

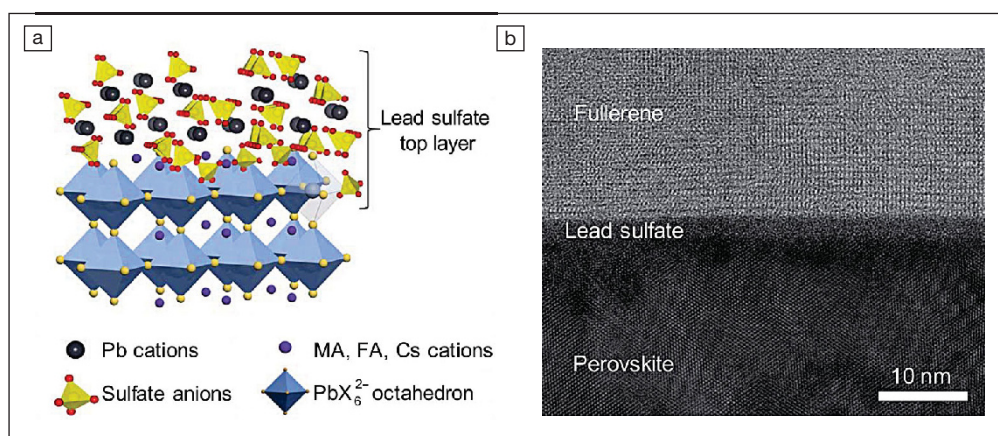
RESEARCH HIGHLIGHTS: Perovskites

By **Prachi Patel**
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Perovskite solar cells are at the edge of commercial success. Device efficiency records break at a regular pace, while stability and optimization is progressing rapidly. The first commercial products could reach the market by 2020, just a decade since perovskite photovoltaics were first discovered. MRS Bulletin usually presents the impact of recent advances in the burgeoning field of perovskite research every quarter. This special October addendum is indicative of the breathtaking pace of perovskite research.

Converting the surfaces of lead halide perovskites to water-insoluble lead oxysalt can significantly stabilize perovskite solar cells, a team led by Shuang Yang, Shangshang Chen, and Jinsong Huang of the University of North Carolina at Chapel Hill reported in a recent issue of *Science* (doi:10.1126/science.aax3294).

Previous approaches have focused on stabilizing perovskites themselves or by physically covering perovskites with organic molecules. “The secondary bonding between passivation molecules and the perovskite surface is typically too weak to protect perovskites from attack by moisture and oxygen,” Huang says. By contrast, the new approach involves forming a compact, strongly bonded lead



(a) Schematic illustration of protection of perovskites through *in situ* formation of a lead sulfate top layer on the perovskite surface. (b) Cross-sectional high-resolution transmission electron microscope image of the perovskite/lead sulfate/fullerene interface (fullerene is the charge-transport layer). Credit: *Science*.

oxysalt layer through a reaction of the perovskites with sulfate or phosphate ions.

The oxysalt capping protects the perovskite and suppresses defects at the surface. Encapsulated solar cells made with the capped perovskites maintained

about 97% of their initial efficiency with simulated solar irradiation for nearly two months at a realistic operation temperature of 65°C. “This is one of the best reported stability so far, if not the best,” Huang says.

A study in the journal *Materials Horizons* offers an insight into the low defect density of halide perovskites. This could help materials scientists search for and design materials with similarly low defect densities for applications in optoelectronics and beyond (doi:10.1039/c9mh00606k).

Defects in semiconductors, including halide perovskites, drastically impact the materials’ electronic and optical

properties. Perovskites typically have very few defects especially when solution-processed near room temperature. David Cahen of the Weizmann Institute of Science and his colleagues had previously found that defects in halide perovskites can repair themselves because of dynamic bonds that can break and reform. “This implies change toward a thermodynamically more stable state,” Cahen says.

These findings, he says, led the researchers to propose the counter-intuitive idea that “the materials’ very small free energy of formation from their binary components, which stabilizes them against decomposition, leads to their ultra-low densities of static defects,” Cahen says. This understanding suggests a new path to defect management in materials, the research team concluded.

Perovskite solar cells are prone to degradation when exposed to humidity and sunlight, and researchers have been devising various ingenious ways to improve their stability. A University of Oxford research team led by Sai Bai, Feng Gao, and Henry Snaith have found that adding ionic liquids to perovskites markedly improves the devices' long-term stability.

