

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Perovskite Materials: Recent Advancements and Challenges

Ashwith Chilvery, Sharvare Palwai, Padmaja Guggilla, Kijana Wren and Devon Edinburgh

Abstract

In the past decade, hybrid organic–inorganic perovskites (HOIP) have emerged as the exotic materials for the futuristic photovoltaics. The viability of low-temperature, solution-processed manufacturing and a unique blend of electronic and optical properties that has further indicated its goal towards a potential commercialization. This article clearly articulates the emergence of HOIPs and various challenges such as toxicity, hysteresis in these devices. Additionally, this chapter also makes an effort to highlight the advancements made in the perovskite materials for solar cells in the recent years, that include the Ruddlesden-Popper (RP) phase that has enabled us reach the power conversion efficiency of 28%. This phase is reportedly a lower dimensional structure than the conventional HOIP and exhibit better stability than the latter. This chapter also focuses to elucidate a few challenges of these RP phased HOIPs such as its synthesis, stoichiometry and process-ability in integrating the organic and inorganic entities.

Keywords: Ruddlesden-Popper, 2D perovskite, photovoltaics

1. Background

In the early 1990s, David Mitzi at the IBM Watson Research Centre extensively explored the structural dynamics of methylammonium lead iodide perovskite (MAPBI₃) material engineered for niche applications such as electronics, thin film transistors, photovoltaics (PV) and light emitting diodes [1–5]. Today, the hybrid halide perovskites are treated as the emerging semiconductor materials, as the past decade witnessed their successful application in highly-efficient photovoltaics [6]. Compounds based on this particular hybrid arrangement of organic and inorganic molecules has emerged in an unprecedented manner by the participation of over 1000 institutes across the globe and over 8000 published articles in its decade-old research efforts [7]. This article outlines a detailed overview about these materials advancements and challenges.

In the past decade, the lead (Pb)-based HOIP have attracted a great deal of interest for applications in high-performance optoelectronics and efficient photovoltaics [8–13] due to their ability to tune optical band-gaps from the violet to near infrared [14], as well as their higher absorption coefficients [15, 16] and potential for long-range electron and hole transport [17]. Furthermore, it is widely understood that perovskites exhibit a plethora of functionalities such as dielectric [18, 19], ferroelectric [5, 15, 20, 21], magnetoresistive [21], thermoelectric [22], electro-optic [23], semiconducting [24], conducting [21, 25], and superconduction [5, 26].

2. Perovskite structure

A three-dimensioned (3D) perovskite structure usually adopts a stoichiometry of ABX_3 cubic structure where A is an organic cation (methylammonium), B is a metal cation (Pb^{2+} or Sn^{2+}), and X is a halide (Cl^- , Br^- or I^-). Dieter Weber first reported the three-dimensional (3D) perovskite structure of methylammonium lead iodide ($MAPbI_3$) in 1978 [27]. There were a few other researchers who were investigating the optical properties of these materials and its feasibility for transistors and other electronics [1, 28–30]. The material was further brought to light in 2009, when Miyasaka reported a 3.81% efficient dye-sensitized solar cell with $MAPbI_3$ coated on TiO_2 surface [16]. This material was later heavily reported by various research groups across the globe due to its potential to transform photovoltaic technology and replace silicon [22, 31–34]. By natural disposition, they could potentially transform the PV technology.

The hybrid organic–inorganic perovskites (HOIP) have strong intermolecular hydrogen bonds between the amino and halide group ions, whereas the weak Vander Waals exists among the organic ions. The divalent metal ions function as the best metal cations for organic–inorganic framework. Among these combinations, those belonging to group 14 (including Sn^{2+} , and Pb^{2+}) attracted more interest due to their good optoelectronic properties and potential for low-temperature device fabrication [25, 35, 36]. The employment of least electronegative halide anions improves the perovskite structures for strong absorption over wide band gaps. The HOIPs, with a stoichiometry of perovskite crystal, have some excellent properties such as long electron–hole diffusion lengths (>100 nm) and carrier lifetimes, direct bandgap with large absorption coefficients, and low-cost solution based processing capabilities that made them best functional materials for solar cells [37, 38].

3. Perovskites for photovoltaics

HOIPs that inherit a diversified set of properties such as stronger and broader absorption, ultra-fast charge transportation, high dielectric, and swift charge recombination makes it the best suitable candidate material for PV [39, 40]. Also, its ease of fabrication, stability, cost, efficiency, and performance rivals the best thin-film PV technologies.

Perovskite materials exhibit excellent optoelectronic properties and superior device performance via two key device architectures—mesoscopic and planar—as illustrated in **Figure 1**. The ultimate goal of the proposed summer project is to study how the contact/electrode interfaces impact the mechanism of charge collection and investigate the role of ionic motion on electronic charge carriers. In the recent years, the $MAPbI_3$ has attracted a great deal of interest for applications in high-performance optoelectronic devices [41, 42] due to their ability to tune optical band-gaps from the violet to near infrared [14], as well as their higher absorption coefficients [15, 16] and potential for long-range electron and hole transport [17]. Moreover, the optical and electrical properties of HOIP single crystals are far superior to their thin film counterparts [43, 44]. So far, researchers have been able to grow perovskite structured single crystals of methylammonium lead triiodide ($CH_3NH_3PbI_3$) and methylammonium lead tribromide ($CH_3NH_3PbBr_3$) with both size and shape controlled capabilities [45, 46].

