TINY CRYSTALS in solution

A Next Step for Solar

Could tiny quantum dots grown in solution make solar energy affordable for everyone? Researchers at the new Los Alamos Center for Advanced Solar Photophysics are exploring that tantalizing possibility.

Every day that goes by, greenhouse emissions from fossil fuels increase the pace of global warming. At the same time, the sun is dousing the planet with thousands of times more light energy than is needed to sustain modern civilization. The solution to global warming would seem to be a no-brainer. Just harness the power of the sun's rays and leave carbon emissions behind. If only it were that simple.

The most direct way to convert the sun's rays into electric power is with a solar cell—a thin wafer of semiconductor material sandwiched between two conducting terminals. When light strikes the cell and passes into the semiconductor, a voltage develops across the solar cell like that in a standard battery. A wire placed across the terminals allows the voltage to drive a current that can power a load. A detailed description is in "Photovoltaics: Converting Sunlight to Electricity," on the next page.

Crystalline silicon, the poster child of the electronics industry, was the photovoltaic material used in the first modern solar cell. That cell was invented at Bell Labs in the 1950s, an unexpected spinoff of transistor development. Today, these Generation-I cells, now made of crystalline silicon wafers, are the most popular cells on the market because of their efficiency.

A Generation-I cell converts up to 25 percent of the incident solar power to electric power (25 percent power-conversion efficiency). Installed solar panels (hundreds of Generation-I cells wired together) have a power-conversion efficiency of about 15 percent. That's very encouraging. When the sun is overhead, each square meter of a solar panel receives, on average, 1,000 watts of solar power, which means solar panels covering 30 square meters (only a portion of a typical roof) produce enough power (around 5 kilowatts) to run a small household.

But Generation-I panels also have a problem: cost. Solar panels for that 5-kilowatt household cost around $15,000 and up, and the whole system, including storage batteries for standalone systems or power connections for the electric grid, double that cost.

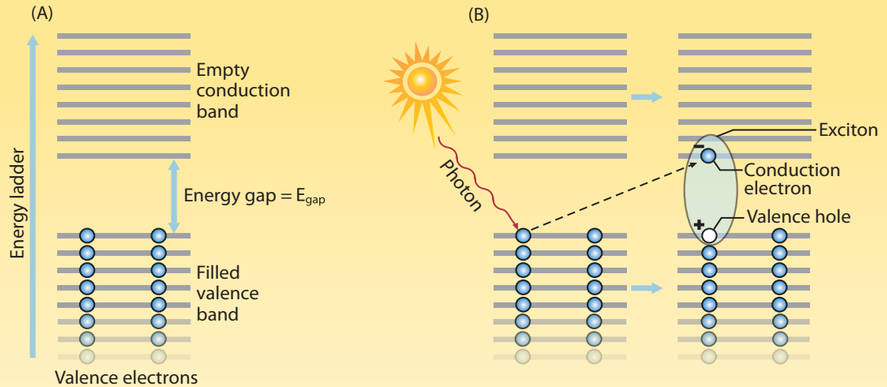
Unfortunately, it's the crystalline silicon wafers in the Generation-I cells that make the solar panels so expensive. Elaborate processes and lots of energy are required to grow large, perfect single-crystal ingots of high-purity silicon, which are then sliced into paper-thin (200-micron-thick) single-crystal wafers (a micron is a millionth of a meter). In the world of electronic devices, 200 microns (500,000 atoms) is very thick and, by industry standards, very expensive to produce.

Scientists have brought costs down in Generation-II cells by abandoning the "thick" single-crystal wafer and instead going to

thin films of different kinds of photovoltaic material, for example, amorphous (noncrystalline) silicon or cadmium telluride. Reducing the amount of material in each cell reduces the fabrication cost, but then the cells also become less efficient. Either they absorb less sunlight, or they are less efficient at transporting the charge carriers to the terminals. So while the public's interest in solar is growing, as long as electric power from solar photovoltaics remains many times more costly than power from fossil fuels, solar photovoltaics will likely remain a minor player in the energy sector. The challenge is to identify an approach that is both cheap and efficient.

