Making a solar energy conversion breakthrough with help from a ferroelectrics pioneer

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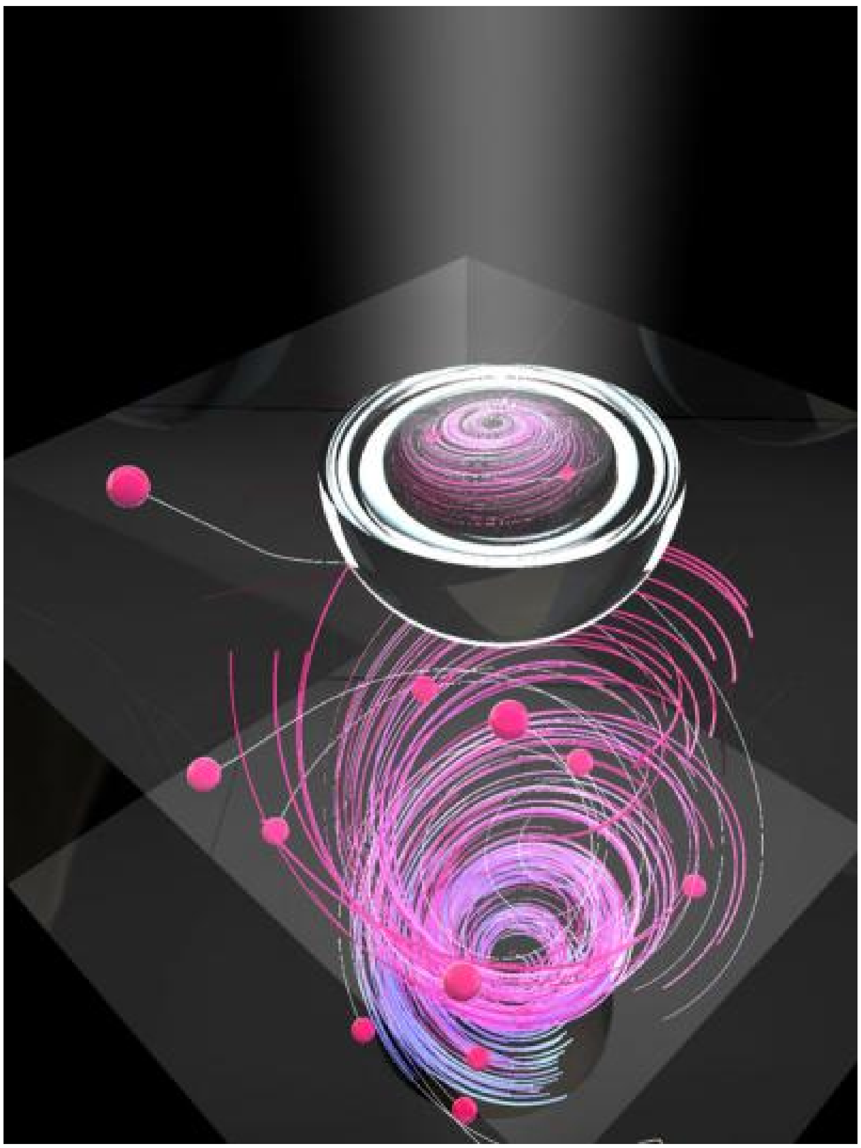

Artist's concept of optically-generated non-thermalized electrons and their collection in a ferroelectric crystal. An intense screening fieldresults in impact ionization, enabling an unexpectedly high conversion efficiency. Credit: Ella Marushchenko

Designers of solar cells may soon be setting their sights higher, as a discovery by a team of researchers has revealed a class of materials that could be better at converting sunlight into energy than those currently being used in solar arrays. Their research shows how a material can be used to extract power from a small portion of the sunlight spectrum with a conversion efficiency that is above its theoretical maximum—a value called the Shockley-Queisser limit. This finding, which could lead to more power-efficient solar cells, was seeded in a near-half-century old discovery by Russian physicist Vladimir M. Fridkin, a visiting professor of physics at Drexel, who is also known as one of the innovators behind the photocopier.

The team, which includes scientists from Drexel University, the Shubnikov Institute of Crystallography of the Russian Academy of Sciences, the University of Pennsylvania and the U. S. Naval Research Laboratory recently published its findings in the journal *Nature Photonics*. Their article "Power conversion efficiency exceeding the Shockley-Queisser limit in a ferroelectric insulator," explains how they were able to use a barium titanate crystal to convert sunlight into electric power much more efficiently than the Shockley-Queisser limit would dictate for a material that absorbs almost no light in the visible spectrum—only ultraviolet.

A phenomenon that is the foundation for the new findings was observed by Fridkin, who is one of the principal co-authors of the paper, some 47 years ago, when he discovered a physical mechanism for converting light into electrical power—one that differs from the method currently employed in solar cells. The mechanism relies on collecting "hot" electrons, those that carry additional energy in a photovoltaic material when excited by sunlight, before they lose their energy. And though it has received relatively little attention until recently, the so-called "bulk photovoltaic effect," might now be the key to revolutionizing our use of solar energy.

The Limits of Solar Energy

Solar energy conversion has been limited thus far due to solar cell design and electrochemical characteristics inherent to the materials used to make them.

