RESEARCH HIGHLIGHTS: Perovskites

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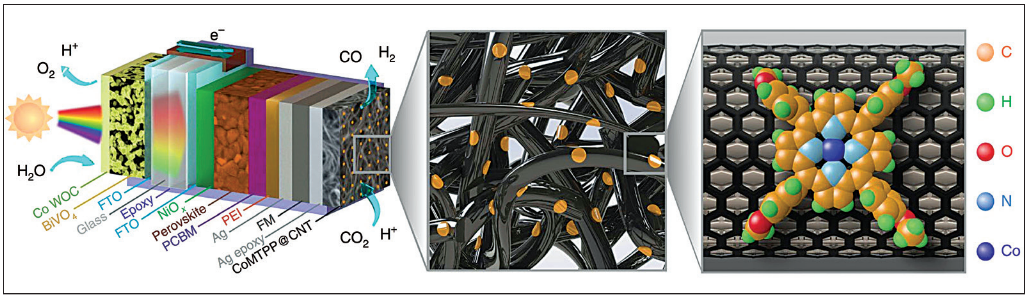
Perovskite solar cells are at the edge of commercial success. Device efficiency records are being broken at a regular pace, while stability and optimization are progressing rapidly. The first commercial products could reach the market within a year. MRS Bulletin *presents coverage of the most recent impactful advances in the burgeoning field of perovskite research.*



An artificial leaf device with perovskite and bismuth vanadate electrodes produces syngas from water and carbon dioxide. Oxygen evolution occurs at the front $BiVO_4$ anode, while a perovskite cathode reduces CO_2 and protons to CO and H_2. WOC, water oxidation catalyst; FTO, fluorine-doped tin oxide; PCBM, [6,6]-phenyl-C_{61}-butyric acid methyl ester; PEI, polyethylenimine; FM, field's metal. Credit: *Nature Materials*.

A photoelectrochemical "artificial leaf" device with perovskite electrodes uses sunlight to produce syngas, a mixture of hydrogen and carbon monoxide, from water and carbon dioxide. "This demonstration is a first step to develop solar technologies that may enable a circular carbon economy in the long term," says University of Cambridge chemistry professor Erwin Reisner, who led the study reported in *Nature Materials* (doi:10.1038/s41563-019-0501-6).

Syngas, which is widely used to produce fuels, chemicals, and fertilizers, is typically made by reforming fossil fuels. Solar syngas production is a cleaner alternative.

The new device contains a bismuth vanadate anode and a cesium formamidinium methylammonium mixed-halide perovskite cathode, with special cobalt catalysts in each. When the device is immersed in water, the anode produces oxygen, and the perovskite cathode reduces CO_2 and protons into CO and H_2, respectively. The perovskite cathodes even reduce aqueous CO_2 for one day at light intensities as low as 0.1 Sun, which means the device would work on cloudy days. The perovskite's high-efficiency sunlight absorption "ultimately allows catalysis with good performance," Reisner says.

Plants take up lead from perovskites in the ground 10 times more effectively than other contamination sources, a study in *Nature Communications* shows (doi: 10.1038/s41467-019-13910-y). The authors call for a need to reassess the safety levels of lead in perovskite solar cells.

Lead content in perovskite modules is typically less than 0.1% by weight, which is the safety limit imposed by many countries. To find out if it can still have an environmental and health impact, Jian Lü of Fujian Agriculture and Forestry University, Antonio Abate of Helmholtz-Zentrum Berlin für Materialien und Energie and colleagues grew mint, chili, and cabbage—which have high, medium, and low lead accumulation ability, respectively—in perovskite-laced soil.

Natural soil samples had a lead level of 36 mg/kg, in line with agricultural lands worldwide. The team added 5 mg/kg of lead to simulate a solar module leaching its entire perovskite content into the ground. Increasing lead concentration by only 10% boosted the lead measured in plants by more than 100%. All the plants blackened and rotted with larger perovskite amounts, which added 250 mg/kg lead to the soil.

The researchers recommend keeping the safety level for lead in perovskites lower than that in other lead-containing electronics. They also "encourage replacing lead completely with more environment-friendly metals to deliver safe perovskite technologies."

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Researchers report a new strategy to make high-quality perovskite quantum dots (QDs), giving QD solar cells with a record certified power-conversion efficiency of 16.6%. Perovskite QD solar cells could be more stable than their thin-film counterparts, but making high-quality QDs with desirable optoelectronic properties has been a challenge.

"This substantial improvement of efficiency and stability paves the way for addressing high-value applications in niche markets," says Yang Bai of The University of Queensland in Australia and an author of the *Nature Energy* paper (doi:10.1038/s41560-019-0535-7).