These materials potential has increased the power conversion efficiencies of solar cells from 1 to 24.2% [47, 48]. Despite these materials were gaining efficiencies but were losing on the stability and durability side due to the anomalous hysteretic effects that is typically exhibited by ferroelectric materials. So, it became critical to understand the significance of hysteresis in these materials.

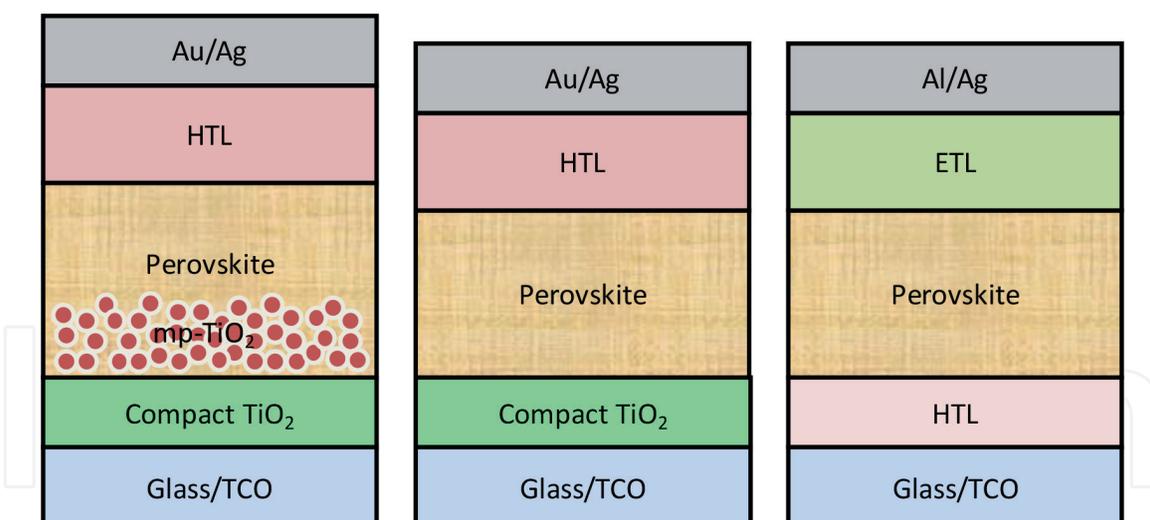


Figure 1. Typical architectures of PSCs—mesoporous (left), conventional planar (middle) and inverted planar (right); HTL—hole transport layer, ETL—Electron transport layer, TCO—transparent conductive oxide (e. g. Indium tin oxide).

4. Hysteresis in perovskites

This unusual property of hysteresis in the J-V characteristics [49–52] of perovskites is understood to originate from various factors impacted by the various electronics parameters used to operate or test device based on these materials, such as the scan rate, sweep direction, thickness of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and TiO_2 . Some researchers report that the abnormal behavior is more extreme in planar structures than the mesoporous architectures [51, 53–56]. Moreover, the presence of anomalous J-V hysteresis makes it difficult to reliably quantify the device performance, which could postpone the timely commercialization of this technology. It was found that the presence of large crystal grain sizes in the perovskite layer and the use of mp- TiO_2 layer can significantly reduce the J-V hysteresis. Recently, Yang et al. reported that hysteresis highly depends on the type of perovskite material used, and device architecture (n-i-p or p-i-n) [47]. The devices with n-i-p architecture and formamidinium lead iodide (FAPbI_3) as the absorber material did not show any hysteresis, whereas devices with p-i-n architecture (FTO/ NiO /perovskite/PCBM/ LiF/Al) showed strong hysteresis.

You et al. [57] reported that their devices with ITO/ NiO_x or PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$ or PCBM/ Al (p-i-n) architecture were shown to exhibit negligible hysteresis (**Figure 2**), which is consistent with some other earlier reports [58, 59]. It was speculated that n-type PCBM layer diffuses into the perovskite layer through pin-holes and grain boundaries during processing, and mobile ions in the perovskite film may interact with PCBM, forming PCBM halide radicals. This was assumed to result in stable electrostatic properties and reduced or no hysteresis [56, 60]. On the other hand, if the PCBM is used as the bottom electron transport layer (n-i-p architecture), no such inter-diffusion occurs, and the unusual ion movement causing hysteresis cannot be suppressed. More recently, Xu et al. reported the fabrication of hysteresis-free PSCs with conventional architecture using a perovskite-PCBM hybrid solid thin film as the absorber [60]. The devices without PCBM, i.e., FTO/ TiO_2 /perovskite/spiro-OMeTAD/ Au , exhibited hysteresis, whereas devices with a perovskite-PCBM hybrid layer showed significantly reduced or no hysteresis. Here, PCBM was shown to neutralize PbI_3^- defects, traps, and perovskite grain boundaries. It also reduced non-geminate recombination, and increased carrier lifetime. This study showed that incorporating a small amount of PCBM into the perovskite layer, or using a thin PCBM layer at the interface of TiO_2 /perovskite, significantly

