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NOBEL PRIZE

Wonder material

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The Nobel Prize in Physics is awarded "for groundbreaking experiments regarding the two-dimensional material graphene".

ANDRE GEIM AND Konstantin Novoselov, who shared the Prize.

Imagine a piece of paper but a million times thinner. This is how thick graphene is. Imagine a material stronger than diamond. This is how strong graphene is. Imagine a material more conducting than copper. This is how conductive graphene is. Imagine a machine that can test the same physics that scientists test in, say, CERN, but small enough to stand on top of your table. Graphene allows this to happen...

– Andre Geim, one of the two winners of the Nobel Prize in Physics 2010, in an interview in November 2006.

GRAPHENE is a form of ordinary carbon but an extremely thin flake of it, just one atom thick. This year's Nobel Prize in Physics has been awarded to 52-year-old Andre Geim and 36-year-old

Konstantin Novoselov, both of the University of Manchester, United Kingdom, for isolating, identifying and characterising this single atomic layer of carbon, a strictly two-dimensional (2D) plane unlike any material forms that one is familiar with – and what had been hitherto considered impossible.

This Russia-born mentor-student combine showed that this monatomic layer of carbon has exceptional properties that originate from the strange world of quantum physics. The Nobel award is “for groundbreaking experiments regarding the two-dimensional material graphene”.

As a material, graphene is completely new, perhaps the thinnest material in the universe. Little wonder, therefore, that the article in the journal Science in October 2004 by Geim, Novoselov and their collaborators from the Institute of Microelectronics Technology, Chernogolovka, Russia, where Geim was a postdoctoral fellow, created a storm in the physics community. For a long time, it was one of the most cited papers in physics. Theoretical studies on it, as a model 2D system, have, however, been carried out for over six decades.

Apart from what Geim listed in the quotation above, as a conductor of heat, graphene outperforms all other known materials. It is also completely transparent, absorbing only 2.3 per cent of the light incident on it. Yet, it is so dense that even helium, the smallest gas atom, cannot pass through it. On the one hand, such exotic properties have rendered graphene a novel platform for physicists to test the theoretical foundations of physics. On the other, a host of applications of graphene now seem possible, including the creation of new strong materials and the manufacture of faster and more superior electronic devices that have the potential of replacing silicon, which is reaching its limits in capacity and speed.

Carbon can exist in several different forms. The most common form of carbon is graphite, the “lead” in the common writing pencil, a kind of pure carbon formed from stacked sheets of carbon atoms. Graphene is the name given to one such sheet. Thus, graphene is nothing but a single plane of carbon atoms. In recent years other molecular forms of graphite have been discovered and investigated by scientists. In 1985, a soccer-ball-shaped molecule (C60 is the simplest one and has 60 carbon atoms) called the “buckyball” was discovered by Robert Curl, Richard Smalley and Harry Kroto. In 1991, Sumio Iijima identified the honeycombed, cylindrical assemblies of carbon called carbon nanotubes. Both these forms are called “fullerenes”.

Graphite, fullerenes and graphene all have carbon atoms arranged in the same structural form. The basic unit of this structure is six carbon atoms, tightly bound together chemically in the shape of a regular hexagon, the well-known benzene ring, with a C-C distance of 0.142 nanometre (nm). At the next level is graphene, a honeycomb network of these hexagonal structures bound together resembling a chicken wire mesh. The other forms of graphite are built up out of graphene. Fullerenes and other nanotubular structures can all be thought of as graphene sheets wrapped up. Carbon nanotubes are essentially graphene sheets rolled into minute cylinders. A graphite block is a 3D stack of graphene sheets with an interplanar spacing of 0.335 nm. This means a one-millimetre-thick graphite block will have three million layers of graphene. As Geim puts it, graphene is the mother of all graphitic forms (see figure).

It is important to emphasise that even materials that are usually referred to as 1D or 2D are never one-dimensional or two-dimensional. A nanotube is often referred to as one-dimensional but is actually a thin and long cylinder, a 3D object. In the case of semiconductors in electronic devices, the thickness typically extends from 10 to 100 atomic layers, and the system is considered 2D only because electron dynamics in the short direction is largely irrelevant. Here, one is talking of a strictly 2D structure: a single plane of atoms.

