

# Perovskite Solar Cells Shine in the “Valley of the Sun”

“Perovskite-Based Photovoltaics and Optoelectronic Devices” (Symposium EP3) was one of the most active symposiums in the *Material Research Society (MRS) Spring Meeting 2016* (March 28–April 1) held in Phoenix, Arizona—the “Valley of the Sun”. A large number of scientists and engineers from academia and industry met together to discuss the progress of perovskite solar cells (PSCs) and the understanding of the critical science related to PSCs. This symposium included 18 invited talks, 67 contributing talks, 130 posters, and more than 300 participants. These numbers clearly indicate that the surge in research interest continues in this emerging solar cell technology. Just a couple of months before this symposium, a new power conversion efficiency (PCE) record of 22.1% was released by Sang Il Seok’s group (KRICT/UNIST, South Korea).<sup>1</sup> Such a swift rise of PSC efficiency within only 6 years has been unprecedented in the history of photovoltaic (PV) technology. Of course, several challenges remain (for example, scaled-up fabrication, stability, toxicity, and hysteresis) before PSCs can successfully enter the PV market. However, the perceived huge potential of this future lab-to-market transition has stimulated myriad efforts from both the scientific community and industry. This symposium reported some of the recent achievements in the context of addressing these challenges.

Is it the time to consider scaling up PSCs? The answer is a resounding “Yes”, as evinced by many exciting talks from different groups worldwide. Trystan M. Watson (SPECIFIC, Swansea University, United Kingdom) discussed a roadmap for commercial-scale PSC production from laboratory hero devices, to print trials, to continuous module fabrication, and finally, into large-scale production. A photograph of a flexible printed PSC fabricated based on the low-cost metal foil from Watson’s group is shown in Figure 1A. Watson noted the following potential bottleneck in the process of continuous (roll-to-roll) perovskite thin-film fabrication: in the conventional “one-step” or “two-step” processing of halide perovskites, a prolonged duration of heat treatment is usually required to form high-purity perovskite films from the precursor phases. Considering a roll-to-roll process rate of 10 m/min, a 90 min heating step will require an oven that is 900 m long. This heat-treatment issue was also discussed by Doojin Vak (CSIRO, Australia), who has been working on the protocol and instrumental development of roll-to-roll fabrication of perovskite thin films on flexible plastic substrates. Instead of using one-step annealing, Vak and co-workers engineered the microstructure of the first-printed  $\text{PbI}_2$  precursor film and subsequently printed the organic halide precursor film to form the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  ( $\text{MAPbI}_3$ ) or  $\text{HC}(\text{NH}_2)_2\text{PbI}_3$  ( $\text{FAPbI}_3$ ) perovskite rapidly, as shown in Figure 1B. It is apparent that lessons learned from research on spin-coating, the most popular film-processing method in the laboratory, cannot be easily transferred to slot-die coating trials. This is because rapid solvent evaporation

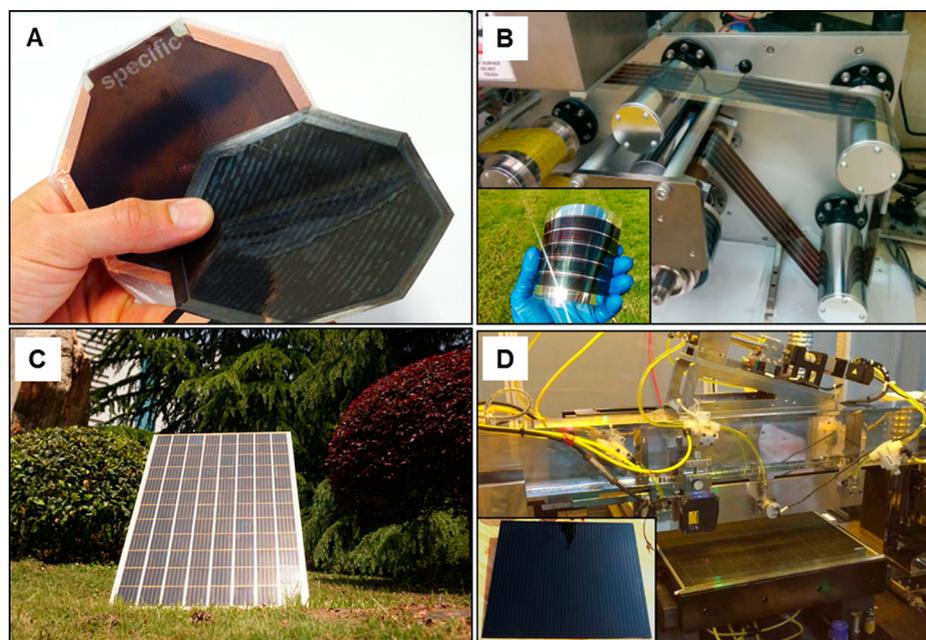
simultaneously occurs during the precursor-solution spin-coating process, which is different from the case of the slot-die coating. This gap needs to be closed by researchers in order to advance the processing science that is suitable for large-scale continuous PSC fabrication. Instead of focusing on the roll-to-roll fabrication of PSCs, talks by Bin Fan (Weihua-Solar Company, China) and Hongwei Han (Huazhong University of Science and Technology, China) showed that carbon-electrode-based hole-conductor-free PSC modules on rigid glass substrates based on batch processing have more promise in the nearest term for PSC commercialization. Both Han and Fan demonstrated large PSC panels (Figure 1C and D) with encouraging power conversion capability and outdoor stability. In particular, PSCs based on carbon-based triple-layer mesoscopic architecture invented by Han’s group have already demonstrated outstanding stability in outdoor tests in a hot desert climate and in indoor long-term light soaking as well as heat exposure for 3 months at 80–85 °C in an earlier report.<sup>2</sup>

