Thin Carbon Is In: Graphene Steals Nanotubes’ Allure

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First, it was buckyballs, molecules of carbon in the shape of soccer balls.

Dr. Andre Geim placed a graphite flake on adhesive tape, repeatedly folded the tape and pulled it apart, and then stuck it to a silicon wafer and rubbed, producing flakes one atom thick.

Dr. Andre Geim
Then came carbon rolled up in nanotubes.

Now, the latest craze in materials science is graphene, a one-atom-thick sheet of carbon that looks like molecular chicken wire.

Graphene is the thinnest of all possible materials in the universe. It shares many of the properties that excited physicists about nanotubes a decade ago, but it is easier to make and manipulate, giving greater hope that it will make the move from laboratory to practical application. Physicists have made transistors out of graphene and used it to explore odd quantum phenomena at room temperatures.

“The hype is bigger,” said Carlo Beenakker, a professor of theoretical physics at Leiden University in the Netherlands, “because the physics is richer.”

It is also one of the few times in history that a roll of sticky tape — the same tape that sits in dispensers on office desks around the world — has played a central role in spurring scientific research. Tape is a surprisingly easy and effective way to split carbon into thin sheets.

A couple of years ago, just a handful of groups was researching anything with graphene. At an American Physical Society meeting last month in Denver, nearly 100 papers about graphene were presented, often to full sessions.

“It’s like discovering a new island” with a host of species to be catalogued and studied, Dr. Beenakker said. In one sense, graphene is not new. A nanotube is just rolled-up graphene. Graphite, the stuff of pencil lead, has long been known to consist of layers of carbon stacked on top of one another like a deck of cards. Pencils produce a black trail, because the friction on the tip rubs off graphite flakes. Beginning in the 1970s, scientists grew graphene flakes in the laboratory.

The laboratory-made flakes were too minuscule to be more than curiosities, and researchers had not mastered the sleight-of-hand needed to slide a single graphene card out of a deck of natural graphite.

Eight years ago, researchers led by Rodney Ruoff, a professor of nanoengineering who is now at Northwestern University, reported that he had rubbed tiny pillars of graphite against a silicon wafer surface, causing them to spread out like a deck of cards. He suggested that the technique could produce single-layer graphene, but he did not measure the flakes’ thickness. Philip Kim, a professor of physics at Columbia, took a similar approach in making a “nanopencil,” attaching a graphite crystal to the tip of an atomic force microscope and dragging it along a surface. He, too, found graphite cleaved into flakes. But the flakes, as thin as five-billionths of a meter, nevertheless consisted of probably at least 10 layers of atoms.

“We were pretty happy with this result back then,” said Dr. Kim, who presented the research in March 2004. “And then everything got changed a few months later.”
In September 2004, Dr. Kim saw a preprint of a paper by researchers led by Andre Geim, a physics professor at the University of Manchester in England. They had made single-layer graphene.

More surprising was the technique. They placed a graphite flake on a piece of adhesive tape, folding the tape over and pulling it apart, cleaving the flake in two. Folding and unfolding repeatedly, the graphite became thinner and thinner. Then they stuck the tape to a silicon wafer and rubbed it. Some graphite flakes stuck to the wafer, and those flakes were occasionally one atom thick.

Reading the preprint, Dr. Kim abandoned his nanopencil. “We rushed to the stationery store and bought Scotch tape,” Dr. Kim said.

Scientists now regularly call Dr. Geim’s innovation “the Scotch tape method.” Dr. Geim originally used Scotch tape but has switched to a different brand.

The utter simplicity makes it possible for almost anyone to jump into graphene research. Dr. Kim’s group pays an undergraduate $10 an hour to make graphene.

Dr. Geim says his main contribution was not the tape, but his way of spotting the single-layer graphene among the thicker flakes. The highest of high-tech microscopes can spot the bumps of a single atom, but using them to measure the thickness of each flake is impossibly slow. A one-atom-thick sheet is generally invisible, but Dr. Geim found that a sheet that thin does change the color of the silicon oxide layer atop the wafer, much as a sheen of oil on water generates a rainbow of colors.

Now, at a glance under a simple light microscope, researchers can tell whether a graphite flake is more than 100 layers thick (yellow), 30 to 40 layers thick (blue), about 10 layers thick (pink) or just a single-layer (pale, almost invisible, pink).

Dr. Geim said he thought the earlier researchers — and indeed, anyone who has written with a pencil — was likely to have produced graphene but simply could not see it.

After researchers had an easy way to make graphene, they started playing with all types of experiments. Techniques borrowed from silicon technology allow them to cut graphene into specific shapes, constructing transistors and other electronic devices. They face years of challenges. The ragged edges can affect the devices’ properties, though they also offer the possibility of tuning the electronics by attaching various atoms at the edges.

Scientists have also explored more esoteric aspects of graphene, including a prediction from more than half a century ago. Because of how the electrons flowing in graphene interact with the honeycomb chicken-wire structure, they behave as if they have no mass, always traveling at the same speed regardless of their energy, like particles of light. Dr. Beenakker at Leiden has proposed taking advantage of graphene’s unusual behavior in a new type of electronics that he calls “valleytronics.”
Independently, Dr. Geim and Dr. Kim at Columbia demonstrated a phenomenon known as the quantum Hall effect, where the electrical resistance perpendicular to the current and an applied magnetic field jumps between certain discrete values. The quantum Hall effect is usually seen just at very low temperatures in semiconductors, but it occurs in graphene at room temperature. A more recent paper by Dr. Geim and his collaborators describes a suspended graphene sheet as not flat, but wavy.

For applications like computer chips, the Scotch tape method would not be a practical method of mass production. Walter de Heer, a professor of physics at the Georgia Institute of Technology, has refined the techniques first developed in the ’70s to grow graphene out of silicon carbide. By heating a silicon carbide wafer to about 1,300 degrees Celsius, the silicon atoms on the surface evaporate, and the remaining carbon atoms rearrange into graphene.

“It’s literally like cooking a turkey,” Dr. de Heer said. “We are really out to produce a new electronic material.”

He said he could reliably grow graphene, usually a few layers thick rather than a single layer, providing, he said, better electronic properties.

Dr. de Heer had been working with nanotubes, but said they looked like a dead end, because of the difficulties in producing nanotubes of a specific type and length, placing them precisely and attaching wires. “The idea was to just unroll the nanotubes and work with the real stuff,” he said.

In 2001, he proposed this research to the National Science Foundation, which rejected his grant proposal. Intel, however, liked the idea and financed it. “What’s remarkable about graphene,” Dr. de Heer said, “is industry is taking notice — and serious notice.”