In some sense, graphene has always been around; only scientists had failed to detect it. Like mica, graphite is a highly layered material and splits into planes very easily. In more technical terms, it is because graphene sheets are held together by the weak attractive (intermolecular) force called van der Waals force, which drops in strength as the seventh power of the distance between the molecules. During a simple trace of a pencil, which is nothing but graphite, on paper, thick graphite flakes are cleaved from the graphite crystal. But, thinner, very nearly transparent crystallites, some perhaps even a single-layer thick (graphene), are also present in every pencil mark. The difficult part is in finding it in the haystack of thicker flakes.

Before Geim and Novoselov, scientists had tried to make graphene for over four decades, but all their attempts failed. The most popular earlier approach was the method of “chemical exfoliation”, that is, intercalating various molecules between atomic planes of graphite to weaken the interplanar bonding and wedge the planes apart. Although graphene layers did probably separate from the graphite, they could not be identified. Instead, the final product was a mix of graphite particles, more like soot. A more direct, brute force, approach was then tried. The graphite crystal was split into progressively thinner wafers by scraping or rubbing against another surface. This method, known as micromechanical cleavage, did surprisingly well despite its crudeness. Scientists succeeded in peeling off graphite films with fewer than 100 atomic layers. By 1990, German physicists at Aachen University had isolated graphite films thin enough to be optically transparent, but not graphene.

A decade later, Philip Kim of Columbia University and his graduate student Yuanbo Zhang refined this micromechanical cleavage method by scratching across a silicon wafer with a graphite microcrystal attached to the arm of an atomic force microscope. But this resulted only in thin slices of graphite, not graphene, being deposited on the wafer. In fact, these failed attempts to create stable sheets of graphene strengthened the belief that such a 2D material could not exist in nature. More than seven decades ago, Lev Landau and Rudolf Peierls argued that strictly 2D crystals were thermodynamically unstable and could not exist. Thermal fluctuations, they said, would cause them to morph into various 3D structures. It was, therefore, a complete surprise when Geim and Novoselov and collaborators succeeded in achieving this. They, in a sense, fooled nature by starting with a 3D material and then peeling a single layer from it. Lego doctrine

The success of Geim and Novoselov, who have been working together for a long time, owes a great deal to their unusual style of research. Geim's research strategy is what he calls the “Lego doctrine”. “You have all these different [Lego] pieces and you have to build something strictly based on the pieces you have got. In research, some of the Lego pieces are facilities, some are random knowledge, and we try to build up something new from that.”

Geim also has a tendency to take up quirky but significant research topics. He made headlines in 1997 by levitating a live frog using a magnetic field to demonstrate the diamagnetic effect. This fetched him the Ig Nobel Prize in 2000. (The Ig Nobel Prizes are given each year in early October for 10 achievements that “first make people laugh, and then make them think”. Geim is the only scientist to win both prizes.) In 2007, his team developed a microfabricated adhesive that mimics a gecko's sticky foot pads, which help it scale walls.

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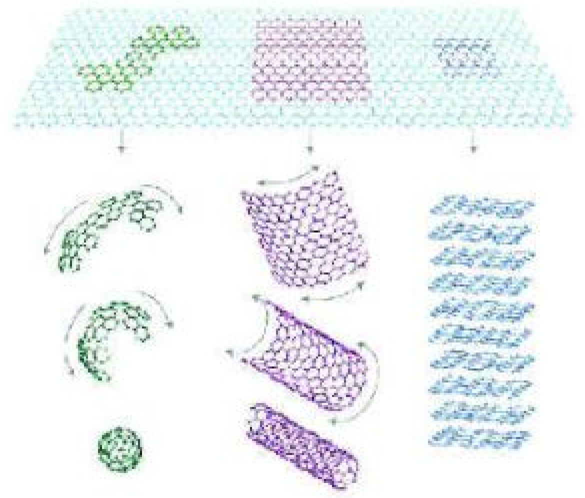

C60 fullerene molecules, carbon nanotubes, and graphite can all be thought of as being formed from graphene sheets, i.e., single layers of carbon atoms arranged in a honeycomb lattice.

Geim's research strategy led to graphene because his laboratory was well-equipped to study small samples. He also had knowledge from low-dimensional systems that he had worked on in Russia. The third element was what he calls “scientific spite”. Inspired by the nice results that the nanotube community had come out with, in 2002-03 he thought of doing something like carbon nanotubes but from a different perspective – carbon nanotubes unfolded. “That was the initial idea: try to do something similar to carbon nanotubes but by starting with graphite and then polishing the graphite down to a few layers thick or at least whatever we could reach. At that time neither I nor anyone else thought it was possible to reach a single layer, but 10 to 100 layers seemed quite reasonable,” Geim has said.

