

# RESEARCH HIGHLIGHTS: Perovskites

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

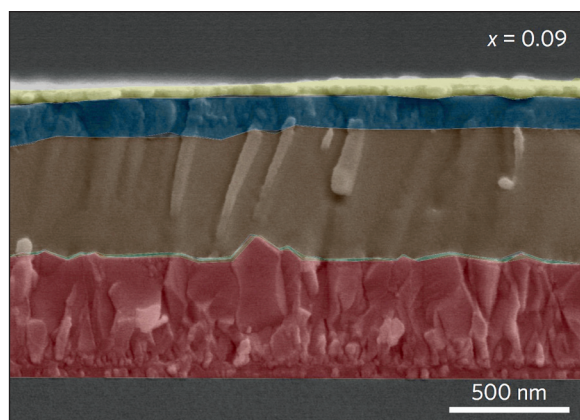
The biggest hurdle perovskite solar cells face before they can reach market is that standard devices made with three-dimensional (3D)

methylammonium-based perovskites degrade when exposed to light, moisture, and oxygen. Two-dimensional (2D) organic metal-halide perovskites, on the other hand, are much more stable but suffer from low power-conversion efficiency.

Henry Snaith and colleagues turned to 2D Ruddlesden–Popper phases  $((\text{RNH}_3)_2(\text{A})_{n-1}\text{BX}_{3n+1})$ , which are layered 2D perovskite films known for their moisture stability. And they used formamidinium-based perovskites, which are more thermally stable than their methylammonium counterparts.

The researchers started with a precursor for a cesium formamidinium perovskite  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ , to which they added butylammonium ( $\text{C}_4\text{H}_9\text{NH}_3^+$ ) iodide. The resulting fully crystalline perovskite films had small 2D plate-like crystals of butylammonium lead halide standing between larger, flat 3D perovskite grains. The films also had remarkably enhanced crystallinity.

Best-performing solar cells made with the film had an efficiency of 19.5%, retained 80% of this efficiency after 1000 hours in air under simulated sunlight, and 4000 hours when encapsulated.



An artificially colored scanning electron microscope image of the cross section of a photovoltaic device shows a perovskite layer (brown) composed of 2D platelets of butylammonium lead halide standing up between the larger, flat 3D cesium formamidinium perovskite  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ . The mixed 2D–3D perovskites result in efficient, air-stable solar cells. Credit: *Nature Energy*.

Oxford University researchers have now made a hybrid of the two by incorporating small 2D perovskite platelets into 3D perovskite films. The 2D platelets enhance stability and prevent charges from recombining nonradiatively, which increases sunlight-to-electricity conversion efficiency, according to their study published in *Nature Energy* (doi:10.1038/nenergy.2017.135).

Researchers at the Swiss Federal Institute of Technology in Lausanne have combined 2D and 3D perovskites to make ultra-stable solar cells that have worked for more than 10,000 hours, or over 400 days, with no loss in efficiency. The solar cells are also low cost and have an efficiency of 11.2%.

Conventional solar cells struggle to reach a goal of less than 10% drop in efficiency for at least 1000 hours in lab-based

accelerated aging tests, the researchers write in *Nature Communications* (doi:10.1038/ncomms15684). This corresponds to the 20–25 year warranty, with less than a 10% drop in performance that a marketable product would require.

The team led by Mohammad Khaja Nazeeruddin covered a methyl ammonium lead iodide perovskite film with a 2D perovskite based on aminovaleric acid  $(\text{HOOC}(\text{CH}_2)_4\text{NH}_3)_2\text{PbI}_4$ . They also

replaced the hole-transport layer found in conventional perovskite solar cells with hydrophobic carbon electrodes because of vulnerability of the former to moisture and oxygen in ambient operating conditions.

The researchers used an industrial-scale process to print a 10 cm × 10 cm solar module, and tested it under continuous light in the presence of oxygen and moisture.

A team from Columbia University and the Italian Institute of Technology has provided the first direct view of an unusual phenomenon thought to be responsible for the excellent optoelectronic properties of perovskite materials.

Charge carriers in lead halide perovskites last for an unusually long time and travel long distances, resulting in high efficiency despite defects in the material. Columbia's Xiaoyang Zhu and his colleagues had proposed previously

that these unique carrier properties are due to polarons—quasiparticles that represent electrons and their self-induced polarization in the lattice—that screen charge carriers and keep them from colliding with defects. But no one had been able to directly observe how, or if, they are formed.

