

Decentralized Energy Generation and Environmental Impact Reduction via Perovskite Solar Cells

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Abstract

Perovskite solar cells (PSC's), and metal-halide variants specifically, continue to be some of the most researched and promising materials for the low-cost energy generation among other applications. Metal-halide perovskites, possess the highly desirable direct band-gap and highly tunable band structures. Furthermore, organic nature of the materials greatly simplifies the deposition of the materials and thus makes them good candidates across a broad range of applications. PSC's consistently demonstrate Power Conversion Efficiencies (PCE's) above 24% through a low temperature simplified deposition that reduces the overall device cost by over 30%. As technology advances the energy consumption increases and Perovskites are key in reducing those operational costs. This paper also focuses on the CO₂ generation and the environmental impact reduction associated with the technology. Successful stabilization of perovskites, in thermal, hydro, and oxygen environments, will enable PSC's to be scaled for applications in multiple markets.

Keywords: perovskite solar cells, stability, semiconductors, radiation

Introduction

Energy remains the most crucial commodity among established and emerging economies. Despite supply chain disruptions energy consumption across all markets continues to grow exponentially [1]. More recently the demand for decentralized sustainable energy sources increased dramatically [2]. Solar energy harvesting has the potential to fill the gap of the energy generation due to the stable, predictable, and continuous supply of solar radiation. Annual solar irradiance is estimated to be nearly 1,361 W/m² in the upper atmosphere which equates to over 170,000 TW of power and over 1 zettajoule of energy [3]. This volume of energy is nearly unfathomable, abundant, steady, and even at 20% Power Conversion Efficiency (PCE) of a conventional solar device is orders of magnitude above current global consumption. Furthermore, solar energy is evenly distributed across the

globe, with solar irradiation exceeding 1,600 kWh/m² between North and South latitudes of 45° [4]. Thus, an enormous opportunity exists to harvest energy locally, reduce energy transportation inefficiencies, and provide sustainable energy to established and emerging markets.

While a variety of semiconducting materials are available for solar energy harvesting, in recent years perovskites emerged as the most promising and novel class of materials for this application. Perovskite materials in general, and methylammonium lead iodide (MAPbI₃) chemistries in particular, demonstrate favorable opto-electronic characteristics for such applications [5, 6]. Hybrid versions of the perovskite materials consist of inorganic-organic, ABX₃, stoichiometries, where the A & B cations and X anions are interchangeable [7]. This interchangeability within the chemical structure of the material enables a highly tunable material that can be optimized for a broad range of applications. Furthermore, both cations and anions can be substituted with materials that possess highly ameliorable, environmentally friendly among other favorable properties besides being readily available.

It has been demonstrated that the perovskite materials can be synthesized via a variety of scalable low-cost methodologies that include spin/spray coating, inkjet printing, chemical bath, chemical vapor among other prevalent techniques [8, 9, 10]. The variety of deposition techniques further broadens the range of chemical constituents that can be leveraged in A & B locations of the structure. Success of various depositions methods has been demonstrated by various research groups with perovskite minimodules of 49 cm² reaching PCE's of 24% [11, 12]. Given the recent success in the maturation of perovskite materials, numerous groups began exploring the scalability of the materials for eventual penetration of the market.

Given the recent successes of these materials, Perovskites are becoming a desired material for multiple applications including the reduction of CO₂ footprint. These materials, however, are unable to penetrate the markets due to their instabilities under thermal and humid conditions [13, 14].

The low activation energy of the anions induces ion migration under light thermal stresses [15]. Migration of the anions leaves a vacancy within the X location of the perovskite structure, hence generating defects and inducing exciton recombination rates. Given the hygroscopic and hydrophilic nature of the materials, materials have been shown to degrade even under low humidity conditions [16]. Thermal and humid stabilities need to be addressed prior to large scale applications of the materials. Perovskites, however, need to be stabilized and ruggedized for a broad range of austere conditions before they can be widely utilized.

