NOVEMBER 21, 2011

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CHEMICAL & ENGINEERING NEWS

CLEAN ENERGY
Political infighting threatens investments **P.26**

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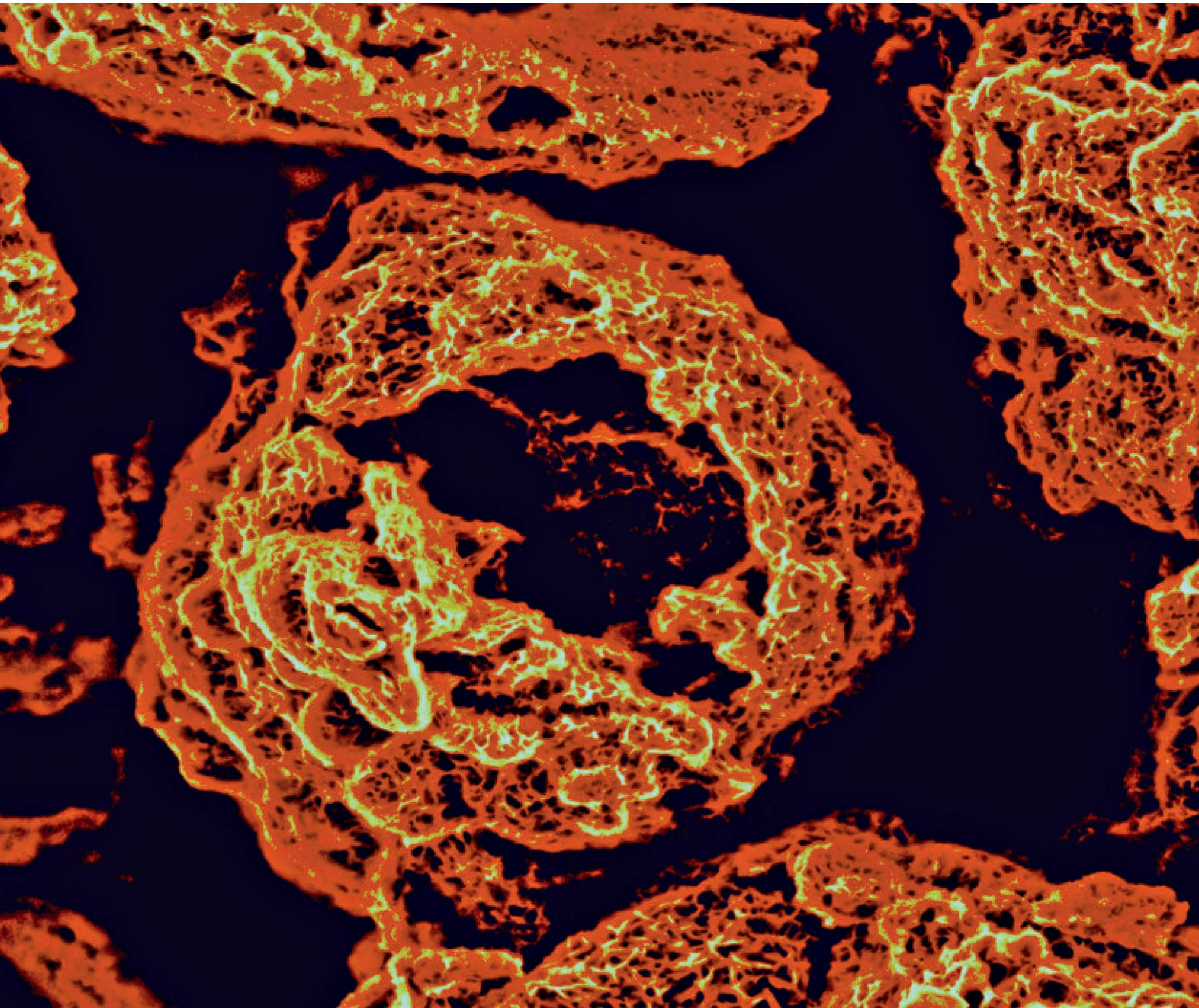

