

Preview

Perovskites: Between the Grains

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Defect reduction and device stabilization will continue to be two important thrusts toward efficient long-lasting polycrystalline perovskite solar cells. Recently in *Chem*, Zong et al. show that a complementary hydrophobic/hydrophilic triblock copolymer continuously incorporates into methylammonium lead tri-iodide grain boundaries. This improves solar cell stability and performance, resulting in a stabilized 19.4% power conversion efficiency, 92% of which is retained after 480 hr of continuous 1-sun illumination.

Crystalline semiconductors are defined by their long-range order, exhibiting near atomic perfection at the millimeter scale and beyond. In contrast, polycrystalline materials, which are typically fabricated using scalable lower-temperature approaches, consist of crystalline grains separated by a boundary layer. Grain boundaries play a complex role in determining the optoelectronic properties of a semiconductor. Most often, they are detrimental. They are a source of dangling bonds, vacancies and voids, and other defects. This often has the effect of producing undesirable sub-bandgap states that, in a solar cell, can pin open-circuit voltage, increase shunt routes, trap charge carriers, and may increase the pathways for degradation ingress throughout the film. For example, in polycrystalline silicon, grain boundaries are well known to create deep energy states that negatively affect optoelectronic device performance.¹

Perovskite thin-film semiconductors are a class of polycrystalline materials that have demonstrated early promise toward lower-cost, large-area solar cells. The exact role of grain boundaries in perovskites is still not robustly understood.² Generally, it is believed that perovskite grain boundaries are areas with an increased density of non-radiative recombination centers, as evidenced by reduced photoluminescence lifetime³ and other carrier-

quenching measurements. Perovskite single crystals, which do not have grain boundaries—but their large dimensions make them unsuitable for solar cell applications—consistently show improved electronic properties over solar-relevant thin films, indirectly supporting the view that grain boundaries in perovskites are detrimental.⁴

While it is typically well-agreed upon that grain boundaries aren't a good thing for solar cell performance, sometimes there are unexpected benefits. Grain boundaries have been shown to assist in electron-hole pair separation in chalcogenide photovoltaics⁵ and there were some early observations of a similar effect in methylammonium lead tri-iodide (MAPbI₃) perovskites.⁶ In the best case, it has been shown that carefully processed polycrystalline MAPbI₃ can possess key electronic properties comparable to that of perovskite single crystals, but the degree to which this is undermining the effects of grain boundaries remains unclear.⁷ Other work found that carrier recombination in MAPbI₃ primarily occurred in bulk and that degradation was not nucleated from grain boundaries.⁸

Knowing that the properties of perovskites are so incredibly sensitive to fabrication methods, light, temperature, electric fields, and environmental conditions, it is not surprising that

there is some disagreement when studying the “same” material. One way to interpret this somewhat conflicting body of evidence is that grain boundary defects in perovskites aren't necessarily performance-killing. This can be partially attributed to the high defect tolerance of this material, which results in defect formation energies near or within band-edges. Perovskite photovoltaics are already so highly efficient that any performance enhancements from grain boundary mitigation will be modest. However, as this technology continues to mature, modest improvements in efficiency and step-change improvements in stability are going to be two important paths toward a commercially relevant perovskite solar cell.

Every part of a solar cell is valuable real-estate; you can either functionalize it to provide some benefit, or it is wasted space (even if it is not harmful to performance). To benefit polycrystalline solar cell stability and performance, finding the right material and developing effective processing methods to passivate grain boundaries is important. Post-hydrogenation of polycrystalline silicon is known to form chemically resistant Si-H complexes, improving the optical and electronic properties.¹ One promising approach to passivate grain boundaries in perovskites has been the use of organic polymers, which have been shown to form stable cross-linkers between grains.⁹ Recently in *Chem*, Zong et al. report on multifunctional triblock copolymers that self-assemble into a continuously incorporated layer between the ever-present grain boundaries in perovskite thin films.¹⁰

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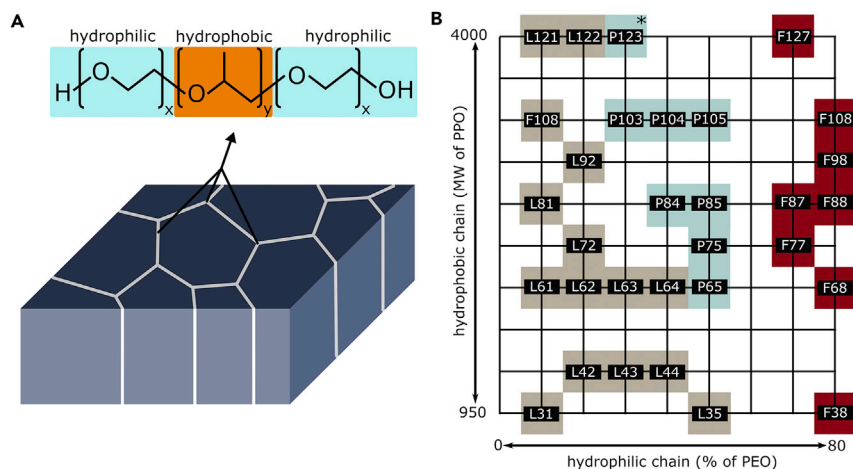


Figure 1. Triblock Copolymer Passivated Perovskite Grain Boundaries

(A) Schematic showing multifunctional triblock copolymer grain boundary passivation. (B) A grid of poloxamers organized by their molecular weight and the ratio of hydrophilic to hydrophobic chain length. L, P, and F suffixes denote polymers that are liquid, paste, or flakes, respectively, at room temperature. * Denotes polymer used in this study. Grid concept adapted from Bahadur et al.¹²

