Gold standard. Silicon solar cells dominate the market, but new competitors are rising fast.

SOLAR ENERGY

Can the Upstarts Top Silicon?

Several nascent technologies are improving prospects for turning the sun's rays into electricity. The success of any one of them could mean a big boost for solar power

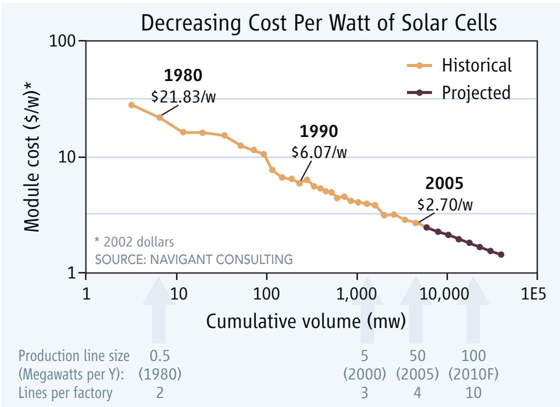
These are bright days for backers of solar power. The exuberance that previously pumped up dot-coms and biotech companies migrated in 2007 to solar energy, one of the hottest sectors in the emerging market for clean energy. Last year, solar energy companies around the globe hauled in nearly $12 billion from new stock offerings, loans, and venture capital funds. And although the markets have taken a bath in recent weeks due to investor fears about a coming recession in the United States, enthusiasm for solar's future remains strong. The industry is growing at a whopping 40% a year. And the cost of solar power is dropping and expected to rival the cost of grid-powered electricity by the middle of the next decade (see figure, right).

Still, there are clouds overhead. Solar power accounts for only a trivial fraction of the world's electricity. Silicon solar panels—which dominate the market with a 90% share—are already near their potential peak for converting solar energy to electricity and thus are unlikely to improve much more. A typical home's rooftop loaded with such cells can't produce enough power to meet the home's energy needs. That limitation increases the need for large-scale solar farms in sunny areas such as the American Southwest, which are far from large population centers. The bottom line is that the future of solar energy would be far brighter if researchers could make solar cells more efficient at converting sunlight to electricity, slash their cost, or both.

That's just what a new generation of solar-cell technologies aims to do. A raft of those technologies was on display here* late last year, as researchers reported how a broad array of recent advances in chemistry, materials science, and solid state physics are breathing new life into the field of solar-energy research. Those advances hold out the promise of solar cells with nearly double the efficiency of traditional silicon-based solar cells and of plastic versions that cost just a fraction of today's photovoltaics (PVs). "It's a really exciting time [in solar energy research]," says chemist David Ginger of the University of Washington, Seattle.

In the past few years, Ginger and others point out, solar researchers have hit upon several potential breakthrough technologies but have been stymied at turning that potential into solar cells able to beat out silicon. "The next couple of years will be important to see if we can overcome those hurdles," Ginger says. Although most of these novel cells are not yet close to commercialization, even one or two successes could dramatically change the landscape of worldwide energy production.

* Materials Research Society meeting, Boston, Massachusetts, 26–30 November 2007.



Heading for parity. Solar electricity still costs about five times as much as electricity from coal. But many experts expect economies of scale could close the gap by 2015.

Minding the gap

Beating silicon is a tall order. Although the top lab-based silicon cells now convert about 24% of the energy in sunlight into electricity, commercial cells still reach only 15% to 20%. In such traditional solar cells, photons hitting the silicon dump their energy into the semiconductor. That excites electrons, kicking them from their staid residence in the so-called valence band, where they are tightly bound to atoms, into the higher-energy conduction band, where they lead a more freewheeling existence, zipping through the material with ease. But if photons don't have enough energy to push electrons over this "band gap," the energy they carry is lost as heat. So is any energy photons carry in excess of the band gap. Given the sun's spectrum of rays and the fact that only certain red photons have the amount of energy that closely matches silicon's band gap, single silicon cells can convert at most 31% of the energy in sunlight into electricity—a boundary known as the Shockley-Queisser limit.

