

Advances and Obstacles on Perovskite Solar Cell Research from Material Properties to Photovoltaic Function

This is a summary of the central topics and discussions presented at the MRS symposium on perovskite solar cells celebrated in Boston, USA, November 27–December 2, 2016. The objective of this Energy Focus is to picture a vivid update of the dominant lines of development of perovskite solar cell research. The topics have been edited and finished by the organizers (authors) based on remarks from David Cahen, Filippo De Angelis, Germà Garcia-Belmonte, Jinsong Huang, Luis K. Ono, Nam-Gyu Park, Prashant Kamat, Teresa S. Ripolles, and Yi-Yang Sun. The text expresses the consensus opinion of the organizers, who are very grateful to the speakers that shared their views for this paper.

Progressing toward Electronic Perfection. The impressive enhancement in inherent properties of photovoltaic perovskite materials during the past few years has allowed one to attain power conversion efficiencies (PCEs) comparable to those exhibited by commercial technologies (Figure 1). Clear indications of the materials quality of semiconductor perovskites are the outstanding values reached by the emission quantum yield of layers as well as the carrier mobility. Perovskite processing and preparation routes are then lending active absorber layers to practically ideal levels. An enormous variety of parameter optimization routes still go unexplained, but they appear to progressively lead to electronic perfection in photovoltaic operation. While in the early stages of development the trial and error approach is understandable, likely it will come back to haunt us, as was and is the case in inorganic thin-film PV technologies, when high reproducibility at high efficiencies with minimal waste and environmental impact become a must. This fact situates further enhancements of performance on the interface engineering side. It also opens the era when photonic control for squeezing the power content of the solar spectrum will begin to be a relevant research and technical issue.

As a matter of fact, photon recycling was raised by several authors in one session because of its impacts on perovskite solar cell efficiency. The photon recycling concept means that photons can be recombined several times with subsequent radiative events, which was raised for GaAs, but its impact to efficiency enhancement is still under strong debate because it is lost if an amount of nonradiative recombination is available to remove long-standing excitations. Under low quantum efficiency of radiative recombination, photon recycling can be ignored, but at a higher level of sample perfection, it could add a component to the open-circuit voltage.

It has been widely recognized that perovskite layers of excellent luminescent quality undergo dramatic decay of performance when contacts are added to form a solar cell. As a consequence, several recent studies have paid close attention to the kinetic processes and energetics of the contacts between

the perovskite materials and the extraction layers. A combination of tools and techniques addressing the chemistry and operation of interfaces is of order at the present time to gain useful knowledge for solar cell improvement. First-principle simulations, reactivity of materials, energy level spectroscopies, and electrical response analyses restricted to the operation of the interfaces would contribute, among other techniques, to a coherent and predictive picture of the perovskite solar cell operating principles.

Understanding Compositional Variations and Traps. Quite a few talks dealt in one way or the other with the presence of electronic traps. The results that were presented add to those already in the literature, but there does not at this point seem to be a clear convergence of numbers. This is so even if one accepts that most of the results are essentially reporting on traps at interfaces, surfaces, and grain boundaries. Likely the great variety of samples that are nominally the same has something to do with the uncanny large spread of data for trap energies and densities.

Besides the intrinsic material properties, such as the absorption coefficient and carrier effective masses, the success of a semiconductor is essentially related to the minimization of trapping and scattering of charge carriers at defect sites. Organohalide perovskites have shown a surprisingly low concentration of traps, ranging from $\sim 10^{11}$ to 10^{16} cm⁻³ in single crystals and polycrystalline thin films, respectively, despite the inherent soft nature of these materials. Defects must however be very abundant in the hybrid perovskites, implying an unusual defect chemistry in the prototypical MAPbI₃ perovskite whereby the typical cation (MA, Pb) and anion (I) vacancies or interstitials would only introduce shallow states in the material band gap. State of the art DFT calculations have however shown that most of the above defects show relatively low formation energies. Some can indeed introduce (deep) states in the MAPbI₃ gap, but they show relatively high formation energies. Nevertheless, additional understanding of the defect photochemistry/physics of lead halide perovskites by dedicated experiments and modeling studies is still needed. One needs to clearly identify the sources and nature of carriers traps and the mechanism behind their apparent inertness toward charge trapping, thus allowing further boost of the hybrid perovskite optoelectronics.

