RESEARCH HIGHLIGHTS: Perovskites

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Research on perovskites has progressed rapidly, with solar-cell efficiencies now at 22%, five times higher than first cells reported in 2009. MRS Bulletin *presents the impact of a selection of recent advances in this burgeoning field.*

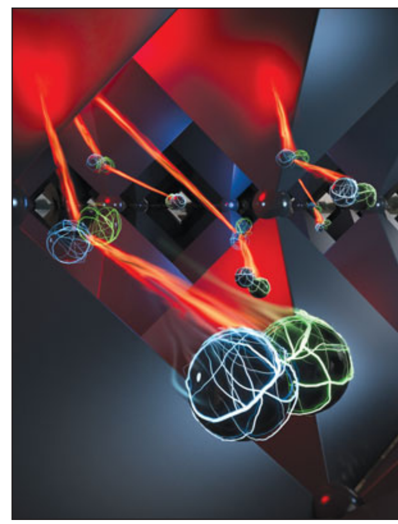
Scientists in the United Kingdom have discovered a property of perovskites that could further boost the efficiency of solar cells made from these materials. Perovskites, the researchers reported in a recent issue of *Science* (doi:10.1126/science.aaf1168), can reuse photons multiple times, increasing the open-circuit voltage of the solar cells.

The best reported power-conversion efficiency (PCE) for perovskite solar cells is over 22%, similar to that of commercial crystalline silicon solar cells. However, solar cells made from gallium arsenide (GaAs) hold the world record for single junction cells with PCE at 28.8%. That is partly because of photon recycling, a phenomenon in which light-generated electrons and holes recombine radiatively, producing a photon again, and the process of charge separation and recombination continues until the charges are extracted at the electrical contacts or the photons escape the film. As a result, the average distance the charges can travel no longer depends only on carrier-diffusion length.

To investigate whether perovskites can recycle photons, Richard Friend, Felix Deschler, and their colleagues at the University of Cambridge focused laser light on a tiny patch of a 100-nm-thick methylammonium lead iodide ($MAPbI_3$) film, and observed light coming out of the cell at 1.5-μm increments away from that excitation spot.

Close to the excitation spot area, the emission spectrum was centered at an expected 765 nm. As the observation distance increased, the spectrum center steadily shifted to lower-energy photons, going beyond 800 nm when the separation reached 50 μm. Yet, the higher-energy 765-nm signal remained in the spectrum, and the 765-nm and 800-nm spectral components decayed much slower with distance than a simple linear absorption model would predict. These high-energy signals would not remain at those distances unless photons were being recycled, the researchers say.

Optimizing solar cells using methods such as highly reflective back mirrors and texturing of the top surface could harness these recycled photons to take efficiency closer to the theoretical Shockley–Queisser limit, they add.



Depiction of photon recycling inside the crystalline structure of perovskite. Perovskites can reabsorb photons that are regenerated inside the material, a feature which could enable researchers to break through the efficiency limits of existing solar cells. Credit: Criss Hohmann.

Another significant advance in the stability of perovskite solar cells comes from a research team led by Kwanghee Lee at the Gwangju Institute of Science and Technology in the Republic of Korea. Perovskite cells are known to self-degrade even under inert conditions, for reasons that scientists have not understood so far.

The Korean team took a rigorous look at the degradation of planar perovskite solar cells with typical silver or aluminum electrodes. They found that halide ions migrate from the perovskite films to the metal electrode and chemically interact with the metal, degrading device performance. To stabilize the ionic defects in the perovskite film, the researchers deposited a thin amine-mediated titanium suboxide layer between the active layer and the electrode. These solar cells maintained nearly 80% of their initial efficiency after one year of storage in inert conditions, and after 200 hours in ambient conditions without any encapsulation. The report is published in *Energy & Environmental Science* (doi:10.1039/c6ee00612d).

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Despite the promise of perovskites for low-cost next-generation solar cells, their toxicity and lack of stability remain significant hurdles to commercialization. The perovskite family with the most commercial promise, $MAPbI_3$, contains lead, and these materials are known to degrade due to moisture, heat, and long-term exposure to light. Researchers have been looking for lead-free materials with good optoelectronic properties.

Two research groups have independently introduced perovskites that might fit the bill. Both materials are based on a double perovskite structure. Conventional perovskites have the formula ABX_3. Double perovskites, in which the unit cell is twice that of the conventional perovskite unit cell, have the formula $AB'B''X_6$. They have attracted much research attention recently for their ferroelectric and ferromagnetic properties, but no one has made compounds with suitable optoelectronic properties for photovoltaics.

Using first-principles calculations and computational methods, Henry Snaith, Feliciano Giustino, and their colleagues at the University of Oxford designed a family of lead-free perovskites based on bismuth or antimony and noble metals. The team started with the formula Cs_2BBX_6 and calculated that compounds where B′ is Sb or Bi and B″ is Cu, Ag, or Au would have the most promising optoelectronic properties, such as a tunable bandgap and low carrier masses, which would both lead to high light-to-electricity efficiency. They experimentally synthesized the perovskite $Cs_2BiAgCl_6$, refined its structure using single-crystal x-ray diffraction, and characterized its optical properties. Optical measurements showed that the material had an indirect bandgap of 2.2 eV, the researchers report in *The Journal of Physical Chemistry Letters* (doi:10.1021/acs.jpclett.6b00376).

A Stanford University team led by Hemamala Karunadasa, meanwhile, reported a new bismuth-based double perovskite with the formula $Cs_2AgBiBr_6$ in the *Journal of the American Chemical Society* (doi: 10.1021/jacs.5b13294). This perovskite has a photoluminescence lifetime of 600 ns, close to that of Pb-based perovskite material. Photoluminescence lifetime is the average lifespan of an exciton—a bound state of an electron and hole—created when a photovoltaic material absorbs a photon; longer lifetime indicates higher efficiency. The material is nontoxic and significantly more heat and moisture stable than lead-iodide perovskites. It has an indirect bandgap of 1.95 eV, which makes it suitable for combining with a top silicon light-absorbing layer to make a tandem solar cell, the researchers say.

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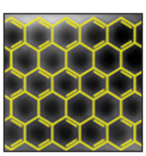

The electronics industry traditionally turns to silicon for its semiconductor needs, but silicon's properties change when manipulated on a nanoscale level, making it less ideal for use in smaller devices and components. Graphene is a possible substitute, but using it as a semiconductor requires first transforming its structure. Now, a team of Swiss and German researchers has come one step closer to achieving that goal of transforming graphene into an ideal semiconductor. As described in a recent issue of *Nature*, they created graphene nanoribbons with zigzag edges featuring antiferromagnetic coupling, or independent channels of electrons exhibiting opposite direction spin on either edge.

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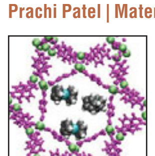

Using a novel approach based on highly porous metal–organic framework (MOF) materials, researchers at Pacific Northwest National Laboratory have developed an efficient way to extract oxygen from air at room temperature. Their findings could enable low-cost, low-energy oxygen separation.

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