NEWS FEATURE

News Feature: Beyond graphene

Fueled by the surge of interest in graphene, scientists are racing to understand other exotic 2D materials; the payoff would be some impressive applications.

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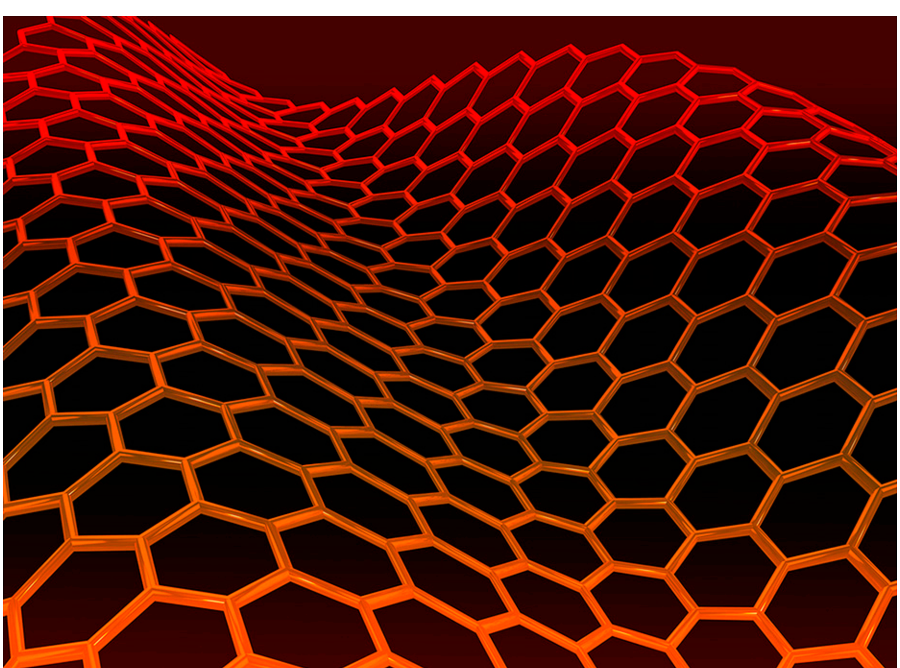
These are the halcyon days of research on graphene, a much heralded superstrong material. Since atom-thin sheets of carbon were first isolated in 2004, thousands of researchers have leapt at the chance to get to know this exotic material better and figure out what to do with it. Not only is graphene robust and relatively easy to prepare in the laboratory, it also boasts an astonishing portfolio of useful properties. Electrons can zip through graphene many times faster than they do through silicon. Graphene is stronger than steel, and can absorb light at any wavelength. Last year, researchers published nearly 18,000 papers on graphene, according to the Thomson Reuters Web of Science database. Although graphene transistors are still in the experimental stage, the material is already starting to appear in commercial applications, from strengthening carbon composite materials to enhancing touchscreens in smartphones.

But graphene's potential has also inspired a scramble for the next breakthrough. Researchers are searching for other materials that can form atomic sheets with extraordinary properties, and the catalog grows every year. Boron nitride, for example, forms a flat hexagonal pattern of atoms very close to graphene's honeycomb structure. Silicon and germanium atoms can be assembled into similar sheets—silicene and germanene—that are more like a buckled honeycomb. And researchers have identified more than 40 transition metal dichalcogenides, such as molybdenum disulphide, that form monolayers. Right now, it's anyone's game, as researchers seek to push the field in new directions that elicit the kind of excitement that greeted graphene.



Following on the success of graphene, various 2D materials are vying to be the next breakthrough. But substantial technical challenges remain. Image courtesy of Shutterstock/Shilova Ekaterina.

Signs of Weakness

This quest to expand the library of 2D materials is partly motivated by graphene's Achilles' heel. It lacks a natural bandgap—the energy hurdle in semiconductors that electrons must overcome before they can flow as a current—which means that it cannot switch between conducting and nonconducting states. This is an essential quality for the transistors at the heart of every electronic gadget, and the main reason why graphene will probably need some help in many applications.