Perovskite Solar Cell

PSC Structures

Unlike their inorganic counterparts, perovskite solar cells (PSC's) consist of three layers, i.e. perovskite material (active layer) is sandwiched between electron- and hole-transporting layers, ETL and HTL respectively. This basic design is analogous to the n-i-p and p-i-n structures of the traditional solar cells, *Figure 1 (a)*. Given the ABX_3 structure of the materials, perovskites band structure is highly malleable and tunable. Given this tunability, a broad range of ETLs and HTL's can be applied to the materials and band structure can be aligned to maximize electron extraction. Sn has been one of the most explored substitutes for the Pb position within the structure, Sn changes the morphological and band structures of the material, but also provides an opportunity for lead free perovskite solar cell in the future, *Figure 1 (b)*.

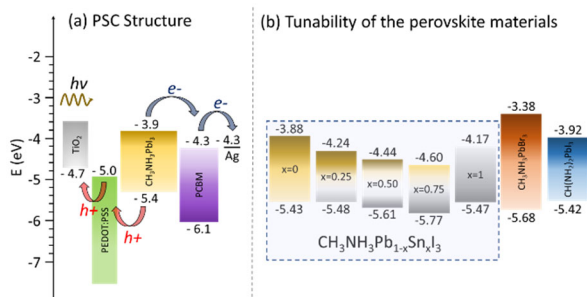


Figure 1. (a) Typical PSC structure.

(b) Tunability of the perovskite materials based on the B location cation replacement.

Materials such as fullerene C_{60} , various fullerene derivatives such as [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM), bathocuproine (BCP), CdS, have all been explored as possible ETLs for the PSC. A broad range of materials for HTLs has also been explored to include poly(3,4-ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS), NiO, and Poly(N,N'-bis-4-butylphenyl-N,N'-bisphenyl)benzidine (polyTPD), tert-butylpyridine (TBP), 2,2',7,7'-tetrakis-(N,N-di-4-

methoxyphenylamino)-9,9'-spirobifluorene (spiro-MeOTAD), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA). Thus it is possible to select stoichiometries with various band-structures that can be optimized for performance under various conditions [17].

Another benefit of the tunability of the perovskite solar structure is the ability to use multiple Transparent Conducting Oxides (TCO's) on either the electron- or hole-extracting layer side. This enables a broader range of deposition techniques where the more stable layers can be deposited earlier in the process. As an example the PEDOT:PSS is often leveraged as an HTL in the PSC. PEDOT:PSS is also known to be highly hydrophobic and thus provides an additional layer of protection against humidity for the functional material, *Figure 2 (a)*. Phase line mapping of the perovskite performance with PEDOT:PSS HTL and various fullerene based ETLs is shown to change significantly based on the stoichiometries of the materials, *Figure 2 (b)*. Hence, conditions must exist where the chemical compositions of the materials are such that enable optimized performance of PSC's.

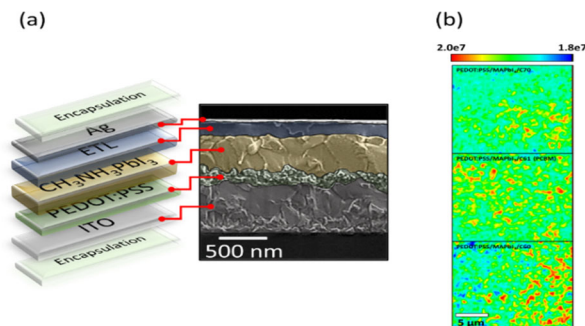


Figure 2. (a) Inverted PSC device configuration with PEDOT:PSS and its associated SEM image **(b)** forward and backward sweeps of the J-V curve comparison for n-i-p and p-i-n PSC structures.

Perovskite Film Degradation

Long term stability continues to plague perovskite materials. This is also the biggest factor that inhibits material deployment and utilization in multiple markets. Humidity has been identified as one of the most detrimental to perovskite performance. Exposure to the environment without the correct encapsulation will rapidly degrade the technology complicating its use. Amine molecules of the materials are known to be hygroscopic and thus absorb humidity from ambient environments which leads to degradation [18]. Since the instability is led by the anion molecules of the materials, similar degradation mechanisms and rates are observed across multiple perovskite stoichiometries.

