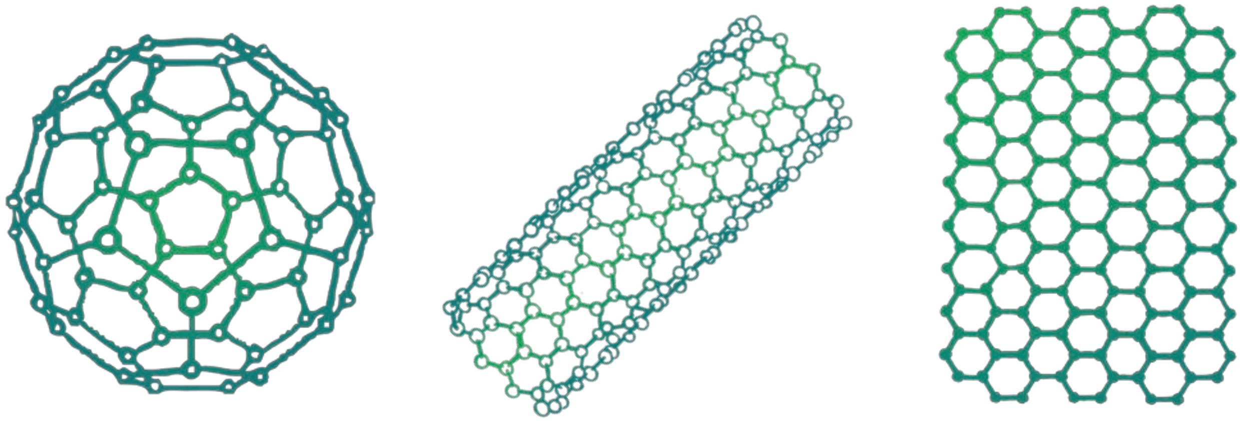


S. J. COLEMAN

THE TRIALS OF NEW CARBON

Researchers have spent 25 years exploring the remarkable properties of fullerenes, carbon nanotubes and graphene. But commercializing them is neither quick nor easy.

By Richard Van Noorden

In fairy tales, third place is often the best: it's usually the third casket that contains the treasure, and the third child who finds fame and fortune. And so it may be for graphene, the third and most recently discovered form of 'new carbon'. The football-shaped fullerenes[1], discovered in 1985, and the hollow cylindrical carbon nanotubes[2], first characterized in 1991, have so far had a limited impact on industry. But now graphene, a one-atom-thick flat sheet of carbon, seems to be surrounded by favourable omens — not the least of which is the speed with which groundbreaking experiments on its properties were rewarded with the 2010 Nobel Prize in Physics.

It has been just six years since Nobel laureates Andre Geim and Kostya Novoselov at the University of Manchester, UK, first reported using sticky tape to peel atomically thin layers of graphene from lumps of graphite[3]. But the material — essentially just an unrolled nanotube — has turned out to have properties just shy of miraculous: a single layer of graphene is simultaneously the world's thinnest, strongest and stiffest material, as well as being an excellent conductor of both heat and electricity.

Graphene has been showered with media attention as companies vie to bring those attributes to market. Last year, graphene was the subject of around 3,000 research papers and more than 400 patent applications. South Korea is planning a US$300-million investment to commercialize the material, and companies ranging from IBM to Samsung are testing graphene electronics — ultra-small, ultra-fast devices that might one day replace the silicon chip. The hype over graphene has reached such a pitch that a casual follower might wonder why it hasn't conquered the technological world already.

The reality is not such a fairy tale. Graphene's carbon forebears were once hyped in much the same way. Yet fullerenes have found hardly any practical applications. And although nanotubes have done better, they are costly to produce and difficult to control. Their subdued industrial impact is a lesson in just how hard commercialization of a new material can be.

Yet the story of nanotubes has some encouraging features. High-tech electronics applications are still years in the future, but a more low-tech application — nanotube-based conducting films for energy storage or touch screens — is much closer to commercialization. Another, comparatively straightforward use — nanotube-reinforced composite materials for aeroplanes and automobiles — is now reaching the market. Anticipating growing demand, nanotube manufacturers have scaled up production to many hundreds of tonnes a year.

