Accelerating Scaling to Rapid Open-Air Fabrication of Robust Perovskite Solar Modules

Investigators

Dr. William J. Scheideler, Nicholas Rolston, and Prof. Reinhold H. Dauskardt

Abstract

The goal of this project was to demonstrate a rapid and scalable open-air processing route to fabricate robust perovskite solar modules, with the goal of seeding a larger scale federally funded program in this area. We report that our efforts to integrate large area spray and plasma processing methods have successfully led to *the first perovskite solar modules produced at Stanford University.*

As detailed in the following report, this ambitious program also provided key data to validate the thermomechanical reliability of inorganic charge transport layers for reinforcing perovskite modules, demonstrating a 4X improvement in the fracture energy of our newly developed spray processed NiO charge transport layers. Detailed characterization of these newly developed charge transport layers has also allowed optimization of the optoelectronic performance of our plasma-processed devices and eliminated moisture sensitive polymeric charge transport layers. These experiments illuminated critical factors unique to *open-air* processing of perovskite solar cells and developed methods for overcoming the impact of ambient humidity on cell performance. Understanding these factors provided a foundation for demonstrating high efficiency cells and modules on 25 cm^2 substrates.

Our GCEP-funded work was instrumental in helping secure a 3-year, $1.9 million grant from the Department of Energy's Solar Energy Technologies Office. This funding will support the work started by GCEP and will continue to strengthen Stanford's position as a world leader in solar energy research. Finally, this demonstration of the application to solar modules at a significant scale helped seed support for ongoing collaborative work with two industry partners (Energy Everywhere and Plasmatreat GmBH).

Introduction

Our perovskite research has centered on innovative and scalable fabrication of highly efficient perovskite solar cells while focusing on the critically important parameters of robustness and reliability. The goal is to design low-cost photovoltaic technologies capable of long service lifetimes. Indeed, while extensive international research (and related "hype") has established hybrid perovskites as the leading materials for next-generation thin-film solar cells in terms of cost and efficiency, our earlier work clearly showed that the primary metrics for thermomechanical reliability of perovskite absorbers and organic transport layers are so low that, without improvement, they altogether *rule out existing perovskite cells as a viable technology*. This mechanical fragility, along with related chemical *instability* and moisture *sensitivity,* threaten to limit the scaling of this promising technology.

With our focus on fabrication and reliability, we previously mitigated these risks

using our rapid spray plasma process (RSPP) for perovskite absorbers which have a factor of ten improvement in thermomechnical properties [1]. The current project has developed additional rapid spray processing methods for fabricating inorganic charge transport layers, a strategy for removing polymeric organic charge transport layers from the device architecture and facilitating larger area perovskite module fabrication. The consecutive combination of these spray plasma processing methods in open-air to form full cells as well as high-voltage *integrated perovskite* modules stands to greatly reduce process complexity and decrease the energy payback time, enabling the commercialization of perovskite technology.

Background

The perovskite solar cell field is an extremely active research area, internationally. Within the last year there have been a large number of groups working on the topics of scaling and reliability domestically and abroad. Below we have summarized a selected few publications which illustrate the context for our work. These papers show recent progress in *up-scaling* of perovskite deposition as well as studies of the cost-models that have described factors influencing the ultimate commercial success of existing cell architectures and processing methods. The work reported here is distinguished from these competitors by the ambitious stability targets set and the development of greater understanding of thermomechanical reliability of module architectures with inorganic charge transport layers.

There have recently been reports of high efficiency perovskite solar modules, ~16% PCE for 25 cm^2 [2] and ~12% PCE for 36 cm^2 [3] respectively, leveraging advances in scalable coating methods of bar-coating. However, there are clear drawbacks to each of the methods described, as the poly (3-hexylthiophene) process only uses bar-coating for the hole transport material and relies on spin-coating for depositing the perovskite layer. In the case of the solvent/vacuum-free process, the approach requires several steps, including a cumbersome peel process which risks mechanical damage to the fragile absorber layer. Neither of the articles operate in open air, use a high-throughput process, nor demonstrate module stability, all of which are key components of the approach taken in this GCEP program.