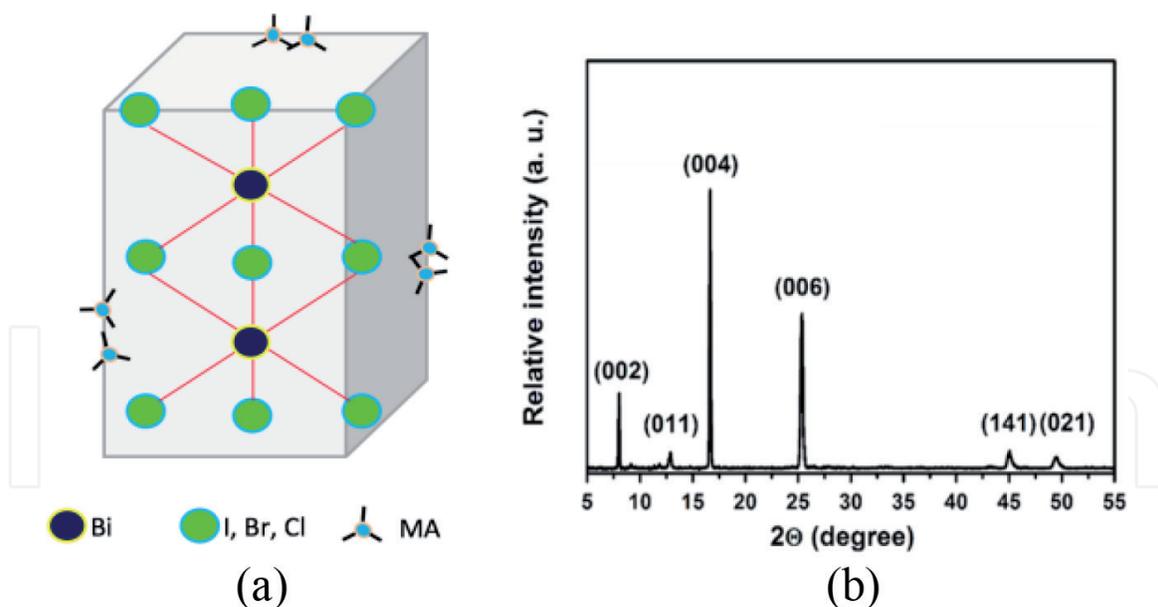


Figure 2.

(a) Schematic of MABi perovskite structure (b) XRD studies of solution grown $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ crystal.

reduces device hysteresis, while improving the device stability. However, these observations are not consistent with the hypothesis that PCBM reduces hysteresis by preventing the diffusion of ionic defects along grain boundaries. In addition to demonstrating the role of interfacial recombination in the presence of mobile ions in a semiconductor, our study targets the demonstration of the viability of controlling this ionic migration. These measurable consequences of ion migration suggests interesting possibilities of exploiting these effects for other electronic applications (e.g. sensing) where a memory of previous operating conditions could enable novel device behavior.

The majority of investigations indicate, that an electronic alignment at the interface between the perovskite absorber and transport layer is likely to become a key ingredient for designing next-generation devices, which can overcome the current performance limits [61, 62]. Considering these various sources potentially contributing to hysteresis, further investigation into device architectures and materials design is required to understand the dominant sources of this unusual behavior.

Further, the architecture of PSCs is also found to affect the level of J-V hysteresis. Planar PSCs on cp-TiO₂ often show more severe hysteresis than mesoporous PSCs based on a mp-TiO₂ scaffold [50]. For mesoporous/planar hybrid PSCs with a perovskite capping layer on top of mp-TiO₂, the grain size and thickness of the capping layer influences the J-V response. As ionic migration was identified as a possible cause of PV current–voltage hysteresis in hybrid perovskite solar cells, it was concluded that the quality of materials and crystal growth kinetics are vital in improving electronic, optoelectronic and PV applications for these classes of hybrid organic–inorganic semiconductors. Apart from hysteresis, another drawback that was hindering these devices into the commercial markets was the toxicity of lead.

5. Bismuth-based perovskites

The HOIP class of materials have displayed promising results for advanced and efficient photovoltaics. However, some of the urgent issues associated with these materials such as lead toxicity, poor stability, and atmospheric impacts are yet to be resolved. So, the focus of research shifted to replace toxic lead with other cations such as Sn²⁺, Ge²⁺, Mg²⁺, Mn²⁺, Ni²⁺, and Co²⁺ [63–65]. Many proposed the

replacement of Pb by tin (Sn) in order to render perovskite light absorbers less toxic or even nontoxic [66, 67]. Yet, compared to their Pb-based counterparts, Sn-based perovskites so far show inferior device performance, and they are even more sensitive to degradation because of self-oxidation [24]. In addition, Sn is also listed as a harmful chemical, raising concerns regarding its suitability as a more environment friendly alternative to lead in perovskite solar cells [68]. The most obvious route to replacing Pb in this compound is via substitution of other group-14 elements, such as Sn which tend to undergo oxidation, for example, from Sn^{2+} to Sn^{4+} , leading to a rapid degradation of the corresponding halide perovskites [69].