Materials are found to be hygroscopic because of the amine molecules and hydrophilic in the A & B cation sites. Thus any effective control of degradation must include elimination or segregation of moisture from the materials. Deposition techniques must thus include inert atmosphere encapsulation and multilayer micro-encapsulation. Moisture has been found to prevent solidification of the films during the deposition. Thus, deposition of the materials must also take place in controlled chambers with limited moisture and controlled ambient environment [19].

Several moisture degradation mechanisms have been proposed in the past, most prevalent however is the hydrolysis reaction of the moisture with the film. This forces the amine group to migrate from the cation sites, effectively forcing ion migration and defects, *Figure 3 (a)*. Inorganic components of the materials can delay the migration of ions and help achieve stability of the materials [20]. Ultimate goal of the perovskite based solar cells, however, is to obtain fully organic materials.

Significant degradations are observed in materials that are deposited in 40% RH and further exposed to ambient atmosphere, *Figure 3 (b)*. Power conversion efficiency of materials degrades by over 50% within 10 days, and degrades nearly completely within 20 days. This data further solidifies the need for robust and ruggedized encapsulation and stabilization of the materials. Furthermore, segregation of ambient atmosphere is crucial with micro- and inert-atmosphere encapsulation. Additional approach to stabilization of materials has been through mesoporous interatomic layers [21]. Mesoporous layers have shown to prevent degradation in environments of up to 45% humidity even after 2,000 hours of operations. Despite significant achievements in stabilizing the materials, significant additional achievements are required for further applications.

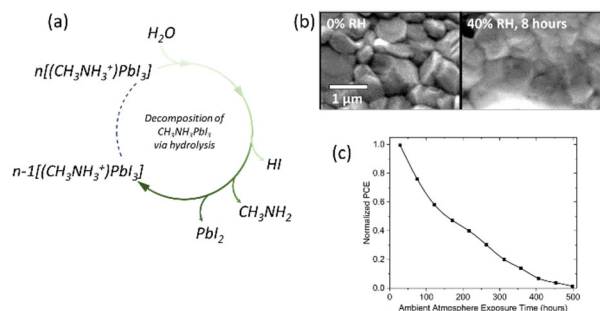


Figure 3. (a) Proposed hydrolysis decomposition of $CH_3NH_3PbI_3$ with the main byproduct of PbI_2 . **(b)** SEM images of perovskite films deposited in 0% and 40% RH. **(c)** Normalized PCE of perovskite films exposed to ambient atmosphere.

A novel methodology of chemical vapor deposition (CVD) with inline micro-scale encapsulation with inert atmosphere capture will provide additional stability to the final device. Goal of this effort is to encapsulate inert atmosphere into a final device, which will enable further deleterious elements segregation and stabilize the materials. Although additional deposition steps are required, this methodology is expected to further expand the lifetime of these materials and nudge the technology towards maturation and deployment.

Perovskites have qualities that supersede current technologies such as the absorption of sunlight, ease of manufacturing, lower cost and flexibility. PSC's possess highly tunable opto-electrical properties, *Figure 4 (a)*. Thus, materials can find applications in multi-junctions of various combinations, making them suitable for innumerable applications. Furthermore, these materials exhibit exceptional radiation-induced photocurrent, *Figure 4 (b)*. Organic components of the perovskites, however, decay under thermal exposure above $\sim 380K$, thus cooling needs to be introduced at temperatures above these temperatures. Perovskites also undergo phase changes at 330K and 160K transitioning from cubic to tetragonal to orthorhombic phases respectively.

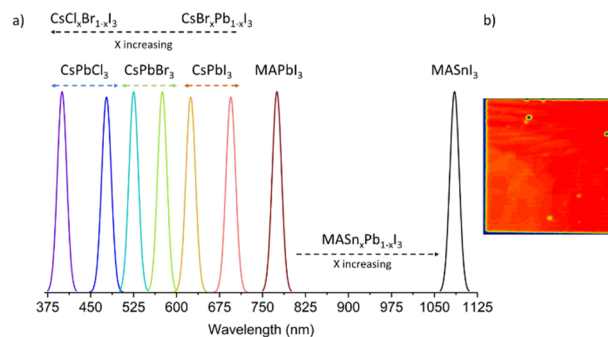


Figure 4. (a) Opto-electrical tunability of ABX_3 perovskite materials. **(b)** Radiation induced photocurrent in perovskite cells.