GRAPHENE FOR SALE

Ultrathin carbon enhances products **P.10**

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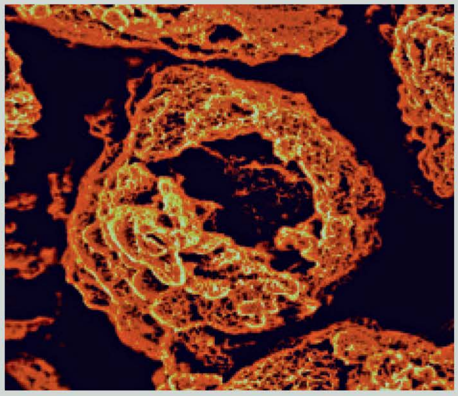
COVER STORY

GRAPHENE PUSHES FORWARD

Voluminous research on the material begins to yield real-world applications.

PAGE 10



QUOTE OF THE WEEK

"Sugar water will change the world."

MIKE HAMILTON, CEO, RENMATIX PAGE 20

NEWS OF THE WEEK

BUSINESS

GOVERNMENT & POLICY

SCIENCE & TECHNOLOGY

EDUCATION

THE DEPARTMENTS

COVER: *Forming a 3-D network of interconnected tunnels with nanoporous walls, this form of graphene may help advance lithium-air battery technology.* Nano Lett.

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LAWRENCE T. DRZAL/XG SCIENCES

INDUSTRIAL SIZE At XG Sciences, in East Lansing, Mich., a worker operates equipment that produces graphene at the multi-kilogram-per-day scale.

GRAPHENE MOVES TOWARD APPLICATIONS

As composites and inks become commercial products, **ADVANCED ELECTRONICS** remain a long way off

MITCH JACOBY, C&EN CHICAGO

EVERY NOW AND AGAIN, some scientific discovery comes along that rivets the world's attention. These days, it's graphene.

By any measure, this ultrathin form of carbon—a single atomic layer thick in some cases, a handful of layers in others—has been the focus of an enormous research effort for the past couple of years (C&EN, March 2, 2009, page 14). A glance at conference programs and the tables of contents of leading journals shows that researchers are inundating these scientific venues with studies of graphene's fundamental properties and reports of the material's application in numerous areas. At the same time, newspapers and other media outlets often run stories about how graphene will revolutionize personal electronics and other technology areas.

But is it realistic to expect that graphene and graphene-based products will be commercialized anytime soon? The short answer is yes. "Graphene products are here today. They're not five years away," says John S. Lettow, president of Vorbeck Materials in Jessup, Md.

The longer answer is—it depends on what's meant by "products." To Vorbeck and the growing pool of companies making and selling some form of graphene, "products" may refer to raw graphene, graphene-based materials, and graphene-enhanced products, including ones headed to retail stores. Nowadays, all of those categories are bustling with commercial activity.

In addition, an intense wave of research activity is directed at exploiting graphene's outstanding electronic, mechanical, and other properties in future products and applications. Even before physicists Andre K. Geim and Konstantin S. Novoselov of the University of Manchester, in England, were honored with the 2010 Nobel Prize

"Graphene products are here today. They're not five years away."

in Physics for their pioneering work with graphene, the range of graphene's potential applications discussed in scientific circles was impressively broad. It's even broader now. Scientists and engineers are searching for ways to use graphene to make the next generation of high-performance batteries and other energy storage devices, light-emitting diodes, organic solar cells, computer displays, and other advanced-technology products.

A SURVEY of today's graphene market shows that a couple of small companies have been selling microscopic amounts of graphene flakes for a few years already, mainly to academic researchers for fundamental investigations. A few other companies, such as Durham Graphene Science, a spin-off of Durham University, in England, now offer gram quantities for sale. Karl S. Coleman, the company's founder and a Durham chemistry professor, says his company is aiming to boost graphene production in the coming months to the multikilogram-per-day level.