Germanium (Ge) has received relatively little attention as a replacement to lead, in part due to its strong lone pair effect, which acts to produce lower dimensionality structures with poor conductivities [70]. The series of perovskite-structured CsGeX_3 compounds, where X is chlorine (Cl), bromine (Br), and Iodine (I) have been known for some time for their nonlinear optical properties [71, 72]. These compounds are stable up to 150°C , and have bandgaps correlated with the A-site cation size [73]. However, the relative stability of the +4 oxidation states decrease and the relative stability of the +2 oxidation states increase down the group IV elements. As this effect is even more prominent for the case of Ge^{2+} , it is presumptive why no successful Ge-based hybrid perovskites have been developed.

These reports indicate that neither Pb nor Sn nor Ge can steer the scientific community to a roadmap for stable and non-toxic optoelectronic devices. Thus, more out-of-the-box approaches such as blending and splitting the anions and cations is required to stimulate the research in these niche areas. Fundamentally, many of the excellent properties seen in hybrid perovskites are thought to be derived from the $6s^2$ electronic configuration of lead, a configuration seen in a range of post-transition metal compounds [74]. Typically, materials containing post-transition metals with an ns^2 electronic configuration (*i.e.* an N-2 oxidation state) possess large dielectric constant, small effective masses, a valence band maximum composed of antibonding states, and high levels of band dispersion properties due to their soft polarizability—leading to high Born effective charges and large spin-orbit effects, which act to increase the bandwidth of the conduction band.

One promising alternative is to incorporate **Bismuth (Bi)** into the perovskite structure. Its size is similar to lead and the impact of steric effects on the optoelectronic properties of the material. Bismuth(III) (Bi^{3+}) compounds are attractive reagents and catalysts in organic synthesis because of their low toxicity, low cost and ease of handling. Preliminary investigations on organic-inorganic methylammonium bismuth iodide (MABiI) shows its advantages of non-toxicity, stability in ambient air and low-temperature solution-processibility, which may address both the toxicity issue of lead-based perovskites and instability concern of tin-based ones [75]. Typically for methylammonium bismuth halides, a Goldschmidt tolerance factor (t) of 0.85–0.87 ($\text{Bi}^{3+} = 1.03\text{\AA}$) is observed for a suitable perovskite structure and to further compliment it an octahedral factor (μ) of 0.46 justifies a stable octahedron perovskite structure [76]. Another study reports that compounds formed with $6p$ block cations show a significantly larger contribution of spin-orbit coupling in the conduction band, *vs.* those formed from the $5p$ block. This implies that the Bi^{3+} compounds show a much stronger spin-orbit contribution than the In, Sn, and Sb compounds. This further reiterates that Bi based compounds are the most suitable for achieving similar shallow vacancy levels as observed in MAPbI_3 [77].

Organic-inorganic bismuth iodide based hybrid materials have attracted interest because of their potential semiconducting character, rich structural diversity and interesting electronic and optical properties, for which the $6s^2$ lone pair of the Bi^{3+} plays an important role in the various material properties [78, 79]. In early 1990's, researchers conducted extensive studies on the phase transitions of various

MBH primarily to investigate its application as scintillators in radiation detectors [80, 81]. Recently, several research groups reported methylammonium bismuth iodides ($(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$) as a stable and lead-free light absorber for PV applications with an efficiency of less than 1% [75, 82–85]. Our basic studies on Bi based single crystals of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ were successful and in agreement with the literature (publication pending). **Figure 2a** illustrates a typical schematic of MABiI structure comprising of bioctahedral $(\text{Bi}_2\text{I}_9)^{3-}$ clusters that are surrounded by methylammonium cations. The MABiI crystal was solution grown at ambient room temperatures with good hexagonal crystalline structural phase and X-ray diffraction as shown in **Figure 2b** is in agreement with the literature [75, 83]. The red single crystals suitable for single crystal X-ray diffraction were grown using a layer crystallization technique by separating the two starting solutions of methyl ammonium iodide and bismuth(III) iodide with dichloromethane. In our preliminary study, all of the peaks in the XRD pattern can be indexed to a hexagonal structure, with no traces of any impurities. There are reports on XRD patterns of thin films, prepared via spin coating techniques recorded in Bragg–Brentano geometry and show good agreement when compared with the pattern calculated from single crystal data demonstrating a high degree of phase purity in the new material [79, 82]. A recent study on $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite crystal, revealed it had a hexagonal structure and its space group is $P6_3/mmc(194)$ which also has a monoclinic phase with space group $C12/c1$ [15] [83]. However, there are no reports for Bi based single crystal nanostructures.

