

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.

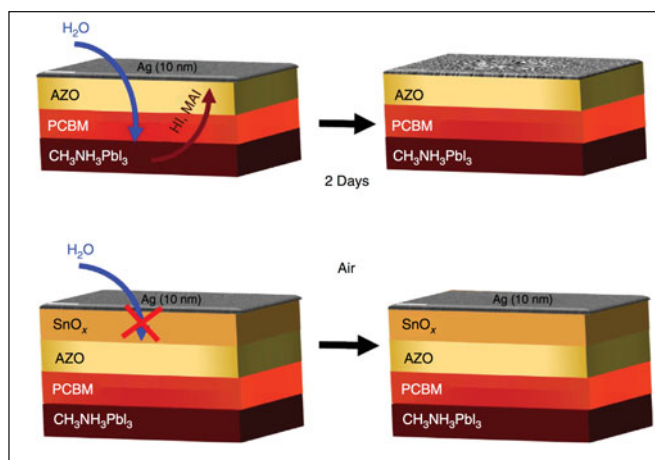
The biggest hurdle to the commercialization of perovskite solar cells is that organic–inorganic metal-halide perovskites tend to decompose into their constituents in the presence of humidity and at high temperatures. Researchers have now made the devices more stable at high temperatures by adding an impermeable tin oxide and an aluminum-doped zinc oxide layer to a conventional perovskite cell architecture.

Typical perovskite solar cells employ an inverted cell architecture, in which positive charge carriers, or holes, are extracted from a PEDOT layer that is deposited on the transparent electrode. Electrons are extracted from the other electrode, which is a metal.

Thomas Riedl of the University of Wuppertal in Germany and his colleagues added a 20-nm-thick tin oxide (SnO_x) layer followed by a 100-nm-thick

aluminum-doped zinc oxide (AZO) layer between the perovskite and the top metal electrode. The AZO is an excellent electron conductor, and the SnO_x layer is crucial for blocking moisture. Cells with the protective bilayer lasted for more than 350

hours in ambient air with 50% humidity, whereas those without the SnO_x layer degraded within tens of hours. The bilayer cells also lasted more than 1000



Credit: *Nature Communications*.

Last summer, physicists at the University of Cambridge discovered that perovskites can reuse photons multiple times.

By depositing thin perovskite films on textured surfaces, the Cambridge team, led by Felix Deschler and Richard Friend, has now been able to extract these recycled photons and boost the external photoluminescent quantum efficiency of devices. “We were surprised at the high gains in photoluminescence quantum efficiency we could achieve with our simple texturing approach, from 20% to almost 60%,” says Johannes Richter, lead author

of the paper in *Nature Communications* (doi:10.1038/ncomms13941). This method could eventually improve power-conversion efficiencies in light-emitting diodes as well as solar cells.

Photon recycling involves light-generated electrons and holes recombining to produce a photon, and the process of charge separation and recombination continuing until the charges are extracted at the electrical contacts or the photons escape the film. The more photons that escape the film, the better the performance of the light-emitting devices or solar cells.

hours at 60°C, while those without the tin degraded within 100 hours. The work is reported in *Nature Communications* (doi:10.1038/ncomms13938).

To increase every photon’s chance to leave the film at the film–air interface, the researchers trapped the photons in the perovskite layer. They achieved this by depositing the perovskite film on a randomly textured glass substrate with structures ranging from 100 nm to 1 μm, which caused the light to bounce around 30 times longer in the perovskite layer, hitting the film–air interface multiple times, explains Richter. On a planar film, the photon would leave the film at the interface between the film and the substrate.

Another approach to address perovskites' thermal stability is to use inorganic perovskites such as CsPbX_3 , where the cesium (Cs) cation is less volatile. There has been growing interest in perovskites for light-emitting field-effect transistors and phototransistors. By integrating organic and inorganic cations, a research

team has made a triple cation perovskite $\text{Cs}_x(\text{MA}_{0.17}\text{FA}_{0.83})_{1-x}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ that has low amounts of electronic defects and better thermally stability.

Mohammad Khaja Nazeeruddin of the École Polytechnique Fédérale de Lausanne, Switzerland, Jin Jang of Kyung Hee University in South Korea, and their

colleagues used the new material to make field-effect transistors that have mobilities over $2 \text{ cm}^2/\text{V}\cdot\text{s}$ and inverters with voltage gains over 20. The researchers say that these are the best reported performances of such perovskite devices. The work is reported in *Advanced Materials* (doi:10.1002/adma.201602940).