Two companies, Vorbeck and XG Sciences, in East Lansing, Mich., have already exceeded that level of production. Lawrence T. Drzal, chief scientist at XG Sciences, notes that his company currently produces a form of graphene known as graphene nanoplatelets (small stacks of graphene sheets) at the 25-lb-per-day level and is on track to reach production capacity of 2,000 lb per day by year's end. The technique for making these nanoplatelets was developed by Drzal's research group at Michigan State University, where he is a professor of chemical engineering and materials science.

In addition to raw graphene, Vorbeck and XG Sciences offer materials made with graphene. XG Sciences, for example, works with resin and polymer compounders to provide commercial customers with new graphene-polymer composites. Michael R. Knox, XG Sciences' president and CEO, explains that depending on the material's intended use—for example to manufacture parts for the automotive and aerospace industries—polymers may be blended with graphene nanoplatelets to increase stiffness, electrical conductivity, and thermal stability or to reduce solvent and gas permeability relative to the pure polymer.

Graphene-based electrically conductive inks are another family of commercial products. Vorbeck makes such products under the trade name Vor-ink for the printed-electronics industry. The company also manufactures sheets and rolls of preprinted Vor-ink-based circuits.

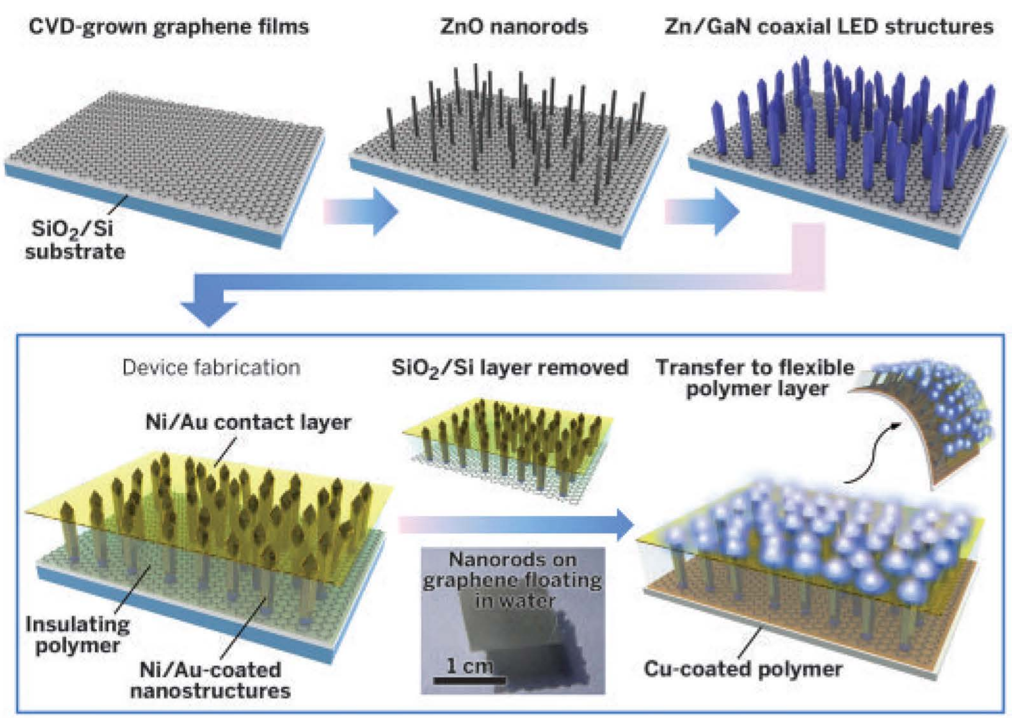
Some of those printed circuits have already made their way to retail store shelves and into customers' hands. These circuits don't sit deep inside the electronic brains of flexible, wearable computers or other futuristic devices. Rather, they are embedded in the cardboard packaging that holds small electronic gadgets, such as memory cards and USB sticks, and other consumer items. Specifically, Vorbeck has teamed up with MeadWestvaco (MWV), a multinational packaging company with headquarters in Richmond, Va., to develop graphene-based printed circuits that are central to a line of theft- and tamper-resistant packaging products marketed as Natralock security packaging.

