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.

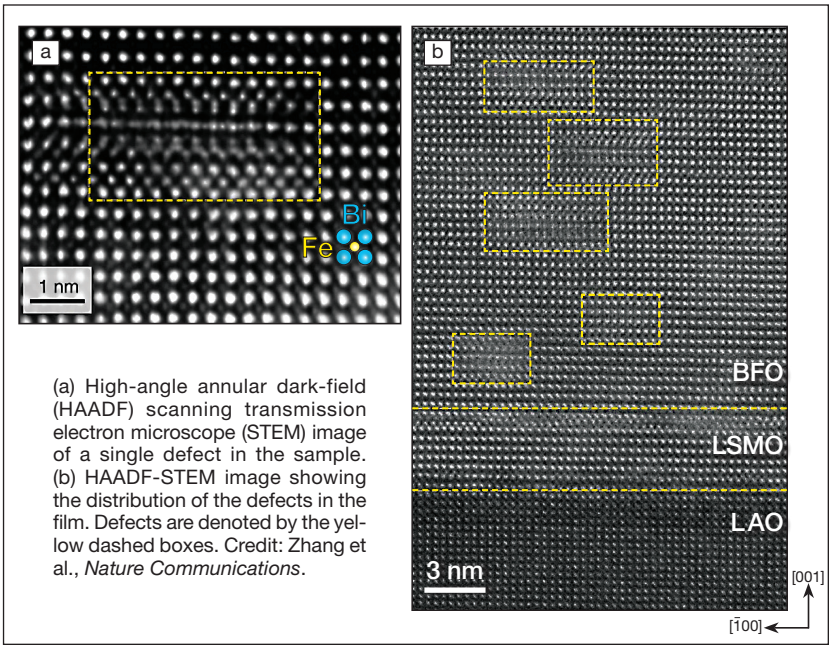
In the LEDs reported in *Nature Photonics* (doi:10.1038/s41566-019-0577-1), energy flowed in the form of excitons, tightly bound electron–hole pairs that traveled together, from the perovskite into the QDs. The devices exhibited a high external quantum efficiency of 8.1% at 980 nm at a radiance of up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

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.



(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*.

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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deposition. The researchers introduced defects in the BFO during the growth process by precisely controlling the temperature, gas pressure, pulse energy, pulse rate, and target composition. High-resolution images of the 60-nm-thick BFO film revealed a high-quality surface with uniformly distributed defects. The defects were larger than a single atom, with an average width of ~5 nm and height of ~2 nm. "Their structure is complex and has not been investigated in detail yet," says Seidel.

To create a memory storage system, the team inserted a 3-nm-thick electrode between the BFO and substrate. Then, using the conducting tip of an atomic force microscope probe, they applied a voltage pulse across the film. The pulse created a stable nucleus of polarization in the film directly below the tip from which the domain spread outward. This spreading can be described by the motion of the domain walls. By systematically varying pulse duration and tip voltage while scanning the film, the team created domains of different sizes.

A statistical analysis of domain diameter as a function of voltage and duration revealed that activating the motion of a domain wall in the film required an electric field 3–6 times larger than in conventional BFO systems. This suggested that the defects exerted local strain that effectively pinned the domain walls in place.

To study the extent of the pinning, the researchers formed domains of various sizes using a tip voltage of –9 V and a pulse duration ranging from 5 ms to 200 ms. They imaged the film with high-resolution piezoresponse force microscopy, which simultaneously captured topography and ferroelectric domains, during a span of 8904 hours. Even after more than one year, the diameters of the domains remained essentially the same.

The normalized polarization retention of this system was at least one to two orders of magnitude better than other ferroelectric systems, the researchers reported. Furthermore, the stability persisted across domains of all sizes. This was surprising because small domains normally decay faster than large domains, and indicates the system's potential for high-density memory applications that utilize small domains. With an optimally sharp tip, the researchers estimate they may be able to achieve a storage density up to 1300 Gbit/in^2.

"[This] work shows a promising path forward to producing superior high-density nonvolatile memories based on ferroelectric materials," according to Matthew Dawber, an expert on ferroelectric materials at Stony Brook University, The State University of NewYork, who was not associated with this project. "[The researchers] show that introduced defects can help stabilize tiny domains for very long times. This is a win-win, normally it's hard work to get rid of defects, and conversely, it's not too hard to introduce them," Dawber says.

The team focused on one kind of defect in this research, but Seidel says that there are many options for pinning domain walls and further improvement may be possible. "Another interesting aspect is the intrinsic properties of domain walls themselves, which can be exploited for nanoelectronics," he says. "[Domain walls have] been known for a long time, but insight into their intrinsic properties and functionality has been investigated in more detail only recently."

Kendra Redmond

Nano Focus

Parallelized two-photon lithography enables submicrometer additive microfabrication

Additive microfabrication—three-dimensional (3D) printing on the micron and submicron level—is relatively new and is expected to have a broad niche market especially in biomedical and wearable electronics industries. The available microprinting techniques, however, suffer from either low throughput that constrains their scaling up to mass production, or poor resolution on the micron scale. A team of researchers has increased the printing speed by more than 1000-fold without sacrificing resolution of the printed pattern. The research team at Lawrence Livermore National Laboratory (LLNL) and The Chinese University of Hong Kong, led by Sourabh K. Saha and Shih-Chi Chen, succeeded in parallelizing two-photon lithography (TPL), a higher resolution lithography method.

TPL is typically a serial method where submicron patterns are printed in a sequential manner rendering it too slow to be practical. The researchers developed a technique where TPL was used to print large areas simultaneously without sacrificing the resolution of the structures that reached length scales as small as 130 nm. The technique, as introduced in a recent issue of *Science* (doi:10.1126/science.aax8760), parallelized TPL-based microfabrication by combining technologies from laser physics, digital optics, and 3D printing.

In two-dimensional (2D) lithography, a 2D pattern is printed on a photosensitive polymer (resist) by exposing it to focused light or a laser through a patterned mask; areas exposed to the light are chemically altered (cured/polymerized) while those covered by the mask are not. By changing the solubility of the exposed volume, a 2D pattern emerges after submerging the polymer into a solvent. The idea was to achieve 3D printing by printing 2D layers on top of each other creating 3D structures.

The main challenge that the researchers overcame was patterning a thin sheet of the polymer while leaving the lower and upper layers unaffected. This allowed layer-by-layer printing by moving a new sheet of the uncured polymer into the focal plane of the laser. The new technique accomplished just that by simultaneously focusing a pulsed near-infrared laser in the time and space domains and thus creating a thin, temporally focused light sheet.

"This was implemented by focusing patterned laser pulses in the time domain such that it has the shortest duration and highest intensity at the spatial focal plane. Basically, the laser pulse was stretched and then compressed in the desired plane, a technique used in designing high-power ultrafast lasers," says Saha, now an assistant professor at the Georgia Institute of Technology.

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