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Wonder Material Ignites Scientific Gold Rush

Atom-Thin Graphene Beats Steel, Silicon; A Patent "Land Rush"

By GAUTAM NAIK CONNECT



Graphene is an extremely thin, strong and flexible material derived from the graphite found in everyday pencils. Scientists are racing to exploit those attributes for an array of new applications. WSJ's Gautam Naik reports. Photo: Daniella Zalcman.

CAMBRIDGE, England—A substance 200 times stronger than steel yet as thin as an atom has ignited a global scientific gold rush, sending companies and universities racing to understand, patent and profit from the skinnier, more glamorous cousin of ordinary pencil lead.

The material is graphene, and to demonstrate its potential, Andrea Ferrari recently picked up a sheet of clear plastic, flexed it and then tapped invisible keys, triggering tinkly musical notes.

The keyboard made at Dr. Ferrari's University of Cambridge lab was printed with a circuit of graphene, which is so pliable that scientists predict it will fulfill dreams of flexible phones and electronic newspapers that can fold into a pocket.

It is the thinnest material known. But it is exceedingly strong, light and flexible. It is exceptional at conducting electricity and heat, and at absorbing and emitting light.



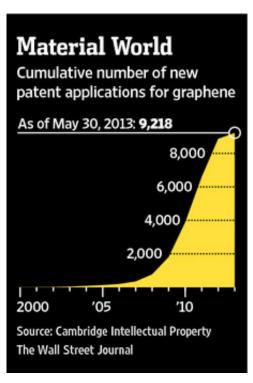
Daniella Zalcman for The Wall Street Journal

Dr. Andrea Ferrari, head of graphene research at the University of Cambridge, inspects equipment used for experiments on the atomthick material.

Scientists isolated graphene just a decade ago, but some companies are already building it into products: <u>Head NV</u> introduced a graphene-infused tennis racket this year. <u>Apple Inc.</u>, <u>Saab AB</u> and <u>Lockheed Martin Corp.</u> have recently sought or received patents to use graphene.

"Graphene is the same sort of material, like steel or plastic or silicon that can really change society," says Dr. Ferrari, who leads a band of about 40 graphene researchers at Cambridge.

Graphene faces hurdles. It is still far too expensive for mass markets, it doesn't lend itself to use in some computer-chip circuitry and scientists are still trying to find better ways to turn it into usable form. "Graphene is a complicated technology to deliver," says Quentin Tannock, chairman of Cambridge Intellectual Property, a U.K. research firm. "The race to find value is more of a marathon than a sprint."



Interest in graphene has exploded since 2010, when two researchers won a Nobel Prize for isolating it. Corporate and academic scientists are now rushing to patent a broad range of potential uses.

"As soon as I find something, boom! I file a patent for it," says James Tour, a graphene expert at Rice University in Houston.

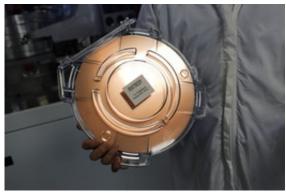
Apple has filed to patent graphene "heat dissipators" for mobile devices. Saab has filed to patent graphene heating circuits for deicing airplane wings. Lockheed Martin this year was granted a U.S. patent on a graphene membrane that filters salt from seawater using microscopic pores.

Others have applied for patents on graphene used in computer chips, batteries, flexible touch screens, anti-rust coatings, DNA-sequencing devices and tires. A group of scientists in Britain has used a graphene membrane to distill vodka.

There were 9,218 published graphene patents and patent applications filed cumulatively as of May around the world, up 19% from a year earlier, says Cambridge Intellectual. Over the past five years, it says, the cumulative number of graphene patent filings has more than quintupled.

"It's a land grab," says Mr. Tannock of Cambridge Intellectual. By trying to patent

just about every finding, "you have the option for suing your competitors later and stopping them." Many graphene patent filings appear legitimate, but some seem speculative and others may be decoys to mislead rivals, he says.