According to David W. Miller, MWV's global director for security packaging systems, the company is about to conduct its second multistore trial with a major retailer. He adds that this type of product can be expected to appear regularly on retail store shelves starting in early 2012.

The security packaging is made from a tear-resistant paperboard and a transparent plastic piece that holds the retail product such that it can easily be seen, held, and examined by customers, Miller explains. The security circuit, in this case printed on a label with graphene ink, is sandwiched together with the product between cardboard sheets (and therefore not visible to the customer) and electrically connects the product to the package and to a small electronic alarm module.

If a shoplifter tampers with, tears, or cuts the paperboard or cuts through the plastic window and removes the product but leaves the paperboard intact, an alarm attached to the package will sound. Likewise, if someone tries to steal the item without damaging or opening the packaging material in the store, the security system can be set to sound the alarm on the package and also trip the store alarm as the thief

SUPPLE The optoelectronic properties of ZnO/GaN core-shell nanorods can be exploited in flexible LEDs by fabricating the devices on an ultrathin graphene film.



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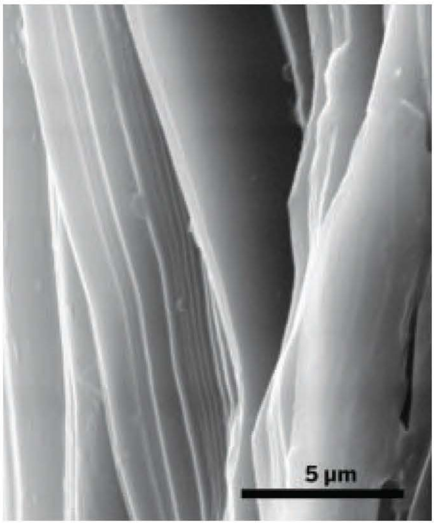
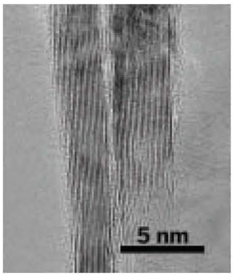


LAWRENCE T. DRZAL/MICHIGAN STATE



STACKED These electron micrographs reveal that each micrometer-scale carbon sheet in the wide-view image consists of a pile of nanometer-thin graphene platelets.

passes through the store's security gates.

Compared with other antitheft strategies, such as locking products in display cabinets or attaching the clunky security devices often found on clothing, MWV's printed-electronic device is unobtrusive, Miller says, and doesn't compromise the appearance of the product or the customer's access to it. "The graphene ink is the enabling factor that makes it all happen," he asserts.

Also, compared with other conductive inks, including ones made from silver particles, graphene inks do not need to be heated to sinter the particles to make the printed lines and traces conducting. Skipping that step simplifies manufacturing and lowers costs. Furthermore, Miller says, "we find that graphene forms a strong conductive circuit that tolerates flexing and bending and stands up well to the rigors of transportation and the retail environment."

GRAPHENE SUPPLIERS tend to be guarded about naming potential customers or commercial partners, but Lettow reveals that Vorbeck has been working with other companies in the printed-electronics industry, including Conductive Technologies, in York, Pa., and Topflight, in Glen Rock, Pa., to develop graphene-based printed-circuit products that are expected to hit the market in 2012.

Meanwhile, XG Sciences announced in June and October, respectively, that it had finalized multi-million-dollar agreements with South Korea's Posco, one of the world's largest steel producers, and with Boston-based Cabot Corp., a major manufacturer of performance materials, to provide production licenses and detailed technical information about the manufacture of graphene nanoplatelets.