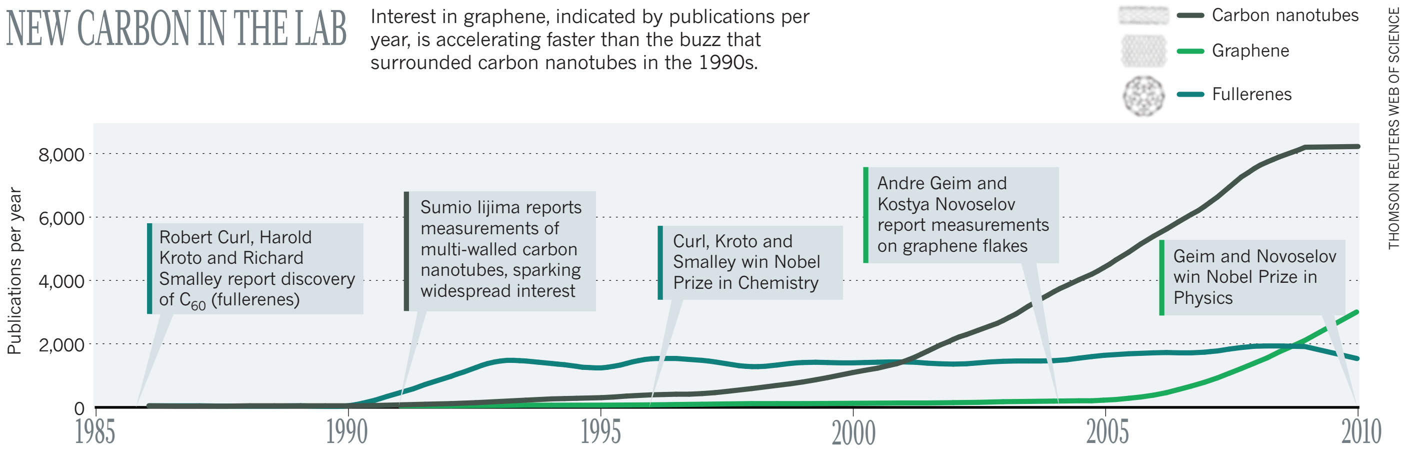
For that very reason, the graphene manufacturers following in their wake may have hit on the right moment to start mass-producing the sheets. Graphene is being considered for the same types of application as nanotubes, but it has some key advantages in ease of production and handling, and should benefit from two decades of research with nanotubes. That hindsight also means that graphene manufacturers have a better idea of which applications are worth chasing, and of how to avoid the false starts that nanotubes made in their first decade.

A CARBON PLAYGROUND

The remarkable properties shared by nanotubes and graphene arise from their common structure: an atomically thin mesh of carbon atoms arranged in a honeycomb pattern. Immensely strong carbon–carbon bonds produce an exceptionally high strength-to-weight ratio. Such is the strength of graphene, for example, that according to the Nobel prize committee, a hypothetical 1-metre-square hammock of perfect graphene could support a 4-kilogram cat. The hammock would weigh 0.77 milligrams — less than the weight of a cat's whisker — and would be virtually invisible.

The symmetry with which carbon atoms are arranged on the hexagonal lattice also allows both forms of nano-carbon to conduct electricity far more easily than the silicon used in computer chips. This means that they have much lower electrical resistance and generate much less heat — an increasingly useful property as chip manufacturers try to pack features ever more densely onto circuits.

Furthermore, even small variations in carbon structure can create a multitude of new properties. In graphene, for example, electronic



behaviour depends on the size of a given sheet, the presence or absence of defects in the sheet's lattice and whether it is lying on a conductive surface. In nanotubes, likewise, a given structure can be made semiconducting or metallic just by changing its diameter, length or 'twist' (the angle between the lines of hexagons and the direction of the tube). And there are differences between single tubes and those in which several cylinders are nested inside each other — called multi-walled nanotubes.