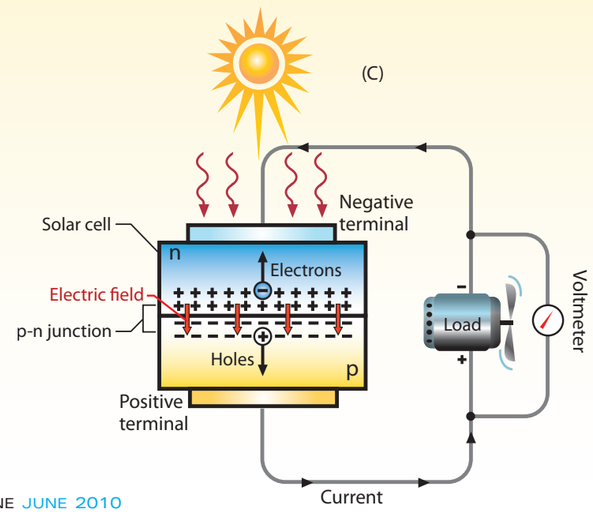
Los Alamos' Victor Klimov and other scientists worldwide are betting that intensive research in the next two decades will produce a quantum leap forward in solar technology, one that will create the higher-efficiency, lower-cost Generation-III solar cells people have been waiting for. Klimov sees the possibility of photovoltaic cells with efficiency above 20 percent and a price low enough to compete with the cost of oil and coal. To develop such things, he's turning to novel physics at the nanoscale.

Photovoltaics: Converting Sunlight to Electricity



(A) The Energy Gap—In a semiconductor, electrons (blue dots) fill up the ladder of allowed energy states to the top of the valence band. An energy region with no energy states (the energy gap) separates the highest rung of the valence band from the bottom rung of the empty conduction band. The gap has an energy value denoted by E_{gap}.

(B) Creating Excitons—An electron absorbs a photon with energy E_{gap} and jumps across the energy gap to the conduction band, where it becomes a negative-charge carrier. The electron leaves a vacancy, a hole that looks like a positive-charge carrier. The electron and hole are slightly bound together, and the pair is called an exciton.



(C) Harvesting the Charge Carriers—A crystalline silicon solar cell quickly separates the excitons' electrons and holes because the cell contains two silicon layers: a p-doped layer containing "acceptor" atoms, which tend to accept extra electrons, and an n-doped layer containing "donor" atoms, which tend to give away their electrons. When these layers are brought into contact, they form a p-n junction—electrons are exchanged, and ionized donors and acceptors create a strong electric field. It is this electric field that drives the electrons and holes apart as soon as sunlight creates them, thereby preventing recombination (in which the electron falls back into the hole, and solar energy is re-emitted as a photon). The charge carriers collect at opposite conducting terminals and flow around a circuit to power, for example, an electric motor.

Betting on Nanocrystals

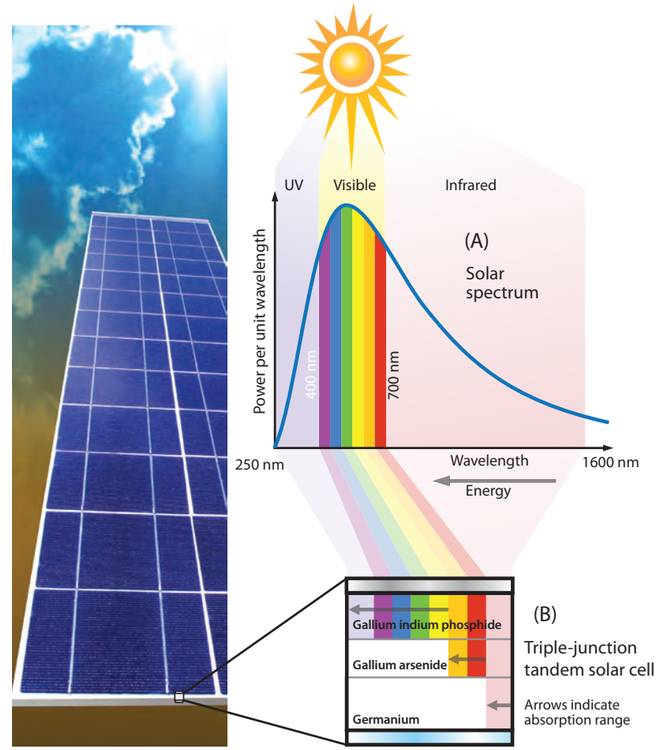
Klimov has just become director of the new Center for Advanced Solar Photophysics at Los Alamos, a collaborative effort with six other institutions: the National Renewable Energy Laboratory (NREL) in Colorado, Rice University in Texas, the University of Colorado, Colorado School of Mines, the University of California at Irvine, and the University of Minnesota. The center is one of the 46 Energy Research Frontier Centers funded by the Department of Energy to do high-risk, potentially breakthrough research for making renewable, carbon-free energy available and affordable across the globe. Of those 46 centers, 13 are devoted in whole or part to harnessing solar energy.