Bai and colleagues made cesium and formamidinium lead triiodide perovskites ($Cs_{1-x}FA_xPbI_3$) QDs by first preparing $CsPbI_3$ and $FAPbI_3$ QDs using a modified hot-injection method. Before mixing them together, they intentionally retained excessive oleic acid (OA) ligands in the parent $CsPbI_3$ and $FAPbI_3$ QD solutions, forming an OA-rich environment. The surface ligands promoted a cation exchange reaction of the Cs and FA cation and suppressed surface defects, boosting efficiency.

The best material, $Cs_{0.5}FA_{0.5}PbI_3$, gave solar cells a remarkable power-conversion efficiency of 16.6% and negligible hysteresis. The cell retained 94% of its efficiency under continuous 1-Sun illumination for 600 hours, a stability comparable to that of thin-film materials.

Infrared (IR) light-emitting diodes (LEDs) used in night vision, optical communications, and medical applications are expensive. Embedding lead sulfide QDs into perovskite films could give low-cost, efficient IR LEDs. These devices combine the tunability of QDs to precise wavelength emissions with excellent charge-transport properties of perovskites. But the QDs tend to aggregate, causing inhomogeneity because of imbalanced charge accumulation.

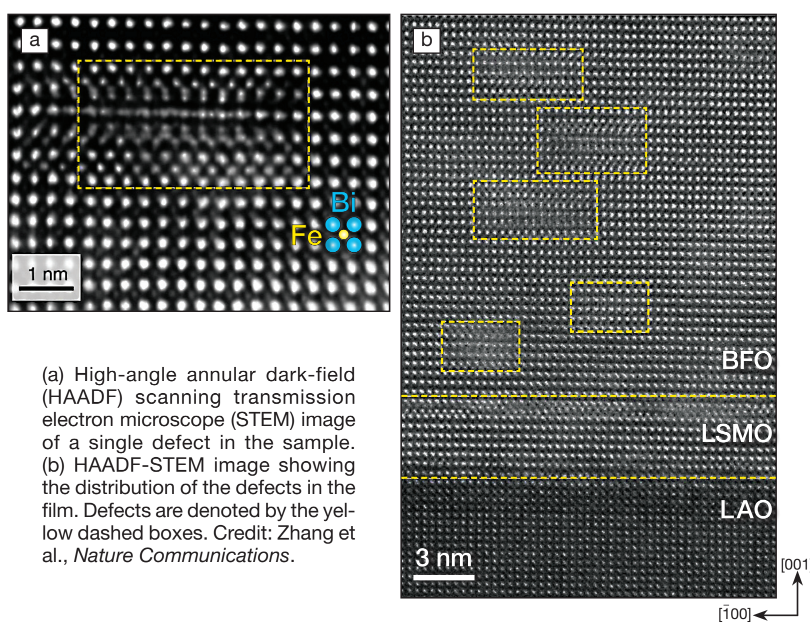
To overcome these issues, a team led by Jiang Tang of the Huazhong University of Science & Technology and Edward Sargent of the University of Toronto turned to low-dimension layered perovskites as a matrix for QDs. They altered the surface of the QDs with perovskite cations, which caused them to disperse evenly through the matrix.

In the LEDs reported in *Nature Photonics* (doi:10.1038/s41566-019-0577-1), energy flowed in the form of excitons, tightly bound electron–hole pairs that traveled together, from the perovskite into the QDs. The devices exhibited a high external quantum efficiency of 8.1% at 980 nm at a radiance of up to 7.4 W $Sr^{-1}m^{-2}$.

Nano Focus

Defect engineering increases polarization retention in ferroelectric thin films

Ferroelectric thin films are intriguing candidates for nanoscale electronics, including memory systems in which information is stored as polarization states equivalent to the 1s and 0s of binary systems. Researchers at the University of New South Wales (UNSW) and Monash University in Australia have recently overcome a key limitation of this technology—the decay of polarization states over short time scales. As they described in *Nature Communications* (doi:10.1038/s41467-019-14250-7), they utilized designer defects in a thin film of bismuth ferrite ($BiFeO_3$, BFO) to set a new record for polarization retention.



(a) High-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) image of a single defect in the sample. (b) HAADF-STEM image showing the distribution of the defects in the film. Defects are denoted by the yellow dashed boxes. Credit: Zhang et al., *Nature Communications*.

In ferroelectric random-access memory (FeRAM) systems, information is stored in the polarization states of nanometer-scale ferroelectric domains. Different states are separated by thin boundary regions known as domain walls. Typical FeRAM systems retain distinct polarization states for just days or weeks before they begin to decay and information is compromised.

Research has shown that BFO films grown on lanthanum aluminate substrates ($LaAlO_3$, LAO) experience strain due to the lattice mismatch between BFO and LAO. At thicknesses of 30 nm or more, this leads to a mixed-phase state, which includes BFO in a tetragonal-like phase and a rhombohedral-like phase.

In this new study, a research team led by UNSW's Jan Seidel fabricated a thin film of BFO in the tetragonal-like phase on a LAO substrate, using pulsed laser

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