Another active area in this field has been that of technoeconomic cost modeling for projecting the commercial viability of perovskite solar technology. A recent study [4] by the University of Toledo has investigated the minimum sustainable pricing for perovskite modules and the overall costs, presenting estimates in the range of $0.05 - $0.08 per kWh. Several variables are discussed that could affect manufacturing cost, and processing throughput is highlighted as a significant factor. On this topic, a related review [5] by Kai Zhu's group at NREL discusses the state-of-the-art developments in scaling up perovskite solar cells and related efforts to enable manufacturing and commercialization of the technology. This includes an overview of module architectures, scalable deposition methods for the perovskite and associated charge-transport layers, and stability. The GCEP sponsored project reported here implements an open-air, rapid spray process of the perovskite and associated charge transport layers to add to the list of conventional solution processing methods with distinct advantages in manufacturability and reliability. This combination of scalable materials and rapid processing methods is

expected to help fulfill one of the foundational assumptions behind the prevailing cost models—a 20 year service lifetime for perovskites modules.

Results

There is significant progress to report towards both aims of this program. The first aim was develop scalable processes and materials for inorganic charge transport layers in perovskite solar cells and the second aim of the program was to integrate these open-air processes to fabricate large area, series-interconnected perovskite solar modules utilizing our rapid spray processing methods. The results reported here demonstrate successful progress towards these aims while also providing key information to inform future studies of the performance and reliability of these materials.

Spray Fabrication of Inorganic NiO Charge Transport Layers

This program involved developing inorganic charge transport layers to improve the thermomechanical reliability of perovskite solar modules. The focus of the first phase of this program was to develop a scalable process for producing high quality NiO films for use as hole transport layers (HTLs) in perovskite cells. Leveraging past experience with spray processing, an ultrasonic spray method was developed for depositing NiO from an aqueous solution of $Ni(NO_3)_2$. Figure 1 illustrates this process and highlights the smooth, pinhole free morphologies obtained for the NiO films with thicknesses controlled from 12 nm to 60 nm. These films exhibit a roughness of 4.5 nm as measured by AFM over small areas and of 9 nm as measured by stylus profilometry over a 200 x 200 µm area.

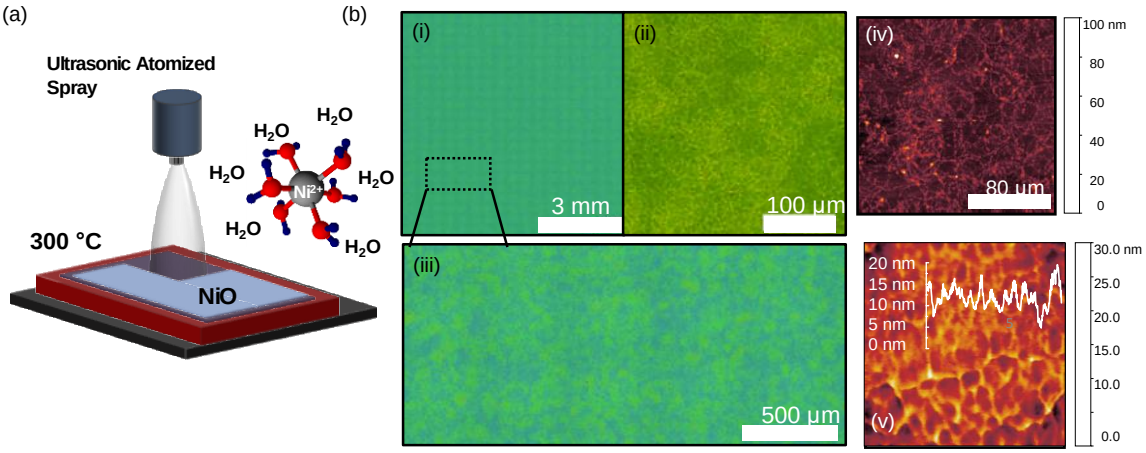

Figure 1: (a) Ultrasonic spray deposition of NiO transport layers. (b) Micrographs (i-iii) of NiO films with height maps measured by stylus profilometry (iv) and AFM (v).

