RESEARCH HIGHLIGHTS: Perovskites

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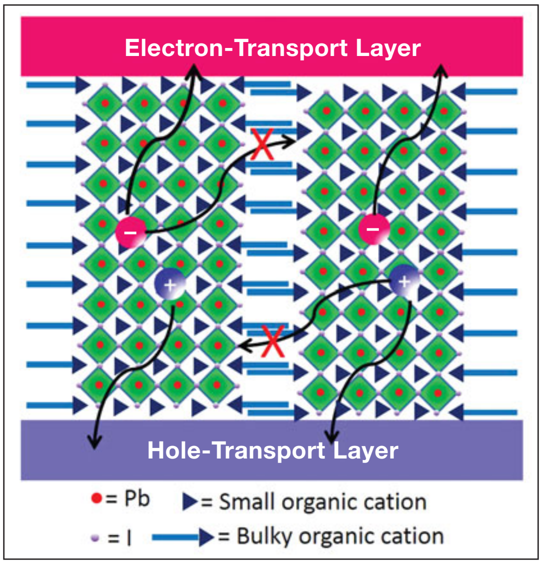
Research on perovskites has progressed rapidly, with solar-cell efficiencies now at 22%, five times higher than first cells reported in 2009. MRS Bulletin *presents the impact of a selection of recent advances in this burgeoning field.*

Three-dimensional organic-metal-halide perovskites are one of the most promising solar photovoltaic materials. However, their instability under operational conditions has been a roadblock to their practical use. By contrast, layered two-dimensional (2D) perovskite films known as Ruddlesden–Popper phases are more stable but have a power-conversion efficiency (PCE) of only 4.73%.

Now researchers have made 2D Ruddlesden–Popper perovskite solar cells with a PCE of 12.52%. When encapsulated, the cells show profound stability over 2000 hours under constant light or humidity, as reported recently in *Nature* (doi:10.1038/nature18306).

Ruddlesden–Popper phases get their layered structure from the presence of bulky organic cations. While smaller organic cations can fit in the cages formed by the metal-halide framework, the bulkier ones come to the edge of the metal-halide framework (see image). The bulky cations are also insulating. So when the metal-halide frameworks are randomly oriented in the thin film, these insulating organic layers obstruct charge transport across the device, reducing device efficiency.

To overcome this, the research team, from Los Alamos National Laboratory and Rice University, used a hot-casting method to prepare uniform, nearly single-crystalline films of the 2D perovskite in which the metal-halide frameworks are flipped on their ends and oriented perpendicular to the substrate. In this configuration, the 2D semiconducting structures act like vertical channels through which photogenerated charge carriers can flow to the respective charge-transport layers without being blocked by the insulating spacers. The researchers used *n*-butylammonium (BA) as the bulky organic cation and methylammonium (MA) as the small organic cation to prepare perovskites with the crystal structures $(BA)_2(MA)_2Pb_3I_{10}$ and $(BA)_2(MA)_3Pb_4I_{13}$.



Schematic for a 2D perovskite in which the metal-halide frameworks are flipped on their ends and oriented perpendicular to the substrate. The photo-generated charges can pass uninterruptedly through the vertical columns formed by the metal-halide framework.

By inventing a simple solution processing method to make high-quality perovskite films, researchers have produced large-area (over 1 cm^2) perovskite solar cells with a certified efficiency of 19.6%.

Michael Gratzel, at the École Polytechnique Fédérale de Lausanne, reported recently in *Science* (doi:10.1126/science.aaf8060) that the new method is reproducible and results in solar cells that have almost no hysteresis. A lag in the current response to applied voltage changes what commonly causes perovskite solar-cell efficiency to drop.

The new method involves applying a vacuum-flash treatment during solution processing of the perovskite. This removes the solvent suddenly but in a well-controlled manner, enabling rapid crystallization of the perovskite precursor. Heating the material results in highly oriented, crystalline perovskite films that have excellent electronic quality.

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https://doi.org/10.1557/mrs.2016.193 Published online by Cambridge University Press

Despite the astounding increase in perovskite solar-cell efficiency, the technology is still far from its theoretical efficiency limit. Knowledge of the material's fundamental properties could help reach this limit. Scientists at the Lawrence Berkeley National Laboratory are trying to understand fundamental processes in perovskite solar cells at the local nanoscale.

In the past, properties of perovskites such as light-generated short-circuit current and open-circuit voltage were assumed to be homogeneous within individual crystal grains. But Ian D. Sharp, Alexander Weber-Bargioni, and their colleagues have found that the current and voltage characteristics vary within the grains.

The team found this by mapping the local open-circuit voltage, short-circuit current, and dark current at the nanoscale (10–100 nm) using conductive atomic force microscopy. The variation depends on the density of charge-trapping defects on the angled facets of the grains. This results in a big difference in energy-conversion efficiency between the facets on individual grains, with some facets approaching the material's theoretical energy-conversion limit of 31%.

The researchers used density functional theory calculations to support their interpretation of the experimental data. This work is published in *Nature Energy* (doi: 10.1038/NENERGY.2016.93). According to the researchers, the results imply that by controlling the growth direction of the grains and the orientation of the facets at interfaces with electron and hole conducting layers, it should be possible to systematically improve the efficiency of perovskite solar cells and light-emitting diodes.

A team of Canadian and Korean researchers have made the brightest, most efficient perovskite near-infrared light-emitting diode (LED) to date. The device, built with a new perovskite mixed material, has an efficiency of 8.8% and a radiance of 80 W/sr/m^2.

In LEDs, under applied voltage, electrons and holes are injected into the device, which in turn recombine and release photons. At normal operational conditions, the charge carriers tend to get trapped at defect sites where nonradiative (thus nonemissive) recombination dominates. This problem can be avoided if the charge carriers are confined in a small space so that all the defect sites are filled and radiative recombination can dominate.

To that end, Edward Sargent at the University of Toronto, Dong Ha Kim at Ewha Womans University in Seoul, and their colleagues prepared a perovskite material where a series of differently quantum-size-tuned grains concentrate the charge carrier in the lowest bandgap light emitter in the mixture.

They synthesized multilayered quasi-two-dimensional perovskite compounds by incorporating the bulky cation PEA, phenylethylammonium ($C_8H_9NH_3$). The large ionic radius of the PEA causes the three-dimensional architecture of $MAPbI_3$ to separate into layers. This gives grains with the composition $PEA_2(CH_3NH_3)_{n-1}PbnI_{3n+1}$, with the average grain comprising $\langle n \rangle$ sheets of PbI_6. The researchers reported their results in *Nature Nanotechnology* (doi:10.1038/NNANO.2016.110). They said the concept could be expanded to make visible LEDs by tailoring the composition of the perovskites.

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