Many researchers hope that by combining different 2D materials in stacks—like a well-filled club sandwich—they will be able to fine-tune the materials' properties, making them useful in transistors, sensors, and a wide range of other electronics applications. That in turn could usher in a new age of faster, cheaper, and more ubiquitous electronics.

"We dream of the day when you go to Starbucks and you get a cup of coffee, and there are electronics in the coffee mug," says Tomas Palacios, who leads the Massachusetts Institute of Technology–Microsystems Technology Laboratories Center for Graphene Devices and 2D Systems in Cambridge, Massachusetts. Such electronics might track temperature, the fill level, or even coffee shop rewards points. As you drink your coffee, you look outside your office, Palacios imagines, through a window outfitted with invisible electronics that moderate the amount of incoming sunlight.

But many hurdles remain that could keep these materials from reaching their potential, cautions Jari Kinaret, director of the Graphene Flagship, the European Union's billion-Euro research effort that aims to shepherd 2D

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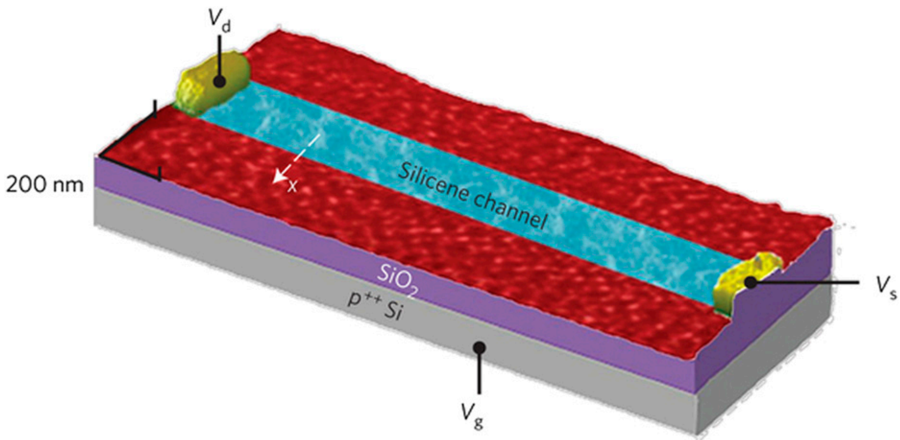

This rendering shows the electrodes (yellow) at either end of a silicene channel (in blue). The silicene was grown on a mica substrate (in gray) and capped with alumina to prevent degradation. Reproduced from ref. 6, with permission from Macmillan Publishers Ltd, *Nature Nanotechnology*.

materials from the laboratory into commercial applications. "Many of the materials beyond graphene are much trickier to deal with than graphene," he says.

Kinaret notes that most of the work done on atomic sheets, other than graphene, has been conducted on the scale of a laboratory. Scaling up production methods to be able to make enough to use in electronic devices could be an insurmountable challenge. He also cautions that because many of these materials are unstable—especially the ones made from transition metals—they quickly bond to the surface on which they're grown and become difficult to separate. "You may say that you're studying some material, but actually you don't have good tools to measure it, so you don't have a perfect grasp of what the material is," he says.

A Growing Family

The rush to understand atomic sheets began in 2004 (1), when physicists Andre Geim and Konstantin Novoselov at the University of Manchester, United Kingdom, announced that they had isolated graphene by using an astonishingly low-tech method. The physicists used sticky cellophane tape to peel away superthin layers of carbon from a graphite pencil, and kept on peeling at the flakes until they were left with an atomic monolayer. The following year, the two showed that by simply rubbing the surface of various crystalline compounds they could scratch off monolayer flakes of boron nitride, molybdenum disulphide, and several other materials (2).