The optoelectronic properties of these NiO films are ideal for use as HTLs in perovskite cells. As characterized in Figure 2, the NiO films have visible range transmittance of 88 - 90 % and conductivity of approximately 10^{-4} S/cm, comparable to spin coated films annealed for much longer durations. Additionally, the work function was found to be approximately 5.30 – 5.40 eV for these films, which positions them in an ideal range as a hole-selective contact layer.

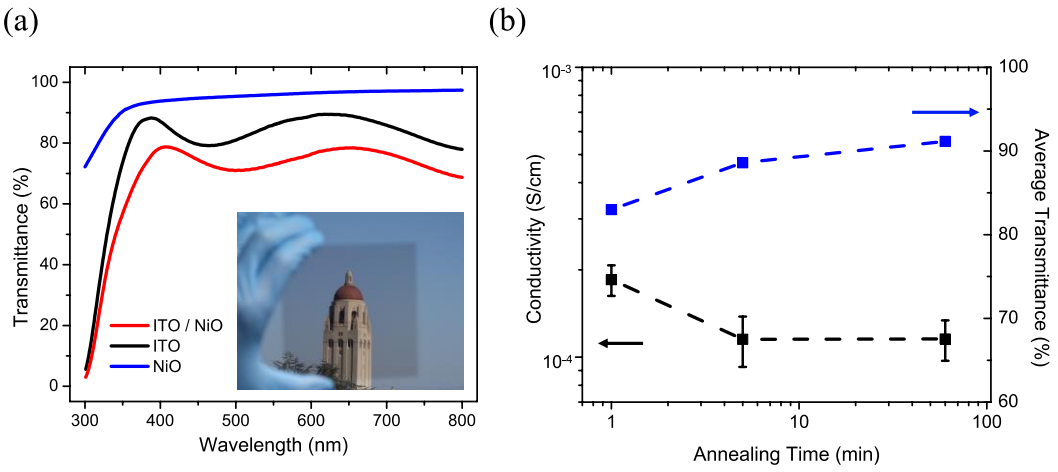

Figure 2: (a) Visible range transmittance of large area sprayed NiO films. (b) Conductivity and average transmittance of NiO films as a function of post-annealing time at 300 °C.

Importantly, these NiO films serve as a platform for high efficiency perovskite solar cells. Perovskite cells fabricated using these inorganic sprayed NiO films have high photovoltaic conversion efficiency (PCE) of approximately 18 %, with average efficiency of 16.2 % and lower variance than those fabricated on spin coated NiO films. The NiO films allow open-circuit voltage of up to 1.08 V and fill factors of above 80 %, as shown in Figure 3. Both of these metrics are significantly improved beyond conventional spin coated NiO films, while offering the scalability of spray processing over large areas.

The thermomechanical reliability of these sprayed NiO films also serves as a motivation for utilizing them in robust perovskite modules. As shown below in Figure 4, double cantilever beam tests were performed on these spray coated NiO films. These mechanical tests allow extraction of the fracture energy of the NiO films, a primary metric of their thermomechanical reliability. The spray coated NiO films achieve a fracture energy (G_c) of 4-5 J/m^2, which is a factor of 4X higher than those measured for spin coated NiO films. This also represents a 10X improvement over nanoparticle based NiO films. This mechanical testing has been critical for designing mechanically stable module structures which will endure long-term environmental testing and additional stresses from encapsulation and packaging.

