



Perovskites' extraordinary properties could revolutionize solar energy

## Perovskites in the spotlight

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Solar power is gaining mass appeal as photovoltaic panel prices fall and efficiencies improve. A watt of power generated from sunlight now costs less than \$0.70, within shot of conventional electricity prices. Slashing that number by half could be a game-changer for solar. An upstart photovoltaic material with astonishing properties provides a potential pathway to that end, and it has set the solar research world ablaze.

Perovskites, materials with the crystal structure of calcium titanate, have only been intensely studied for solar cells since 2012. The progress in two years has been astounding: light-to-electricity power conversion efficiency has soared from a few percent to a certified 17.9%. “That’s never happened before,” said Michael McGehee, a Stanford University materials science and engineering professor. “Normally a doubling of efficiency takes 10 years, if not 20.”

The best crystalline silicon solar cells—which form most of today’s commercial panels—have efficiencies around 25%. Established thin-film devices made of cadmium telluride and copper indium gallium selenide are around 20% efficient. Gallium arsenide yields thin-film devices with efficiencies over 28%, but the material is expensive to process.

Perovskite solar cells could combine the high efficiency of silicon and GaAs with the low cost, easy processing of thin-film technologies. Making crystalline perovskites requires gently heating inexpensive precursor salt solutions deposited on a substrate. This solution processing opens up the possibility of printing them on flexible substrates using inexpensive roll-to-roll processes.

Perovskites are extraordinary light absorbers, so solar cells can be made with layers only 300–500 nm thick, which also lowers cost. Tweaking the materials’ chemical composition gives a range of optical and electronic properties. For example, the type and ratio of elements can be tuned to engineer the bandgap, which determines the swath of the light spectrum the material can absorb. Perovskite cells also have a high open-circuit voltage—necessary for high efficiency—of over 1 V. Crystalline silicon solar cells, by comparison, have an open-circuit voltage of 0.6 V and are typically 500 times thicker.

The original perovskite was a mineral composed mainly of calcium titanate. But the term now refers to any compound with an  $ABX_3$  composition and a three-dimensional network of corner-sharing  $BX_6$  octahedra, where A is a larger inorganic or organic cation, B a metal, and X is generally a halogen or oxygen. Methylammonium, lead, and iodide have been the most common

picks for the three respective components in hybrid perovskites used for PV.

Tsutomu Miyasaka and his colleagues at Tooin University of Yokohama were the first to use perovskites in a dye-sensitized solar cell (DSSC) configuration in 2009. In traditional DSSCs, a nanoporous titania film coated with a light-absorbing dye and infused with a liquid electrolyte is sandwiched between two glass electrodes. When the dye absorbs light, it gets excited and creates electrons and positive charge-carriers called holes. The electrons are injected into the titania, which shuttles them to the electrode, while the electrolyte conducts the holes. Miyasaka’s team replaced the dye with  $CH_3NH_3PbI_3$  nanocrystals. The resulting devices were 3.8% efficient but were unstable because the liquid electrolyte dissolved the perovskite.

Then in 2012, Nam-Gyu Park at Sungkyunkwan University in South Korea together with Michael Grätzel at École Polytechnique Fédérale de Lausanne in Switzerland made 9.7% efficient cells with  $CH_3NH_3PbI_3$  nanocrystals and a solid hole-conductor based on spirobifluorine. About the same time, Miyasaka teamed up with University of Oxford physicist Henry Snaith to make solar cells with a mixed iodide-chloride perovskite and with alumina instead of titania as a scaffold. Efficiencies jumped to 10.9%, and since alumina cannot conduct electrons, the results hinted that the perovskite wasn’t just absorbing light but also transporting charge.

The photovoltaic world has since been hooked. Researchers have made swift, persistent strides in efficiency by making higher quality perovskites, developing different device architectures, and investigating new materials combinations.

“Underpinning everything has been improvements in the material’s crystallinity,” Snaith said. “The crystal domain size is increasing, and their quality is getting higher.” Larger, more uniform crystal grains mean fewer boundaries and defects at which electrons and holes can recombine. This results in more charge-carriers getting out of the device, boosting efficiency.

In July 2013, for example, Grätzel and colleagues reported 15% efficiency by using a two-step method to make more uniform, better-crystallized perovskite films. Until then, researchers had deposited a mixture of lead halide and methylammonium halide on porous titania. Grätzel’s team first deposited lead iodide and then exposed it to methylammonium iodide solution to create the perovskite.

Two months later, Snaith’s group reported a 500-nm-thick

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perovskite film using vapor deposition in a vacuum chamber. Unlike direct crystallization from solution, which gives small non-uniform crystals, this technique creates an amorphous film that crystallizes upon heating, leading to long, platelet-like crystals. The uniform, flat film allowed the researchers to do away with the DSSC-type nanostructured design. Instead, they sandwiched the film between charge-transporting layers and a pair of electrodes to make a 15.4% efficient planar solar cell.