These properties have long sparked hopes of game-changing electronics applications. And researchers have made great progress — in the laboratory. In 1998, for example, physicists demonstrated a transistor made from a single, semiconducting nanotube[4]. And in 2007, researchers reported the synthesis of a carbon-nanotube-based transistor radio[5].

But for industrial-scale mass production of such circuits, the great variability of nanotubes is a curse. They are most commonly produced in a reactor, in which catalysts guide formation of the tubes from a carbon-rich vapour. This typically leaves a jumble of multi-walled, single-walled, semiconducting and metallic tubes of various lengths and diameters, all with different electronic properties. "Diversity is great until you have too diverse a population: then it becomes a real headache," says John Rogers, a physical chemist at the University of Illinois in Urbana-Champaign.

Only in the past five years have researchers worked out how to sort nanotubes into semiconducting and metallic types[6]. But there are further difficulties in assembling selected nanotubes in predetermined places on a chip and connecting these separate tubes together without compromising performance, so most physicists have come to believe that it is impractical for carbon nanotubes to replace silicon. "An integrated circuit would have to involve billions of identical carbon-nanotube transistors, all switching at exactly the same voltage," says Phaedon Avouris, who works on nanoscale electronics at IBM's Thomas J. Watson Research Center in Yorktown Heights, New York. This is not feasible with current technology.

Graphene offers a bit more cause for optimism. The highest-quality sheets are currently made by heating a wafer of silicon carbide in a vacuum, leaving a layer of pure graphene on the top surface. This method has fewer problems with uncontrollable variety from batch to batch than does nanotube synthesis, and the flat sheets that result are bigger and easier to handle than nanotubes.

But graphene has problems too. A single graphene sheet conducts charge so well that it is hard to make the current stop, something that must be solved if the material is ever going to be used in digital devices such as transistors, which control the flow of current like on–off switches. To change the material's electronic properties in the appropriate way — creating a 'band gap', or break in electron energy levels, which essentially turns it into a semiconductor — the sheet must be sliced up into thin ribbons. This is probably easier than trying to place billions of nanotubes on a chip, says Avouris — but it is still not currently possible with commercial technologies.

> **"A lot of companies are bringing new capacity online at the same time right now."**

These processing difficulties suggest that graphene won't soon displace silicon chips. "There have been millions of person-years and trillions of dollars put into the development of silicon electronics," notes James Tour, an organic chemist who specializes in nanotechnology at Rice University in Houston, Texas. "Asking graphene to compete with silicon now is like asking a 10-year-old to be a concert pianist because we've been giving him piano lessons for the last six years."

In the meantime, nano-carbon structures may be more competitive in less demanding electronics, such as conductive flat films for transparent electrodes in touch-screen displays or in solar cells. Bundles of dissimilar carbon nanotubes might very well provide enough conductivity for such electrodes, as might cheaper, lower-quality graphene sheets made by methods other than the silicon carbide process.

LOWERING THE SIGHTS

In June 2010, for example, a team led by Byung Hee Hong at Sungkyunkwan University in Suwon, South Korea, reported using carbon-rich vapour to deposit graphene films measuring 75 centimetres diagonally on copper plates, which are then etched away and recycled[7]. South Korean electronics giant Samsung is already testing this technique for use in commercial touch screens, which Hong estimates could be just two to three years away.