As the research was plateauing on the lead alternatives and the observed hysteresis, the scientific community has identified a new breakthrough for these materials i.e., a lower dimensional perovskite- halide based two dimensioned organic–inorganic perovskite.

Recently, Benabdallah et al., have reported on the advantages of MABiI over lead-based perovskites [86]. The first principle calculations based on DFT have revealed that the Bi-based perovskites could be engineered to better bandgaps and have superior absorption coefficients than its lead counterparts. Separately, Sanders et al., have also reported on a novel chemical vapor deposition method to fabricate Bi-based perovskite solar cells that could potentially pave way for large scale and cost-effective commercial markets [87].

6. Transition from 3D to 2D crystal structures

Lately, these materials have unlocked a new stoichiometry-two-dimensional (2D), that features improved stability against atmosphere than the 3D materials. This process of lowering the dimensionality is gaining momentum and potentially serve the needs of specific applications such as solar cells, light emitting diodes (LEDs) and other optoelectronic devices. Although, there are various techniques to obtain this exotic and new 2D material, there has been significant interest for a specific kind of perovskites, namely Ruddlesden-Popper (RP) which was discovered in 1957 [88]. These perovskites have Vander Waals crystal structure carrying a general chemical formula of $\text{L}_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$, where L is a large molecular chained cation, A is a regular cation, B is an inorganic metal cation, X is the halide anion and $n = 1, 2$, etc., this arrangement of alternating organic–inorganic layers develops an ordered and ideal 2D quantum well. Additionally, these 2D structured quantum wells play a vital role in neutralizing the higher exciton binding energies formed due to contrasting dielectric constants. A simple structure is illustrated in **Figure 3**.

The insulating nature of the organic spacer cations creates a competitive advantage of greater atmospheric stability for the 2D HOIPs when compared to their 3D counterparts. It was rightly indicated by Mao et al. that the discovery of these 2D

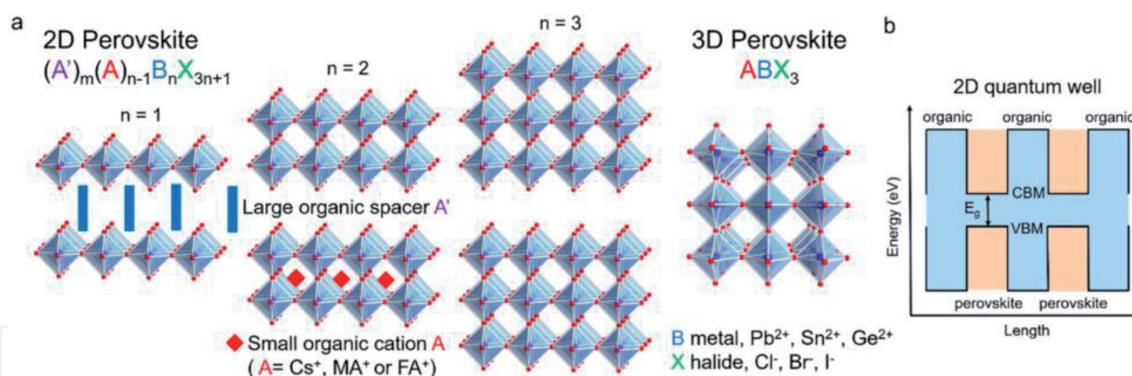


Figure 3.
 (a) An illustration of the evolution from 2D perovskite to 3D perovskite with key components.
 (b) Representation of a 2D quantum well structure. “Reprinted with permission from Mao et al. [6].
 Copyright (2019) American Chemical Society.”

	L	A	B	X	n
Notation	Bulky organic cation	Small organic cation	Inorganic cation	Halide ion	integer
Features	Must contain functional cations to interact with inorganic anions	Insulating nature	Divalent transition metals	Key for photoconductivity	Indicates number of metal halide layers held between the two cation layers
Most commonly used materials	Butyl ammonium (n-BA), 2-phenylethylammonium (PEA), ethylenediammonium (EDA)	Cs^+, MA^+	Pb^{2+}, Sn^{2+}	Cl^-, Br^-, I^-	1,2,3...
Impact on the device	Its hydrophobic nature exhibits superior ambient stability	Longer diffusion lengths for electrons and holes	Organic–inorganic layers generate quantum wells	Makes the charge transport anisotropic	Critical factor to tune the layer thickness

Table 1.
 Key requirements of 2D HOIPs.