Although the scale-up of solution fabrication of perovskite thin films has been shown, it remains a challenge to form continuous, smooth, high-purity perovskite thin films at large scale, which is associated with difficulty in controlling the crystallization behavior of perovskites at different scales. In this context, Nitin P. Padture (Brown University, United States) discussed the solution evolution of hybrid perovskites from a fundamental material science perspective, including classical nucleation and growth theory as well as the coarsening mechanism. Padture and his co-workers showed that using (anti)solvent–solvent extraction to induce the nucleation of perovskites at room temperature is a feasible way to form highly smooth perovskite thin films rapidly. This can be attributed to perovskite nucleation and growth occurring in the red-band region in Figure 2, where the growth rate is suppressed and the nucleation rate approaches the maxima. In contrast, using conventional annealing with elevated temperature, the growth dominates the crystallization process, as shown in the green-band region in Figure 2, and the resultant perovskite film usually contains large crystal domains with pinholes. Interestingly, Padture, Yabing Qi (Okinawa Institute of Science and Technology, Japan), and Yixin Zhao (Shanghai Jiao Tong University, China) all reported use of methylamine ( $\text{CH}_3\text{NH}_2$ ) gas for rapid (in seconds) processing of ultrasmooth perovskite thin films at room temperature, where the aforementioned nucleation and growth theory may be in play. It is worth noting that the kinetics of the perovskite crystallization process in Figure 2 are based on the simplest assumption that the perovskite evolves directly from its precursor solution, which may not be the exact case in many real situations. For example,

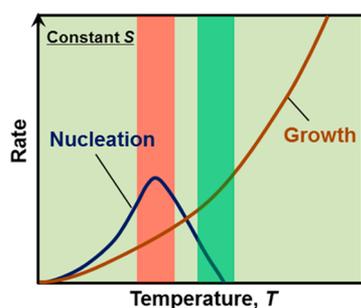
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**Figure 1.** (A) Photograph of a printed PSC on low-cost metal foil (courtesy of Dr. Trystan M. Watson, Swansea University). (B) Photograph of roll-to-roll fabrication of the MAPbI<sub>3</sub> perovskite thin films based on a “two-step” slot-die coating process (reproduced with permission from ref 3; Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). The inset shows a printed flexible module (courtesy of Flexible Electronics Lab, CSIRO Manufacturing, Clayton, VIC, Australia). (C) Photograph of carbon-based hole-conductor-free mesoscopic PSC modules (courtesy of Professor Hongwei Han, Huazhong University of Science and Technology). (D) Photograph of the process of slot-die coating the hybrid perovskite thin film on a rigid substrate. The inset is a photograph of an encapsulated carbon-based hole-conductor-free planar PSC module (size: 45 cm × 65 cm) based on the slot-die coating technology (courtesy of Dr. Bin Fan, Weihua-Solar Company).



**Figure 2.** Schematic profile of nucleation and growth rates as a function of temperature at constant supersaturation ( $S$ ). The red and green bands indicate the nucleation and grain growth of materials at a lower and higher temperature, respectively. Reproduced with permission from ref 4; Copyright 2015 American Chemical Society.

as implied in talks by Prashant V. Kamat (University of Notre Dame, United States) and Aryeh Gold-Parker (Stanford University, United States), the first crystallized phases from a nonstoichiometric perovskite precursor solution are usually solid-state iodoplumbate complexes, which then transform into the perovskite. Here, the complex chemistry of the precursor components (organic precursor, inorganic precursor, and solvent molecules) can play important roles. Correlating this with nucleation and growth theory can be critical for understanding the evolution of perovskites. These fundamental understandings on chemistry and material science questions are expected to provide insight to guide the development of optimum processing protocols for large-scale perovskite thin films.