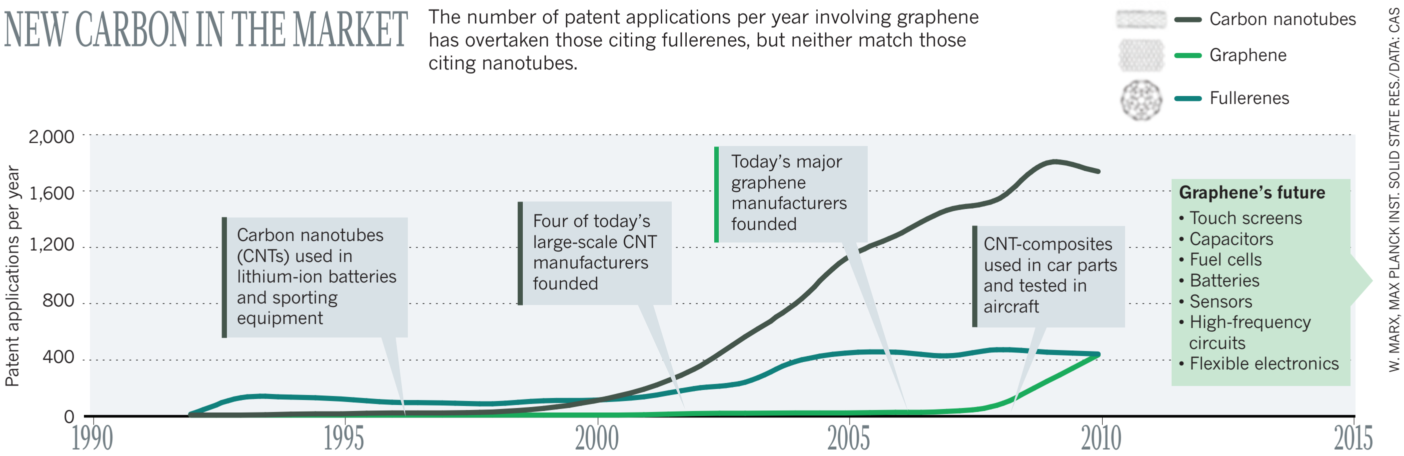
The question is whether the graphene films can compete with existing touch-screen materials such as indium tin oxide (ITO). Hong is optimistic; the cost of ITO has been increasing rapidly, because indium is scarce. But again, carbon nanotubes offer a cautionary tale. Early on, it was hoped that the tubes would form the television screens of the future, thanks to their ability to emit electrons from their tips to excite phosphors on the screen. In practice, competing plasma and liquid-crystal displays got better faster — and these are the screens most commonly used today.

One sweet spot for nano-carbon may be in the still-emerging market for flexible electronics. These are displays and sensors that could be worn on clothes, stuck to walls or printed on rollable sheets. Here, the only competition is from organic conducting polymers, because other materials cannot be printed on plastic. The performance of these polymers is quite low, says Rogers, so nanotubes and graphene circuits — which can be transferred to flexible substrates — could compete effectively.

But even these specialist electronics are still in the future. For now, the hundreds of tonnes of commercial nano-carbon being turned out every year are mostly going into composites for sporting goods, lithium-ion batteries and cars.

NEW CARBON IN THE MARKET

The number of patent applications per year involving graphene has overtaken those citing fullerenes, but neither match those citing nanotubes.



W. MARX, MAX PLANCK INST. SOLID STATE RES./DATA: CAS

The aim is to disperse nano-carbon sheets or tubes within resins or polymers, so that they not only make the material tougher by blocking cracks that would otherwise spread, but also help to dissipate heat and electrical charge. For example, the Audi A4 car now has plastic fuel filters containing carbon nanotubes, which protect against static electricity. And nanotube additives in lithium-ion battery electrodes were one of the first nanotube applications marketed by Showa Denko, a Tokyo-based chemical-engineering company.

CUTTING COSTS

Basic processing problems with nanotubes initially hampered progress. They tended to clump together like tangled string as they came out of the reactor, making it hard to disperse the nanotubes evenly through plastic or resin. Despite improvements, this limits nanotube content to 1–2% by weight in the final product, compared with the 20–30% typical of conventional carbon fibre. The other problem was, and still is, cost. Materials such as steel, aluminium and plastics, and fillers such as carbon black, sell for just dollars or cents a kilogram, says David Hwang at Lux Research, a technology-evaluation company in New York. Meanwhile, multi-walled nanotubes retail for $100 a kilogram. The price is coming down as production scales up, but will drop only to about $50 a kilogram by 2020, according to Lux forecasts.