Klimov says, "Our center is focused on semiconductor nanostructures, mainly nanocrystal quantum dots because they're cheap to make—and that's because they can be grown and processed in solution." Klimov is a world leader in the physics of quantum dots, tiny specks of matter that each contain from 100 to 10,000 atoms and extend only 2 to 20 nanometers (billionths of a meter) in each direction.

Nanocrystal quantum dots have a number of properties that fit right in with the needs of photovoltaics. First, they are easy to grow and process. Jeff Pietryga, a leading chemist on Klimov's Los Alamos team, and other chemists at the center have refined the methods for growing nanocrystals in solution, achieving excellent uniformity in their size and composition. Making a uniform film of these can be as easy as pouring drops of crystals in solution onto a spinning surface and allowing the fluid to spread and dry. Such films can be much cheaper to fabricate than ordinary semiconductor thin films, which require expensive deposition techniques.

Second, a thin film of nanocrystals (50 to 100 nanocrystals thick) can absorb as much light as the standard single-crystal silicon wafer, which is 1,000 times thicker.

Third, nanocrystals can be grown to many different sizes, an advantage that requires some explanation.

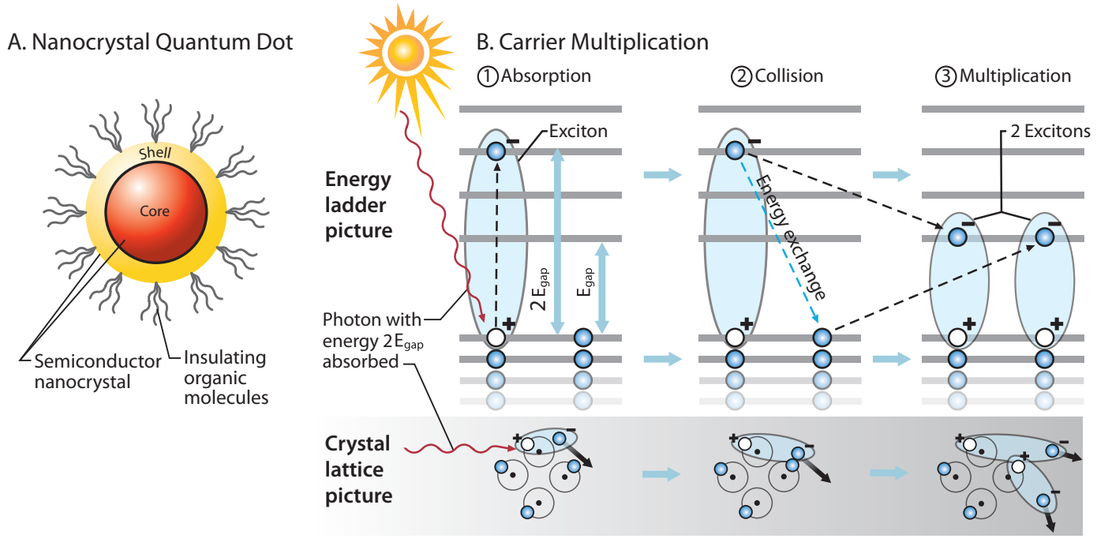


Above: (A) Sunlight contains photons with a spectrum of colors, or energies. (B) A high-efficiency tandem solar cell developed by NREL has three thin-film layers of different semiconductors. As shown, each starts absorbing light at a different wavelength (color). Together they operate like batteries in a series (the same current flows through each, and the total voltage equals the sum of their separate voltages). The cell operates at more than 40 percent power-conversion efficiency, but the expense of producing the thin-film layers limits use of the tandem solar cell to satellites and other niche applications.

Consider first how a voltage develops when light strikes a solar cell made of bulk silicon. Individual photons (quantum particles of light) are absorbed by individual electrons that are bound to atoms in the semiconductor's crystal lattice. The solar photons have the right amount of energy to free the electrons from their bound positions and give them a certain voltage. It is those freed (conduction) electrons that collect at the negative terminal of the solar cell and flow as current when the cell is placed in a circuit.