Another major concern regarding PSCs is stability. The intrinsic thermal stability of the most-popular MAPbI<sub>3</sub> perovskite has been questioned, while the thermally more stable FAPbI<sub>3</sub> has been attracting increasing attention. However, FAPbI<sub>3</sub> has a yellow nonperovskite polymorph that appears more stable in the ambient; thus, the phase transition from the perovskite polymorph to the undesirable nonperovskite polymorph can occur. Mei Gao (CSIRO, Australia) showed that a printed FAPbI<sub>3</sub> perovskite thin film degrades rapidly in the ambient without encapsulation. To address this issue, Nam-Gyu Park (Sunkyunkwan University, South Korea) and Zhen Li (National Renewable Energy Laboratory, United States) reported the hybridization of FAPbI<sub>3</sub> with inorganic CsPbI<sub>3</sub> to stabilize the perovskite structure. Such composition-mixing strategies were also discussed by Michael McGehee (Stanford University, United States), whose group focuses on developing stable perovskites for tandem cell applications. Interestingly, MA–FA mixed perovskite fabricated at elevated temperature also showed improved stability (Yehao Deng, University of Nebraska—Lincoln, United States), which is similar to the Cs–FA situation. To gain insights into the degradation of perovskites due to moisture, the behavior of the perovskite–moisture interaction was discussed by Ajay Kumar Jena (Toin University of Yokohama, Japan) and Christian Mueller (TU Braunschweig, German). Encouragingly, Yang Yang (UCLA, United States) and Liyuan Han (NIMS, Japan) showed significantly improved PSC stability by adopting metal oxide charge-transporting layers in the cell structure. Fan (Weihua-Solar, China) also showed that the large carbon-electrode-based PSC panels maintain their efficiencies for several months in outdoor conditions after proper glass encapsulation. These results imply that the low moisture tolerance of the perovskite absorbers can be mitigated by

engineering of the other components in PSCs and developing proper sealing procedures. Other aspects of stability were also discussed. Considering the promise of flexible PSCs with roll-to-roll processing, a study on the mechanic stability of the perovskites was reported by Nicholas Rolston and Brian Watson (Stanford University, United States). Further, Tsutomu Miyasaka (Toin University of Yokohama, Japan) reported the results on the space-environment tolerance of a typical MAPbI<sub>3</sub>-based PSC in aerospace applications, showing that the PSCs using a polymeric hole-transporting layer have excellent tolerance under high proton radiation whereas the ultraviolet stability needs to be further improved. The comprehensive testing results were also presented in a poster by Yu Miyazawa (JAXA, Japan). These and other various aspects of stability have important implications on the specific applications of PSCs.

At present, the state-of-the-art PSCs are still based on lead halide perovskites, but the potential lead toxicity of the PSCs is still being debated. Miyasaka indicated that the lead pollution from PSCs to soil in nature can be negligible due to the ultrasmall amount of perovskite materials contained in the PSCs, considering the as-existed level (~20 ppm) of lead in soil. Nevertheless, to explore lead-free photovoltaic material alternatives, David B. Mitzi (Duke University, United States) suggested guidelines for screening the candidate materials: a good candidate should have a direct or near-direct band gap of 1.0–1.6 eV, a high joint density of states, a low effective mass and high mobilities for electrons/holes, and lack of deep traps. The compounds based on Bi<sup>3+</sup> with lone-pair electrons similar to those of Pb<sup>2+</sup> could be potential candidates. In another talk by Constantinos C. Stoumpos (Northwestern University, United States), the Sn<sup>2+</sup>- and Ge<sup>2+</sup>-based compounds were reported in the application to PSCs. However, the results shown by Mitzi and Stoumpos indicated that these lead-free materials exhibit far inferior PV performance to the Pb-based counterpart. Thus, a stable high-performance lead-free compound still awaits development.

The understanding and eliminating of hysteresis in PSCs appears related to device engineering as well as the fundamental properties of perovskites, which is one of the hottest subjects in PSC research. Possible origins of the hysteresis include ion migration, interfaces (charge trapping), and ferroelectricity. Giuliano Gregori (Max-Planck-Institute for Solid State Research, Germany) emphasized that the popular hybrid halide perovskite is one typical halide material with mixed electronic/ionic conduction. Gregori and co-workers measured electronic ( $\sigma_{\text{con}}$ ) and ionic ( $\sigma_{\text{ion}}$ ) conductivity of MAPbI<sub>3</sub> using the classic ion-blocking method and showed the significance of ionic conduction ( $\sigma_{\text{con}} = 1.9 \times 10^{-9} \text{ S cm}^{-1}$  and  $\sigma_{\text{ion}} = 7.7 \times 10^{-9} \text{ S cm}^{-1}$ ). By constructing a galvanic solid-state electrochemical cell consisting of Pb/MAPbI<sub>3</sub>/AgI/Ag (Figure 3) as the experimental platform, iodine (I<sup>-</sup>) was concluded as the dominant migrating species. However, in another talk by Jungseok Chae (National Institute of Standards and Technology, United States), it was suggested instead that the MA<sup>+</sup> cation was the migrating species based on the nanoscale photothermal induced resonance (PTIR) technique. Further investigation on this aspect is required to elucidate the discrepancy. Regardless of the exact migration species, such significant ion conduction and the existence of the stoichiometric polarization in hybrid perovskite under electric bias can be responsible for both the large value of the apparent dielectric constant occurring at low frequencies as well as the hysteresis in

