***NATURE* | OUTLOOK**

Come into the light

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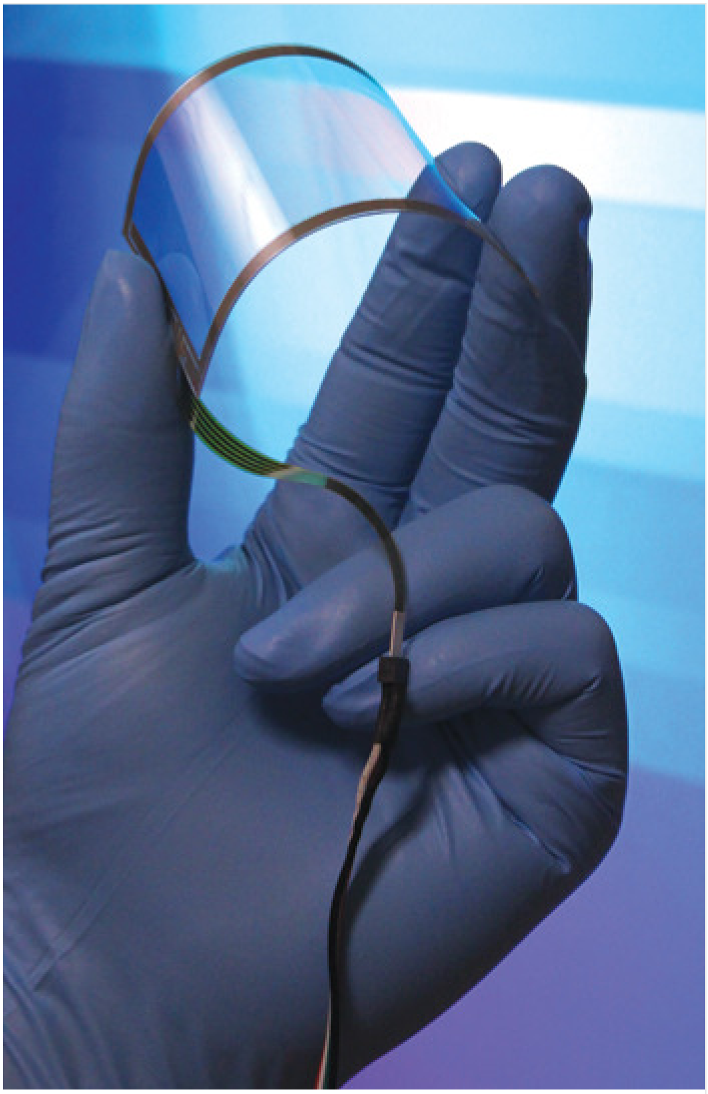
Transparency across the spectrum combined with electronic prowess makes graphene an ideal photonic material.



BYUNG HEE HONG

creens with a graphene electrode could bring flexibility to mobile
and other devices.

Graphene's first major appearances outside laboratories may be at the intersection of electronics and optics, in the form of transparent electrodes. Such electrodes — which carry current but allow light to pass through — let touch screens operate, collect current from solar cells without blocking the light needed to produce that current, and inject current to power organic light-emitting diodes (OLEDs) while allowing most of the photons to escape.

Much graphene research has focused on the material's remarkable electronic abilities and the possibility of using it to build transistors. However, it competes there with a well-established technology — silicon. As James Tour, a chemist at Rice University in Houston, Texas, puts it: “Silicon has had a 50-year head start, trillions of dollars and millions of person years.” So some researchers are starting to explore possibilities that combine graphene's electronic properties with its light-handling characteristics, as well as other attractive properties such as strength and flexibility. Transparent electrodes today generally rely on indium tin oxide (ITO). But indium is rare, and its price is rising as demand for smartphones and tablets soars. And because ITO is brittle, it must be deposited on an unbending surface (usually glass), thus placing constraints on device design. With a thin film of graphene as a conductive material, manufacturers could build flexible organic solar cells; OLED panels could be wrapped around furniture, automobile frames or a wrist. Graphene electrodes could make possible light-weight smartphones that could be folded or rolled up and whose screen won't crack when dropped. At the Consumer Electronics Show in early 2011, Korean electronics firm Samsung displayed a flexible active-matrix OLED phone screen based on graphene, but the company has not announced any products incorporating this technology.