What is the "right amount" of energy to free the electrons? As shown in "Photovoltaics: Converting Sunlight to Electricity" (facing page), a semiconductor's electrons exist on an ascending hierarchy (ladder) of energy levels (allowed energy states). The ladder is divided into the valence band, for bound electrons, and the conduction band, for conduction electrons, with an energy gap between the two bands.

The bound electrons on the highest "rung" of the valence band can move to the lowest rung of the conduction band (becoming conduction electrons) only by absorbing enough energy to jump the gap—



energy equal to or greater than the amount of energy represented by the gap (E_{gap}). Solar photons have energies in that range, so a bound electron that absorbs a solar photon can take the leap, becoming a conduction electron.

But the electron does something else as well: it leaves a vacancy where it once sat in the valence band. That hole (it's in the crystal lattice) acts like a positive charge, attracting the new conduction electron's negative charge. Together, the two are called an exciton. Electricity is created when an electric field causes the conduction electrons and holes to move to opposite terminals.

In macroscopic samples of a given semiconductor, the energy gap is always the same, independent of the sample size, but in tiny nanocrystals, quantum effects cause the energy gap to vary with size: the larger the nanocrystal, the smaller its energy gap. Klimov points out that solution chemistry can be used to grow nanocrystals of a precise size, thus "tuning" the energy at which the crystals begin absorbing photons.

To take advantage of that fact, one could layer three nanocrystal thin films, each with progressively smaller nanocrystals (and therefore larger energy gaps). The smallest nanocrystals (in the top layer) would selectively convert the highest-energy photons into charge carriers at a voltage about equal to the energy gap. Lower-energy photons would pass through to the second or third layer, where they'd produce charge carriers at successively lower voltages. The total voltage would equal the sum of the voltages derived from the three layers. Thus, the layering would allow a higher voltage to be extracted from the solar spectrum and result in higher power output than is obtained from a single layer. Potentially, this three-layer device could perform as efficiently as the very costly tandem solar panels used to power satellites (see figure on p. 5).

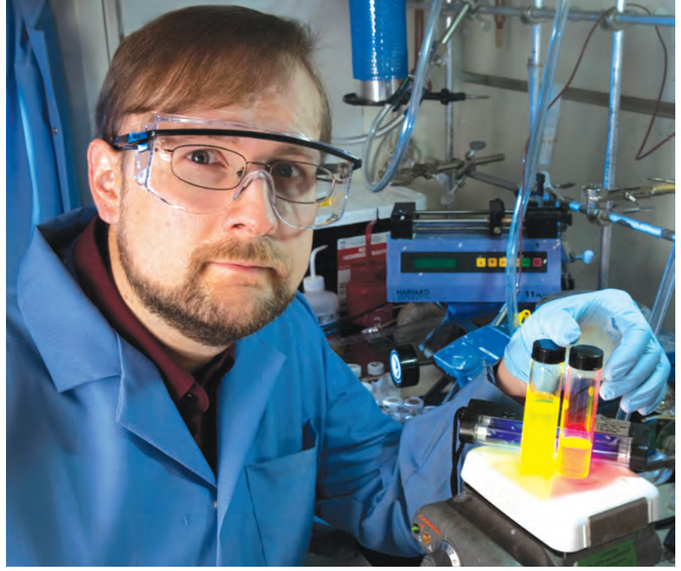
Most intriguing of all, the new center will try to exploit a number of novel nanoscale phenomena that could raise the maximum possible power-conversion efficiency of a single-layer device, dramatically increase its light-absorption properties, and circumvent present difficulties of transporting the charge carriers to the terminals.

Step One—Getting Two for One

First, the question of maximum efficiency for a single-layer device. Typically, in a macroscopic semiconductor, each photon with energy of E_{gap} or greater gets absorbed, freeing one electron. If the photon energy equals E_{gap}, it boosts an electron to the bottom rung of the conduction band, where it becomes a negative-charge carrier with a voltage equal to E_{gap}.