Temperature ranges can vary greatly, the Perovskite material will have the ability to undergo all three phase changes. While optimal performance of the materials is observed in orthorhombic phase, maintaining temperature of the materials below 380K will be crucial to prevent degradation.

Anion migration under thermal stresses also plays a role in generating defects and leaving to degradation. Activation energy for anions has been reported to be between 0.37 and 0.50 eV [22]. This low activation energy results in a significant portion of the anions to leave their sites, thus degrading the morphology of the materials and generating recombination sites. Ion migration has been mitigated via

functionalized and engineered ionic fluids, control of the nucleation during deposition, and gradual crystallization of materials. 2- and 3-dimensional perovskites with varying quantum-well depths have also been explored to stabilize anions and prevent material degradation.

Material stability continues to be one of the most pursued research efforts in the field of perovskites. Preliminary data demonstrates that no ‘silver-bullet’ exists to resolve the stability issues. Thus, a combination of stabilization methodologies needs to be explored in order to achieve significant results.

Conclusion

Perovskites are an emerging class of hybrid materials that have enormous potential. While perovskites have applications well beyond energy harvesting, material applications for energy generation would be of great interest and impact. Application of these materials for energy harvesting will bring significant impact in reducing energy reliance on traditional fuel based sources and reduce the overall CO₂ footprint. Despite their promising nature and performance, perovskites still suffer from stability which needs to be addressed before wider acceptance. Extensive work is done to ensure that the stability of the materials is obtained thermal, humid, and ambient atmospheric environments. Additional stability is pursued via packaging and inert atmosphere encapsulation. CO₂ emissions to the atmosphere are the major cause for global warming and worldwide environmental disasters. Hence the potential for energy generation via resilient, cost-effective, and sustainable energy source is of great interest.

Having the ability to produce a technology that would be economically accessible, rugged, diverse, sustainable, and effective in reducing carbon footprint will be critical in the years to come..

References

- [1] C. Chen, M. Pinar and T. Stengos, "Renewable energy consumption and economic growth nexus: evidence from a threshold model," *Energy Policy*, vol. 139, p. 111295, 2020.
- [2] M. Blondeel, M. J. Bradshaw, G. Bridge and C. Kuzemko, "The geopolitics of energy system transformation: A review," *Geography Compass*, vol. 15, no. 7, 2021.
- [3] M. Wild, "The global energy balance as represented in CMIP6 climate models," *Climate Dynamics*, vol. 55, pp. 553-577, 2020.
- [4] A. Slonopas, L. Rodriguez-Cabanas, C. Duong, D. Baker, V. Parameshwaran and B. Stanley, "Low-cost perovskite materials for decentralized energy generation and Department of Defense environmental impact reduction," *SPIE Organic Photonics + Electronics: Organic, Hybrid, and Perovskite Photovoltaics XXIII*, vol. 12209, 2022.
- [5] M. K. Nazeeruddin and G. Grancini, "Dimensional tailoring of hybrid perovskites for photovoltaics," *Nature Reviews Materials*, vol. 4, pp. 4-22, 2019.
- [6] A. Slonopas, H. Ryan and P. Norris, "Ultra-high energy density CH₃NH₃PbI₃ perovskite based supercapacitor with fast discharge," *Electrochimica Acta*, vol. 307, pp. 334-340, 2019.
- [7] J. Teuscher, A. Ulianov, O. Müntener, M. Grätzel and N. Tetreault, "Control and study of the stoichiometry in evaporated perovskite solar cells," *ChemSusChem*, vol. 8, no. 22, pp. 3847-3852, 2015.
- [8] A. Slonopas, B. Kaur and P. Norris, "Role of the colossal frequency and temperature dependent dielectric constant in the performance of the organo-metallic tri-halide perovskites," *Applied Physics Letters*, vol. 110, no. 22, p. 222905, 2017.
- [9] I. A. Howard, T. Abzieher, I. M. Hossain, H. Eggers, F. Schackmar, S. Ternes, B. S. Richards, U. Lemmer and U. W. Paetzold, "Coated and Printed Perovskites for Photovoltaic Applications," *Advanced Materials*, vol. 31, no. 26, p. 1806702, 2019.
- [10] Z. Li, P. Li, G. Chen, Y. Cheng, X. Pi, X. Yu, D. Yang, L. Han, Y. Zhang and Y. Song, "Ink engineering of inkjet printing perovskite," *ACS Applied Material Interfaces*, vol. 12, no. 35, p. 39082–39091, 2020.
- [11] Z. Song, C. L. McElvany, A. B. Phillips, I. Celik, P. W. Krantz, S. C. Wathage, G. K. Liyanage, D. Apul and M. J. Heben, "A technoeconomic analysis of perovskite solar module manufacturing with low-cost materials and techniques," *Energy & Environmental Science*, vol. 10, pp. 1297-1305, 2017.
- [12] A. Roy, B. Ding, M. Khalid, M. Alzahrani, Y. Ding, A. A. Tahir, S. Sundaram, S. Kinge, A. M. Asiri, A. Slonopas, P. J. Dyson, M. K. Nazeeruddin and T. K. Mallick, "Certified high-efficiency ‘‘large-area’’ perovskite solar module for Fresnel lens-based concentrated photovoltaics," *iScience*, vol. 26, p. 106079, 2023.
- [13] S. Ruan, M. A. Surmiak, Y. Ruan, D. P. McMeekin, H. Ebendorff-Heidepriem and Y.-B. Cheng, "Light