Tour concedes that graphene's performance characteristics are not as good as ITO's, at least not yet. A thin film of ITO lets about 90% of the light pass through it, and has electrical resistance of 50 ohms. A single-layer sheet of pristine graphene allows more light through — 97.7% — but has far higher resistance, between 2,000 and 5,000 ohms. Adding more layers of graphene improves resistance but worsens transparency; four layers provide transparency roughly comparable to ITO's but, at 350 ohms, it still has seven times the resistance.

But graphene may not need to be as good electrically as ITO to get into the marketplace — being cheaper may be enough. And in the meantime, researchers are working to enhance the carbon monolayer's performance. Tour is building a touchscreen that contains a thin mesh of aluminium nanowires between the substrate and the graphene. Only 5 micrometres in diameter, the wires are too slender to block light but they make the device dramatically more conductive. A screen with 90% transparency now has a resistance of only 20 ohms. Researchers at Samsung and at Sungkyunkwan University in Seoul have collaborated to obtain similar results — 90% transparency with 30 ohms resistance — by mixing in nitric acid. And these South Korean groups have shown they can produce sheets of the improved graphene that measure 30 inches diagonally, using a roll-to-roll process that would be convenient for manufacturing.

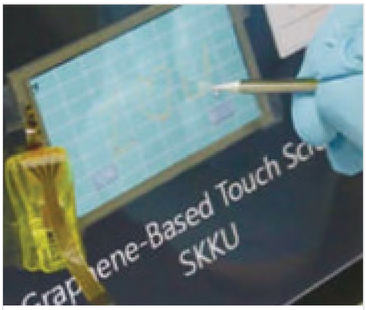
Finding efficient production processes is part of the challenge of introducing graphene transparent electrodes. Tour has devised a method to create thin ribbons of graphene by treating carbon nanotubes with sulphuric acid, causing them to unzip into ribbons. He then attaches to the ribbons' edges molecular groups that allow the material to be suspended in a solution and sprayed onto a surface. This approach could allow transparent electrodes to be painted onto large-area solar cells or OLEDs, potentially providing an inexpensive alternative to silicon solar cells.

Andrea Ferrari, a nanotechnologist at the University of Cambridge in the United Kingdom, has made graphene-based inks that an inkjet printer can use to make transparent electrodes and circuits; graphene ink and polymers could be used to create thin-film solar cells, he suggests. These wouldn't convert as much light to electricity as a silicon solar cell, but because they're so lightweight and transparent they could be installed on the facades of buildings, capturing sunlight that would otherwise go to waste without inducing any structural strain or ruining the aesthetics. A thin-film solar cell could be transparent enough to cover a window pane, yet still produce enough energy to make a dent in an electricity bill. Filling niches where silicon isn't appropriate could be a small but still valuable role for graphene, Ferrari says. “Even though it works much worse than the state of the art, it has the advantage of being flexible and cheap.”

Gaps in the spectrum

Graphene's most attractive optical property, according to Ferrari, is that it “works at absolutely any wavelength whatsoever”. That is, the material absorbs the same fraction of light — roughly 2.3% — all across the spectrum, from the ultraviolet into the far infrared. This property arises from the electronic structure of graphene: it lacks a bandgap — a range of energy states where electrons are prohibited from existing. Graphene's ability to absorb across the spectrum is important because the way light interacts with different materials — whether it's absorbed or scattered or passes though — varies depending on its wavelength. One wavelength may be ideal for cutting a certain material, another for detecting particular organic molecules. But at some wavelengths, there's no device to perform those tasks, at least one that isn't prohibitively expensive. Much of the electromagnetic spectrum, Ferrari notes, has “never been exploited, because it's hard to make semiconductors that work at those wavelengths.”

