

## Metal Halide Perovskite Polycrystalline Films Exhibiting Properties of Single Crystals

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## Preview

# Tailoring Perovskite Thin Films to Rival Single Crystals

Brandon R. Sutherland<sup>1,\*</sup>

**High temperature epitaxial growth has been a long-standing requirement for forming semiconductor thin films with exceptional optoelectronic properties. In this issue of *Joule*, Brenes and coworkers have demonstrated that atmospheric and photoinduced post-treatments of solution-processed polycrystalline metal halide perovskites can improve the diffusion length, carrier lifetime, and surface recombination velocity to values previously only achievable by single crystal materials.**

Metal halide perovskite materials have invigorated the field of solution-processed optoelectronic devices. They have been predominantly studied as the active layer in third-generation thin film solar cells—a burgeoning area of research with an aim to augment or displace commercial silicon solar panels with inexpensive, lightweight, and scalable materials. Perovskites have seen extensive progress in this application with certified power conversion efficiencies advancing from 14.1% in 2013<sup>1</sup> to now 22.1%.<sup>2</sup> The latter result cements perovskites as a leading competitor in beyond-silicon photovoltaics.

One of the performance-critical physical parameters for the active material in a conventional solar cell is the carrier diffu-

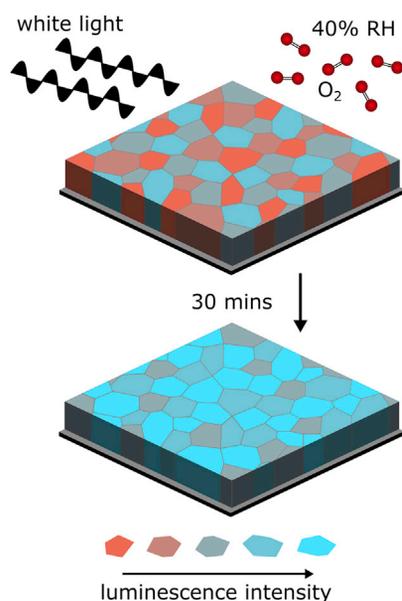
sion length. This parameter is a measure of how far a charge carrier can travel through a semiconductor medium due to a concentration gradient before recombining. It limits the thickness of the absorbing layer in solar cells and is overall a strong measure of the electronic quality of a semiconductor. In early 2015, two research groups near simultaneously demonstrated that perovskites can be grown into large-dimension single crystals and reported diffusion lengths in the 10 to >100  $\mu\text{m}$  range.<sup>3,4</sup> Despite having physical dimensions ill-suited for solar energy harvesting, this was a key result for the perovskite community as it was one of the first reports of solution-processed semiconductors possessing diffusion lengths comparable to their epitaxial counterparts (such as silicon). Re-

searchers have since developed methods to scale down the wider-bandgap bromide perovskite to solar-relevant thicknesses.<sup>5</sup> However, it remains challenging to control the growth of high-quality iodide perovskite single crystals, which possess a bandgap required for efficient single junction photovoltaics. Additionally, single crystal growth is substrate-seeded and is not directly compatible with most mass-manufacturable printing techniques. This new study by Brenes and coworkers published in the inaugural issue of *Joule* has shown, for the first time, that thin film perovskites can be tailored to have key semiconductor material properties—including diffusion lengths—comparable to those of single crystal materials.<sup>6</sup>

Perovskite materials are well known to be incredibly sensitive to both light and humidity.<sup>7</sup> Fully fabricated devices generally prefer exposure to as little of each as possible. However, there has been considerable progress in improving both fronts of device stability through compositional control, electrode engineering, and encapsulation.<sup>8</sup> What is interesting is that perovskite films during

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**Figure 1. Grain-Dependent Photoluminescence Intensity**

Upon treatment with light and humid air, improved luminescence efficiency is observed.

fabrication do not necessarily want to be kept in a dark and dry atmosphere. Experimentalists have long danced back and forth between the glovebox (inert or dry air) and the wet bench (air ambient) for perovskite device fabrication, often favoring one or the other depending on the weather and season. Ummadisingu and colleagues recently reported that, depending on the exact method of film fabrication, perovskites actually switch their preference between light and dark environments during crystallization.<sup>9</sup> It is clearly apparent that on a chemical and morphological level, perovskites change in the presence of light and humidity and, while undeniably chaotic, it is a space to explore and optimize.

In this work, Brenes and colleagues have systematically developed a methylammonium lead triiodide (MAPbI<sub>3</sub>) perovskite treatment process that uses light and humidity to enhance the optoelectronic properties. The method is wonderfully uncomplicated, consisting of exposure to white light at near air mass 1.5 solar irradiance (1000 W/m<sup>2</sup>)

for 20–30 min in a 40%–50% relative humidity environment. This procedure is shown to benefit MAPbI<sub>3</sub> thin films formed via two conventional one-step deposition precursors: (1) 1:1.06 MAI to PbI<sub>2</sub> in an acetonitrile + methylamine solvent, and (2) 1:3 molar ratio of lead acetate trihydrate to MAI in a dimethylformamide solvent with a small amount of hypophosphorus acid additive.