The researchers added the ionic liquid 1-butyl-3-methylimidazolium

tetrafluoroborate to the formamidinium-methylammonium-cesium lead halide perovskite. They made a solar cell by using this light-absorbing layer between electron and hole extraction layers. The most stable encapsulated devices lost just 5% of their roughly 20% power-conversion efficiency after being exposed to simulated sunlight for more than 1800 hours at 70–75°C. The team estimates that device efficiency drops to

80% of its peak performance in about 5200 hours.

Ions migrate in the perovskite layer, especially under light and heat, creating defects that can trap charges and bring down efficiency. The ionic liquid unpredictably suppressed this ion migration, and it also facilitates better charge transfer between the perovskite and charge-transport layer, the team reported in a recent issue of *Nature* (doi:10.1038/s41586-019-1357-2).

Researchers at Kyushu University in Japan have made exceptionally thick organic light-emitting diodes (OLEDs) by combining thin organic light-emitting films with hybrid perovskite charge-transport layers. They published their results in *Nature* (doi:10.1038/s41586-019-1435-5).

OLEDs hold promise for low-cost, flexible displays and lighting. They are made of

a layer of organic light-emitting molecules sandwiched between organic charge-transport layers. The transport layers need to be thick to completely cover the defects and residues on a substrate. But this requires high driving voltage because organic materials are usually poor conductors.

Toshinori Matsushima, Chihaya Adachi, and their colleagues used the

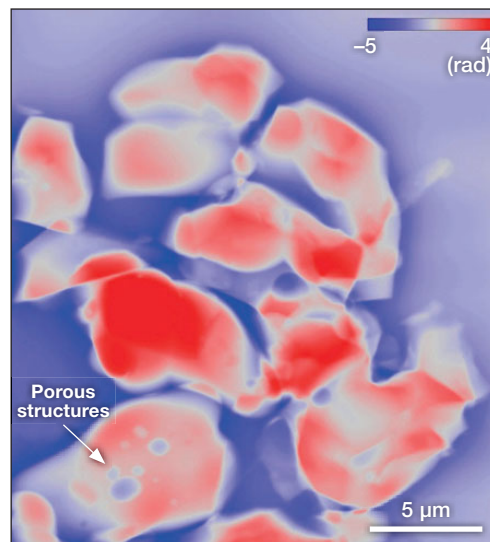
perovskite methylammonium lead chloride to make transport layers that were 2000-nm thick, more than 10 times the thickness of standard OLEDs, without requiring high driving voltage. The thick OLEDs could be used to make large, low-cost, efficient displays that emit the same color from different viewing angles.

Advanced instrumentation enables continuous high-resolution x-ray ptychography

X-ray ptychography differs from more commonly known x-ray techniques that rely on attenuation in x-ray intensity to detect matter. In contrast, ptychography functions on diffraction of coherent x-rays. Diffraction patterns result from interference (i.e., superposition) of x-rays scattered by the structural features of the material under investigation. Accordingly, ptychography can provide information at much smaller dimensions than radiography. In principle, this diffraction imaging technique offers wavelength-limited resolution. However, in practice, spatial resolutions are also limited by inaccuracies while positioning the incident beam. Junjing Deng and his colleagues at Argonne National Laboratory have introduced an instrument called the Velociprobe to relax this limitation and advance ptychography imaging. They reported this design in a recent issue of the *Review of Scientific Instruments* (doi:10.1063/1.5103173).

Unlike the traditional ptychography, the Velociprobe provides continuous scanning with about two orders of magnitude improved positional accuracy down to a couple of nanometers (traditional ptychography performs “step scan” where the scanning stage is first moved and then scanned, while the Velociprobe scans as it moves). Such advanced spatial and temporal control is facilitated by (1) a granite stage for higher stiffness, thermal stability, and vibrational response; (2) laser interferometry for accurate position detection; and (3) a specialized control algorithm to interpret position data and effect adjustments without time lags. The name—Velociprobe—implies fast (velocity) measurements with x-rays as a probe.

The Velociprobe exhibits high spatial resolution down to the pixel size, as shown in the Figure where a $\text{LaFe}_{0.3}\text{Co}_{0.7}\text{O}_3$ perovskite structure is imaged. As the x-rays used in the Velociprobe penetrate the sample, structural information is retrieved rather than just from the surface.



Ptychographic reconstruction of a perovskite sample of about $21\ \mu\text{m} \times 24\ \mu\text{m}$ dimensions with a fine resolution close to 6.2 nm. Credit: Junjing Deng.

For a given sample placement, the probe beam moves to scan an area (typically a raster-like motion), and then the sample is repositioned to image the adjoining portion. The resulting array of diffraction images are stitched to reconstruct the sample. For example, the perovskite structure shown in the Figure is composed of nine