CONNECTING THE QUANTUM DOTS

Optoelectronic materials that can be applied like paint will yield cheap solar cells

BY EDWARD H. SARGENT

NOT SO LONG AGO, ARTISTS ROUTINELY MADE their own paints using all sorts of odd ingredients: clay, linseed oil, ground-up insects—whatever worked. It was a crude and rather ad hoc process, but the results were used to create some of the greatest paintings in the world.

Today I and other scientists are developing our own special paints. We're not trying to compete with Vermeer or Gauguin, though. We hope to create masterpieces of a more technical nature: optoelectronic components that will make for better photovoltaic cells, imaging sensors, and optical communications equipment. And we're not mixing and matching ingredients quite so haphazardly. Instead, we're using our blossoming understanding of the world of nanomaterials to design the constituents of our paints at the molecular level.

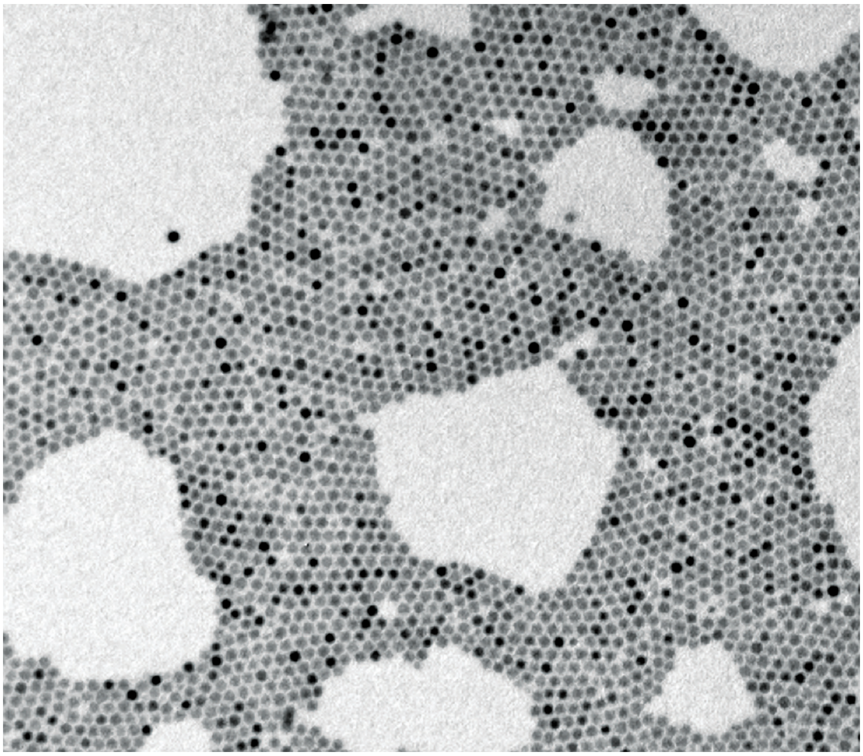
For well over a decade, researchers have been investigating ways to make optoelectronic devices by painting, spraying, or printing the active materials onto an appropriate backing. This work has generated various commercial products, including flexible photovoltaic cells and ultrathin, high-contrast displays, Sony's XEL-1 being a prime example of the latter. The organic polymers from which these devices are built absorb or emit light at visible wavelengths. But making paint-on optoelectronic materials that are sensitive to the infrared—that is, to wavelengths longer than those of visible light—opens up even further possibilities.

Infrared wavelengths are particularly valuable in solar cells. Such a cell must absorb infrared as well as visible light, lest it squander half the sun's energy. And imaging devices that are sensitive to infrared provide a remarkable way to pierce through fog and to view outdoor scenes at night, using the faint infrared glow of the upper atmosphere as illumination. And for optical communications, the equipment must operate in

ILLUSTRATION: JAMES ARCHER/ANATOMY BLUE

the infrared, because outside of certain wavelength bands in this range, glass fibers tend to absorb or distort the light sent through them. Infrared is also useful for conducting secure line-of-sight optical communications.