Engineers can boost the efficiency with a number of conventional strategies. One is to layer several light-absorbing materials that capture different portions of the solar spectrum—for example, by having one cell that absorbs mostly blue photons, while others absorb yellow and

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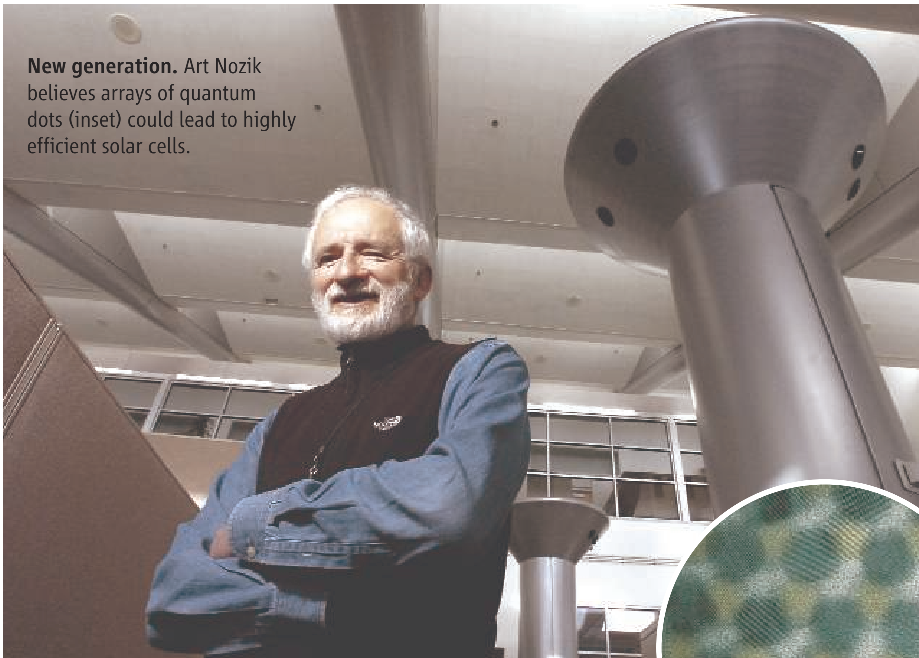
red photons. But such "tandem" cells are expensive to produce and thus are currently used primarily for high-end applications such as space flight.

But there may be other ways to capture more energy from the sun. One strategy that has drawn a lot of attention in recent years is to find materials that generate multiple electronic charges each time they absorb a photon. Traditional silicon solar cells generate just one. In them, a layer of silicon is spiked with impurity atoms so that one side attracts negatively charged electrons, while the other attracts positively charged electron vacancies, known as holes. Most light is absorbed near the junction between the two layers, creating electrons and holes that are immediately pulled in opposite directions.

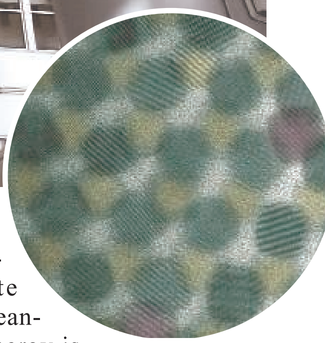
In 1997, however, chemist Arthur Nozik of the National Renewable Energy Laboratory (NREL) in Golden, Colorado, and colleagues predicted that by using tiny nanosized semiconductor particles called quantum dots to keep those opposite charges initially very close together, researchers could excite two or more electrons at a time. A paired electron and hole in close proximity, they reasoned, increases a quantum-mechanical property known as the Coulomb interaction. The greater this interaction, the more likely it is that an incoming energetic photon with at least twice the band-gap energy will create two electron-hole pairs with exactly the energy of the band gap—instead of one electron-hole pair with excess energy above the band gap, the other possible outcome that quantum mechanics allows. At least that's how Nozik and his colleagues see it. Several other models of multiple-electron excitation exist, and theorists are still debating just what is behind the effect.

Four years ago, researchers led by Victor Klimov of Los Alamos National Laboratory in New Mexico reported the first spectroscopic evidence showing that multiple electron-hole pairs, known as excitons, were indeed generated in certain quantum dots. Nozik's team and others have since found the same effect in silicon and other types of quantum dots. And according to calculations by Nozik and NREL colleague Mark Hanna, the multiple exciton generation (MEG)–based solar cells hit with unconcentrated sunlight have a maximum theoretical efficiency of 44%. Using special lenses and mirrors to concentrate the sunlight 500-fold, they predicted, could boost the theoretical efficiency to about 80%—twice that of conventional cells hit with concentrated sunlight.