The physicists found that molybdenum disulphide monolayers have a sizeable bandgap, and hexagonal boron nitride is an insulator. In February 2015, a team of physicists led by Novoselov showed that monolayers of these two materials could be sandwiched between layers of graphene to create a light-emitting diode (3). In the device, an applied voltage across the graphene layers frees electrons to leave behind positively charged "holes." The electrons and holes tunnel through the hexagonal boron nitride and combine in the transition metal dichalcogenide, emitting red light. In laboratory experiments, the LED monolayer sandwich was almost as energy-efficient as conventional LEDs. Unlike conventional LEDs, however, those built from 2D dimensional materials are transparent and flexible, and other researchers suggest they may emit electromagnetic waves in the wavelength ranges used by telecommunications devices. Molybdenum disulphide's bandgap also makes it useful for molecular-scale measurements, including as a gas sensor (4).

Other researchers think that silicene might prove to be a better fit for the microelectronics industry. Not only has silicon been the mainstay of computer chips for more than 50 years, but also silicene itself can be made with a suitable bandgap, and its electrons may also flow at high speeds. Several research groups isolated silicene in 2012, including physicist Guy Le Lay at the Aix-Marseille University in France (5), whose team created the material by condensing hot silicon atoms onto a silver crystal in a vacuum chamber.

But silicene is tricky to work with. "Once you remove it from the vacuum chamber, it degrades in a matter of minutes," says nanomaterials researcher Deji Akinwande at the University of Texas, Austin. Like Kinaret, Akinwande cautions that silicene tends to stick to the underlying substrate, making it difficult to transfer into a device. Indeed, researchers at Argonne National Laboratory in Illinois last year questioned previous silicene research, claiming that the material being studied was actually a combination of silicene and its silver substrate, in which case the experiments revealed little about the behavior of isolated silicene.

Researchers are already finding ways to deal with these problems. In February 2015, for example, Akinwande and Alessandro Molle at the Institute for Microelectronics and Microsystems in Agrate Brianza, Italy, unveiled the first silicene transistor (6). They relied on techniques that effectively circumvented silicene's tendency to fall apart.

After creating their silicene layer on silver, the researchers protected it with a thin coating of alumina. This process allowed them to move the silicene sheet, still sandwiched between silver and alumina, to an insulating silicon substrate. Then they etched away some of the silver to create a transistor that worked for a couple of minutes. "We have hope because we've seen the first silicene transistor," says Le Lay, who is applying the method in his own laboratory. Akinwande and Le Lay are collaborating to try the same trick with germanene, which Le Lay's team first isolated last year (7).

In August, a group led by physicists from China's Shanghai Jiao Tong University reported the first successful growth of stanene, a single layer of tin atoms (8). Stanene is predicted to have a large bandgap, like other materials, and may let electrons flow without resistance, but the paper on the material's first synthesis did not confirm those behaviors. Researchers at the Stanford Linear Accelerator Center National Accelerator Laboratory in Menlo Park, California, suggest the material could be used to make topological insulators, which allow electrons to travel freely on their surface but not in the interior (9). Right now, topological insulators are still more interesting from a pure science standpoint because they can shed light on quantum electronic behaviors, but proposed applications for these materials range from quantum computing to new ways to store information.

And in November 2014, a team of researchers in China, led by Xian Hui Chen and Yuanbo Zhang at Fudan University, created a transistor using black phosopherene, a few-layers-thick sheet of phosophorous atoms arranged in a puckered honeycomb shape (10). Akinwande's group is also working on protecting black phosphorene by coating it with Teflon (11).

This catalog of atomic sheets is still growing quickly. "These materials have such large potential, and it is clear that something very interesting is coming out," says Kinaret. But Kinaret cautions that it is difficult to pinpoint which materials or combinations will lead to marketable devices.

The literature is already rife with proposed applications that extend into almost every field related to energy, heat, or electricity. Some researchers propose that 2D materials could bolster the efficiency of solar cells when used as photosensitizers or charge transporters. As good heat conductors, atomic sheets might make efficient thermoelectric devices. And because they can quickly shuttle charge, they might show up in high-performance batteries and conductors. Some researchers have proposed novel ways to use these materials to sequence DNA (12) or detect genetic translocations (13).