One of the major downsides to metal halide perovskites is their inherent instability. This is especially true for MAPbI₃, one of the more unstable perovskite semiconductors in the presence of elevated temperature and moisture. MAPbI₃ is known to thermally degrade one crystal layer at a time from a surface-initiated breaking of the Pb-I-Pb bond along the [001] direction.¹¹ This process can revert the material to PbI₂ within minutes of heating at temperatures above 80°C. Encapsulation of an entire solar cell made with perovskites is likely required, but it can quickly become an expensive (and incomplete) solution if the material itself is highly unstable. In this work, the authors sought to use polymers possessing some hydrophobic component that would help increase moisture tolerance. Further, to improve their solubility in common polar perovskite precursor solutions (such as dimethylformamide, DMF) as well as to strengthen their interaction with perovskite grains, some element of hydrophilicity is needed. The authors elected to use Pluronic® P123, a multifunctional triblock copolymer of the poloxamer family consisting of hydrophilic

poly(ethylene oxide) (PEO) ends and a hydrophobic poly(propylene oxide) (PPO) core. P123 is shown to have up to 40 weight % solubility in DMF; therefore, the authors simply added it into the precursor solution and studied how it incorporates into the perovskite film.

Careful transmission electron microscopy analysis of the perovskite-P123 composites reveals continuous amorphous regions accumulating at the grain boundaries. The thickness of these amorphous between-grain regions is found to be a controllable function of the amount of the copolymer added to the precursor solution. Using density functional theory, they show that the hydrophilic ends favorably bind to the perovskite surface. The authors posit that, since the copolymer cannot be incorporated into the crystal lattice, during nucleation they are pushed outward to the grain boundaries.

The authors employ the copolymer-P123 material as the active layer in a standard n-i-p heterojunction solar cell. The best-performing device with

optimized P123 concentration exhibits an outstanding stabilized power conversion efficiency of 19.4%, relative to the 17.6% pure MAPbI₃ control. A significant gain in open-circuit voltage was observed, from 1.03 V to 1.11 V. Local atomic force microscopy probing reveals a voltage enhancement consistent with the passivation of defects. Their control device without the copolymer degraded to 59% of its original performance after 480 hr of continuous testing in a dry atmosphere, whereas the copolymer device retained 92% of its initial efficiency.

Rather interestingly, it was observed that as the amount of P123 is increased, the grains get smaller (typically thought of as undesirable for efficiency). It is a somewhat surprising case of performance increasing with a significant decrease in the grain size. The authors have attributed this to the combined benefits from the filling-in of pinholes, the increase in film smoothness, and the passivation of grain boundary defects. It was found that when the boundaries get too thick, as expected, the electronic transport is impeded and the performance subsequently decreases. The presence of the copolymer is believed to act as a nucleation site, which is why the number of grains increases. The authors further supported this view by forming films without an antisolvent, showing that film coverage increases with increased P123 incorporation.

This work presents a generic grain boundary passivation strategy consisting of complementary hydrophilic/hydrophobic triblock copolymers. Encouragingly, the authors have demonstrated this stability and performance enhancement with one of the most common off-the-shelf poloxamers. This motivates further exploring of different triblock or diblock copolymers, and studying their effects on a wider range of materials, such as those based on more complex blended

cation/anion compositions, and all-inorganic or lead-free perovskites. Other members of the poloxamer family—depending on their ratio of hydrophobic to hydrophilic chain lengths and specific molecular weights (Figure 1B)—may be promising to explore toward a more optimal combination of stability, solubility, and defect passivation. Grain boundaries are not going away anytime soon in perovskite thin films, and every nanometer cubed in a solar cell is valuable space; it's increasingly encouraging to see efforts like this to functionalize them.

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Preview

Separating the Heat from the Gap

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Increasing the conversion efficiency of incident solar energy to electricity is a key goal in the solar R&D community. In this issue of *Joule*, a conceptual hybrid photovoltaic/thermal (PV/T) receiver design is reported by the research groups of Evelyn Wang and Gang Chen. High exergetic efficiency is achieved by absorbing below-bandgap and excessively high-energy photons as thermal energy, while allowing photons at the PV's bandgap to pass through to the underlying cell.

One need go no further than the first paragraph of any article on solar energy technology to confront the mind-boggling scale of the available energy resource. The deployment of solar technology has experienced incredible growth in the past decade. This deployment has been dominated by single-junction silicon photovoltaic (PV) technology. These devices are

characterized by a single bandgap, which is unable to convert a significant fraction of the incident solar spectrum. The Shockley-Queisser efficiency limit¹ for single bandgap silicon PV devices is 32.2%, accounting both thermal losses of photons below and greatly above the bandgap and radiative recombination losses, and deployed systems experience a much lower con-

version efficiency. Besides conversion efficiency, another barrier to ever-increasing solar penetration is the lack of cost-effective grid-scale electricity storage technologies, since storage is necessary for solar electricity to be available overnight or during extended periods of clouds.

Another approach to solar energy conversion to electricity is via concentrated solar power (CSP), where the incident solar energy is concentrated and used to heat a storable high-temperature working fluid, which is then used to drive a heat engine. Increases in system efficiencies are therefore achieved by increasing the collector temperature. CSP based on conventional molten salts has been limited by the vapor

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