But reaching those higher efficiencies isn't easy. "One big hang-up is that no one has yet shown that you can extract those extra electrons," Nozik says. To harvest electricity, researchers must first break apart the pairs of electrons and holes, using an electric field across the cell to attract the opposite charges. That must happen fast, as electrons in excitons will collapse back into their holes within about 100 trillionths of a second if left side by side. If those charges can be separated, they must hop between successive quantum dots to find their way to an electrode, again without encountering an oppositely charged counterpart along the way. Unfortunately, the organic chemical coatings used to keep quantum dots stable and intact push the particles apart from one another, slowing down the charges.



New generation. Art Nozik believes arrays of quantum dots (inset) could lead to highly efficient solar cells.



CREDITS: MARTY CAIVANO/DAILY CAMERA; (INSET) A. NOZIK

Still, Nozik's group seems to be making progress. At the Materials Research Society meeting, Nozik reported preliminary results on solar cells made with arrays of lead selenide quantum dots. In such cells, a layer of quantum dots, and their organic coats, is spread between two electrodes. According to Nozik, spectroscopic studies indicate that two or three excitons are generated for every photon the dots absorb. And the researchers managed to separate the charges and get many of the electrons out, boosting the efficiency of the solar cells to about 2.5%, up from 1.62% from previous MEG-based cells.

To boost that efficiency further, Nozik says, one key will be to pack quantum dots closer together and in more regular arrays, making it easier for electronic charges to hop from one dot to the next to the electrodes where they are collected. Nozik's group is already experimenting with strategies for doing that, such as shrinking the organic groups that coat each dot and keep them separated from one another. Another needed improvement will be to find quantum dot materials better at generating multiple excitons. Nozik's lead selenide dots, for example, must be hit with about 2.5 times the energy of a single excited electron to generate two excitons, meaning that extra energy is wasted. In the November 2007 issue of *Nano Letters*, however, Klimov and his colleagues reported that dots made from indium arsenide generate two excitons almost as soon as the energy of the incoming photons exceeds twice the band gap.

Other groups are hoping to use quantum dots as steppingstones to cross the band gap in conventional semiconductor materials. The idea is to seed a semiconductor with an array of quantum dots, which will absorb photons that have too little energy to raise electrons above the band gap. The photons would excite electrons in the quantum dots to an intermediate level between the valence and conduction bands, then a hit from a second low-energy photon would boost them the rest of the way into the conduction band.

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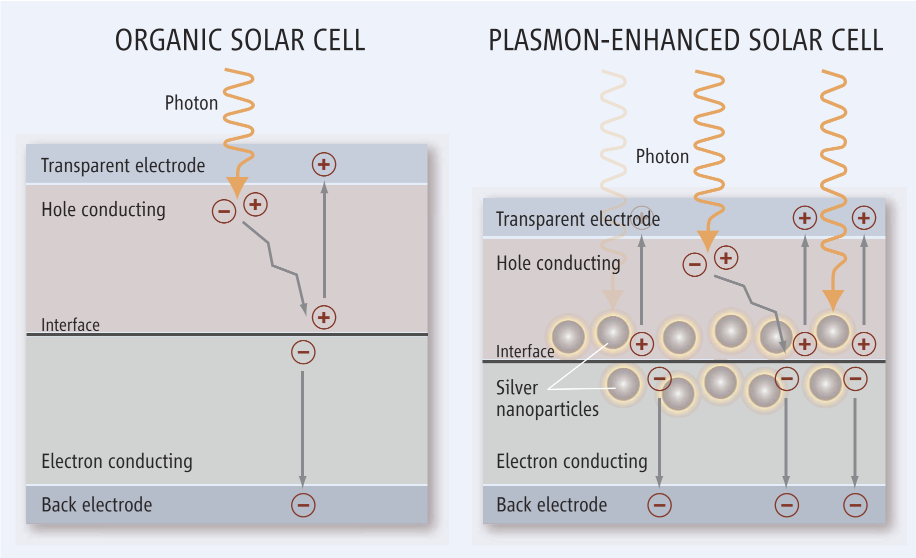
Theoretical work by Antonio Luque of the Universidad Politécnica de Madrid in Spain suggests that such cells could achieve a maximum efficiency of 63% under concentrated sunlight. But here, too, the potential has been hard to realize. In practice, adding quantum dots to materials such as an alloy of gallium arsenide seems to cause more losses than gains; the quantum dots also seem to attract electrons and holes and promote their recombination, thus losing the excess energy as heat.

