

RESEARCH HIGHLIGHTS: Perovskites

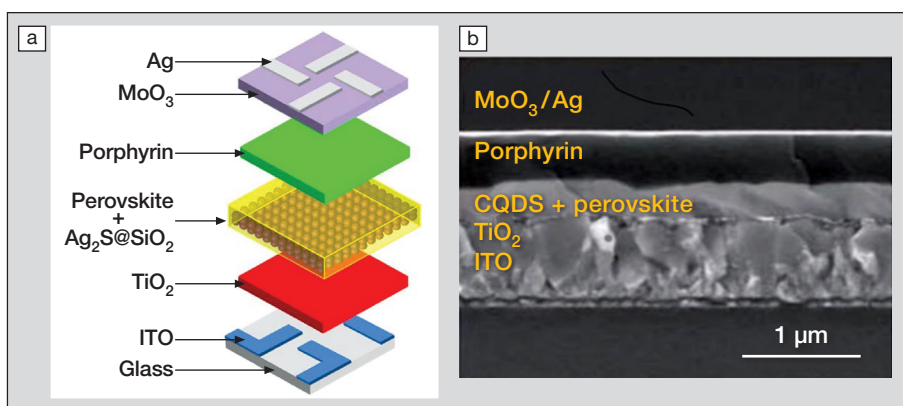
By **Prachi Patel**

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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 are progressing rapidly. The first commercial products could reach the market within the next year; only a decade since perovskite photovoltaics were first discovered. MRS Bulletin presents coverage of the most recent impactful advances in the burgeoning field of perovskite research.

Near-infrared (NIR) wavelengths of 1000–1700 nm have negligible absorption and scattering in living tissue, which makes this an ideal range for fluorescent probes used in medical imaging. Quantum dot (QD) light-emitting diodes (LEDs) can emit light in this NIR window, but their efficiencies have been impractically low, reaching only about 8%. A new study published in *Nature Photonics* (doi:10.1038/s41566-019-0526-z) shows the first QD LED emitting at a long wavelength of 1397 nm with an external quantum efficiency of nearly 17%. A perovskite matrix plays a key role in the device's high efficiency.

To achieve this, the team, led by Abdul Rashid bin Mohd Yusoff at Swansea University, made silica-encapsulated silver sulfide quantum dots with “careful control of both the shell composition/thickness and



(a) Schematic illustration of a multilayered near-infrared-emitting quantum dot-in-perovskite light-emitting diode consisting of ITO/TiO₂/perovskite+Ag₂S@SiO₂ quantum dots/porphyrin/MoO₃/Ag. (b) Cross-sectional scanning electron microscope image of the fabricated device. ITO, indium tin oxide; CQDS, carbon quantum dots. Credit: *Nature Photonics*.

QD size,” Yusoff says. They incorporated the QDs in a highly conductive yet passive cesium-based perovskite matrix, which suppresses nonradiative recombination

of charges—where charges recombine without releasing photons—and ensures the speedy movement of charges, both of which increase efficiency.

A new technique to significantly improve the stability of tin-lead perovskite solar cells could pave the way for high-efficiency tandem solar cells.

Tandem solar cells, made by stacking devices that absorb different parts of the solar spectrum, have higher power-conversion efficiencies than single-junction devices. For perovskite tandem cells, researchers typically use a wide-bandgap lead-based perovskite layer on top and a narrow-bandgap tin-lead perovskite layer underneath. But tin is prone to oxidation,

so the efficiency of tin-based devices drops drastically within a few hours in ambient conditions.

University of Colorado Boulder Materials Science and Engineering Professor Michael McGehee and his colleagues reported that the commonly used hole transporter poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) reacts with tin-lead perovskites, severely reducing charge extraction. The team made a solar cell without a hole-transport layer,

with the tin-lead perovskite deposited directly on the indium tin oxide (ITO) electrode. The Schottky-type junction at the ITO-perovskite junction obviates the need for a separate hole-transport layer. They made the perovskite film with compact, large crystal grains, which increased resistance to oxidation. The cells had an efficiency of 15.4%, which they retained after running under 1-sun illumination for more than 1000 hours. The results were published in *Nature Energy* (doi:10.1038/s41560-019-0471-6).

In another *Nature Energy* article (doi:10.1038/s41560-019-0466-3), a team led by Hairen Tan of Nanjing University presented a different way to suppress tin oxidation in tin-lead perovskite layers. Their “simple and effective strategy” is to add metallic tin powder to the precursor solution from which perovskite films are made.

In the precursor, the species Sn^{2+} oxidizes to Sn^{4+} . But the metallic tin reduces

the Sn^{4+} back to Sn^{2+} , the researchers found. They filtered out the leftover metallic tin granules before making a perovskite film. “By using this strategy, we are able to reduce the Sn vacancies inside the grains and thereby achieve a long carrier-diffusion length of 3 μm in mixed Pb-Sn perovskite films,” they wrote.