Surprisingly, a photon with still more energy that boosts an electron to a higher conduction rung does not result in a higher-voltage electron and potentially higher power-conversion efficiency (electric power is equal to current times voltage). Instead, that electron immediately begins to lose energy to heat through collisions with the atoms of the crystal lattice. Like the operation of a pinball machine, but in energy space not real space, each collision sets off a lattice vibration (phonon), causing the electron to lose energy and descend another rung of the energy ladder until its energy (voltage) is E_{gap}, that is, until it's sitting on the bottom rung of the conduction band. The descent takes

Above: (A) Nanocrystal quantum dots are surrounded by a layer of organic molecules (surfactants) that allows precise size control, prevent conduction electrons from getting trapped at the surface, and make nanocrystals soluble. (B) The process of carrier multiplication—the freeing of two electrons (or creation of two excitons) with one high-energy photon—is depicted two ways: on the energy ladder and within the crystal lattice. In the latter, the valence electons orbit the atomic nuclei, and the conduction electrons move freely.



Jeff Pietryga shows two vials of different-size nanocrystals, each emitting light of a different color (energy) that corresponds to the nanocrystal's size (and energy gap).

a few picoseconds (trillionths of a second) at most. Thus, irrespective of the photon energy absorbed, the generated photovoltage (and electric power) in a semiconductor photocell is the same, and a single semiconductor layer can never have 100 percent power-conversion efficiency. In fact, the maximum power-conversion efficiency is 31 percent.

"Nanocrystals can beat that limit," explains Klimov excitedly, "because when you confine the electrons to small nanocrystals, all of sudden, for each high-energy photon absorbed, you can free not just one but two or more negative-charge carriers with voltage E_{gap}. If you can transport those carriers to the terminals, you can get a higher electric current, and that's the kind of effect we're looking for."

Called carrier multiplication, this phenomenon of creating two free electrons with one high-energy photon was first measured in nanocrystals in 2004 at Los Alamos by Klimov and Richard Schaller. The original motivation for searching for this effect in nanocrystals traces back to the concept of a "phonon bottleneck." As shown in the figure on the facing page (part B) the energy ladder of a nanocrystal is different from one in a macroscopic sample; namely, the rungs are so widely spaced that the energy difference between rungs is much larger than the energy it takes to create a single phonon. An electron boosted to a high-energy rung in a nanocrystal (step 1, B), must create several phonons at once to descend to the next rung down, but that process is much slower (has lower probability) than creating a single phonon. Therefore, the "hung-up" electron with its extra energy courses back and forth through the nanocrystal and is more likely to strike a bound electron (step 2, B), boosting the latter up to the conduction band and bumping itself down to a lower rung (step 3, B). Now absorption of a single high-energy photon has created two electrons in the conduction band instead of one.

Victor Klimov, director of the Center for Advanced Solar Photophysics.

Klimov notes, however, that "while energy loss through phonon emission is likely suppressed in nanocrystals relative to bulk solids, experiments indicate that other energy-loss processes compete with carrier multiplication. Understanding those is one area of the center's research.

Klimov estimates that if carrier multiplication worked perfectly, the extra current created would raise the power output, thereby increasing the maximum possible power-conversion efficiency for a single-layer device to about 41 percent. "Right now, we seem to need two and one-half to three energy gaps of photon energy to create two excitons. We would like to learn enough of the fundamental physics to reduce that threshold to the theoretical limit given by energy conservation, which is two energy gaps for two excitons," says Klimov.

Another approach to exceeding the 31-percent limit is to increase the voltage by harvesting the "hot" (high-energy) electrons directly, before they either lose their energy to phonons or create multiple carriers. In particular, a phonon bottleneck could be used to maintain the photogenerated electrons in the hot state for times sufficient to collect those electrons at the negative terminal and send them down a wire. The hot electrons would drive a voltage that is greater than the energy gap, resulting in increased power output. Researchers for the Center for Advanced Solar Photophysics hope to develop novel nanoscale materials that exhibit a pronounced phonon bottleneck and, in addition, to develop efficient schemes for harvesting hot electrons.

Step Two—Getting Them Out There

Whether solar photons create a single conduction electron, multiple electrons, or hot electrons, the real bugaboo for nanocrystal devices is transporting, or conducting, the charge carriers to the terminals.