My colleagues and I at the University of Toronto have made great progress in recent years building devices using what are essentially paints that respond well to infrared wavelengths. This work is still in the research stage—products remain between one and five years away, depending on the application—but the pace of advance has been so swift that it's not too soon to look forward to the many exciting possibilities.



QUANTUM DOTS: This electron-microscope image shows close up the nanometer-scale quantum dots used by the author and his research team to fashion infrared-sensitive optoelectronic devices. *IMAGE: EDWARD H. SARGENT*

Yearly sales of photovoltaic panels now amount to tens of billions of dollars, and the overall energy market is measured in the trillions. The ideal that solar-cell developers are seeking is a device that is both efficient and inexpensive. Solar cells constructed from costly semiconductor wafers have yielded the greatest efficiencies—upward of 40 percent—but because they are so difficult to manufacture, such high-efficiency cells are too pricey for all but the most demanding applications, such as for the solar panels attached to spacecraft.

Photovoltaic cells made out of organic polymers cost far less, but the best efficiencies they've shown have typically been around 5 or 6 percent. That's stunningly good for something that can be manufactured so cheaply, but it's still less than the 10 percent figure experts say will be needed for this technology to take off commercially.

One common strategy to boost the efficiency of solar cells of any kind might be called the layer-cake method. The top layer of the cell absorbs photons of relatively short wavelengths, and thus of high energy, turning them into electricity. These wavelengths include visible light and some of the ultraviolet as well. Photons of lower wavelengths pass through this layer into a second one below, which is designed to absorb them and transform their energy into electric power. Some of these layer-cake designs include a third stratum at the bottom to capture the even lower-energy photons that penetrate the top two layers.

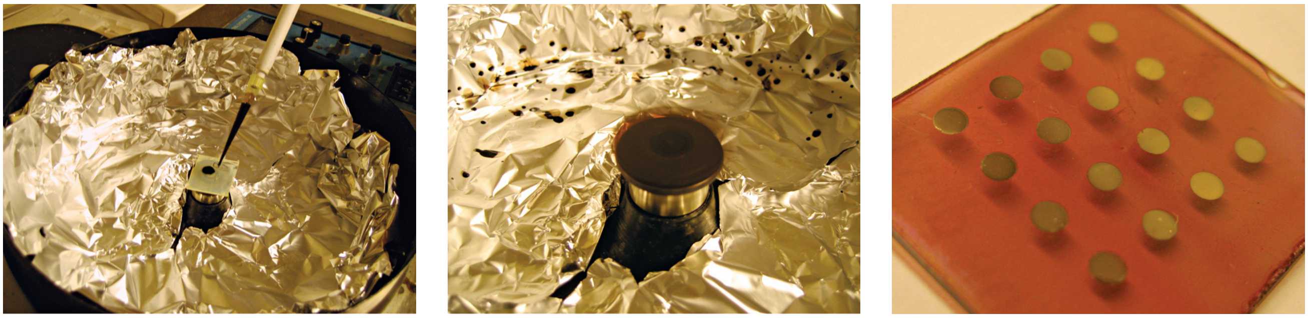
Companies making paint-on or print-on solar cells have been unable to take advantage of this strategy, however. The reason is that for years the only paintable photovoltaic materials have been based on organic molecules that are sensitive to visible wavelengths or to infrared wavelengths that are very close to the red end of the visible spectrum. So manufacturers had nothing that could be used for the lower layers.

Fortunately, the researchers on my team have lately made good progress in devising paint- or print-on solar cells sensitive to infrared wavelengths that are well separated from the visible spectrum, which is to say wavelengths of 1 micrometer or longer. Five years ago, when we first proved the concept, the efficiencies at these wavelengths for our pioneering devices were less than 1 percent. But in 2008 we showed how to boost efficiencies to just under 4 percent. That's only about a third of the efficiency figure you'd need for commercialization, but it represents a huge step forward, and we expect further progress as we continue to devise new and better designs.