Initially, Geim had asked his PhD student to make films as thin as possible with a big piece of what is called “highly oriented pyrolitic graphite (HOPG)”, but he only managed to polish the block down to 10-micrometre-thick films (about 100 layers). Geim and Novoselov then got the brilliant idea of using the normal plastic adhesive tape, the Scotch tape. Starting with a thick flake, they stuck the tape to its surface and carefully pulled it to peel a thin graphite layer off.

Repeating this action of “mechanical exfoliation” produced increasingly thinner films, and after 10 to 20 successive peelings, they obtained extremely thin and transparent layers.

The tape with attached optically transparent flakes was dissolved in acetone, and the layers were transferred to a silicon wafer and a standard optical microscope was used to look for the graphene layer. When the silicon wafer is placed under a microscope, one sees a rainbow of colours, similar to what is seen when oil is spilled onto water, and this enables determination of the number of graphene layers in the flake. The colour of very thin layers has a very specific hue owing to the interference of light. When Geim and company carefully examined the many fragments of exfoliation, they found that some were only one atom thick. More significantly, the newly identified bits of graphene were found to have high crystal quality and to be chemically stable even at room temperature.

The “research as fun” element intrinsic to their style of working is what eventually got them there. Geim had introduced in his laboratory the idea of devoting 10 per cent of the time to what were called “Friday evening experiments”, where all kinds of crazy ideas were taken up. “Ninety-nine times out of hundred, you don't succeed, but sometimes there are very simple experiments and very simple discoveries to be made using what is at hand.... Graphene was within this series of very many failures, but this was a successful one,” Geim said in his interview to the Nobel website.

Serendipity also played a significant role in their success. “We had what you could call a stream of coincidences that brought us some very remarkable results very quickly – within a week or so,” Novoselov has said. The two got the idea of using the Scotch tape from their knowledge of the standard technique used for preparing samples for low-temperature scanning tunnelling microscope investigations. The samples are cleaned by peeling the top layer off with the tape. The other critical step, which was also serendipitous, was the method used to identify the monolayer graphene from the other thin layers of graphite in the debris. One can see graphene only on a very special substrate, silicon dioxide. But coincidentally they had exactly that substrate, and of the correct thickness. Even a 5 per cent difference (from the standard 300 nm) can make single-layer graphene completely invisible.

“If not for this simple yet effective way to scan substrates in search of graphene crystallites, they would probably remain undiscovered,” Geim and Novoselov wrote in *Nature Materials*. “I still don't understand how that worked out, but the substrate we had was exactly the one required,” Novoselov has remarked. “This was a huge coincidence – just unbelievable. It was only a few months later that we understood how lucky we had been. If not for that, I'm sure we would be there anyway, but a bit later.”

However, with the “Scotch tape method”, the laureates could only obtain micro flakes of the new material. Despite the miniscule size, they discovered the two most remarkable properties of graphene, which make it not only an exceptional material but give it its electrical properties as well. First, despite the relative crudeness of the tape method, it produced very high-quality graphene, both in terms of purity of the carbon content and the error-free ordering of carbon atoms in the lattice. So far, defects, such as a vacancy at some atomic site on the lattice or a misplaced atom, have not been seen in graphene. According to scientists, this perfect crystalline order arises from the strong, and yet highly flexible, interatomic bonds. These not only make graphene harder than diamond but allows it to bend or stretch by as much as 20 per cent of its original size when force is applied.

In normal electric conductors, electrons bounce off at various points and move like balls in a pinball machine. This scattering happens when electrons encounter imperfections and impurities in the lattice that impede their motion. In graphene, however, Geim's team found that electrons could travel without being scattered off course. Even the pushing of electrons by the surrounding carbon atoms as they vibrate is minimal because the vibrations are relatively small owing to the high strength of the interatomic bonds. This results in the remarkably high conductivity of graphene, which opens up the possibility of ultrafast electronics. The intrinsic mobility of graphene (which is related to conductivity), which governs the speeds the material devices are able to provide in electronics, is 200,000 cm^2 per volt-second at room temperature, as compared to 8,500 cm^2/Vs for gallium arsenide and just 1,500 cm^2/Vs for silicon.

The second remarkable feature is that the current-carrying electrons, besides travelling unhindered through the lattice, behave almost like massless photons. They travel at enormous speeds of about one million metres/s, only about 300 times less than light, as if they had far less mass than the electrons in metals and semiconductors. Because of their quantum nature, electrons are not localised objects; they are spread over space because of their wave-like properties. This leads to interactions among the electrons, and the dynamics of these interacting charged entities is described collectively as a quasiparticle, which acts like the electron but with an effective mass, which can be larger or smaller than that of the electron.

