

Polymer-based transistors bring fully stretchable devices within reach

Researchers harnessed nanoconfinement effects to achieve elasticity and efficient charge transport in a semiconducting material.

Zhenan Bao wants to give robots the sense of touch. The Stanford University professor is among a contingent of materials scientists, chemists, and engineers who have been working to develop stretchable electronic materials that could serve as artificial skin for robotics (see *PHYSICS TODAY*, October 2008, page 18). Such materials could benefit people too, as medical sensors that can be worn like temporary tattoos or as implantable devices that could, say, monitor an internal organ without inhibiting its function.

Now Bao and her coworkers have reported their biggest advance yet in the pursuit of stretchable electronics: They've demonstrated a method for fabricating polymer films that are both stretchable and good semiconductors.¹ Comments John Rogers of the University of Illinois at Urbana-Champaign, "I don't think those two attributes had ever been found in the same material before."

The Stanford group has already fashioned their films into stretchable transistors such as the one shown in figure 1. Supple and durable, the transistors function whether they're twisted like a candy wrapper, stretched to twice their length, or jabbed with a nail.

Disorderly conduction

The notion that a polymer can be semiconducting isn't new. The first semiconducting polymers were discovered 40 years ago by Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa, who shared the 2000 Nobel Prize in Chemistry for the achievement (see *PHYSICS TODAY*, December 2000, page 19). The polymers' electronic behavior is the result of a bond structure that allows electrons to delocalize along the length of



FIGURE 1. A POLYMER TRANSISTOR, visible as a 20-mm-wide translucent patch in the film pictured here, is resilient to stretching, twisting, and poking. (Photo credit: Amir Foudeh, Jie Xu, and Sihong Wang of Zhenan Bao's group at Stanford University.)

the molecules' long backbones. But first-generation semiconducting polymers exhibited modest charge-carrier mobilities. Although electrons could zip along an individual molecule, slow intermolecular hopping limited the bulk charge transport.

To improve the polymers' performance, researchers sought to coax them

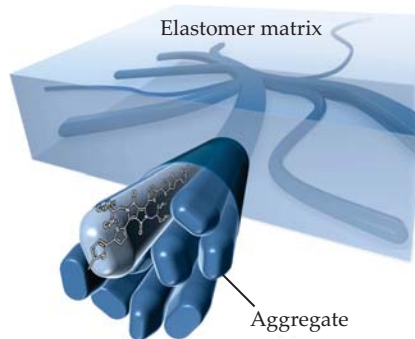


FIGURE 2. TIGHT SQUEEZE. Under certain conditions, a mixture containing a semiconducting polymer and an elastomer will spontaneously separate into a network of nanofiber aggregates embedded in an elastomer matrix. Due to confinement effects, the semiconducting nanofibers become soft and stretchy—at no cost to their electronic performance. (Adapted from ref. 1.)

to assemble into ever more perfect crystals. The thinking was that electrons should hop more efficiently on a compact, ordered lattice than they could in a disordered tangle of molecules. The strategy paid off, and by the 2000s the polymers' carrier mobilities had surpassed $1 \text{ cm}^2/\text{V}\cdot\text{s}$. Although still far below the $10^3 \text{ cm}^2/\text{V}\cdot\text{s}$ typical in commercial silicon, that was still good enough to make them legitimate candidate materials for flexible electronic devices. Before long, semiconducting polymers began showing up in LED displays, solar panels, and other commercial electronics.

Soon, however, the electronics community set their sights on stretchability. In 2006 Rogers's research group reported the fabrication of buckled silicon nanoribbons, designed to flex like an accordion when pulled.² Mounted on an elastomer substrate, the ribbons could withstand strains of up to 100%—a doubling in length. (The flexible electronics of the day typically failed at strains of around 1%.)

Polymers seemed in many ways like ideal stretchable electronic materials. Besides their inherent potential for elasticity, they would be far cheaper than nanostructured silicon to produce at scale. But decades of optimizing semiconducting

polymers for crystallinity had rendered them brittle. And it wasn't clear that one could impart stretchiness without reverting to poor electronic performance.

Around 2010, however, experimental results began to challenge the idea that long-range order was essential to efficient charge transport. Several groups discovered a class of semiconductors, known as donor-acceptor polymers, that showed high carrier mobilities despite their apparent lack of crystallinity. The polymers tended to aggregate into bundles containing segments of many molecular chains. In any given aggregate, electrons could easily hop between molecules, just as they would in a crystal. If the aggregates formed a connected network and had diameters larger than the typical electron mean free path—roughly 1 nm—then the polymer transported charge with efficiencies rivaling those of pristine crystals.

Bao saw in that revelation a golden opportunity. Aware of the vast body of fundamental research on nanoconfined polymers, she knew that a polymer's mechanical properties changed dramatically if the polymer was constricted to, say, a nanopore or nanochannel: It became softer, more ductile, and less prone to cracking—all ideal qualities for stretchable electronics. She thought if she could get a donor-acceptor polymer to form a network of aggregates inside a porous elastic medium, she could create a semiconductor that would stretch like rubber but transport charge like a crystal.

A perfect blend

The theory of phase separation offered Bao and her coworkers a potentially convenient way to implement the idea. Mixed in the right proportions, certain combinations of polymers separate spontaneously into a matrix-embedded network of nanofibers. The trick would be to pair a semiconducting polymer with a soft elastomer such that the semiconducting polymer isolated itself in the nanofiber domain, as illustrated in figure 2. Because phase separation theory for semiconducting polymers is still relatively immature, however, determining which polymers and elastomers to pair, and in which proportions, took patient trial and error.