The resulting tin-lead perovskite films have electronic quality comparable to high-quality lead-based perovskites. This,

in turn, yielded tin-lead perovskite solar cells, with the highest reported power-conversion efficiency of 21.1%. Tandem cells made with these narrow-bandgap devices have a certified 24.8% efficiency for small-area devices (0.049 cm^2) and 22.1% for large-area devices (1.05 cm^2). The tandem devices retained 90% of their performance following 463 hours of operation at the maximum power point under full 1-sun illumination.

While most efforts on perovskite solar cells have focused on methylammonium lead trihalide perovskites, with bandgaps of 1.55 eV or higher, formamidinium-lead-iodide (FAPbI₃)-based systems, with their slightly narrower bandgap, have the potential to give more efficient photovoltaic devices.

The material’s drawback is that within 10 days at room temperature, it transforms from a black phase to a yellow phase—which has trigonal versus hexagonal

crystal symmetry, respectively—that has a wider bandgap. In a recent *Science* article (doi:10.1126/science.aay7044), researchers reported a method to stabilize the trigonal phase to make efficient, stable FAPbI₃ solar cells.

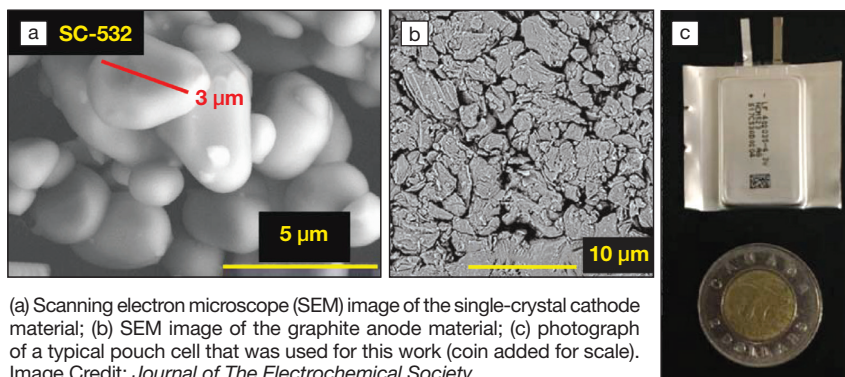
In the past, others have tried to stabilize FAPbI₃ by mixing in cations and anions such as methylammonium, cesium, and bromine. But these additives can also widen the bandgap and reduce stability. Sang Il Seok and his colleagues at the

Ulsan National Institute of Science and Technology made highly efficient and stable perovskite solar cells by adding methylenediammonium dichloride (MDACl₂) to the a-FAPbI₃. The device had a certified efficiency of 23.7% and maintained over 90% of that initial efficiency after 600 hours of operation under full sunlight. Even unencapsulated devices exhibited better thermal and humidity stability over a control device in which FAPbI₃ was stabilized by MAPbBr₃.

Energy Focus

High-performance, long-lasting battery comes with test protocol

Electric automobiles are becoming more popular and more common on the roads each year. These cars are viable because their battery banks store enough energy to facilitate daily commutes. They also deliver steady day-to-day performance and do not degrade rapidly. However, everyday commutes that are short and intermittent rarely tap the full capacities of these batteries. As long-haul trucks and driverless taxis transition from gasoline to electric power, their constant run time will have an adverse impact on the longevity of their batteries. Furthermore, hot and cold environments also affect the operational capabilities of electric vehicles. There is, therefore, a significant drive to deliver “beyond-lithium” cell chemistries for the next generation of batteries. The aforementioned host of dynamic variables presents a formidable challenge for these efforts: what is the most reliable



(a) Scanning electron microscope (SEM) image of the single-crystal cathode material; (b) SEM image of the graphite anode material; (c) photograph of a typical pouch cell that was used for this work (coin added for scale). Image Credit: *Journal of The Electrochemical Society*.

protocol to evaluate these cells and, over a viable laboratory-scale test process, assess expected lifetime and failure mechanisms that accurately apply to real-life batteries that operate for several years?

A research group from the Department of Physics and Atmospheric Sciences and Department of Chemistry at Dalhousie University recently reported a lithium-ion cell chemistry design with excellent longevity. Their resulting battery design, which uses finely tuned electrode and electrolyte designs, also withstood

temperature extremes, allowed fast charging, and was durable enough to power an electric vehicle for over 1 million miles. The group published their findings and methodology in a recent issue of the *Journal of The Electrochemical Society* (doi:10.1149/2.0981913jes).

A crucial component of the success of Jeff Dahn and his colleagues was the design of the cathode electrode in the battery cell. A single-crystal electrode composed of a lithium nickel manganese cobalt oxide yielded the highest and most durable