One such untapped portion of the spectrum is between the far infrared and microwaves, or frequencies between about 100 and 10,000 gigahertz (0.1–10 terahertz). Because such terahertz radiation penetrates a wide variety of materials but is non-ionizing, it has potential applications in security scans, environmental sensing, and medical imaging. Currently, however, sources and detectors that operate at those frequencies are few and complex; some terahertz detectors require cryogenic cooling, whereas a graphene detector could work at room temperature. “Some people refer to it as the last gap in the electromagnetic wavelengths,” says physicist Feng Wang, head of the Ultrafast Nano-Optics Group at the University of California, Berkeley.



NATURE NANOTECHNOLOGY

A graphene-based touch screen in operation.

Wang built a terahertz detector based on nanoribbons of graphene ranging in width between 1 and 4 micrometres. The detector is based on plasmon resonance: when light strikes a material whose electrons resonate with a frequency that matches the light's wavelength, the result is oscillations in electron density called plasmons, which can enhance the strength of a signal. (The colours in stained glass windows are so vibrant because of plasmon resonance between visible light and metal nanoparticles embedded in the glass.) In graphene, this plasmon resonance happens at terahertz frequencies. Wang designs devices to detect particular frequencies by choosing the width of the ribbons, and then further tunes the device by applying an electrical field. Creating such a detector is the beginning of developing a set of tools for the terahertz range, he says.

Graphene may be valuable not only as a detector of terahertz radiation, but also as a source, Wang says. There are already quantum cascade lasers that emit at frequencies of 10 to 100 THz. The most useful frequencies, however, lie between about 500 GHz and 4 THz, and the only existing sources in that range are limited to very low output power. Wang points out that as researchers push to create faster transistors that operate at these speeds, they could in effect be creating an emission source in that range as well — just as conventional megahertz-speed transistors produce radio waves. Pushing emitters to higher and higher frequencies opens up the possibility of higher bandwidth communications.

Although the terahertz range is the area that's most sorely lacking emitters and detectors, graphene could fill in other gaps in the spectrum as well, because “you have a sort of universal detector”, says Phaedon Avouris, head of the nanoscale science and technology group at IBM's Watson Research Center in Yorktown Heights, New York. Current technology does not offer fast photodetectors at mid- to far-infrared wavelengths; Avouris's team built an experimental graphene-based detector for this region of the spectrum that operates at a speed of 40 GHz. And, Avouris contends, because of imperfect measurement tools, it's possible that the graphene device could actually operate at 500 GHz or higher.

As for emitters, Ferrari says graphene might soon be used in ultrafast lasers. Such lasers produce short, high-energy bursts of light, lasting only picoseconds (trillionths of a second) or femtoseconds (thousandths of a picosecond). Delivering a lot of energy in a short burst lets the lasers cut very precisely without damaging nearby material or tissue; they're used in applications from eye surgery to printed-circuit-board processing. Most ultrafast lasers use a technique called mode-locking, in which a device known as a saturable absorber soaks up continuous laser emission and releases it in a series of pulses. The absorbers are usually semiconductor mirrors. But such systems are complex to build, and they generally emit light at only a narrow range of wavelengths. Using graphene as the saturable absorber would not only allow a simpler design but also permit broader spectrum operation.

Small and fast

In addition to emitting and detecting light, photonics systems often require an optical modulator, which encodes signals onto light beams. Optical telecommunications use a modulator built of lithium niobate, and that's unlikely to be displaced for the majority of applications, says Wang. His group demonstrated a graphene modulator about 25 square micrometres in size — 4 million times smaller than a conventional modulator made from lithium niobate. Such a small device could be integrated on a computer chip for optical interconnections, replacing copper wires with light beams and clearing a bottleneck for processing speed. The modulators should also work up to 10 times faster than existing devices and, unlike lithium niobate, could be used in the mid-infrared, giving system designers more flexibility.

It will take some time to figure out the impact on photonics of these emerging graphene technologies, Ferrari says. “Graphene optoelectronics is only three years old,” he says. “We need to give it another two or three years to see where we are going.” By that time, this toddler technology might be starting to light the way forward in ways not yet conceived.

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