Many manufacturing details are a close-kept secret. In general, the method by which graphene is made—and there are several of them—determines the product's microscopic structure, surface area, electronic and mechanical properties, and other characteristics that dictate suitable applications.

One common method treats graphite

with strong acids and oxidizers. The procedure exfoliates graphite and yields a high-surface-area product consisting of defective oxidized crystallites. Researchers typically refer to the product as graphite oxide or graphene oxide. Oxidation is generally followed by chemical or thermal treatment, which partially reduces the material and renders it electrically conducting. Princeton University's Ilhan A. Aksay and Robert K. Prud'homme developed a modified version of that procedure to more thoroughly oxidize graphite and functionalize it with hydroxyl and epoxy groups. Vorbeck holds an exclusive license to that technology, which yields mainly single-layer wrinkled graphene sheets.

XG Sciences, in contrast, does not use the graphene oxide route to prepare its graphene. Instead, according to Knox, the company uses a proprietary process to drive an intercalating compound between the layers of the graphite starting material and follows that step with rapid microwave-driven heating. The heat vaporizes the intercalant, which generates high internal pressures, which, in turn, expand and exfoliate the graphite. The procedure produces nanoplatelets that measure from 5 to 25 µm in diameter and roughly 5 nm (about 10 layers) in thickness.

Much thinner and more pristine graphene films are made by various chemical vapor deposition (CVD) methods. The films can also be isolated from thin graphite flakes by successively splitting the flakes apart with adhesive tape. The Scotch tape method, as it's known in the field, was central to the Nobel Prize work.

The rougher forms of graphene tend to be used in composite materials and energy storage devices. The CVD-quality samples generally play a key role in advanced electronics. Regardless of preparation method, graphene samples are accessible to any lab. And that availability has led to a growing torrent of journal papers reporting results of application studies.

In the energy storage arena, for example, last year, Jun Liu and coworkers at Pacific Northwest National Laboratory (PNNL) and Aksay and coworkers at Princeton developed a surfactant-based self-assembly method to make graphene-metal oxide films and evaluated their utility as lithium-ion battery anodes. In a study demonstrating the structural control afforded by the method, the team found that graphene-tin oxide films' specific energy values nearly match the theoretical one for the lithium insertion and extraction process. They also found that the material remains electrochemically stable over the course of 100 charge/discharge cycles (*ACS Nano*, DOI: 10.1021/nn901819n).

And just last month, the PNNL team together with Aksay reported a procedure to convert functionalized graphene sheets into a new material endowed with a three-dimensional network of large (submicrometer-sized) interconnected tunnels featuring walls with nanosized pores. From that material, which is shown on the cover of this issue, the team fashioned an electrode for a lithium-air battery, a power system widely studied for electric-vehicle use (C&EN, Nov. 22, 2010, page 29).

The group found that the battery provides a record-breaking charge capacity of 15,000 milliampere hours per gram of carbon in a cell tested with pure oxygen. That characteristic corresponds to an energy density three times greater than that of state-of-the-art Li-ion batteries. They attribute those results to the electrode's unique porosity and surface chemistry, which facilitate rapid oxygen diffusion and provide numerous sites for $Li-O_2$ reactions (*Nano Lett.*, DOI: 10.1021/nl203332e).

VORBECK MATERIALS

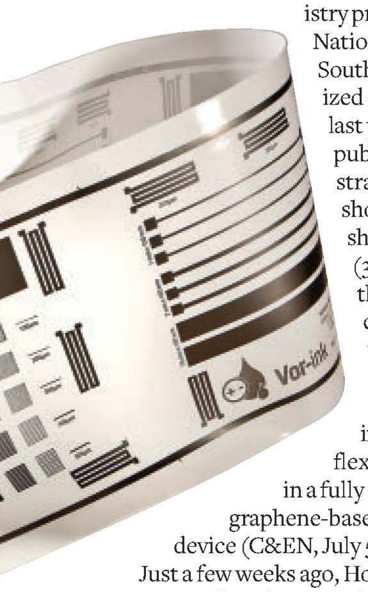
IN STORES NOW Made with electrically conductive graphene-based ink, printed-circuit labels like the ones shown here are being tested in national retail stores in antitheft/antitamper packaging.