- induced degradation in mixed-halide perovskites," *Journal of Materials Chemistry C*, vol. 7, no. 30, pp. 9326-9334, 2019.
- [14] J. Yang, B. D. Siempelkamp, D. Liu and T. L. Kelly, "Investigation of CH₃NH₃PbI₃ degradation rates and mechanisms in controlled humidity environments using in situ techniques," *ACS Nano*, vol. 9, no. 2, p. 1955–1963, 2015.
- [15] P. Vashishtha and J. E. Halpert, "Field-driven ion migration and color instability in red-emitting mixed halide perovskite nanocrystal light-emitting diodes," *Chemistry of Materials*, vol. 29, no. 14, p. 5965–5973, 2017.
- [16] A. Bouich, J. Mari-Guaita, F. Baig, Y. H. Khattak, B. Mari Soucase and P. Palacios, "Investigation of the surface coating, humidity degradation, and recovery of perovskite film phase for solar-cell applications," *Nanomaterials*, vol. 12, no. 17, p. 3027, 2022.
- [17] H. S. Jung and N.-G. Park, "Perovskite solar cells: from materials to devices," *Small*, vol. 11, no. 1, pp. 10-25, 2014.
- [18] C. Fu, Z. Gu, Y. Tang, Q. Xiao, S. Zhang, Y. Zhang and Y. Song, "From structural design to functional construction: amine molecules in high-performance formamidinium-based perovskite solar cells," *Angewandte Chemie*, vol. 61, no. 19, 2022.
- [19] J. A. Christians, P. A. Miranda Herrera and P. V. Kamat, "Transformation of the excited state and photovoltaic efficiency of CH₃NH₃PbI₃ perovskite upon controlled exposure to humidified air," *Journal of American Chemical Society*, vol. 137, no. 4, p. 1530–1538, 2015.
- [20] D. Li, P. Liao, X. Shai, W. Huang, S. Liu, H. Li, Y. Shen and M. Wang, "Recent progress on stability issues of organic–inorganic hybrid lead perovskite-based solar cells," *RSC Advances*, vol. 6, no. 92, pp. 89356-89366, 2016.
- [21] C. Worsley, D. Raptis, S. Meroni, A. Doolin, R. Garcia-Rodriguez, M. Davies and T. Watson, "γ-Valerolactone: a nontoxic green solvent for highly stable printed mesoporous perovskite solar cells," *Energy Technology*, vol. 9, no. 7, p. 2100312, 2021.
- [22] S. R. Pering and P. J. Cameron, "The effect of multiple ion substitutions on halide ion migration in perovskite solar cells," *Materials Advances*, pp. 7918-7924, 20223.