

Link Foundation Fellowship Final Report

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Development and non-toxic and stable perovskites for high efficiency solar cells

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Introduction.

The efficiency of halide perovskite solar cells has dramatically increased from 9% to 22% in less than 5 years.¹ They have shown promise toward the future for low cost and highly efficient solar electricity. While there are still considerable rooms for device optimization, it is now the time to tackle the device long-term stability and toxicity challenges. The presence of Pb in the champion material, methylammonium lead iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$, may prevent this technology from large-scale deployment due to environmental and health concerns. Attempts have been made in replacing Pb with other non-toxic metals such as Sn, Bi, or Sb.²⁻⁶ Long-term device stability is another challenge that needs to be addressed. To meet the commercialization standard, solar cells are required to produce stable performance for at least 10000 hours. This is at present still a goal to reach because halide perovskite thin films are relatively unstable to moisture, heat, and light. Preventing the interaction of halide perovskite with moisture is thus a crucial task. Successful examples of improving the moisture-stability of halide perovskite solar cells are layered two-dimensional perovskites,⁷⁻⁹ metal oxide overlayers,¹⁰ and carbon-based encapsulation.¹¹

The goal of this project is two-fold: to address the moisture instability of halide perovskites by introducing a new class of moisture-resistant light absorbing materials, namely two-dimensional (2D) Ruddlesden–Popper hybrid lead iodide perovskites, where hydrophobic butylammonium $\text{CH}_3(\text{CH}_2)_3\text{NH}_3^+$ long chains are intercalated into the three-dimensional (3D) $\text{CH}_3\text{NH}_3\text{PbI}_3$ framework, and ultimately to develop stable, environmental-friendly, and efficient halide perovskite solar cells by employing 2D lead-free Sn-based perovskites.

Results.

Large scale synthesis, crystal structure, and optical characterization of the 2D $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1, 2, 3, 4, \infty$) perovskites, a family of layered compounds with tunable semiconductor characteristics have been successfully demonstrated. These materials consist of well-defined inorganic perovskite layers intercalated with bulky butylammonium cations that act as spacers, adopting the crystal structure of the Ruddlesden–Popper type. The perovskite thickness (n) can be synthetically controlled by adjusting the ratio between the spacer cation and the small organic cation, thus allowing the isolation of compounds in pure form and large scale. The compounds are noncentrosymmetric, supported by measurements of the nonlinear optical properties of the compounds and density functional theory (DFT) calculations. The band gaps of the series change progressively between 2.43 eV for the $n = 1$ member to 1.50 eV for the $n = \infty$ member adopting intermediate values of 2.17 eV ($n = 2$), 2.03 eV ($n = 3$), and 1.91 eV ($n = 4$) for those between the two compositional extrema. The

compounds exhibit intense room-temperature photoluminescence with emission wavelengths consistent with their energy gaps, rendering them potential use in photovoltaics and light-emitting diodes. Moreover, thin films of the semi-2D perovskites display an ultrahigh surface coverage as a result of the unusual film self-assembly that orients the $[\text{Pb}_n\text{I}_{3n+1}]^-$ layers perpendicular to the substrates. This 2D perovskite family has been successfully implemented in solid-state solar cells, and yielded an initial power conversion efficiency of 4.02%, featuring an open-circuit voltage (V_{oc}) of 929 mV and a short-circuit current density (J_{sc}) of 9.42 mA/cm^2 from the $n = 3$ compound. This result is even more encouraging considering that the device retains its performance after long exposure to a high-humidity environment.

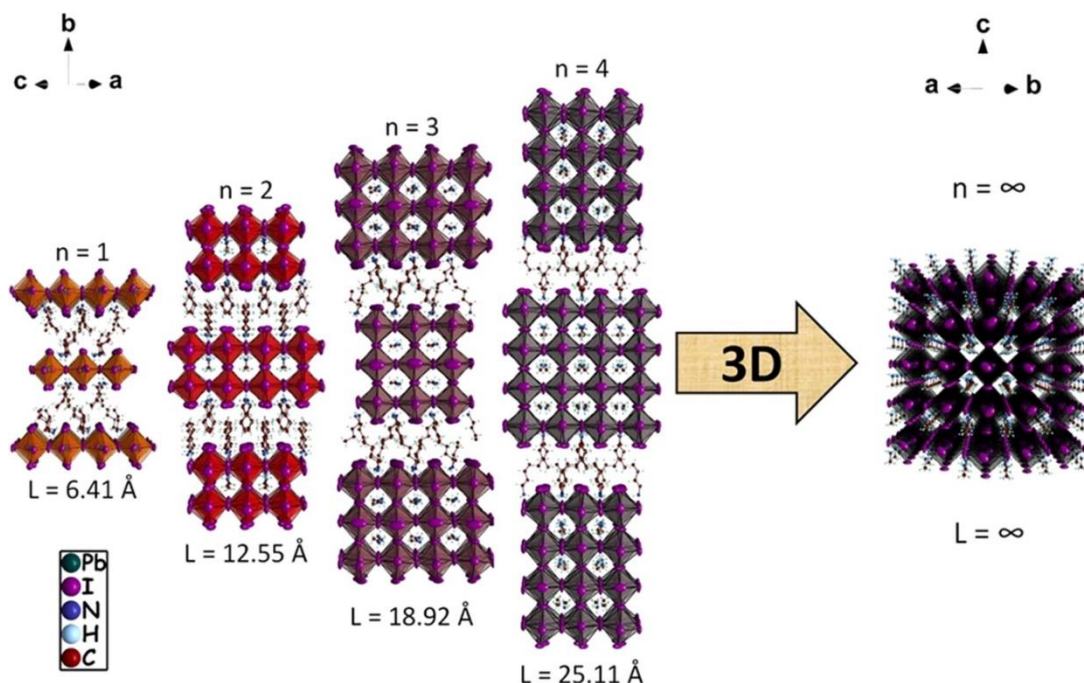


Figure 1. Crystal structures of the 2D lead iodide perovskites, $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, extending from $n = 1$ to $n = \infty$. The n -value denotes the thickness of the inorganic layer in each compound. The L -value refers to the distance between the terminal iodide ions of each layer and was determined directly from the refined crystal structures.