Perovskite surface and grain boundary passivation by organic insulating materials has been attempted. Though polycrystalline organic–inorganic lead halide perovskite thin films have shown superior optoelectronic properties, their surfaces and grain

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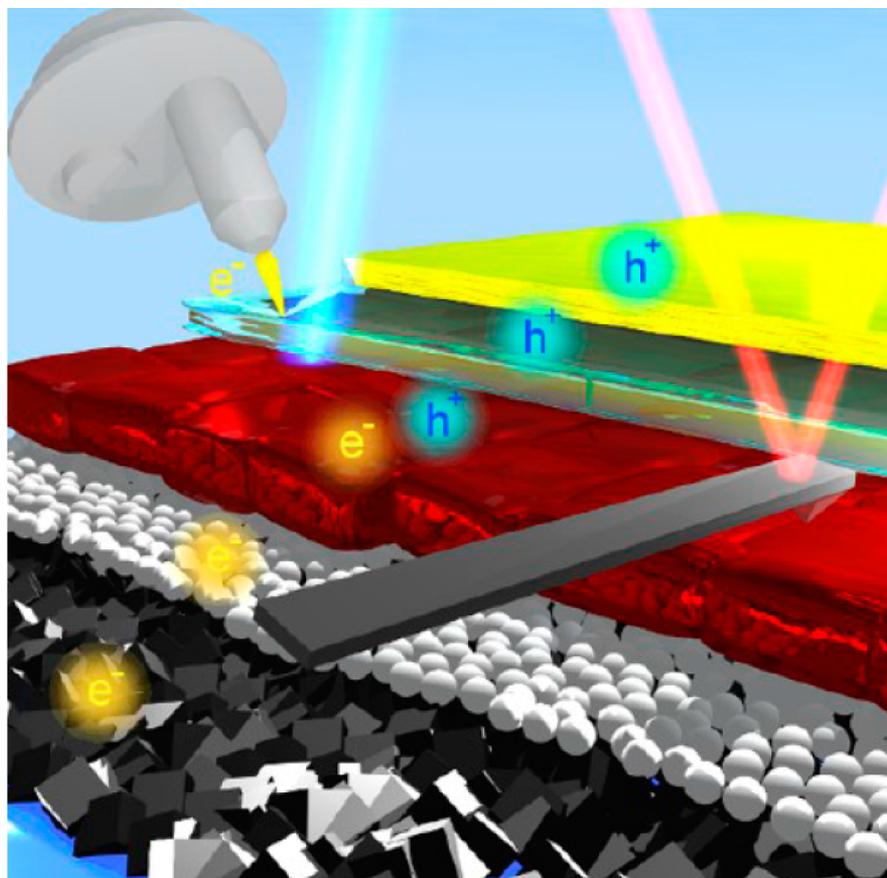


Figure 1. Material properties to photovoltaic function of perovskite solar cells. Reprinted from *J. Phys. Chem. Lett.* 2016, 7 (22), 4764–4794.

boundaries can still cause charge trapping and recombination, which is detrimental for solar cell performances. It has been reported that fullerenes and organic insulating materials can effectively passivate the surfaces and grain boundaries of perovskite thin films. If these materials are kept thin enough so that they do not block current flow between perovskite and charge transfer materials, the open-circuit voltage of the resultant perovskite solar cells can be increased, leading to significantly improved device performance. Unavoidable grain boundary is a pro and a con of solution-processed perovskite films, which is likely to act as a recombination site. An in situ grain boundary healing layer using the nonstoichiometric adduct method was reported. A slight excess of methylammonium iodide in the precursor solution forms an in situ thin methylammonium iodide layer on the surface of perovskite grains, which improves charge conductance at the grain boundary and the carrier lifetime of perovskite grains. The grain boundary healing process can produce a PCE exceeding 20%. However, there is a strong and difficult-to-resolve debate about the role of grain boundaries in electronic operation because definitive correlation of structure and properties remains to be seen, and other authors believe that the contact interfaces introduce the main slow kinetic effects. Hopefully the spread of large single-crystal formation methods devoid of internal grains will assist to separate grain boundary and contact layer effects.

Compositional variation of the halide ratio (e.g., ratio of Br/I) is commonly employed to continuously tune the band gap of mixed halide perovskites. The ease of this approach can be used to design gradient perovskite structures or tandem cells and

maximize capture of energetic photons in solar cells. The recent demonstration of halide ion migration and segregation under photoirradiation and its reversibility upon stopping illumination has intrigued scientists. Several models including entropy of mixing, defect-mediated migration, and polaron-induced effects have been proposed, yet no consensus on this phenomenon has emerged. There is a need to better understand halide ion migration and segregation in lead halide perovskites. Understanding of photoinduced segregation effects in mixed halide perovskites is important as it would influence the performance of solar cells and other photonics applications as well as long-term performance. Theoretical models that could explain the reversibility of photoinduced segregation can shed new light on this intriguing process.