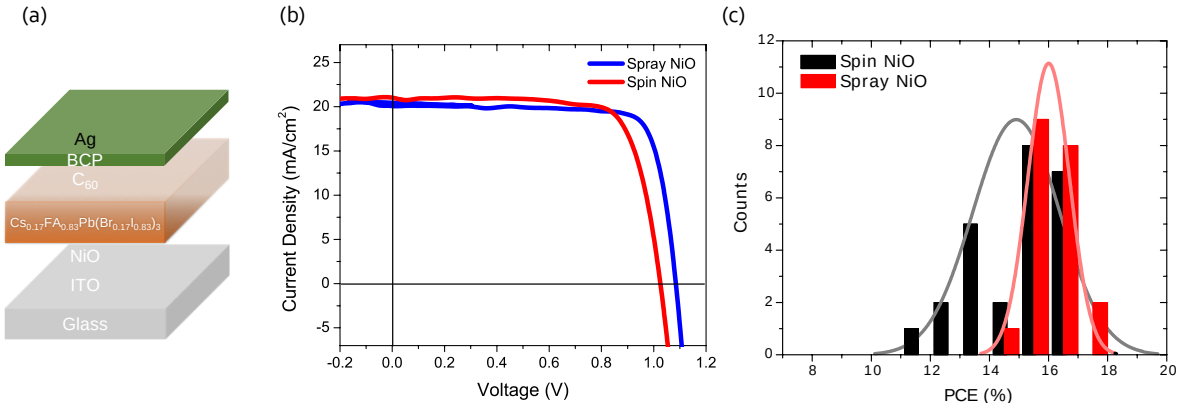

Figure 3: (a) Layer architecture of perovskite cells and modules reported here. (b) Comparison of current-voltage characteristics of perovskite cells with spin coated and spray coated NiO films. (c) Distributions of device efficiencies for perovskite cells incorporating spin (red) coated and spray coated (black) NiO hole transport layers.

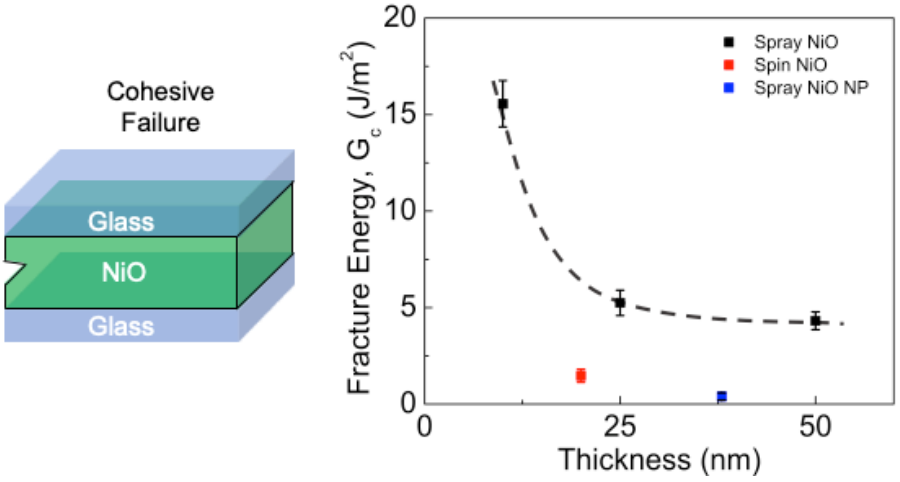

Figure 4: (a) Double cantilever beam fracture energy test structure. (b) Measured fracture energy of NiO films produced by aqueous spray coating (black) vs spin coating (red) and sprayed NiO nanoparticles (blue).

Integration of Spray-Plasma Perovskite Absorbers with Sprayed NiO Layers

The inorganic NiO charge transport layers developed in this program were integrated with spray plasma deposited double cation $Cs_{.17}Fa_{.83}Pb(I_{.83}Br_{.17})_3$ absorber films. The plasma deposited perovskite films were selected to match the composition and thickness of perovskite films utilized in spin coated devices on spray coated NiO. The scheme illustrated in Figure ZZ below was adapted from earlier work in rapid spray plasma processing [1] to allow fabrication of double cation perovskite absorber films with enhanced environmental and thermal stability. This is a significant advancement in plasma processing of perovskites since previous work was focused primarily on $MAPbI_3$ perovskites with simpler precursors.