Our infrared solar cells contain something called quantum dots—tiny bits of semiconducting materials that absorb or emit light. For our work, we used particles of a lead-sulfur compound. We and others are also experimenting with compounds of bismuth, tin, and indium with sulfur, selenium, and oxygen. Whereas typical optoelectronic devices operate at fixed wavelengths defined by the nature of their constituent chemistry, quantum dots can be tuned to absorb or emit light of different wavelengths simply by varying their size.

Quantum dots work this way because the electrons moving within them "feel" the nearby boundaries of the semiconductor. That's because the quantum-mechanical waves associated with these electrons are constrained by the margins of the dots. As is the case with sound vibrations reverberating in a box or microwaves reflecting back and forth in a cavity with conductive walls, the size of the container determines which wavelengths can exist within. For semiconductor quantum dots, increasing the diameter of the particles from, say, 1 to 10 nanometers shifts the action from the visible portion of the spectrum well into the infrared.

Early research in this area mostly involved embedding quantum dots relatively sparsely in a semiconducting polymer. Investigators believed that if they didn't keep the dots spaced well apart this way, they wouldn't remain tuned to the desired wavelength. But in 2007, my colleagues and I omitted the polymer entirely and merely glued the dots



THIN FILM: To create an experimental device, a drop of a quantum dot–rich solution is placed on a 2.5- by 2.5-centimeter glass plate that has already been coated with a transparent electrode [left]. Held to the central shaft by suction, the glass plate is rotated rapidly, forming a thin, even coating of quantum dots [center]. After the solvent evaporates, an array of metal electrodes is deposited on top [right]. *PHOTOS: EDWARD H. SARGENT*

together using extremely small organic molecules. We laid a quarter-micrometer film of this material on top of a transparent electrode, and although the quantum dots clumped together, they worked just fine—indeed, better than dots dispersed in a polymer did.

Such quantum dots make for good solar cells. Here's why: When a photon hits a dot, it kicks an electron free of the nanoparticle, leaving behind a deficiency of negative electric charge, or a "hole" in the lingo of semiconductor mavens. The hole acts like a positive charge; the electron is, of course, a negative charge. So they are attracted to each other and stay together in the same way that a hydrogen atom's single electron orbits its single-proton nucleus.

To get electrical current out of a quantum dot–based photovoltaic cell—or any solar cell for that matter—such electron-hole pairs must be broken up, with the electrons going in one direction (to the negative electrical contact of the cell) and the holes going in the other (to the positive contact). In conventional organic solar cells, the separation of charges comes about because two types of organics are used—one attracts mobile electrons while the other draws holes into it. When the two types of polymers are joined, electrons and holes created by the absorption of incoming light move in opposite directions, providing an electrical current to drive the load attached to the solar cell.

Whereas organic chemists focus on the materials' different affinities for electrons or holes, electrical engineers view the resultant driving force as arising from an internal electric field. In our cells, we use only one type of photosensitive material, so it's not immediately obvious where this internal electric field comes from. Remember, though, that the quantum dots are sandwiched between two electrodes. One electrode is a piece of glass coated with indium tin oxide, a transparent conductor. The other is just a metal—magnesium or aluminum in our experiments. We found that different metals produce widely different results, which leads us to believe that the internal electric field of our solar cells forms at the boundary between the metal and the quantum dots.

The great thing about these cells is that they are so easy to make. Coating glass with indium tin oxide is routine. (Liquid crystal displays, for example, have such glass electrodes.) And painting this transparent electrode with a film of quantum dots is simple enough. We did that with a technique called spin coating, which spreads a droplet of a quantum dot–rich solution evenly over a rapidly rotating surface. It's a little like the system you sometimes see kids using to drip paint on rapidly spinning cards, which spreads the paint outward into colorful patterns. All we had to do was deposit metal on top of the film to serve as the second electrode.