Daniella Zalcman for The Wall Street Journal

'As soon as I find something, boom! I file a patent,' says an expert in graphene, which coats the disc, pictured.

Graphene's biggest short-term promise is in high-speed electronics and in flexible circuitry such as that in Dr. Ferrari's keyboard, because of expected demand for use in pliant electronic displays. Companies such as South Korea's <u>Samsung Electronics</u> Co. and Finland's <u>Nokia</u> Corp. have filed for patents covering various graphene uses in mobile devices.

One of the hottest areas is graphene ink used to lay down circuitry, which a few companies have begun to sell. Dr. Ferrari's lab last year filed for a patent on a

graphene ink that can be deposited by inkjet printers. <u>BASF SE</u> is experimenting with graphene ink to print flexible circuits into upholstery that can heat car seats, a technology it says could be in the market in a few years.

"Graphene combines various effects" that make it distinctive, says Matthias Schwab, a lab team leader in BASF's graphene-research operation. "I am seeing no other materials that can do it."

In effect, graphene has only two dimensions, in a microscopic structure that resembles chicken wire. In a study published five years ago, Columbia University researchers concluded it was the strongest material measured. They calculated it would take an elephant balanced on a pencil to puncture a graphene sheet the thickness of Saran Wrap.

It absorbs and emits light over the widest range of wavelengths known for any material. It conducts electricity far better than silicon. Unlike silicon, which is brittle, graphene is flexible and stretchable.



Graphene circuitry promises to eventually be cheaper than conductive materials such as copper and silver because it can be made from graphite—the plentiful stuff of an ordinary pencil lead—and can also be created by combining certain gases and metals, or synthesized from solid carbon sources.

Rice University's Dr. Tour demonstrated in 2011 that graphene can be synthesized

using carbon from sources as diverse as grass, Girl Scout cookies and cockroach legs.

Dr. Tour's lab has filed for multiple graphene patents, including for ribbons to

reinforce composites that he says are strong enough to use in high-pressure naturalgas tanks that can be molded into cars. Patenting quickly, he says, "gives us a foothold on the technology."

One factor holding graphene back is cost. Some U.S. vendors are selling a layer of graphene on copper foil for about \$60 a square inch. "It needs to be around one dollar per square inch for high-end electronic applications such as fast transistors, and for less than 10 cents per square inch for touch-screen displays," estimates Kenneth Teo, a director at the Cambridge unit of Germany's <u>Aixtron SE</u> that makes machines to produce graphene.

Graphene must often be combined with other materials to exploit its properties, and scientists are still trying to figure out how to do that effectively.

It also has a significant shortcoming: It can't easily be made into a switch. <u>International Business Machines</u> Corp. was initially optimistic about using graphene in computer chips but found electrons travel too fast in it to switch off easily, making it hard to turn current into the "ones" and "zeros" of digital code.

Labs around the world are trying to solve the problem. But for now, "we don't see graphene replacing silicon in microprocessors," says Supratik Guha, director of physical sciences at IBM's research unit, who says he remains a big proponent of graphene. IBM is a major graphene-patent filer.

Graphene could still meet the fate of other touted materials that failed to live up to their promise. The discovery of high-temperature superconductors garnered a Nobel Prize in 1987 and led to a flood of patents and predictions of technologies such as superfast magnetically-levitated trains. The world is still waiting.

That still leaves plenty of scientific enthusiasm. In 2012, scientists published 45% more papers on graphene than in 2011, according to Thomson Reuters Web of Science, an index of journals.

It's a global race: Chinese entities had filed for the most graphene-patent applications cumulatively as of May, followed by U.S. and South Korean filers, says Cambridge Intellectual. Samsung accounted for the most filings, followed by IBM and South Korea's Sungkyunkwan University.

While labs work out graphene's kinks, some of the patents have found their way into products. Vorbeck Materials Corp., of Jessup, Md., makes a graphene ink it says is being used to print circuits in antitheft packaging in a few U.S. stores, which it declined to name.