In this new plasma-process for perovskite deposition (Figure 5), the addition of substrate heating aided in control of drying kinetics for the more complex, multiple component double cation perovskite liquid precursors. Additionally, the influence of the plasma power and air flow shaping on film formation were investigated to guide selection of a linear, slot-type nozzle with improved uniformity for larger area films critical for module integration. The other significant improvement that this spray plasma processed double cation perovskites offered beyond previous work was excellent photostability. Under constant illumination and maximum power point tracking, the plasma deposited unencapsulated perovskite devices retained over 96% of their efficiency for > 10^3 s, an encouraging indication of longer term stability. The current-voltage characteristics of these cells are provided in Figure UU (a) below, alongside the efficiency (~ 15 %) and current density throughout maximum power point tracking under full illumination. With these double cation perovskites, plasma processing is also able to achieve high open circuit voltages above 1.0V and current density of up to 22 mA/cm^2.

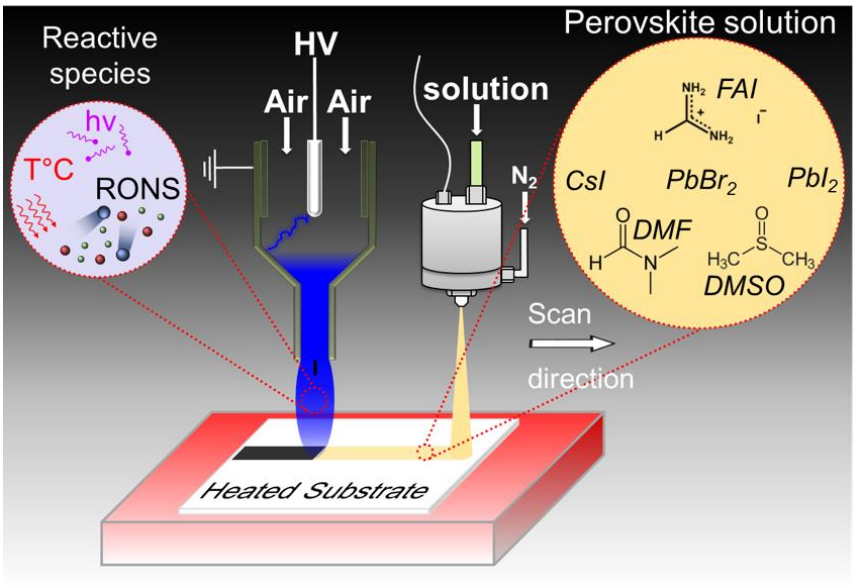

Figure 5: Schematic illustrating rapid spray plasma processing (RSPP) of perovskite double cation $Cs_{.17}Fa_{.83}Pb(I_{.83}Br_{.17})_3$ absorber films.

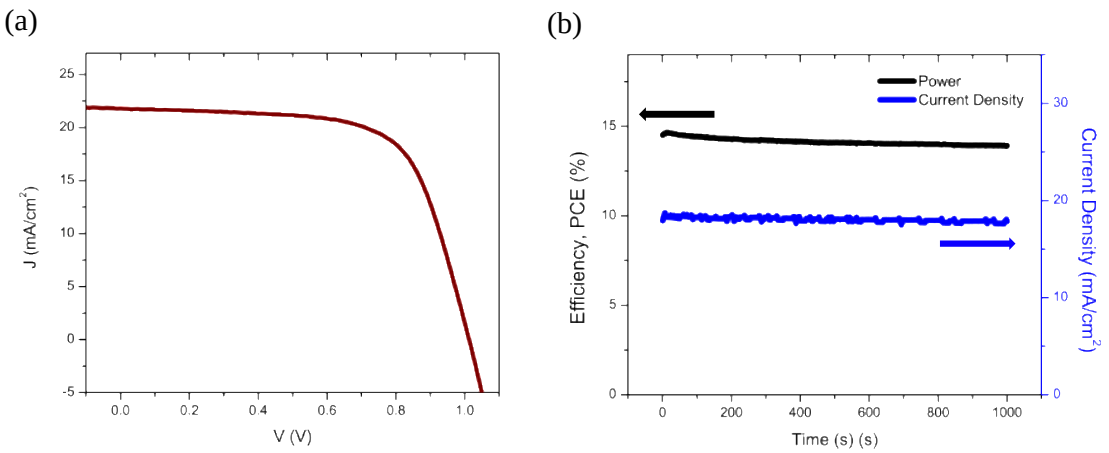

Figure 6: (a) Current-voltage characteristic of plasma-processed perovskite solar cell and maximum power point tracking stability under full illumination (b).