Researchers at Florida State University have made a new organic–inorganic metal halide perovskite with a one-dimensional (1D) structure. The material has a 1D perovskite structure where the edge-sharing octahedral lead bromide chains $[\text{PbBr}_4]^{2-}n$ are surrounded by columnar cages formed by an organic

cation ($\text{C}_4\text{N}_2\text{H}_{14}^{2+}$) to form core–shell wires. Millions of these wires are stacked together to form a crystalline bundle.

The 1D structure is excellent at trapping electron–hole pairs called excitons. This leads to efficient bluish white-light emissions with photoluminescence quantum efficiencies

of approximately 20% for the bulk single crystals and 12% for the microscale crystals, as reported in *Nature Communications* (doi:10.1038/ncomms14051). The material could open up a new way to make efficient light-emitting devices and phosphor materials for display applications.

High pressure and small spaces create order from disorder

Geologists have long studied the effects of high pressure on water in the porous media of rocks and minerals in the earth's crust, mainly to explore deformation properties. Now Gloria Tabacchi, a computational chemist at the University of Insubria, Italy, has enlisted the help of her earth science colleagues to study the effects of high pressure on an ethanol/water solution in the channels of a zeolite. The result is a new material that separates ethanol dimers in one channel of the zeolite and water tetramers in another channel. Perhaps most significantly, the material maintains its structure when the pressure is removed, opening up the possibility of room temperature, ambient pressure devices that could separate more complex molecules for various applications, such as solar energy conversion.

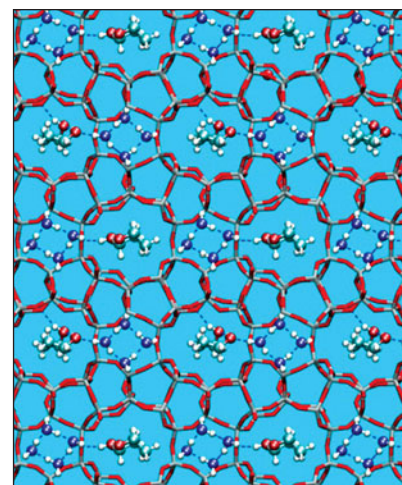
“Usually, when you create something under pressure, all the interesting properties disappear when you release the pressure,” Tabacchi says. “So this was a very nice surprise.”

In this proof-of-principle research published in a recent issue of *Angewandte Chemie* (doi:10.1002/anie.201610949), the investigators chose a simple ethanol/water solution because it was easier to

study experimentally and computationally. Also, the solution is not explosive at high pressures. They chose the hydrophobic all-silica zeolite ferrierite (Si-FER, formula $\text{Si}_{36}\text{O}_{72}$) because it has channels that intersect to form two-dimensional (2D) arrays, along with the right diameters to contain the ethanol and water molecules. They hypothesized that high pressure might enhance the shape-directing action of the zeolite matrix, triggering the formation of organized arrangements.

Experimentally, the geologists, led by Rossella Arletti of the Department of Earth Sciences at the University of Turin, Italy, injected a 1:3 solution of ethanol and water into the zeolite at pressures ranging from 0.20 to 1.34 GPa using a diamond anvil cell. They analyzed the resulting material using high-pressure synchrotron x-ray powder diffraction. At 0.84 GPa, the x-ray analysis showed the inclusion of four ethanol molecules and 6–8 water molecules per unit cell.

Taking the experimental data as a starting point, Tabacchi and colleagues used density functional theory and molecular dynamics simulations suitable for complex organic–inorganic systems. To determine precisely the number of water molecules per unit cell, the computational chemists built Si-FER models containing four ethanol molecules and a range of 6–14 water molecules per unit cell.



Ethanol dimers (cyan, red, and white ball-and-sticks) and water tetramers (blue and white ball-and-sticks) in Si-ferrierite (gray and red sticks). Dotted lines indicate hydrogen bonds. (Image created with VMD: www.ks.uiuc.edu.)

Density functional theory-based structural optimizations showed that the lowest energy (most stable) structure contained eight water molecules per Si-FER unit cell.

Further study of the model revealed that the ethanol molecules formed wires of hydrogen-bonded dimers, while the water molecules formed square tetramers with a closed chain of strong hydrogen bonds. Surprisingly, the zeolite/water/ethanol structure remained stable when