Head's racket is reflected in an application it filed for a patent on graphene in a wide range of sports gear, from golf clubs to ski bindings. A Head representative referred inquiries to its website, which says graphene's strength lets it use less material in the racket, allowing the designer to redistribute the weight for more power.

Bluestone Global Tech Ltd., a Wappingers Falls, N.Y., startup, makes graphene sheets it says it ships to customers in the U.S., Singapore and China. "Within half a year, graphene will be used for touch screens in commercially available cellphones,"

predicts Chung-Ping Lai, its chief executive officer.

The graphene frenzy was unimaginable before 2003, when many scientists believed an atom-thick layer of anything couldn't keep from falling apart.

That year, Andre Geim stumbled upon graphene's wonders. A Russian-born scientist at the University of Manchester in Britain, he wanted thin graphite to study its electrical properties. A doctoral student suggested using cellophane tape.

Dr. Geim and his colleagues used the tape to peel off layers of graphite until they got to a layer so thin it was transparent. When they could peel no further, they had graphene. Not only did it not fall apart, it was strong, flexible and possessed astonishing electrical properties.

Other scientists were initially skeptical. "Not many people believed us," says Dr. Geim. But by March 2006, when he presented at a Baltimore conference, his session was packed, recalls Cambridge's Dr. Ferrari. "Finally, I understood how significant the material was going to be," he says.

In 2010, Dr. Geim and a colleague, Konstantin Novoselov, won the Nobel Prize in physics for their graphene work. By that time, corporate labs, universities like Rice and Harvard University, and academic institutions in China had begun to increase graphene research. In 2010, Japanese and South Korean scientists unveiled prototype graphene touch screens.

Labs at Samsung and Sungkyunkwan University, in particular, began to stand out for the volume of their research. "Although the basic research on graphene started in Europe and the U.S., the early research for commercial applications started in Korea," says Changgu Lee, a Sungkyunkwan graphene researcher. "We want to keep the lead."

A Samsung spokeswoman declined to comment on the company's graphene work.

Among those expressing enthusiasm for graphene is the U.S. military. In late 2011, the U.S. Army Research Laboratory in Adelphi, Md., signed an agreement to study graphene's properties with Northeastern University in Boston. The agreement is mainly funded by a \$300,000 grant from the Defense Advanced Research Projects Agency, or Darpa.

The university plans to use graphene to design better night-vision goggles and other such detectors, says Srinivas Sridhar, a Northeastern physics professor. A Darpa representative, in an email, confirmed the project.

A walk through Dr. Ferrari's labs this summer gave a window into the research. One of his associates, Felice Torrisi, showed how tape could peel graphene from a graphite clump. "This is obviously not scalable" for industrial purposes, said Dr. Torrisi.

That speaks to a big goal in the graphene race: finding the best ways to manufacture it. A large number of patent filings describe methods of manufacturing graphene.

Dr. Torrisi next held up a vial of ink consisting of graphene in water. A nearby inkjet

printer whizzed away, depositing the ink on a plastic sheet to form a near-invisible circuit. Ink printed on plastic was the trick behind the keyboard Dr. Ferrari tapped to trigger music from attached electronics.

In other Cambridge lab rooms, researchers showed off an early prototype of a graphene-based laser that can shoot out ultrafast pulses of light and graphene sensors that can detect any wavelength of light.

Graphene's heat-conducting properties appear to be at the heart of Apple's patent application, which includes drawings of a graphene "heat dissipator" behind components in a "portable electronic device." An Apple spokeswoman declined to comment.

Saab wants to take advantage of graphene's lightness and conductivity by embedding it in wings for deicing. The research is still in early stages, "but it is certainly part of our plan for introducing flying applications," says Mats Palmberg, who oversees future products at Saab's aeronautics unit.

Lockheed expects its graphene membrane to be "more effective at seawater desalination at a fraction of the cost" of current technologies, it says in a news release.

The discovery of graphene has also led scientists to hunt down scores of other twodimensional materials with unusual properties, says Dr. Geim, the Nobel laureate. "Graphene opened up a material world we didn't even know existed."

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