IN ANOTHER ENERGY storage advance, Rodney S. Ruoff and coworkers at the University of Texas, Austin, developed a microwave-KOH treatment to convert graphite oxide to a porous form of graphene with exceptionally high surface area. The group found that supercapacitors made from the new material significantly outperform commercial activated-carbon supercapacitors in terms of energy and power density (*Science*, DOI: 10.1126/science.1200770). Ruoff's earlier graphene work is the basis of the technology portfolio of Graphene Energy, a start-up company that was formed

“Graphene forms a strong conductive circuit that tolerates flexing and bending and stands up well.”

to commercialize graphene-based supercapacitors.

One attractive feature of graphene is that it can be flexed and rolled yet remain electrically conductive. Byung Hee Hong, a chemistry professor at Seoul National University, in South Korea, capitalized on that property last year in a highly publicized demonstration. His team showed that large sheets of graphene (30 inches along the diagonal) could be made via an industrial-style roll-to-roll process and incorporated as flexible electrodes in a fully functioning graphene-based touch-screen device (C&EN, July 5, 2010, page 31).



Just a few weeks ago, Hong and coworkers at Sungkyunkwan University in Suwon and Seoul National University reported a method to impart flexibility to nanostructured inorganic light-emitting diodes. Inorganic LEDs are generally rigid, yet they exhibit useful optoelectronic and other properties not found in organic LEDs, which can tolerate flexing and stretching.

To get the best of both worlds and broaden the range of possible applications, the group grew a forest of GaN/ZnO core-shell nanorods on a graphene film supported on SiO_2/Si. After filling the space between the rods with an insulating polymer and depositing a metal film on top of the nanorod forest, the team etched away the SiO_2/Si layer and transferred the assembly to a flexible support. The nanostructured LED worked reliably without significant degradation in performance throughout flexing tests, the team reported (*Adv. Mater.*, DOI: 10.1002/adma.201102407).

Graphene’s flexibility, coupled with its transparency, makes the ultrathin carbon material a popular candidate to replace expensive indium tin oxide (ITO), the most common transparent electrode material in organic solar cells. But simply swapping graphene for ITO will reduce the solar cell’s power conversion efficiency (ratio of light in to electricity out) because of several factors including an energy mismatch between graphene and adjacent layers.

To address that problem, National University of Singapore chemist Kian Ping Loh and coworkers modified the graphene interface in a commonly studied organic solar cell. Specifically, they inserted a layer each of MoO_3, a polythiophene, and poly(styrenesulfonate) between the graphene anode and the photoactive layer. As a result, the custom cell reached an efficiency 83% of that seen in control devices made with ITO anodes (*Adv. Mater.*, DOI: 10.1002/adma.201003673).

WITH SO MANY graphene application papers being published now and a steady stream of media reports touting graphene as the miracle material that may replace silicon, it’s easy to get lost in the hype. Phaedon Avouris, manager of nanometer-scale science and technology at IBM’s Thomas J. Watson Research Center in Yorktown Heights, N.Y., is quick to help with a reality check. Earlier this month, at the AVS science and technology conference in Nashville, Avouris acknowledged that “graphene has a number of extremely useful properties, including very fast electron mobility and high mechanical strength.” But many of the extreme values that have been reported apply only to isolated graphene, he asserted. “We need to study graphene’s properties under the complex conditions that are present in real technological devices,” Avouris stressed.

Other researchers also sound a note of caution. “Graphene has great potential for some applications, but it’s not the solution for everything,” says PNNL’s Liu. And for any application to be successful, extensive research is needed, and that requires a lot of time. In the electronics industry, Hong says, it often takes well over a decade from the time a new material is discovered until it is optimized and then commercialized in technology. These graphene developments “are a nice start,” he says, “but we’re just at the beginning.” ■