Two posters showing very different experimental methods concluded that MAPI in its tetragonal form is ferroelectric, formally, although whether this has any bearing on photovoltaic activity at room temperature or not is far from clear because the strong dynamic disorder, for which more experimental and theoretical evidence was presented, may wash any effects out.

Fabrication. For a long time, $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells with PCEs above 20% are exclusively fabricated by solution-based processes. It is now reported that fully evaporated perovskite solar cells can also achieve PCEs above 20%. The full evaporation process offers many advantages as compared to solution processes, including not using toxic and expensive solvents, accurate control of film compositions and morphology, ease of synthesizing films at large scale and on flexible substrates, and the possibility of fabricating all-perovskite tandem solar cells. The highly efficient fully

evaporated $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin film solar cells were enabled by the use of new small-molecule electron and hole transfer layers. These carrier transfer materials significantly enhance charge extraction from perovskite absorbers. Importantly, these carrier transfer materials can also be evaporated, making fully evaporated perovskite solar cells possible. Understanding the charge extraction and transfer processes between perovskites and these new carrier transfer materials can provide guidance on designing new charge transfer materials for further improving the PCEs of perovskite solar cells.

Pb-based perovskite solar cells face great challenge for commercial and industrial applications due to the toxicity of Pb-based perovskite materials. One report showed that Pb and Sn affect the human nervous system as well as the reproductive system. Due to the easy decomposition of the perovskite materials in a humid environment or under strong UV radiation, the process would produce Pb and Sn cations. In addition, the decomposition procedure of the perovskite is irreversible. Bi-based perovskites are considered to be a good candidate. Several groups reported hybrid double perovskites, such as $(\text{MA})_2\text{BIBiX}_6$ (BI = K, Tl, and Ag; X = Cl and Br), which show strong similarities to the lead analogues. They used solvent evaporation and hydrothermal methods to synthesize the hybrid perovskites. The results give the possibility of making new bromide and iodide double perovskites as potential light absorbers. Their findings provide a new and viable route toward lead-free, hybrid semiconductors. A report also examined the Cs_2MBiX_6 family by using hybrid DFT to evaluate the electronic structure. It considered the effects of thermodynamic stability and cationic disorder and their consequences on the applicability. These results provide an outlook for the future of the double perovskites in photovoltaics. The overall performances of the Pb-free cells are still relatively low compared to the lead-based ones. However, Pb-free perovskite solar cells are also promising materials for next-generation photovoltaic devices. Much more research effort is expected in the area of developing new materials and new structures of the device to improve performance and stability of Pb-free solar cells.

The adduct approach, mentioned above, is one of the effective methods for highly reproducible perovskite films, which is based on Lewis acid–base interaction. Polar aprotic solvents are good Lewis bases, which can form an adduct with PbI_2 . Instead of direct formation of a perovskite phase from the spin-coating process, homogeneous and higher-quality perovskite films can be formed via an adduct intermediate. Power conversion exceeding 18% could be attained by the adduct approach.

Stability. Perovskite solar cells achieved almost the theoretical maximum photoconversion efficiencies of over 22%. Despite this, stability is still an issue to improve, among other factors, in order to implement the perovskite semiconductor in numerous applications. Here, we summarize some achievements so far in this field.

Although the shorter lifetimes of perovskite solar cells have been frequently attributed to the degradation of the perovskite layer, at this symposium, several talks drew our attention to the stability of adjacent layers such as electron and hole transporting layers (ETLs and HTLs) as well as the electrode materials. For example, the top gold electrode is not completely stable, and gold atoms/clusters can diffuse into the underneath layers, generating an irreversible degradation process in

perovskite-based solar cells. As a remedy, a layer of Cr as thin as 5 nm was shown to prevent the diffusion of Au atoms into the perovskite layer. Another talk highlighted the instabilities of the TiO_2 material as it can induce UV-induced degradation of the perovskite layer, that is, photocatalysis. Spiro-MeOTAD-based HTLs were also pointed out as the cause of severe degradation of the entire perovskite solar cell. From the presented reports, it definitely became clearer that several interfaces, and not just TiO_2 , are not innocent but are loci of reactions or allow ready diffusion across them (e.g., for Au atoms from a Au contact). It is also possible that they are so active because that is where point defects can be annihilated or originate.