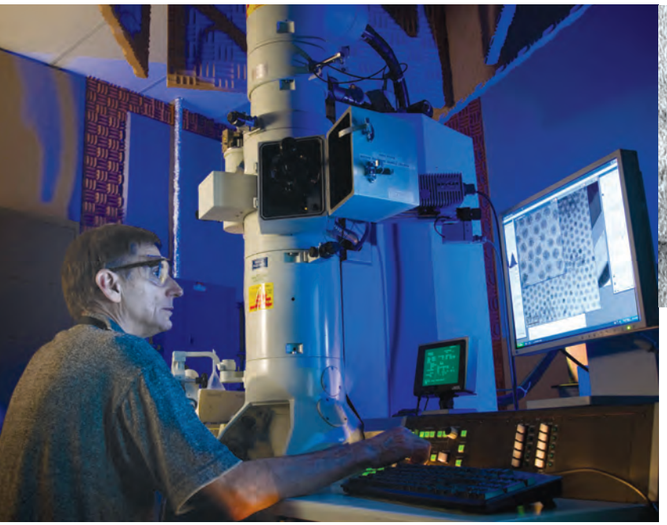
It's been mentioned that each electron is not completely free but instead slightly bound to a hole, forming an exciton. What's not been said is that these two charge carriers must be separated and transported very quickly; otherwise, the exciton will decay in less than a microsecond through recombination, the electron falling back into the hole and emitting the absorbed solar energy as a photon.

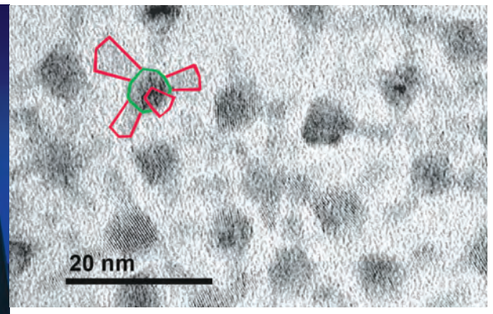
In Generation-I cells, charge separation and transport happen readily. First, the silicon wafer is doped with impurities that provide ready-made charge carriers (conduction electrons and holes) and therefore a high conductivity. Second, as shown in "Photovoltaics" (part C), the doping creates an interface with electron-donating impurities on one side (the "n" layer) and hole-donating impurities on the other (the "p" layer). Electrons migrate across this interface, or "p-n junction," setting up a permanent electric field that separates electron-hole pairs as soon as they are created, and helps transport the electrons with their negative charges to the negative terminal and the holes with their positive charges to the positive terminal.

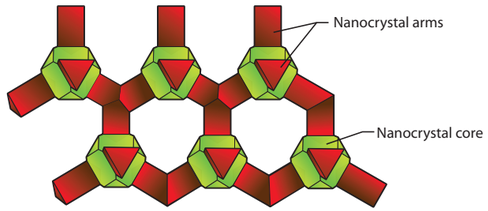
This method of charge separation and transport doesn't work in nanocrystal thin films. Nanocrystals tend to expel impurities during crystal growth, making it difficult to create well-defined p-n junctions. Furthermore, nanocrystals are surrounded by insulating organic molecules (see figure on p. 6), and the charge carriers, once created, must tunnel through that layer and then hop from nanocrystal to nanocrystal to reach the terminals. All of this is inefficient. Charge carriers can be trapped in the insulating layers or lost through recombination with an oppositely charged carrier as they hop to the terminals.

Recombination becomes a very serious and immediate problem when carrier multiplication creates two excitons. Those two can interact and share energy so that one electron gets boosted back up to a higher energy, and the other electron recombines with its hole. This process, called Auger recombination, happens in tens of picoseconds (trillionths of a second). To take advantage of the carrier-multiplication effect, the carriers have to be extracted from the nanocrystal more quickly than Auger recombination can occur. Finding ways to do that is another research objective within the center.

One approach is to give the electrons someplace to go to get away from the holes. Pietryga and center postdoctoral fellow Doh Lee have done this by growing projections (arms) on the nanocrystals. These arms are bits of semiconductor that can act as electron acceptors (see figure below). Each time a photon generates an electron-hole pair, the electron rapidly separates from the hole (it stays in the central core) by traveling to the arms. That separation buys time because it reduces the chance that the electron will recombine with a hole before being extracted from the nanostructure.