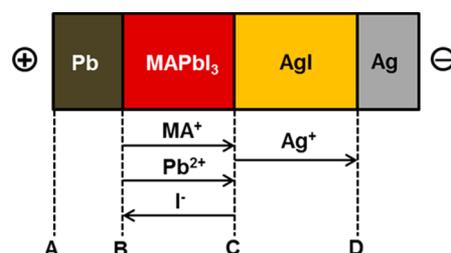


Figure 3. Flow directions of the charged ion species in a Pb/MAPbI<sub>3</sub>/AgI/Ag cell under electrical bias (reproduced with permission from ref 5; Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

the cyclic current–voltage (*I*–*V*) sweep experiments, which was shown in Gregori’s talk. Instead of ion migration, Satoshi Uchida (University of Tokyo, Japan) proposed a self-consistent surface boundary model to explain the *I*–*V* hysteresis in the planar perovskite cell with a TiO<sub>2</sub> compact layer (this type of PSC exhibits the most pronounced hysteresis). Uchida suggested that the lattice mismatch or voids present at the TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interface create high electrical capacitance, and the other CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/hole transport layer interface with fewer defects exhibits low capacitance, which results in the hysteresis behavior. A similar idea was presented by Sang Hyuk Im (Kyung Hee University, South Korea), who further showed that hysteresis-less PSCs can be achieved by balancing the electron flux and hole flux via reducing the surface traps. Alex K.-Y. Jen (University of Washington, United States) also showed that the hysteresis of the PSCs can be significantly alleviated via a variety of strategies to improve the charge extraction (e.g., incorporating a fullerene interfacial layer between the compact TiO<sub>2</sub> and perovskite), which is consistent with the capacitance model. Bo Chen (University of Nebraska—Lincoln, United States) analyzed the influence of both the capacitive effect and ion migration on the *J*–*V* response of PSCs to understand the origin of hysteresis. He concluded that the interface capacitance, which could be due to electron or ion accumulation in PSCs, is the main cause of hysteresis. The ferroelectricity of the MAPbI<sub>3</sub> perovskite and its relationship with the PSC hysteresis are still under debate. Nevertheless, it was impressive that Holger Roehm (Karlsruhe Institute of Technology, Germany) claimed observing ordered ferroelectric domains in a uniform MAPbI<sub>3</sub> perovskite thin film with micrometer grain size. Nevertheless, Tejas S. Sherkar (University of Groningen, The Netherlands) quantified the influence of mesoscale ferroelectric polarization on the PSC performance based on a 3-D drift diffusion model. Sherkar concluded that in the case of a microstructure with random correlated polarization, which is a realistic scenario, the existence of polarization channels for efficient charge transport in the device can reduce charge recombination, but the high open-circuit voltage in PSCs is not likely explained by the presence of ferroelectric polarization and a conclusion correlating ferroelectric polarization with hysteresis has not been drawn.

In addition, other topic areas have also demonstrated significant progress, including advanced spectroscopic techniques to study charge-carrier formation, separation, transport, and recombination processes in various sample configurations. Perovskites have also shown great promise in applications beyond solar cells (e.g., light-emitting diodes, lasers). This is not surprising because, counterintuitively, efficient external

luminescence is a necessity for approaching the Shockley–Queisser efficiency limit.<sup>6</sup> In other words, a great solar cell also needs to be a great light-emitting diode, which was emphasized in the talk by Iván Mora-Seró (Universitat Jaume I, Spain).

In summary, this symposium has demonstrated the prominent progress in addressing issues of lead halide perovskites in high-performance PSCs, such as scaling up perovskite film fabrication, manipulating perovskite crystal growth, improving stability, reducing toxicity, and understanding hysteresis. This progress is made possible by efforts from groups with diverse backgrounds (e.g., materials scientists, chemists, physicists, engineers, and entrepreneurs). These efforts lead to simultaneous advances in the fundamental understanding of perovskite materials and the performance development of PSC devices. The continued success of PSC research will likely lead to ultimate solutions to the problems that are still present in the state-of-the-art PSC technology.

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### Notes

The authors declare no competing financial interest.

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