Several methods to make thin perovskite films have been reported since, each with a slight twist. Some researchers have, for example, exposed metal halide-coated substrates to methylammonium iodide vapors or dipped them into methylammonium iodide solution.

Scientists have also been experimenting with different materials to improve performance and appeal. In December 2013, for example, Dianyi Liu and Timothy Kelly at the University of Saskatchewan in Canada made flexible, 10-plus percent efficient perovskite solar cells by replacing the titania with a much thinner zinc oxide layer that could be processed at room temperature. Meanwhile, Snaith's group and, independently, Robert Chang and Mercuri Kanatzidis from Northwestern University replaced the potentially worrisome lead with tin to make methylammonium tin iodide solar cells. While the cells have much lower stability and a third of the efficiency of their lead counterparts, the advance demonstrates that the perovskite family extends beyond lead.

What makes perovskites the photovoltaic material of dreams? The exact mechanisms are unproven, but researchers have proposed various explanations. For one, they are up to 10 times better at absorbing sunlight compared to traditional thin-film photovoltaic materials, said Yanfa Yan, a University of Toledo physicist. Yan and colleagues have proposed that this is due to the presence of more states in the material's conduction band for light-generated electrons to occupy.

Another precious trait, recently revealed through spectroscopic studies, is that photogenerated electrons and holes can travel for long distances of over 1  $\mu\text{m}$  through perovskites. Yan speculates that this is because most of the defects in the materials are shallow, so they cannot trap electrons and holes, and that the boundaries between crystals are electrically inactive. "In other words, electronically the materials perform like single-crystal films," he said.

Aron Walsh and his colleagues at the University of Bath have proposed a different theory for the material's charge-transport properties. Their theory rests on the cation molecule at the center of the cubic perovskite crystal. This cation is a rotating electric dipole, and the researchers propose that there could be regions in the perovskite where the dipoles of several molecules are aligned, creating paths for electrons and holes to travel in opposite directions.

Unraveling the fundamental physics of perovskites will be crucial for tapping their full potential. But researchers also face other challenges. For one, perovskite solar cells are notoriously unstable. Their ionic metal-halogen bonding makes perovskites degrade easily in humidity. "Labs have more success with the devices in winter than summer," McGehee said. "It's unclear that these materials can last for 20-plus years."

McGehee's team and others have pointed out another troublesome aspect of perovskite solar cells. Every solar cell has a current-voltage curve—plotted by applying a fixed range of voltages across the device and measuring the current—that is useful for calculating power and efficiency. The researchers found that the values depended on the direction in

and speed at which they swept the voltage. Scanning quickly in reverse, going from high voltage to low, gave higher efficiencies than in the forward direction. This effect, called hysteresis, makes it hard to nail down a perovskite solar cell's real efficiency, and resolving it will be necessary for market-ready devices.

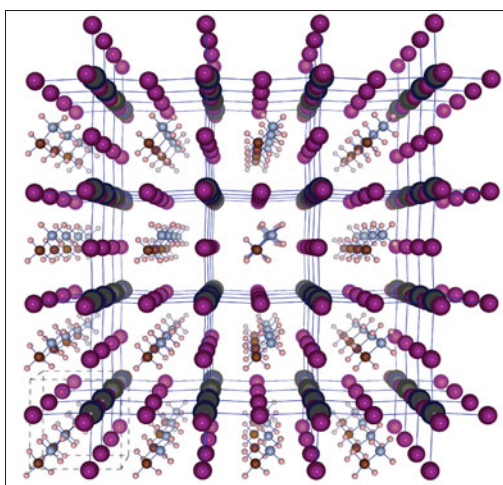
According to Yang Yang, a materials science and engineering professor at the University of California, Los Angeles, making long-lasting high-efficiency cells will require marrying basic materials research with device engineering, as well as an academia-industry partnership. Researchers need to focus on the fundamentals of crystal growth to

reduce defects; find better contact materials to increase current and voltage; improve the interfaces between perovskites and contact materials; and work on device encapsulation. "Now's the time for industry to work with academics and take this technology into a more mainstream production approach for large-area devices and encapsulation," Yang said.

Snaith aims to address both stability and large-area device manufacturing with his company, Oxford Photovoltaics. In simulated sunlight conditions, he said, some of their cells last 1000 hours with a slight decrease in efficiency at the start.

Several researchers are also working on tandem perovskite-silicon cells, which they believe hold more immediate commercial promise. The idea is to place a visible light-absorbing perovskite on top of a silicon solar cell, which is good at absorbing infrared light. This should add little cost to a typical silicon module but could boost efficiency up to maybe even over 30 percent, said McGehee.

The surge in perovskite solar cells is bound to continue as researchers advance their understanding of known materials and engineer better devices. And, per Snaith, perhaps most enticing about this large material family is what is yet to be uncovered. "We might be on the tip of an iceberg in terms of types of materials that could be possible." □



Optimized structure for (pseudo) cubic  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .