Miracle material
A DECADE AFTER ITS DISCOVERY, GRAPHENE IS HOT

It’s the thinnest material on Earth but 200 times stronger than steel. It is exceptionally conductive—10 times better than copper—and can stretch, bend, twist, and bounce right back. And it’s everywhere; if you’ve used a pencil, you’ve likely made some yourself.

If ever there was a “miracle material,” graphene is it. The substance is enabling faculty and students from across McCormick to pursue research areas that once seemed unimaginable.
Discovering the miracle material

Molecularly speaking, it doesn’t get much simpler than graphene. It is the thinnest possible slice of graphite, a virtually two-dimensional, one-atom-thick layer of carbon densely packed in a honeycomb-shaped lattice. But the potential this simple material holds is tremendous. Bendable electronics, superfast computers, lightweight cars and airplanes, nanoscale water purifiers—if it lives up to its promise, graphene could enable all of these and more.

Researchers were speculating about the amazing properties of single-layer carbon sheets as far back as the 1940s, but for years attempts to make the material failed. Fabricating it wasn’t the problem; by the 1970s researchers knew how to grow graphene on top of crystal surfaces. But the material interacted with the surfaces on which it grew, making it impossible to study its properties. Some researchers attempted to make graphene by inserting molecular spacers between layers of graphite in an attempt to wedge them apart, but that tended to degrade the graphite into particles too small to be of use. Others scraped graphite against another surface to slowly wear the graphite down, a technique that proved moderately successful; some scientists whittled the thickness down to fewer than 100 atoms.

Most scientists concluded that isolating graphene in any usable form was impossible, however; a single sheet, they thought, would be thermodynamically unstable and, if isolated, would immediately roll into a cylinder. (The cylindrical form of graphene, the carbon nanotube, had been discovered in 1991.) Graphene, it seemed, was doomed before it had been discovered.

But, as scientists are wont to do when something is declared impossible, some researchers persisted, including Andrei Geim, a physics professor at the University of Manchester in the UK, and a former PhD student of his, Kostya Novoselov. In 2004 Geim and Novoselov realized they could place a small flake of graphite onto a piece of clear tape, fold the tape over, and pull it apart to split the graphite in two. They split layer after layer this way, and when they had a thin enough sample—in some places, only one atom thick—they transferred it to a silicon substrate where it could be characterized.

The discovery of graphene won Geim and Novoselov the Nobel Prize in physics in 2010. The race to develop applications was just beginning.

A global race

Thousands of research groups are developing and patenting graphene products worldwide, but three countries—China, the United States, and Korea, in that order—have filed more than two-thirds of patented discoveries. Recognizing graphene’s potential, other countries are pooling resources to become more competitive.

Despite thousands of patent filings, graphene technologies have been slow to come to market. Mark Hersam, Bette and Neison
Harris Professor in Teaching Excellence and professor of materials science and engineering at McCormick, says it’s largely an issue of integrating graphene with other materials. “No doubt, graphene is the new, hot material, but there is a big difference between winning the Nobel Prize and making a functional technology,” Hersam says. “The solid-state transistor was invented in 1947, and it took 14 years to make the first integrated circuit. Integrating materials takes time.”

While some graphene products are almost ready for the marketplace—such as graphene coatings that could make rechargeable batteries safer and longer lasting—others remain at the exploratory phase. That’s partially because until the past few years, scientists lacked a large-scale graphene production method; unsurprisingly, Scotch tape turned out not to be an effective or cost-efficient method. (In 2008 graphene produced by mechanical exfoliation, or the Scotch tape method, was one of the most expensive materials on Earth, costing $1,000 for a piece smaller than the thickness of a human hair.)

Today’s graphene-making methods have become more efficient. Some labs can create graphene sheets that measure several feet across: stiff, semitransparent pieces that can be seen with the naked eye. There are various ways to make graphene, each with strengths and weaknesses; some lend themselves to certain end products. One of the most popular involves oxidizing graphite via acidic chemical treatments, then applying heat to reduce the resulting graphene oxide to pure graphene. While quick and inexpensive, that process introduces imperfections into the material, so it cannot be used for applications that require optimal conductivity, like computer chips.

For researchers like Hersam, who focus on high-performance applications—such as graphene electronics, now under development—it is vital that the graphene be pristine, even if the growing process is more energy intensive. Hersam’s labs are full of high-performance scanning tunneling microscopes that enable him to carefully analyze each piece he creates. “Our laboratory works on the surface functionalization of graphene to better control the interface between it and other materials,” Hersam says. “When you have a one-atom-thick material, individual atoms matter.”

Electronics of the future

Many experts believe graphene could rival silicon, transforming integrated circuits and leading to ultrafast computers, cellphones, and related portable electronic devices. Among these high-tech visions are flexible electronics, such as a tablet computer that folds to become a smartphone, or electronics that can be integrated into clothing or the human body. Recently Hersam developed a highly conductive, bendable graphene-based ink that could enable such devices, and his lab has used it to inkjet-print patterns that could be used for extremely detailed, conductive electrodes.