Composite-quality graphene has the potential to be a lot cheaper, although costs are currently similar. As Geim and Novoselov showed in 2004, graphene platelets of varying sizes can easily be peeled away from graphite[3], a raw material that costs a few dollars a kilogram. Graphene is also easier to disperse in a resin than are nanotubes.

But promising as this is, says Steve Hahn, a senior scientist with Dow Chemical's Ventures and Business Development Group in Midland, Michigan, the reality is that these applications are still niche. "I've been trying to find outlets for graphene for a couple of years," he says. But there is usually something quite a lot cheaper that does the same job, says Hahn.

Michael Knox, president of XG Sciences, a start-up graphene-manufacturing company in East Lansing, Michigan, agrees. Adding graphene platelets to composites is not a transformational application, "it's an incremental improvement", he says. Yet that is not to be sniffed at. "If I could demonstrate a 10–20% improvement in a polypropylene composite at a reasonable price, I could probably sell a million tonnes of it a year — and car manufacturers would be pretty excited by that," says Knox.

The trick for young graphene-manufacturing companies is to find specific applications and then work out how to scale up production capacity without overstretching themselves. Vorbeck Materials in Jessup, Maryland, for example, has decided to focus on making graphene-based conducting inks. John Lettow, co-founder and president of Vorbeck, says that the inks will be in smart cards and radio-frequency identification tags in retail stores in the first quarter of 2011.

> "Graphene will have its place, but it will just take longer than people think."

One near-term application may be supercapacitors, which use crumpled-up sheets of graphene to pack a massive surface area into a small space — to store more electric charge per gram than any other material. Other researchers are looking at using nano-carbon to make catalyst electrodes in fuel cells, or even to make water-purification membranes — but, as usual, finding clear advantages over existing materials such as activated carbon will be the problem.

Carbon nanotubes do have one property that graphene sheets don't: they can be very long. The nanotubes currently mixed into resins and plastics are typically short stubs, but Nanocomp Technologies in Concord, New Hampshire, says that it can spin long nanotube fibres into lightweight, electrically conducting yarns or sheets that could replace copper wiring in some applications. "There are about 60 miles of copper wire in an aeroplane," says Nanocomp chief executive Peter Antoinette — so replacing this with the much lighter nanotube wire could save substantially on weight and fuel use.

Such activity is very encouraging for carbon nanotubes, says Hwang. "There was a huge amount of research that had to be done before nanotubes got to be commercially viable. Now if you look at the next five years, the commercial trajectory will be very different."

But have carbon nanotubes really taken a disproportionate time to get going? It takes 20 years or more for any new material to make an impact in industry, point out many nanotube makers. "Research on carbon fibre started in the 1950s; it took 15 years or so before aerospace and military used it — and we didn't hear about that until much later — and it wasn't until the mid-1970s that you started seeing commercial aircraft with small quantities of structures made out of carbon-fibre composites," says Brian Wardle, who directs the nano-engineered aerospace structures consortium at the Massachusetts Institute of Technology in Cambridge. Nanotubes may simply be on the usual trajectory from discovery to industry — and graphene may find that it follows the same path. "Graphene will have its place, but it will just take longer than people think," says Antoinette.

And what will happen in the meantime? "A lot of companies are bringing new capacity online at the same time right now," notes Hahn. "They will either go out of business or find a market somewhere. Whatever happens, it'll be a great lesson to all of us in how new materials are commercialized." ■

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1. Kroto, H. W. *et al. Nature* **318,** 162–163 (1985).
2. Iijima, S. *Nature* **354,** 56–58 (1991).
3. Novoselov, K. S. *et al. Science* **306,** 666–669 (2004).
4. Tans, S. J. et al. *Nature* **393,** 49–52 (1998).
5. Jensen, K. *et al. Nano Lett.* **7,** 3508–3511 (2007).
6. Arnold, M. S. *et al. Nano Lett.* **5,** 713–718 (2005).
7. Bae, S. *et al. Nature Nanotech.* **5,** 574–578 (2010).