HOIPs could possibly be a solution to stabilize a few metastable phases that are found in the form of perovskite nanocrystals. As Spanopoulos et al., has rightly observed that the room-temperature PXRD measurements of these 2D perovskites have indicated that there are no residual low-angle peaks ($<13^\circ 2\theta$) which would be an indication of coprecipitation of more than one inorganic layer in each case [89]. Although there has been significant progress in the [90], (110) and (111)-oriented perovskites, there has been undivided attention for the (100)-oriented HOIPs due to their dimensional variability. Furthermore, this particular orientation is the most favored geometry to tune the layer thickness. A few researchers have expanded the family of 2D RP perovskites by increasing the organic spacer molecules ($n = 1-5$) and concluded that for n values higher than 5 does not exhibit sufficient thermodynamic

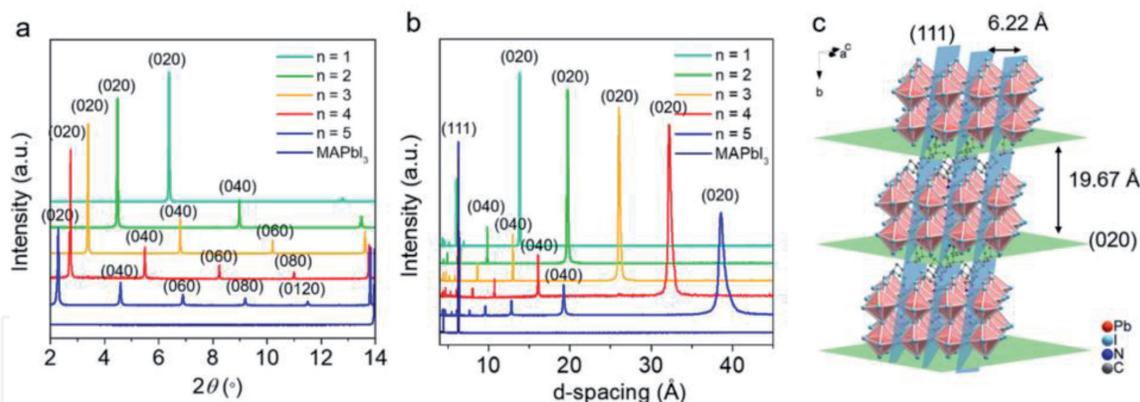


Figure 4. (a) High-resolution PXRD of $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1-5$). (b) PXRD plotted in d-spacing. (c) Structure of $(\text{BA})_2(\text{MA})\text{Pb}_2\text{I}_7$, with the illustration of respective diffraction planes. “Reprinted with permission from Mao et al. [6]. Copyright (2019) American Chemical Society.”

stability [6]. Separately, other study indicated that these materials have demonstrated unique optical characteristics with high air, heat and light stability especially for $n = 4$. Additionally, other discoveries such as the stability increases with increasing layer thickness and the need for crystalline substrates for improved orientation and long-term air stability [89]. So, a plethora of permutations are to be considered to build an effective, stable and functional 2D HOIP. **Table 1** delineates key features about individual elements of these HOIPs.

As a result of its ability to dimensionally customize the n-layer, the [90] oriented 2D HOIPs are paving way for a precise tailoring of the quantum well electronic structures. A simple X-ray diffraction analysis as shown in **Figure 4** would help us track the number of perovskite layers. This particular orientation exhibits a level of resistance to the thermodynamic phase. For example, this phase is more evident in the 2D perovskites at $n = 2$ versus a non-perovskitic phase in a 3D perovskite [6]. This further reinforces the belief that these 2D materials can further emerge with unexplored photophysics and optoelectronic properties.

7. 2D perovskites for photovoltaics

Despite the fact that, these Vander Waal layered 2D structure of RP perovskites has complicated the growth kinetics of thin 2D perovskites, yet the mechanical exfoliation process of inserting the long organic cation into a 3D perovskite structure was investigated by various research groups [6, 91, 92]. A few other groups have explored other methods such as colloidal synthesis [6, 74, 93], chemical vapor deposition (CVD) [94] and solution-based methods to obtain these 2D perovskites.

Another key feature that distinguishes 2D perovskites with their 3D counterparts is its superior susceptibility towards atmospheric moisture. By far, this is believed to be the single largest factor holding its foray into commercial markets. Apart from photoinduced oxidative degradation, 3D perovskites react with water, leading to collapse of the structure and to formation of either a 0D hydrated phase or to irreversible decomposition into the precursors, for example, MAPbI_3 starts to decompose at a relative humidity of 55%, which induces a color change from dark brown to yellow owing to conversion into a lead iodide [95]. Separately, other factors such as localized UV heating and light induced ion movement has also accelerated the perovskite degradation [90, 96–98].

Although, there are various synthesis methods for these 2D perovskite materials such as CVD, liquid and mechanical exfoliation, solution and colloidal based methods that have shown promise. But, there seem to be a critical need for controlled growth