Graphene ink is a smart choice for next-generation electronics: the graphene is extremely conductive and tolerant of bending, and printing provides an inexpensive and scalable method for exploiting these properties. Researchers previously explored the method, but it has remained a challenge because it is difficult to harvest a sufficient amount of graphene without compromising its electrical properties. But a new method that Hersam developed for mass-producing graphene—which uses ethanol and ethyl cellulose to exfoliate the material, resulting in a powder with a high concentration of nanometer-sized graphene flakes—alleviates that problem.

Hersam’s printing technology has caught the attention of the US Office of Naval Research, which is funding Hersam to advance the technology in hopes of someday creating a brain-machine interface for Navy pilots, a skull-conforming cap with millions of printed sensors that could detect the brainwaves of pilots and wirelessly communicate their intentions to the vehicle’s control center. The device would speed response times in combat, and it could also have medical applications, such as understanding brain damage and disorders in veterans. “It sounds a bit like science fiction,” Hersam says, “but it’s possible. Flexible electronics are key.”

To realize this technology, Hersam’s ink must mesh with materials from other labs, most likely semiconducting inks, to build full circuits—millions of electrodes acting in unison. Hersam is collaborating with Tobin Marks, Vladimir N. Ipatieff Professor of Catalytic Chemistry and (by courtesy) Materials Science and Engineering, who is creating metal oxide inks that could prove compatible.
Clean energy with graphene

Because of its unique combination of properties, graphene could also move solar cell technology forward. Solar cells require materials that are conductive and optically transparent—a rare combination. “If you think of optically transparent materials, you think of glass, which is not conductive. And if you think of conductive materials, you think of materials like copper that are optically opaque,” Hersam says. Today’s commercial solar cells rely on silicon and indium tin oxide, brittle and heavy materials that make the cells stiff and bulky, severely limiting their applications. Organic solar cells—which are made of polymers with carbon-based electronics—are lightweight and flexible, but with existing technology, their lifetime is shorter than silicon’s because their polymer layer degrades in wet or humid conditions.

By replacing the faulty polymer layer with graphene treated with ultraviolet light and ozone, Hersam has developed an organic solar cell with much higher environmental stability. The technology could increase organic cell lifetimes 20-fold. “This is one of the places where graphene really shines, because it is an inert material. You can heat it to 100 degrees and expose it to humidity, and it doesn’t degrade,” Hersam says. “This longevity is important, because solar power is more financially viable as a long-term investment.”

Researchers are also eyeing graphene for improvements to lithium-ion batteries, rechargeable batteries that power cellphones and electric vehicles. Most of today’s battery makers use graphite for the anode, the electrode in which lithium ions are stored when the battery holds a charge. Silicon has a benefit: it can hold more lithium ions, which flow from the cathode to the anode during charging. But silicon also rapidly deteriorates after just a few charge cycles, making it impractical in the long term.

Harold Kung, Walter P. Murphy Professor of Chemical and Biological Engineering at McCormick, proposes a solution: sandwiching clusters of nano-size silicon particles between graphene sheets. The combination allows more lithium ions into the electrode while using the flexibility of graphene to deter deterioration. The result is “the best of both worlds,” Kung says. “We have much higher energy density because of the silicon, and the sandwiching reduces the capacity loss caused by the silicon’s expanding and contracting. Even if the silicon clusters fracture and break up, the silicon is held within the graphene and won’t be lost.”

Kung makes his graphene through the oxidation technique—in which graphite is oxidized, then reduced to graphene, leaving behind imperfections in the form of tiny holes—and has found a way to use the material’s imperfection to his advantage. In his battery design...
the holes provide a shortcut for lithium ions to percolate into the anode, speeding the battery’s charging time by up to 10 times. The result is improved charge capacity, charge time, and longevity. “Even after 150 charges, which would be one year or more of operation, the anode is still five times more effective than those in the lithium-ion batteries on the market today,” Kung says. The anode is currently being commercialized by SiNode, a Northwestern student startup founded in the NUvention: Energy course. (Read about SiNode on page 11.)

Where graphene falls short
Graphene is not perfect; some of its intrinsic properties pose a significant challenge. Unlike semiconductors like silicon, pure graphene is a zero-band-gap material, making it difficult to electrically turn off the flow of current through it. (Silicon has a band-gap closer to one.) As it is now, graphene cannot replace silicon in electronics. Researchers are pursuing ways to chemically alter graphene to make it more functional.