Spray Plasma Fabrication of Perovskite Solar Modules

Our work on scaling up perovskites has involved developing monolithically integrated solar modules which have higher voltage output. The series interconnection of the individual cells is accomplished via laser scribing processes, which isolate regions of the bottom electrode (P1 scribe) and open vias (P2 scribe) for the top metal electrode to interconnect the cells. Our work has involved iterative development of our spray plasma processes to produce perovskite films with ideal geometries for these modules to limit resistive losses due to series interconnection.

The cross-section structure of our perovskite modules is shown below in Figure 7, which highlights the scribing marks which separate each cell and interconnect the individual diodes in series. The areas and currents of each subcell are carefully matched to ensure minimal losses in voltage due to interconnection and prevent hot spot development during prolonged operation.

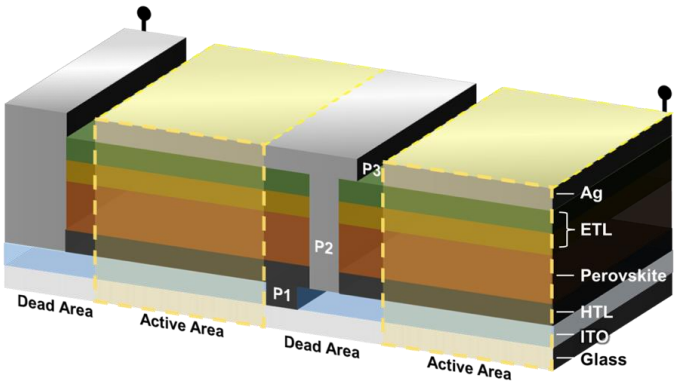

Figure 7: Layer cross section of perovskite module architecture showing scribing marks used to isolate and then connect individual subcells.

The plasma processes developed for producing high quality perovskite films have been adjusted and extended to larger areas (50 mm x 25mm) to produce these prototype modules with six interconnected subcells. The performance of these modules (Figure 8)

has reached a maximum efficiency of 10.5 % PCE while outputting greater than 5.50 V, but further improvements are expected with continued optimization of the module architecture and reduction in open-air related processing artifacts (pinholes, particles, etc.). The current density achieved in these plasma-processed perovskite devices has been validated via external quantum efficiency measurements (EQE) as shown in Figure YY part b. The continued work in this area supported by a new grant from DOE's Solar Energy Technologies Office is expected to boost the efficiency and areas of these modules to achieve our long-term goals of > 16 % module efficiency and larger areas (> 100 cm^2).