There are two possible ways to improve long-term stability. One is encapsulation, and the other is material engineering. Thermal stability of perovskite solar cells relies on not only perovskite materials themselves but also other layers in the full cell, for example, selective contacts. Selection of materials for selective contacts is critical for thermal stability of perovskite solar cells. Regarding interface and contact effects, many researchers confirmed that the standard hole extraction transport layer, spiro-OMeTAD, damaged the perovskite film, and cavities on its surface were observed. Several materials such as undoped organic C_{60} or inorganic NiO can reduce perovskite degradation in an inverted architecture. However, the cell performance achieved in these kinds of structures is still far from the standard perovskite devices.

Ion migration resulting in reactions at electrodes may cause severe materials modification of perovskite solar cells. Insertion of a two-dimensional perovskite in between three-dimensional perovskite grains may help improve stability due to suppression of iodide migration. The above-mentioned examples highlight the need for a solar cell architecture by a rational design approach selecting proper and robust adjacent layer materials.

Regarding the FAPbI_3 perovskite layer, several studies demonstrated that a new perovskite composition is required to avoid structural phase transitions. To that end, structural changes were controlled by adding a small amount of cesium into the standard perovskite configuration which achieved thermal stability. Recently, a new approach consisting of perovskite dimensional stacking was studied. That is, the combination of three-dimensional and two-dimensional perovskite layers hinder ion migration due to the two-dimensional layer, reducing the hysteresis and improving the stability.

As a conclusion, these results suggest that other routes than the conventional methods are imminent toward understanding the critical role of the perovskite films and the contact materials for low-cost, highly efficient, and stable perovskite solar cells.

Tandem. The PCE of single-junction solar cells is limited by a Shockley–Queisser limit of about 33%. However, there are principles that can be explored to overcome this limit. One of the most successful approaches is the tandem cell. So far, high-efficiency tandem cells have been exclusively based on III–V semiconductors and germanium. The stacking of different layers in tandem cells requires good tunability of the band gap of light absorber materials. In the meantime, the lattice constants and band edge positions need to be well matched between layers to allow a high-quality interface and smooth carrier transport across the interface. Perovskites are capable of both cation and anion alloying, which allows the band gap to be tunable from 1.2 eV (e.g., MASnI_3) to above 2 eV. Lattice constant matching can be achieved by simultaneous cation and anion alloying, which could compensate for their changes in

lattice constants. Because these materials have closely related atomic and electronic structures, they may also offer suitable band alignments. With these promising properties, there is a reason to anticipate that perovskite tandem cells will be a widely pursued direction in the years to come.

Combining wide-band-gap perovskite thin-film solar cells with market-proven crystalline silicon solar cells to form a tandem device is a viable approach to improve the solar cell efficiency and reduce manufacturing costs. Four-terminal perovskite/Si tandem solar cells have demonstrated feasibility of achieving efficiency of >25%. Recent device modeling considering various radiation conditions, locations, and temperatures has shown that perovskite/Si tandem solar cells can achieve maximum efficiencies of >30%. Surprisingly, the perovskite/Si tandem solar cells show even better angular dependence for cell efficiency than crystalline Si solar cells. The device modeling results suggest that the perovskite/Si tandem solar cell technology holds great potential for realizing low-cost solar electricity.

Final Remarks. Empiricism and understanding remain strongly imbalanced for halide perovskites. Thus, very few “hero” experiments are done, such as GIWAXS measurements during film formation via antisolvent dripping and femtosecond electron diffraction. The enormous efforts in terms of characterization still seem to be accompanied by no or insufficient awareness of the damage that the probing beams and/or applied voltages can have on the halide perovskites. The issue is not just an academic topic because, for example, more evidence was presented for light-induced structural changes and this needs to be clearly separated from possible damage.

A great advantage of the very large research effort should be the availability of multiple results of similar or identical experiments or of different experiments that should lead to the same result. We have the general impression that there is yet too much randomness and improvisation in the field while we lack coherent and robust results on the front of physical understanding. We need insights corroborated by divergent experimental methods so that we can trust the occurrence of the property. Perhaps the research community is being more cautious about continuous reports of striking novelties and values more patience, confirmation, and similarity that leads to a strong knowledge basis about the perovskites properties and operation. With the widespread availability of high-quality samples that has occurred in very recent times, we should be in good shape to carry out cross-checks. Alas, that is not yet the case, and one way to start would be standardization of samples and a larger degree of large-scale exchange for cross-checks of results and a combination of techniques in different laboratories. To do that, though, a proven way for sample transport and handling has to be found and agreed upon.

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Notes

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