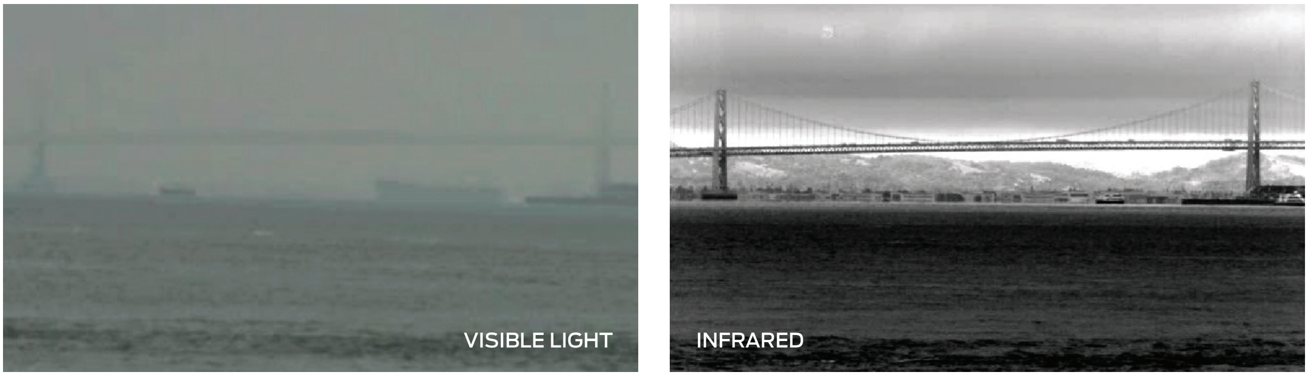
The solar cells we've built this way have very respectable efficiencies already, and we expect to do even better. But there will be other hurdles to overcome. For one, we have to find chemistries that remain stable over time. Our earliest photovoltaic cells lasted only a few minutes in air. Now we have devices that can operate for days and even weeks while exposed to regular room air. And they'll work much longer when encapsulated in an air-free plastic package. Just as it took engineers many years to figure out how to build organic light-emitting diodes that could shine for decades, developing the chemistries and packaging that will allow these solar cells to function for decades will take a great deal of time and effort. But I see no reason why it won't eventually happen.

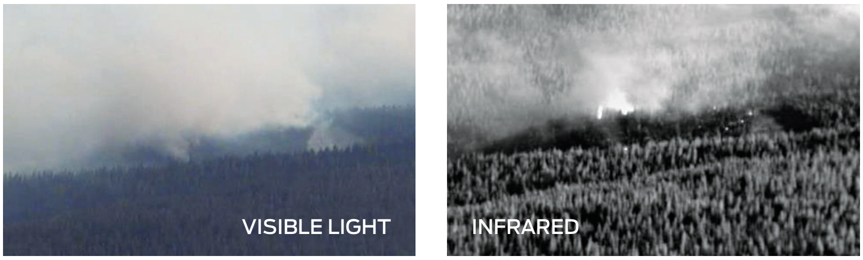
MUCH CLOSER to commercial development are quantum dots that are exquisitely sensitive to faint infrared light. With only a few years of research behind them, these devices now perform as well as the best traditional infrared detectors.

One reason these new quantum-dot sensors work so well is that they provide a built-in gain: Each photon of light produces not just one but many electrons of output current. Since 2004, when Victor I. Klimov of Los Alamos National Laboratory and his team first measured this effect in quantum dots, other scientists questioned the observations, which only indirectly showed multiple-electron generation. But this past summer my research group confirmed this phenomenon by measuring the actual current flowing in real devices. That showed beyond a shadow of a doubt that multiple-electron generation was going on.

In this regard, quantum dot–based sensors are similar to another kind of light detector: the tried-and-true photomultiplier tube. But quantum-dot detectors work very well at infrared wavelengths, while infrared photomultipliers are costly, noisy, and hard to integrate with an imaging chip.