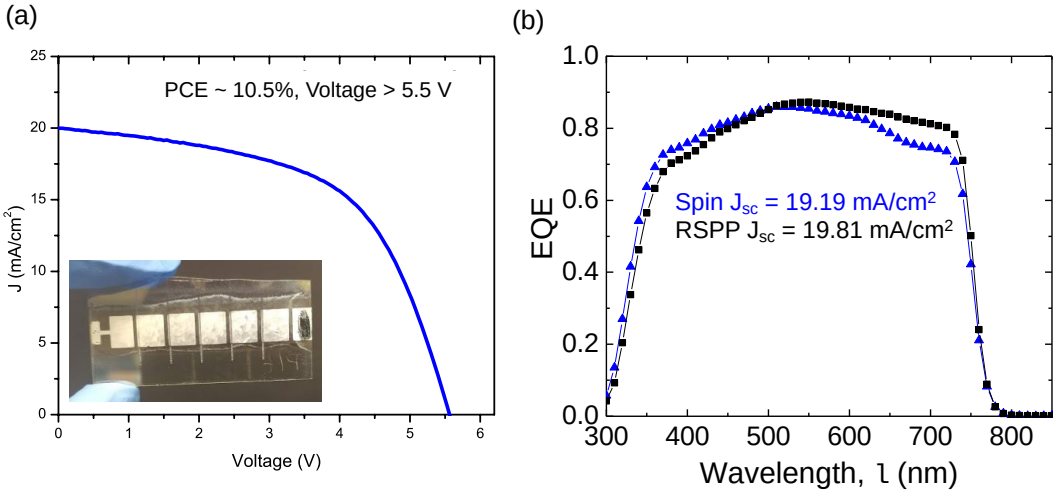

Figure 8: (a) Current-voltage characteristics of spray-plasma fabricated perovskite module formed by series-integration of 6 individual subcells. (b) External quantum efficiency (EQE) of perovskite subcells formed by rapid spray plasma processing (RSPP).

Conclusions

The goal of this work was to accelerate the scaling of high-efficiency perovskite solar modules by employing our group's leading position in open-air spray plasma processing and solar reliability. We expect that continued research building off of our successful initial demonstration of plasma-fabricated perovskite modules will establish a clear **pathway for the most promising current photovoltaic technology to enable a low carbon future** that depends so sensitively on not only efficient, but reliable and low-cost approaches. Importantly, the potential for flexible form factors and the lightweight nature of these thin film solar modules can facilitate a range of new applications, for example, in transportation and energy efficient buildings that are posed to significantly expand the scope of renewables. Here the intent is not necessarily to displace incumbent, GW-scale energy generation with these perovskite technologies, but to develop low-cost manufacturing that can, for example, launch functional microgrids in developing nations with limited infrastructure for power distribution. These parallel advances in solar technology scaling and reliability may then deliver swift, but enduring reductions in greenhouse gas emissions on a global scale.

Publications and Presentations

The following publications and presentations were supported by GCEP.

Publications

1. W.J. Scheideler, N. Rolston, O. Zhao, J.B. Zhang, and R.H. Dauskardt, Rapid Aqueous Spray Fabrication of Robust NiO: A Simple and Scalable Platform for Efficient Perovskite Solar Cells," *Adv. Energy Mater*., 2019, 1803600. DOI: 10.1002/aenm.201803600.

Presentations

1. R.H. Dauskardt, "Accelerated Scaling to Rapid Open-Air Fabrication of Durable Perovskite Solar Modules," invited presentation at the 2nd International Forum on Clean Energy, Dalian, China, Aug., 2018.
2. W.J. Scheideler, N.J. Rolston, O. Zhao, and R.H. Dauskardt, "Rapid Aqueous Spray Fabrication of Robust NiO – A Simple and Scalable Platform for Efficient Perovskite Solar Cells," Materials Research Society Spring Meeting, Phoenix, USA, Apr. 25, 2019.

References

[1] F. Hilt, M. Q. Hovish, N. Rolston, K. Brüning, C. J. Tassone, R. H. Dauskardt, *Energy & Environmental Science* **2018**, *11*, 2102.

[2] E. H. Jung, N. J. Jeon, E. Y. Park, C. S. Moon, T. J. Shin, T.-Y. Yang, J. H. Noh, J. Seo, *Nature* **2019**, *567*, 511.

[3] H. Chen, F. Ye, W. Tang, J. He, M. Yin, Y. Wang, F. Xie, E. Bi, X. Yang, M. Grätzel, L. Han, *Nature* **2017**, *550*, 92.

[4] Z. Song, C. L. McElvany, A. B. Phillips, I. Celik, P. W. Krantz, S. C. Watthage, G. K. Liyanage, D. Apul, M. J. Heben, *Energy & Environmental Science* **2017**, *10*, 1297.

[5] Z. Li, T. R. Klein, D. H. Kim, M. Yang, J. J. Berry, M. F. A. M. van Hest, K. Zhu, *Nature Reviews Materials* **2018**, *3*, 18017.

Contacts

Reinhold H. Dauskardt: rhd@stanford.edu
William J. Scheideler: wjs10@stanford.edu
Nicholas J. Rolston: rolston@stanford.edu