"In a conventional solar cell—made with a semiconductor—absorption of sunlight occurs at an interface between two regions, one containing an excess of negative-charge carriers, called electrons, and the other containing an excess of positive-charge carriers, called holes," said Alessia Polemi, a research professor in Drexel's College of Engineering and one of the co-authors of the paper.

In order to generate electron-hole pairs at the interface, which is necessary to have an electric current, the sunlight's photons must excite the electrons to a level of energy that enables them to vacate the valence band and move into the conduction band—the difference in energy levels between these two bands is referred to as the "band gap." This means that in photovoltaic materials, not all of the available solar spectrum can be converted into electrical power. And for sunlight photon energies that are higher than the band gap, the excited electrons will lose it excess energy as heat, rather than converting it to electric current. This process further reduces the amount of power can be extracted from a solar cell.

"The light-induced carriers generate a voltage, and their flow constitutes a current. Practical solar cells produce power, which is the product of current and voltage," Polemi said. "This voltage, and therefore the power that can be obtained, is also limited by the band gap."

But, as Fridkin discovered in 1969—and the team validates with this research—this limitation is not universal, which means solar cells can be improved.

New Life For an Old Theory

When Fridkin and his colleagues at the Institute of Crystallography in Moscow observed an unusually high photovoltage while studying the ferroelectric antimony sulfide iodide—a material that did not have any junction separating the carriers—he posited that crystal symmetry could be the origin for its remarkable photovoltaic properties. He later explained how this "bulk photovoltaic effect," which is very weak, involves the transport of photo-generated hot electrons in a particular direction without collisions, which cause cooling of the electrons.

This is significant because the limit on solar power conversion from the Shockley-Queisser theory is based on the assumption that all of this excess energy is lost—wasted as heat. But the team's discovery shows that not all of the excess energy of hot electrons is lost, and that the energy can, in fact, be extracted as power before thermalizing.

"The main result—exceeding [the energy gap-specific] Shockley-Queisser [power efficiency limit] using a small fraction of the solar spectrum—is caused by two mechanisms," Fridkin said. "The first is the bulk photovoltaic effect involving hot carriers and second is the strong screening field, which leads to impact ionization and multiplication of these carriers, increasing the quantum yield."

Impact ionization, which leads to carrier multiplication, can be likened to an array of dominoes in which each domino represents a bound electron. When a photon interacts with an electron, it excites the electron, which, when subject to the strong field, accelerates and 'ionizes' or liberates other bound electrons in its path, each of which, in turn, also accelerates and triggers the release of others. This process continues successively—like setting off multiple domino cascades with a single tipped tile—amounting to a much greater current.

This second mechanism, the screening field, is an electric field is present in all ferroelectric materials. But with the nanoscale electrode used to collect the current in a solar cell, the field is enhanced, and this has the beneficial effect of promoting impact ionization and carrier multiplication. Following the domino analogy, the field drives the cascade effect, ensuring that it continues from one domino to the next.

"This result is very promising for high efficiency solar cells based on application of ferroelectrics having an energy gap in the higher intensity region of the solar spectrum," Fridkin said.

Building Toward a Breakthrough

"Who would have expected that an electrical insulator could be used to improve solar energy conversion?" said Jonathan E. Spanier, a professor of materials science, physics and electrical engineering at Drexel and one of the principal authors of the study. "Barium titanate absorbs less than a tenth of the spectrum of the sun. But our device converts incident power 50 percent more efficiently than the theoretical limit for a conventional solar cell constructed using this material or a material of the same energy gap."

This breakthrough builds on research conducted several years ago by Andrew M. Rappe, Blanchard Professor of Chemistry and of Materials Science & Engineering at the University of Pennsylvania, one of the principal authors, and Steve M. Young, also a co-author on the new report. Rappe and Young showed how bulk photovoltaic currents could be calculated—which led Spanier and collaborators to investigate if higher power conversion efficiency could be attained in ferroelectrics.

"There are many exciting reports utilizing nanoscale materials or phenomena for improving solar energy conversion," Spanier said. "Professor Fridkin appreciated decades ago that the bulk photovoltaic effect enables free electrons that are generated by light and have excess energy to travel in a particular direction before they cool or 'thermalize'—and lose their excess energy to vibrations of the crystal lattice."

Rappe was also responsible for connecting Spanier to Fridkin in 2015, a collaboration that set in motion the research now detailed in *Nature Photonics*—a validation of Fridkin's decades-old vision.

"Vladimir is internationally renowned for his pioneering contributions to the field of electroxerography, having built the first working photocopier in the world," Rappe said. "He then became a leader in ferroelectricity and piezoelectricity, and preeminent in understanding light interactions with ferroelectrics. Fridkin explained how, in crystals that lack inversion symmetry, photo-excited electrons acquire asymmetry in their momenta. This, in turn, causes them to move in one direction instead of the opposite direction. It is amazing that the same person who discovered these bulk photovoltaic effects nearly 50 years ago is now helping to harness them for practical use in nanomaterials."

More information: Power conversion efficiency exceeding the Shockley–Queisser limit in a ferroelectric insulator, *Nature Photonics*, DOI: 10.1038/nphoton.2016.143