Making graphene processable for industry can also be difficult. Graphene has one of the largest surface-to-weight ratios of any known material; one gram of it could cover nearly half of a football field. All that surface area is useful for applications like water purification, ultracapacitors, and batteries, but often the surface area is lost during processing. “Graphene is basically an ultrathin sheet of paper,” says Jiaxing Huang, associate professor of materials science and engineering at McCormick. “When you try to process a number of these papers in a solvent, they stack together like a deck of cards.” This leaves the graphene rigid and far less effective.

Researchers have tried to alleviate the problem, with varying levels of success. Some have tried to insert “spacers” between the graphene sheets to physically separate them, but that changes graphene’s chemical composition. Huang has developed another solution: crumpling the sheets into balls. “If you imagine a trash can filled with paper crumples, you really get the idea,” Huang says. “The balls can stack up into a tight structure. You can crumple them as hard as you want, but their surface area won’t be eliminated, unlike face-to-face stacking.”

To make the balls, Huang and his team created freely suspended water droplets containing graphene-based sheets, then used a carrier gas to blow the aerosol droplets through a furnace. As the water evaporated, the thin sheets were compressed into near-spherical particles by capillary force. The resulting particles have the same electrical properties as the flat sheets but are more useful for applications that require large amounts of the material.

For other applications, graphene’s tendency to aggregate can be used to researchers’ advantage. Huang found that stacking inexpensive graphene-based sheets creates a flexible paper with tens of thousands of useful channels between the layers. The channels interconnect and water and electrolytes can flow through, creating nanoscale rivulets (or streams) that can be readily scaled up. Researchers in Huang’s lab used a surprisingly low-tech “manufacturing” method—a pair of ordinary scissors—to cut the paper into a desired device shape. “Using such space as a flow channel was a wild idea,” Huang says. “In a way, we were surprised that these nanochannels can be made so easily and actually work. This can help to create new materials for use in water purification and as fast ionic conductors for fuel cells.”

Fine-tuning the mechanics
Much of the work of L. Catherine Brinson, Jerome B. Cohen Professor of Mechanical Engineering at McCormick, has involved directing the assembly of graphene-based materials, creating interesting
opportunities for engineers to tune its properties to create functional materials. Working with research assistant professor Karl Putz, Brinson has made strides in understanding the layered structures that result when individual graphene oxide nanosheets assemble into thicker papers that can be used as macroscopic materials.

Graphene oxide papers—stiff, strong, and lightweight papers with electrical properties distinct from those of individual graphene sheets—are made through a process called vacuum-assisted self-assembly. Researchers filter sheets of graphene oxide in a batch process that results in a self-assembly process of the individual sheets into a layered paper. Upon closer inspection, Brinson and Putz observed that the papers form a hierarchical structure made of multiple different length-scales—that is, patterns emerge both on the level of individual graphene sheets and of multiple sheets aggregated together into thin, plate-like structures called lamellae. Bones and other biological structures are similarly ordered; this multiscale patterning makes structures more robust.

Understanding the process enables Brinson and Putz to manipulate it for their needs. “We’re developing functional ways to make new materials, and at the same time we’re learning fundamental aspects of what controls graphene oxide paper’s properties,” Putz says. By adding polymers into the vacuum filtration mix, Brinson and Putz created nanoscale composites that incorporate the most useful characteristics of both materials, and they have experimented with replacing water in the solution with other chemical compounds to make the papers stiffer and stronger.

Brinson and Putz recently worked on a project with Boeing regarding the conductivity of composite materials used in the bodies of aircraft. To effectively withstand lightning strikes, engineers often place metal foils within the composites to effectively channel the current. But the foils add weight and cost, so Boeing sought alternatives. “Using nanomaterials like graphene in addition to carbon fibers would create a conducting network inside the polymer matrix and could save both weight and cost,” Brinson says. “But you need graphene composites that are not just conductive but also mechanically durable.”

Getting that combination of strength, toughness, and conductivity in a composite can be tricky. Pure graphene is stiff and conductive, but it is hard to integrate into a composite readily, and it leads to brittle composites. Conversely, when graphene sheets are functionalized to integrate into the matrix robustly, they become tougher but lose some of the conductivity of pure graphene. “There is a trade-off there,” Brinson says. “The goal is to find something in the ‘Goldilocks regime,’ with both superior mechanical performance and requisite conductivity.”

Recently, Brinson and Putz have worked with Jiaxing Huang to create a sandwich composite, layering Huang’s crumpled graphene particles between two pieces of their layered graphene paper. The resulting structure could provide the best of both worlds—a stiff, strong outer layer with lower conductivity, paired with a highly conductive, mechanically weak inner layer.

The ability to create tailored materials at several length scales may provide insight into strong, layered materials made in nature, such as bone or an armored fish with an exceptionally pierce-resistant outer shell. “We want to learn from functional layers in biological structures, like the armored fish, and learn to recreate them,” Putz says. “In the next 10 years, using our unique capability to make tuned layered structures, we will create functional materials with tunable property gradients to satisfy specific application needs.”