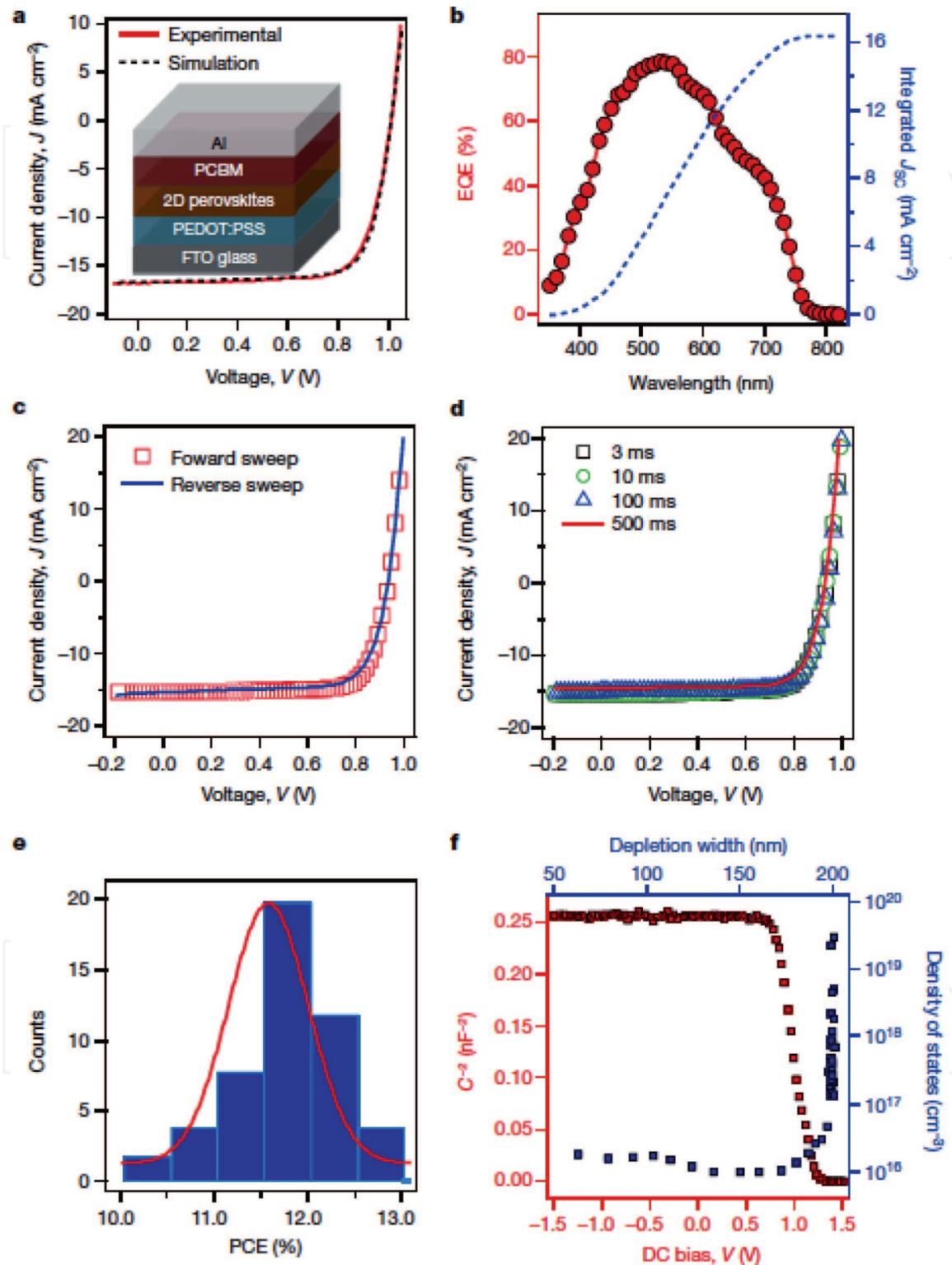


Figure 5. Solar cell architecture and characterization. (a) Experimental (red line) and simulated (black dashed line) current-density–voltage (J – V) curves under an AM1.5G solar simulator for planar devices. (b) External quantum efficiency (EQE; red circles and line) and integrated short-circuit current density (J_{sc} ; blue dashed line) as a function of wavelength. (c) and (d) J – V curves for hysteresis tests under AM1.5G illumination measured with the voltage scanned in opposite directions and with varying voltage delay times. (e), histogram of $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ device power conversion efficiency (PCE) over 50 measured devices, fitted with a Gaussian distribution (red line). (f), C – V curves for a typical device detected by a small-amplitude a.c. field (peak-to-peak voltage $V_{pp} = 20$ mV) at an AC frequency of 100 kHz. Reprinted with permission from Tsai et al. [99].

monitoring especially the thickness and lateral crystal sizes is still a challenge [92]. So, new synthesis methods that warrant controlled thickness and large lateral sizes are highly preferred to institute a seamless pathway towards commercial markets.

Tsai et al., have reported a uniform and thin layered films for planar PV applications as shown in **Figure 5**. These hot-casted films of 2D $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ perovskite was reproducible and highly efficient with 12.51% with an open circuit voltage of 1.01 V, short circuit current density of 16.76mAcm^{-2} and a fill factor of 74.13% [99]. Also, from **Figure 5c** it can be noticed that the J–V curves for hysteresis tests under AM1.5G illumination measured with the voltage scanned in opposite directions were observed to be no effects.

8. Conclusions

With the least scope for degradation and hysteresis, these 2D HOIPs have rejuvenated the scientific community at large and paved the way for a larger role in the commercial markets. Contrarily, as many consider that the dimensional transition of perovskite materials from 3D to 2D clearly outlines the scope of these materials and applications that it could create, there are equally concerning challenges such as complex growth mechanism, low thermal conductivity and high exciton binding energies. So, a reproducible and scalable fabrication mechanism is highly required to lock its potential. Also, the emergence of 2D nanostructures of HOIPs could be leading the research and evaluate the potential of these materials to its fullest. So, a methodology that can create a scalable and efficient PV devices with longer stability and improved functionalities could change the dynamics of these materials.