But it is in microelectronics where 2D materials could eventually have the biggest impact, by offering an alternative to the ubiquitous silicon chip.

Ubiquitous Electronics

In 1965, when integrated circuits had been around only a few years, semiconductor researcher Gordon Moore made a simple but prescient forecast about how much computer power could be crammed onto a single computer chip. The number of transistors on an integrated circuit would double every year, he predicted; he later amended the prediction to say the number would double every two years. That idea became known as "Moore's Law." Moore, who went on to found chipmaker Intel, later admitted that he expected the trend to continue for only a decade. Instead, it has held true for five decades thus far.

Now it faces huge challenges. As chips grow smaller, the transistors are packed so closely together they risk overheating, and smaller transistors are increasingly expensive to manufacture. Experts say that it is simply not tenable to make ever-smaller silicon chips.

That is where 2D materials might save the day. "The new physics of these materials can lead us beyond Moore's Law," says Akinwande. More transistors lead to more processing power, and transistors made from 2D materials—even if they are stacked—will take up less space and require less energy than conventional silicon.

According to Palacios, 2D materials could help to produce electronic devices that are so small—and so cheap—that they are embedded in everything from clothing and wallpaper to glass and paper. He imagines a "wired world," where every object is connected to the Internet. In this "Internet of Things" everyday objects would have the ability to communicate with everything else. Imbued with machine intelligence, countless devices and even entire buildings could become more energy-efficient, and precisely tuned to the tastes and preferences of users. "We want ubiquitous electronics," says Palacios.

> **"The new physics of these materials can lead us beyond Moore's Law."**
> **–Deji Akinwande**

Such a future requires high-performing materials with low energy demands. Future devices must be smaller, faster, and cheaper than anything around today. They'll also need to be durable, flexible, maybe rollable, environmentally friendly, and recyclable. Such a vision seems a far cry from the rigid tablets and smart phones that dominate the market.

Right now, though, high-volume and cost-effective manufacturing of stable forms of these materials remains a daunting challenge. Processes that make atomic sheets on a large scale typically introduce defects into the material that can, for example, cripple their electronic properties; physicists do not yet understand exactly how to mitigate these effects. "One challenge is to produce a perfectly crystalline, very large area sheet of one- or two-layer material," says Palacios. "There's been a lot of recent work on using chemical vapor deposition for that process, but scaling is still a big issue."

Still, graphene's rapid rise offers hope for its flat cousins. Kinaret notes that graphene's trajectory from isolation to market has been unusually quick. For comparison, he says, carbon fibers developed in the 1960s took about 15 years to get to high-end products. Plastics, first developed in the mid-19th century, didn't become mainstream until the 1930s and 1940s.

For now, graphene remains the front-runner of all of the atomic sheets, thanks to its robust research history and its tendency to remain stable at room temperature. And it keeps delivering surprises: in February 2015, researchers showed how graphene nanoribbons can be fashioned to let electrons move more efficiently than previous studies have predicted (14). In June, physicists in the United States and South Korea reported "the world's thinnest light bulb," using light-emitting graphene as an ultrathin filament (15). And in September, an international team of researchers reported that, at low temperatures, the material becomes a superconductor when coated with lithium (16).

And although most people want to know how 2D materials can be used to make better gizmos, physicists are increasingly interested in how these atomic sheets can be used to uncover new physics. Paring a material down to such thinness gives rise to bizarre quantum electronic properties. For example, 2D materials are believed to be able to shuttle electrons so quickly because the electrons behave as though they have no mass. Researchers are also investigating 2D materials for their use in spintronics, a concept that would see data represented by the spins of electrons, rather than the flow of charge.

Even though graphene was the first 2D material to make a splash, Palacios says he's thrilled that it won't be the only player in the field. "Graphene was first, but it doesn't have to be the most successful. Two-dimensional materials are no longer about graphene, they're about a completely new family of materials with truly unique properties," he says. "We have a wide variety to play with."

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