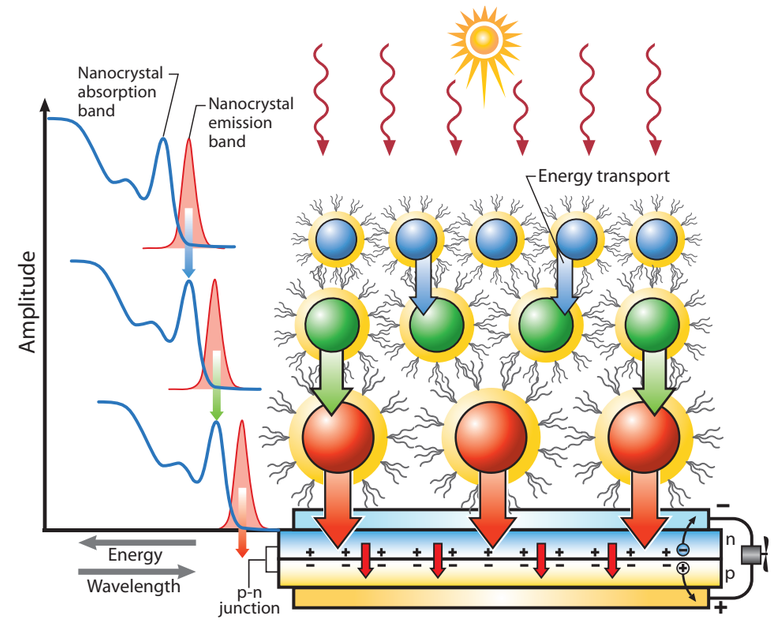


Don Werder (left) works at a transmission electron microscope to image nanocrystals. Those with electron-accepting "arms" (shown in the electron micrograph, upper right), could be grown into a continuous network (lower right) that would dramatically enhance electron transport in nanocrystal thin films.

"If we can assemble a nanocrystal thin film with the arms forming a continuous network and the nanocrystals and arms are embedded in a material that conducts holes, charge transport and charge collection might happen pretty easily, a key to efficient photovoltaics," explains Pietryga (see figure on p. 8).

Energy Transport—Beyond Charge Hopping

An interesting solution to harvesting current avoids the need for having charge carriers hop between nanocrystals. Instead, the exciton in one nanocrystal decays (electron and hole recombine), and the energy emitted goes not into a photon, but into an electric field that *acts like* a photon, exciting an exciton in a neighboring nanocrystal. That transport of energy between nanocrystals repeats until the exciton reaches a p-n junction, where it is split into an electron and a hole by an electric field (see figure, this page).



To understand this energy-transport process, consider that at a distance the exciton's electron-hole pair looks like a positive charge and a negative charge separated by a very small distance, what physicists call an electric dipole. The dipole produces a characteristic electric field that extends well beyond the nanocrystal. That dipole field puts one nanocrystal in contact with another and allows nanocrystals to transport energy from one to the other.

Because the energy emitted when an exciton decays is lower than the energy absorbed to create it, the energy-transport process is especially favored from a small nanocrystal with a large energy gap to a larger nanocrystal with a smaller gap. In that case, each energy exchange produces an exciton with slightly less energy than its predecessor.

Researchers with the center are actively exploring these different mechanisms of charge and energy transport in the hope that one or more will actually pan out, dramatically increasing the efficiency of harvesting usable electricity from nanocrystal thin-film solar cells.

Where the Rubber Meets the Road

The real test comes when these processes are integrated into a working device. The Los Alamos team has built a clean room and other facilities specifically designed to fabricate and test nanocrystal thin-film devices. It's now positioned to benefit from the unique expertise of its center partners from NREL, who have been dealing with issues of practical photovoltaics for two decades. Says Klimov, "I am very excited by the productive relationships we're already developing with our collaborators outside Los Alamos. Clearly, our biggest chance for success is for all of us to work closely together."

The center is also developing novel materials that can find almost immediate use in photovoltaics. One example is inexpensive germanium nanocrystals that can be made in different sizes and applied in inexpensive multilayered devices that absorb energy from the infrared to the ultraviolet.

Klimov emphasizes that new physics being developed at the center will eventually lead to real-life devices capable of replacing bulky and expensive silicon solar panels. The researchers are studying fundamental physics on the nanoscale, but the goal of making solar truly affordable has their attention riveted on the practical. ❖

—*Necia Grant Cooper*

Above: Energy transport in a layering of nanocrystal thin films that have progressively larger quantum dots. The top layer, the smallest quantum dots, will absorb, say, a blue photon and create an exciton. The exciton moves from smaller to larger quantum dots through a two-step sequence of decay and excitation (arrows) and then to the p-n junction, where the electric field splits the exciton into an electron and a hole that travel to different terminals. This process eliminates charge hopping.