Zhu, Filippo De Angelis, and their colleagues used time-resolved optical Kerr effect spectroscopy to give a time domain view of polaron formation in  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  and  $\text{CsPbBr}_3$  perovskites.

The results, reported in *Science Advances* (doi:10.1126/sciadv.1701217), revealed that deformations of the soft  $\text{PbBr}_3^-$  lattice are mainly responsible for the polaron formation, and having an organic cation is not essential. Polarons form more than twice as quickly in the methylammonium perovskite than the cesium one because of its higher frequency of  $\text{PbBr}_3^-$  vibrations. The researchers also confirmed the formation of the polarons using density functional theory calculations.

A new method to heal defects and make them electronically less reactive in hybrid halide perovskite films could provide a path to further improve the efficiency and stability of perovskite solar cells.

Perovskite surfaces and grain boundaries have a high density of ionic defects, where charges can get trapped and recombine, reducing efficiency. Oxygen or moisture can also seep into perovskite films at defects, setting off degradation,

which makes devices less stable. So far, researchers have passivated charged defects in perovskites by adding molecules that act as electron donors or acceptors. But most passivation molecules only passivate one type of defect, either positively or negatively charged.

University of Nebraska–Lincoln's Jinsong Huang reported in *Nature Energy* (doi:10.1038/nenergy.2017.102) that quaternary ammonium halides with

the structure  $\text{NR}_4^+\text{X}^-$ , where R is an alkyl or aryl group and X is a halide, can efficiently passivate charged defects in mixed-cation halide perovskites with quaternary ammonium and halide ions. With a passivation layer of quaternary ammonium halides—choline chloride or choline iodide—deposited on the perovskite film, the efficiency of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solar cells went up from 17% to a certified value of over 20%.

## Bio Focus

### Small tissue reprogramming device designed to heal damaged tissues

The advent of cellular reprogramming technologies (those that convert one specific cell type into another) in recent years has opened the possibility for doctors to be able to use on-site, cell-based therapies to treat a range of health issues. For example, these technologies could one day be used to treat Parkinson's disease by converting certain brain cells into nerve cells that produce the chemical messenger dopamine, which helps coordinate body movements. Approaches thus far, however, have numerous hurdles to overcome before becoming viable, such as the risky reliance on viruses to deliver genes that drive the reprogramming process.

Researchers at The Ohio State University (OSU) have now developed a technology called tissue nanotransfection (TNT), which uses a nanochannel device and small electric charge to deliver

reprogramming factors that directly transform skin and other adult cells into other types of cells on-site. Described recently in *Nature Nanotechnology* (doi:10.1038/NNANO.2017.134), TNT was used to reprogram skin cells in mice to become vascular (blood vessel) cells in badly injured legs that lacked blood flow, ultimately saving the legs within a short time. In other experiments, researchers used TNT to reprogram skin cells into nerve cells, which they injected into brain-injured mice to help them recover from a stroke.

“We've moved from a stem cell concept to a stem tissue or tissue reprogramming concept that understands that individual cells work with other [cells] in their environment,” says study lead author Chandan K. Sen, director of OSU's Center for Regenerative Medicine and Cell-Based Therapies. “Our technology aims at converting tissues as a whole.”

The ability to reprogram adult cells to other types of cells is not new. A decade ago, researchers from Japan and the United

States showed that they could use gene-carrying viruses to transform adult skin cells into so-called induced pluripotent stem cells (iPS cells)—cells resembling embryonic stem cells that can then develop into other types of cells. While viral vectors are efficient tools for cell reprogramming, they cause inflammation in the body and can even switch on cancer genes, making them unsafe for use in people.

More recently, researchers have devised other nonviral techniques to reprogram cells, but the intermediate step involving iPS cells is still an issue. “Even pluripotent cells themselves can be cancerous,” Sen says. A major issue with these techniques, in general, is that they focus on developing and studying cells outside of the body. “But how much of that is relevant to scenarios within the body is questionable,” Sen says.

Sen and his team instead wanted to develop a method to reprogram cells *in vivo* without needing viruses or iPS cells. But current *in vivo* transfection technologies deliver genes in a stochastic manner,