As is the case also for photomultiplier tubes, a small amount of current will flow when a voltage is applied across these quantum-dot devices, even in complete darkness. We figured out how to minimize this background current and its fluctuations by optimizing the chemistry of the starting solution of quantum dots and the films we made from it. In the end, our devices achieved record-breaking, indeed near-ideal performance. They are as sensitive as the indium gallium arsenide photodiodes currently being used for detecting light at infrared wavelengths that are well separated from the visible spectrum.





PEA SOUP: Infrared light is less prone than visible light to scattering. So infrared wavelengths that are well separated from the visible spectrum penetrate well through fog [top two photos] and smoke [bottom two], making scenes clear that would otherwise appear murky. The cameras used to obtain such infrared pictures are, however, expensive. Quantum dot–based sensors promise to make such imagers more affordable.

PHOTOS: SENSORS UNLIMITED, PART OF GOODRICH CORP.

Paint-on technology simplifies the construction of image sensors enormously. No longer do you need to fabricate the matrix of sensor elements from exotic semiconductor materials. Instead, you can use standard silicon fabrication technology to lay down any pattern you want. A quick overcoat of the quantum-dot film then gives you an imaging device that registers infrared light.

What could you do with such infrared cameras? Lots. For example, you could use them to see through what otherwise would be an impenetrable fog—infrared light being less prone to scattering off water droplets. Or you could produce image sensors tuned to a wavelength of 1.7 µm, which matches the peak of what atmospheric physicists call hydroxyl nightglow. This is the faint infrared radiation given off by excited hydroxyl (OH) groups high up in the atmosphere.

We don't normally think about this radiation, because it's at a wavelength that's invisible to our eyes, but if it were shining down on us at visible wavelengths, the night sky would never seem very dark. Deep twilight would be about it, with only the brightest stars ever becoming visible. With an imager sensitive to this infrared wavelength, outdoor scenes at night would be easy to view. It doesn't take much imagination to appreciate the appeal of such sensors for security, police, and military operations. And because of how they will be made, these stunning new imagers needn't be particularly pricey. I can say that with confidence because I am working right now to commercialize quantum-dot image sensors.

Although a little further off, another project my research team has been working on may also prove its value in the marketplace. We've created a device that can modulate the amplitude of the infrared light reflecting off it. Such modulators can be used to add an information-bearing signal to a beam of light, typically one coming from a laser. While other research groups produced quantum-dot infrared modulators before we did, in 2008 ours became the first to break the 1-megahertz barrier. That's key, because modulation speed translates directly to the bandwidth of the communications link. And modulation rates better than 1 MHz mean that truly useful megabits-per-second communication rates are within reach.

What's more, making these modulators out of easily applied quantum dots allows you to create devices big enough to work with low levels of incident light. So it wouldn't be hard, for example, to fashion a helmet or shoulder patch that would let soldiers communicate with an aircraft shining an infrared beam on them. Unlike the case with radio, such a link would be hard to eavesdrop on.

As WITH any form of cutting-edge research, plenty of challenges remain in the field of quantum dot–based infrared optoelectronics. And the development of practical devices will require a lot more than just the kind of fundamental research that's gone on so far. Someone will also need to tackle the many engineering problems involved—how to apply the dots uniformly over large surfaces, how to stabilize the resulting films, and how to mass-produce the ultimate product. I don't mean to minimize the difficulty of these many nuts-and-bolts engineering issues. But I am optimistic, especially considering the fundamental barriers that researchers have lately overcome.

As this technology matures, the devices built with it will surely turn out to be much less expensive than the semiconductor chips or wafers used to handle these jobs today. Indeed, when the fabrication of optoelectronic devices becomes almost as easy as splashing paint on a canvas, our normal assumptions about the high cost of high-performance optoelectronic devices will be turned on its head.

Wouldn't it be grand if, for example, people no longer had to struggle with the problem of harvesting solar energy economically? If mixtures of quantum dots help to accomplish that goal, future generations will surely appreciate them more than any paints ever before devised, even those Vermeer and Gauguin once concocted. ❑

TO PROBE FURTHER Additional information about the author's research on optoelectronic devices is available at http://www.light.utoronto.ca.