The toxicity of Pb present in the champion $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite is problematic. The ultimate goal of this project is to develop not only efficient but also stable and environmental-friendly halide perovskite solar cells. In parallel with 2D lead iodide perovskite studies, lead-free perovskite analog, $\text{CH}_3\text{NH}_3\text{SnI}_3$, was also investigated. However, this Sn-based perovskite material has proven challenging because the Sn^{2+} cation is susceptible to oxidation in minimum humidity, causing an increase in dark carrier concentration (conductivity) in the $\text{CH}_3\text{NH}_3\text{SnI}_3$ semiconductor. The most apparent effect of this self-doping event in solar cells is short-circuiting. By employing 2D structure, namely $(\text{BA})_2(\text{MA})_{n-1}\text{Sn}_n\text{I}_{3n+1}$ compounds, electrical resistivity and moisture-stability of Sn-based perovskites are considerably improved compared to the parent 3D $\text{CH}_3\text{NH}_3\text{SnI}_3$ perovskite. These 2D perovskites are semiconductors with optical band gaps progressively decreasing from 1.83 eV ($n = 1$) to 1.20 eV ($n = \infty$). The $n = 3$ and $n = 4$ members with optimal band gaps of 1.50 eV and 1.42 eV were chosen for solar cell application. It was demonstrated that thin films of 2D perovskites orient the $\{(\text{CH}_3\text{NH}_3)_{n-1}\text{Sn}_n\text{I}_{3n+1}\}^{2-}$ slabs parallel to the substrate when DMSO solvent is used for deposition, and this orientation can be flipped to perpendicular when DMF solvent is used.

Additionally, it was observed that high purity, single-phase films can only be grown by using precursor solutions of “pre-synthesized” single-phase bulk perovskite materials. Triethylphosphine (TEP) was introduced for the first time as an effective antioxidant which suppresses the doping level of the 2D films and improves film morphology. The resulting semiconducting 2D Sn-based iodide perovskite films were incorporated in solar cells yielding a power conversion efficiency of 2.5% from the Sn₄I₁₃ member. From the temporal stability standpoint, the 2D Sn perovskite solar cells outperform their 3D analogs.

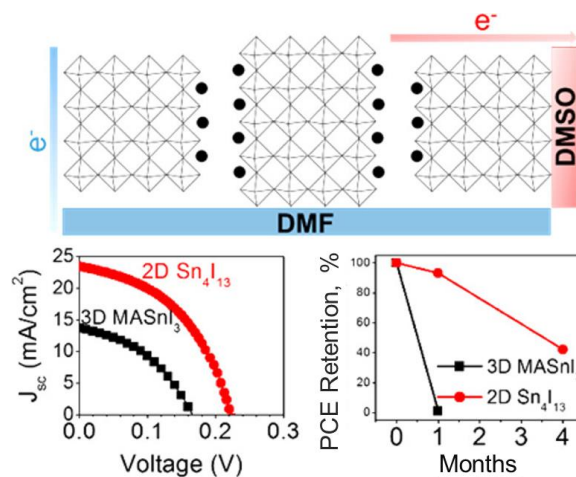


Figure 2. Cartoon illustrating 2D perovskite slabs grow perpendicular to the substrate if DMF solvent is used and parallel if DMSO solvent is used, current vs. voltage curves of 3D MASnI₃ and $n = 4$ Sn₄I₁₃ perovskite devices and their power conversion efficiency (PCE) retention vs. air exposure time.

Significance and impact.

Halide perovskites present a versatile class of solution-processable semiconductors made from earth abundant elements with remarkable electrical and optical properties. This project has delineated strategies in developing lead-free and moisture stable 2D Ruddlesden–Popper (BA)₂(MA)_{*n*-1}Sn_{*n*}I_{3*n*+1} perovskites for photovoltaic application. High quality semiconducting 2D tin iodide perovskite films have been obtained and incorporated in solar cells demonstrating an encouraging PCE of 2.5% from the Sn₄I₁₃ member. Encapsulated devices retained more than 90% of their initial performance after one month.

Where might this lead?

The 2D hybrid perovskites have proven to be a new source of moisture-stable, functional and tunable semiconductors where both the organic and inorganic moieties can be tuned to create multifunctional materials. The Sn-based perovskite solar cell efficiencies are steadily picking up. Given the high susceptibility to oxidation of the Sn²⁺ ions, slight modifications of the remaining constituents A⁺ and X⁻ ions to strengthen the framework might be useful. Using additives to control the semiconducting-relevant parameters in Sn-based perovskites is also an important task. Moreover, the fabrication of high quality, large grain thin films will be essential to push the device efficiency closer to the theoretical limit.

List of published journal papers that have acknowledged Link Foundation support

1. **Cao, D. H.;** Stoumpos, C. C.; Yokoyama, T.; Logsdon, J.; Song, T. B.; Wasielewski, M. R.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G., Thin films and solar cells based on semiconducting two-dimensional Ruddlesden-Popper $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Sn}_n\text{I}_{3n+1}$ perovskites, *ACS Energy Lett.*, **2017**, 2 (5), 982–990
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How did the Fellowship make a difference?

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