"We tested a lot of materials—some

from a group in South Korea, some from a group in Hong Kong, and some that we synthesized in my own lab," explains Bao. "We had some guidance from the known surface-energy parameters of different polymers, but actually obtaining the right morphology required a lot of hard work."

Ultimately, the group found success with five semiconducting polymers, all paired with the same polystyrene–

polybutylene elastomer. In their unstretched states, all five films exhibited electron mobilities on par with those of their pure, conventionally prepared counterparts; in four of the five, mobilities exceeded 1 cm²/V·s. But unlike the conventional films, the composite films could be stretched to double their length with virtually no loss in electron mobility.

Thin-film transistors fashioned from the stretchable semiconductors passed a

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preliminary test of wearability: They maintained functionality through 1000 cycles of stretching to 25% strain. The researchers used the transistors to build a primitive wearable device: a small patch, shown in figure 3, that drives the on-off switching of an LED.

To Simone Napolitano, a polymer physicist at the Université libre de Bruxelles, the achievement is an impressive application of basic research. “You always see in the introductions of papers that this fundamental work on confinement effects will bring marvelous applications, but when I actually asked around, no one could give an example of a real success story,” he says. “Bao’s group has been able to apply these ideas in a very direct way and arrive at excellent results.”

The body electric?

Last year Bao and her colleagues reported a different method for imparting stretchability to semiconducting polymers.³ The resulting films exhibited lower carrier mobilities than the new composite films do, but they had one trait that the new materials lack: Due to their hydrogen-bonding chemistry, they



FIGURE 3. FINGER FILMS. A stretchable, polymer-based thin-film transistor (TFT) worn on the knuckle of an index finger is used to control an LED on the middle finger. The transistor switches on when a sufficiently large gate voltage V_G is applied, remains on as the finger flexes, and switches off when the gate voltage is turned off. (Photo credit: Jie Xu and Sihong Wang of Zhenan Bao's group at Stanford University.)

could heal themselves. Bao thinks that by incorporating similar chemistry into the new semiconductors, she and her coworkers may be able to make them self-healing too.

But other matters will also demand the group's attention: The stretchable transistors' operating voltages, around 40 V, are still relatively high; their carrier

mobilities remain far lower than those of crystalline silicon; and techniques for patterning them into circuits will have to be developed essentially from scratch. Those patterning techniques are unlikely to rival the exquisitely honed methods developed for silicon. “In terms of cost per transistor,” says Bao, “I don’t think we’ll be able to beat silicon. The feature size is so small and the design is so sophisticated.”

Still, says Bao, polymer-based electronics will have significant advantages in applications that demand sensors distributed over large areas or that call for electronics in close contact with skin or soft tissue. “They can be used to make simple circuits that amplify and condition sensor signals, which could then be wirelessly transmitted and processed using silicon chips,” she explains. “We could imagine potentially having a whole bodysuit made of stretchable electronics.”

Ashley G. Smart

References

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Electron diffraction sees hydrogen atoms

The detection of the small, light atoms heralds the emergence of the technique as a powerful crystallographic tool.

For finding the atomic structures of new molecules and materials, x-ray crystallography remains the reigning technique of choice. But it's hampered by a major limitation: Its simplest and most powerful form requires a crystalline specimen tens of microns on a side—a size that's beyond crystal growers' reach for many substances. The size requirement results from two factors: the relatively weak scattering of x rays off atoms in the crystal and the impracticality of focusing x rays onto a submicron spot.

Electrons, because of their charge, scatter orders of magnitude more strongly

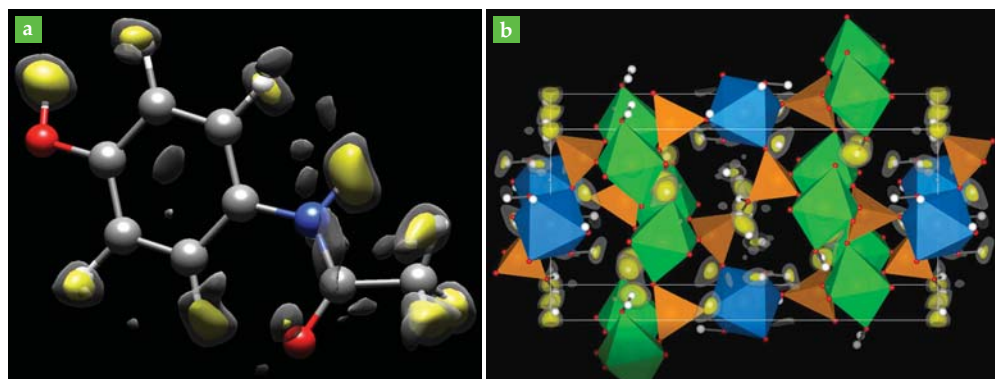


FIGURE 1. STRUCTURAL MODELS of (a) paracetamol and (b) framework cobalt aluminophosphate, derived from electron-diffraction data. Non-hydrogen atoms are shown explicitly, and the hydrogen-atom positions are established from electrostatic potential peaks. Large peaks are shown in yellow and smaller ones in gray; in each case, the largest peaks agree well with the known or expected locations of H atoms. (Adapted from ref. 1.)

than x rays do, and they can be focused much more tightly. Electron diffraction, therefore, has the potential to solve the

structures of submicron crystals, which are much easier to grow than larger ones. But the strong scattering has also been