Last year, Stephen Forrest and Guodan Wei, both of the University of Michigan, Ann Arbor, suggested a way around that problem: designing energetic barriers into their solar cells that discourage free charges from migrating to the quantum dots. At the meeting, Andrew Gordon Norman of NREL reported that his team has managed to grow such structures. The cells didn't outperform conventional GaAs cells, because too few quantum dots were packed into the structure to absorb enough low-energy photons to offset recombination losses. But Norman says he's working on solving that problem.

A silver lining

Many of the approaches to boosting the efficiency of solar cells require expensive materials or manufacturing techniques, so they are likely to increase capital costs. Some groups are exploring low-cost alternatives: light-absorbing plastics or other organic materials that can be processed without the expensive vacuum deposition machines most inorganics require. Unfortunately, organics waste much of the incoming light because they typically absorb only a relatively narrow range of frequencies in the solar spectrum. The key to boosting their efficiency, some groups believe, could be precious metals.

A layer of tiny silver or other metal nanoparticles added to a solar cell encourages an effect known as surface plasmon resonance, in which light triggers a collective excitation of electrons on the metal's surface. This causes the nanoparticles to act like antennas, capturing additional energy and funneling it to the active layer of the material to excite extra electrons (see figure). At the meeting, electrical engineer Peter Peumans of Stanford University in Palo Alto, California, reported that when he and his colleagues added a layer of silver nanoparticles atop a conventional organic solar cell, they increased the efficiency of the device by 40%. Even though the overall efficiency of Peumans's devices is still dismally low—less than 1%—Ginger says the big jump in efficiency is "very promising."



Better reception. In an organic solar cell, sunlight frees an electron (–) and an electron vacancy, or hole (+), which migrate to the border between different materials and then to oppositely charged electrodes (*left*). Adding metal nanoparticles (*right*) increases the light absorption and the number of charges generated.

Peumans notes that the silver nanoparticles work best when placed at the interface between two semiconducting layers in organic solar cells, one of which preferentially conducts electrons, the other, holes. In organic solar cells, excitons must migrate to just such an interface so that they can split into separate charges, which are then steered to opposite electrodes.

Other researchers have found in recent years that they can increase the efficiency of their organic solar cells by expanding the surface area of this interface. Instead of having flat layers lying atop one another like pages in a book, they create roughened layers that interpenetrate one another, a configuration known as a bulk heterojunction. Last year, researchers led by physicist Alan Heeger of the University of California, Santa Barbara, reported that they could use low-cost polymers to create tandem bulk heterojunction solar cells with an overall energy conversion efficiency of 6.5% (*Science*, 13 July 2007, p. 222). At the time, Heeger said that he expected that further improvements to the cells would propel them to market within 3 years.

Researchers are pursuing several strategies to improve these cells. One approach that may pay off down the road, Peumans says, is to incorporate metal nanoparticles into the random surface in these solar cells. That's not likely to be easy, he adds. But it may be possible to outfit the nanoparticles with chemical tethers that encourage them to bind to tags designed into the interface of the material. In theory, Peumans says, that would offer researchers the best of both worlds.

In addition to improving solar cell efficiencies, researchers and companies are also working on a host of technologies to make them cheaper. Nanosolar in San Jose, California, for example, has spent millions of dollars perfecting a new roll-to-roll manufacturing technology for making solar cells from thin films of copper indium gallium selenide atop a metal foil. Although they haven't reported the efficiency of their latest cells, they began marketing them in December 2007. Konarka, another roll-to-roll solar cell company in Lowell, Massachusetts, is working on a similar technology with plastic-based PVs. Other groups, meanwhile, are pushing the boundaries on everything from replacing quantum dots with nanowires that can steer excited charges more directly to the electrodes where they are harvested to using modified ink-jet printers to spray films of quantum dots and other solar-cell materials.

For now, there appears to be no shortage of ideas about creating new high-efficiency, low-cost cells. But whether any of these ideas will have what it takes to beat silicon and revolutionize the solar business remains the field's biggest unknown. "There are a lot of ways to beat the Shockley limit on paper, but it's difficult to realize in the real world," Nozik says. So far, it's not for want of trying.

–ROBERT F. SERVICE

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