manufacturing method called metal-organic chemical vapor deposition (MOCVD) to grow graphene directly where it's needed on devices. "That's what sets us apart," Conway says. "We can grow directly on the substrates. That makes a huge difference, because you just get much better reproducibility."

The company claims it is the first to use standard semiconductor processes to mass-produce graphene-based electronic devices, including magnetic sensors and biosensor FETs, and is producing thousands of devices per year for customers. Its magnetic sensor exploits graphene's high sensitivity to the Hall effect, "so you can measure very small magnetic fields much more accurately," Conway says. Automakers are now testing the sensors to monitor the health of electric vehicle batteries.

Over the next decade, Paragraf plans to use MOCVD to deposit other 2D materials, such as molybdenum disulfide, into devices alongside graphene. Creating stacks of different 2D materials is now a major basic research frontier because each material can bring specific properties and modify those of its neighbors, allowing researchers to fine-tune how the whole stack behaves. For example, sandwiching graphene between two layers of an insulating 2D material called hexagonal boron nitride can help preserve graphene's superlative electronic properties within devices.

Solid state physicist Roman Gorbachev is already building these kinds of graphene club sandwiches at NGI, using a homemade production line. It consists of a 5-meter-long gleaming steel pipe, bristling with joints, side arms, and analytical instruments, that encloses an ultraclean, high-vacuum environment. Inside one part of the system, a robot assembles stacks of 2D materials; a small train then ferries these stacks into other chambers where they are connected to electrical contacts and studied. "Building this machine absorbed roughly 5 years of my life," Gorbachev says. "At the moment, this is one of a kind."

Recently, Gorbachev has used his machine to study how twisting the sandwich layers can dramatically alter their electronic properties. Other researchers in the burgeoning field of "twistronics" have found that in two-layer graphene, twisting one layer by 1.1° transforms the material into a superconductor, for example.

Gorbachev says his modest assembly line is an important step along the long road to commercializing the 2D layered structures. "If we're talking about these really high-end applications, we will need more time," he says. "But they are happening, they are coming."

Geim agrees that this wider world of 2D materials might eventually have a greater impact in electronic devices than graphene itself. "In terms of applications, I would spread my bets on many different materials," he says. "But graphene was certainly an adventure, and I didn't expect that it would last 20 years, for sure." ■

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