In the case of graphene, since electrons are confined to two dimensions, the wave-like characteristic is heightened and these quasiparticles behave as if they are almost massless. They do not obey the rules of non-relativistic quantum mechanics, described by the Schrodinger equation, but those analogous to relativistic quantum mechanics, described by the Dirac equation. The Dirac equation predicts many paradoxical phenomena that cannot be verified in the laboratory but only in high-energy cosmic phenomena or high-energy particle accelerators. But with graphene, whose charge carriers mimic relativistic quantum mechanics, these phenomena, Geim feels, can be verified in the laboratory.

One such phenomenon is Zitterbewegung, a German phrase meaning jittery motion, a consequence of the fact that particles in the relativistic world are accompanied by their antiparticles, which are identical but for their opposite charge. Dirac's equation predicts the existence of antiparticles as a consequence of which a relativistic particle moving from one point to another will not move in a straight line but will oscillate rapidly. Geim believes that a similar effect should be detectable in graphene, allowing this crucial piece of relativistic quantum mechanics to be tested for the first time. Instead of producing positrons, the charge-carrying fast quasiparticles will generate fast-moving holes – gaps in a sea of mobile electrons in a conductor as if they were real particles with opposite charge – and jitter on the scale of about 100 nm. According to Geim, this should be detectable using a high-resolution microscope. The other spooky effect arising from relativistic quantum theory that has so far been discussed only theoretically is Klein tunnelling, which was formulated by the Swedish physicist Oskar Klein in

1929. In non-relativistic quantum mechanics, particles, because of their wave-like nature, have a finite probability of passing through a barrier that would normally block them.

However, in relativistic quantum theory, a particle will always pass through irrespective of the height of the barrier. This phenomenon is also because of the existence of antiparticles and is related to Zitterbewegung. Geim and associates showed that it should be possible to see this effect by applying an electric field barrier across a strip of graphene and observing the tunnelling quasiparticles. This effect has probably been observed recently by some experiments.

Once the technology to fabricate, identify and attach electrodes to the graphene layers was established, the Manchester group, and other groups as well, quickly made a large number of new experiments, and the field virtually exploded. Though various methods of fabricating graphene have been attempted, the preferred method is still the mechanical exfoliation, or Scotch tape, method. The other method is chemical vapour deposition (CVD), which is carried out by burning methane over copper foil.

“Peeled graphene is still the best way to get clean graphene,” says Mandar Deshmukh of the Tata Institute of Fundamental Research (TIFR), whose group has developed graphene electromechanical resonators to measure thermal expansion coefficients and is currently engaged in making sensitive detectors of mass, charge and stress. “The mobility of electrons in CVD graphene is significantly lower. One expects this to be fixed as more research is done on graphene,” he pointed out. The advantage in CVD is one can get significantly larger area flakes as compared to exfoliation. Recently, researchers in South Korea made 75 centimetres × 75 cm graphene using the CVD technique. Many possible technological applications of graphene are still on the horizon, but a few specialised applications could hit the market in a few years.

As Geim has pointed out, more than a decade of research on carbon nanotubes has given graphene a platform from which to take off. “It is not unreasonable,” he and Philip Kim wrote in *Scientific American* in 2008, “to think that nearly every useful role envisaged for nanotubes is also open to their flat cousin.… Meeting demand for such applications will call for graphene output on an industrial scale.” Although graphene powder is currently made in industrial quantities, production of sheet graphene on an industrial scale has been difficult, and graphene is perhaps the most expensive material now.

Scientists and engineers the world over are trying to exploit the highly desirable physical and electronic properties of graphene. Today, many institutions have grown graphene films on silicon carbide (SiC) wafers similar to the ones common in the semiconductor industry, and graphene transistors have already been demonstrated. Because of its high surface to volume ratio, graphene can be useful in making tough composite materials. Thin films fabricated from overlapping patches of graphene are a promising material for transparent and conducting coatings for touch screens, for liquid crystal displays and solar cells.

Also, plastics could be made into conductors with just 1 per cent of graphene mixed into them. Similarly, mixing just less than 0.1 per cent of graphene can increase the heat resistance of plastics by 30 per cent and at the same time make them mechanically more robust. The perfect structure of graphene also makes it suitable for the production of extremely sensitive sensors that can register even the smallest levels of pollution. Even a single molecule adsorbed onto a graphene surface would be detected.

What graphene holds for us in the future cannot be predicted, least of all by the laureates themselves.