After treatment, spatial photoluminescence mapping shows an overall enhancement in emission intensity, as well as a reduction in grain-to-grain emission variability (Figure 1). The resulting internal quantum photoluminescence efficiency approaches 89%, compared to 1% prior to treatment. Using time-resolved microwave conductivity (TRMC) measurements, the authors report long-lived effective carrier lifetimes in treated films of up to 32 μs for holes. The thickness of the film over the full lifetime yields a hole surface recombination velocity of 0.4 cm/s. From the lifetime and the inferred TRMC mobility, a hole diffusion length of 77 μm is calculated. These values are among the best-ever reported for a polycrystalline thin film and are comparable with monocrystalline perovskites and electronics-grade silicon. These impressive values come with two caveats to consider: (1) the TRMC method may underestimate the effect of grain boundaries on charge transport and (2) photon recycling through successive emission and reabsorption events are included in the lifetime.

The exact mechanism leading to this improvement is still under investigation. The authors show experimental and theoretical evidence that it may be attributed to the combination of atmospheric oxygen diffusion and light-induced superoxide O<sub>2</sub><sup>•−</sup> formation passivating iodide vacancies. This has the effect of reducing the shallow state density in the film, thereby suppressing nonradiative recombination and inhibiting ion migration.

The researchers applied the light and humidity exposure method to the bottom half of a perovskite solar cell and then subsequently deposited the hole transporting and electrode layers atop the treated film. These devices demonstrated a stabilized power conversion efficiency of 18.4% and a near-instantaneous rise to this value upon illumination. This is in comparison to 17.4% for the untreated devices, which show a slow rise to the saturated value. While still unoptimized for devices, the initial proof-of-concept performance is encouraging for the pure MAPbI<sub>3</sub> phase perovskite. Importantly—and unlike many previous attempts to optically enhance perovskite properties and device performance—the effects are long-lived.

With an active material possessing an effective diffusion length significantly larger than the extraction length, as well as long carrier recombination lifetimes—suggesting promise for a minimal open circuit voltage deficit—what are the remaining factors inhibiting perovskite solar cells from reaching efficiencies beyond 23%? Even with a perfect active material, interfacial recombination can pin both voltage and current, thereby constraining performance. Grain boundaries still play an important role in transport, and more work is needed to definitively elucidate their effects on limiting efficiency.

It would be interesting to see the method applied to new materials. The entire study focuses on the pure phase of MAPbI<sub>3</sub> perovskites fabricated using various one-step methods. It is known that even different fabrication processes of the same material can alter the light and humidity dependence. Does the same process benefit perovskites formed via sequential deposition or thermal co-evaporation? Many of the latest efficiency and, importantly, stability breakthroughs in perovskite solar cells have relied on compositional tuning of the A-site cation, such as MA

blending with formamidinium<sup>2</sup> and/or cesium,<sup>10</sup> as well as the X-site halide (mixed iodide/bromide).<sup>2,10</sup> Applying systematic environmental control as a processing step on these films and studying its impact on simulated solar cell performance and stability is a natural follow-up investigation on this work.

Brenes and coworkers have fabricated a solution-processed thin film semiconductor with an electronic landscape comparable to monocrystalline semiconductors. This is a significant achievement for polycrystalline materials broadly and suggests promise for

a future of large-area high-performance optoelectronic devices formed using inexpensive and scalable solution-cast materials.

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## Preview

# The Expanding Energy Prospects of Metal Organic Frameworks

Chong Xiao<sup>1</sup> and Yi Xie<sup>1,\*</sup>

**Metal-organic frameworks (MOFs) and their composites and derivatives, with high porosity and tailorable chemical components, have recently aroused tremendous research interest in renewable energy and environmental science. In this inaugural issue of *Joule*, Lou and coworkers<sup>1</sup> summarize the latest progresses in the fabrication strategies of MOF-based materials and their applications in gas adsorption, energy conversion, and storage, while Dincă and colleagues<sup>2</sup> demonstrate the promising application of MOFs in thermoelectrics.**

Global energy consumption has been on the rise over the past few decades, but about 80% of the world's energy consumption comes from fossil fuels,<sup>3</sup> which has caused serious energy shortages and environmental pollution. These pressing issues urge scientists to explore renewable, safe, clean, and sustainable energy conversion and storage technologies. Hydrogen is an ideal energy carrier, and the clean hydrogen evolution through photo-/electrochemistry underpins various innovative approaches to the pursuit of sustainable energy conversion tech-

nologies, which represents one of the most promising solutions to the upcoming exhaustion of the fossil fuels and the ever-worsening environmental problems.<sup>4</sup> On the other hand, the increasing accumulation of CO<sub>2</sub> in air due to the excessive consumption of fossil fuels is the most serious environmental concern associated with global warming and climate change. Therefore, the environmental and economic incentives to develop processes for the CO<sub>2</sub> capture, storage, and conversion from process streams and flue gases are enormous, which is one of

the crucial challenges in the 21<sup>st</sup> century.<sup>5</sup> Although the current energy shortage is extremely serious, more than 50% of the energy is squandered in the form of waste heat.<sup>6</sup> Recycle and reuse of waste heat by thermoelectric generators is one of the best ways to improve the sustainability of our electricity base,<sup>7</sup> which can generate electricity from the waste heat of automobile exhaust and various industrial processes, and thus are increasingly being seen as having the potential to make important contributions to mitigate the energy crisis and environmental pollution and providing cleaner forms of energy. Meanwhile, a variety of new technologies such as water splitting, fuel cells, batteries, supercapacitors, and solar cells have been proposed to address the foreseeable severe energy issues.

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