Acknowledgements

This work is partly supported by Louisiana NASA SAR project and NSF Awards #1546965.

Author details

Ashwith Chilvery^{1*}, Sharvare Palwai², Padmaja Guggilla², Kijana Wren¹ and Devon Edinburgh¹

¹ Department of Physics, Xavier University of Louisiana, New Orleans, Louisiana, United States

² Department of Physics, Alabama A&M University, Huntsville, Alabama, United States

*Address all correspondence to: achilver@xula.edu

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Kagan C, Mitzi D, Dimitrakopoulos C. Organic-inorganic hybrid materials as semiconducting channels in thin-film field-effect transistors. *Science*. 1999;**286**:945-947
- [2] Mitzi DB, Prikas MT, Chondroudis K. Thin film deposition of organic-inorganic hybrid materials using a single source thermal ablation technique. *Chemistry of Materials*. 1999;**11**:542-544
- [3] Mitzi DB. Templating and structural engineering in organic-inorganic perovskites. *Dalton Transactions*. 2001;**1**:1-12
- [4] Mitzi DB, Chondroudis K, Kagan CR. Organic-inorganic electronics. *IBM Journal of Research and Development*. 2001;**45**:29-45
- [5] Mitzi DB. Synthesis, Structure, and Properties of Organic-Inorganic Perovskites and Related Materials. West Sussex, England: John Wiley & Sons; 1999
- [6] Mao L, Stoumpos CC, Kanatzidis MG. Two-dimensional hybrid halide perovskites: Principles and promises. *Journal of the American Chemical Society*. 2019;**141**:1171-1190
- [7] Kumar Jena A, Kulkarni A, Miyasaka T. Halide perovskite photovoltaics: Background, status, and future prospects. *Chemical Reviews*. 2019;**119**:3036-3103
- [8] Huang J, Shao Y, Dong Q. Organometal Trihalide perovskite single crystals: A next wave of materials for 25% efficiency photovoltaics and applications beyond? *Journal of Physical Chemistry Letters*. 2015;**6**:3218-3227
- [9] Bade SGR et al. Fully printed halide perovskite light-emitting diodes with silver nanowire electrodes. *ACS Nano*. 2016;**10**:1795-1801
- [10] Pasquarelli RM, Ginley DS, O'Hayre R. Solution processing of transparent conductors: From flask to film. *Chemical Society Reviews*. 2011;**40**:5406
- [11] Fan J, Jia B, Gu M. Perovskite-based low-cost and high-efficiency hybrid halide solar cells. *Photonics Research*. 2014;**2**:111
- [12] Chilvery AK et al. Perovskites: Transforming photovoltaics, a mini-review. *Journal of Photonics for Energy*. 2015;**5**:057402
- [13] Chilvery AK, Guggilla P, Batra AK, Gaikwad DD, Currie JR. Efficient planar perovskite solar cell by spray and brush solution-processing methods. *Journal of Photonics for Energy*. 2015;**5**:053093
- [14] Knutson JL, Martin JD, Mitzi DB. Tuning the band gap in hybrid tin iodide perovskite semiconductors using structural templating. *Inorganic Chemistry*. 2005;**44**:4699-4705
- [15] Frost JM et al. Atomistic origins of high-performance in hybrid halide perovskite solar cells. *Nano Letters*. 2014;**14**:2584-2590
- [16] Kojima A, Teshima K, Shirai Y, Miyasaka T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*. 2009;**131**:6050-6051
- [17] Xing G et al. Long-range balanced electron- and hole-transport lengths in organic-inorganic CH₃NH₃PbI₃. *Science*. 2013;**342**:344-347
- [18] Juarez-Perez EJ et al. Photoinduced Giant dielectric constant in Lead halide Perovskite solar cells. *Journal of Physical Chemistry Letters*. 2014;**5**:2390-2394

- [19] Batra AK et al. Simulation of energy harvesting from roads via pyroelectricity. *Journal of Photonics for Energy*. 2011;**1**:014001
- [20] Bokov AA, Ye ZG. Recent progress in relaxor ferroelectrics with perovskite structure. *Journal of Materials Science*. 2006;**41**:31-52
- [21] Loi MA, Hummelen JC. Hybrid solar cells: Perovskites under the sun. *Nature Materials*. 2013;**12**:1087-1089
- [22] Takahashi Y et al. Charge transport in tin-iodide perovskite: Origin of high conductivity. *Dalton Transactions*. 2011;**40**:5563-5568
- [23] Bhalla A, Guo R, Roy R. The Perovskite structure- a review of its role in ceramic science and technology. *Materials Research Innovations*. 2000;**4**:3-26
- [24] Stoumpos CC, Malliakas CD, Kanatzidis MG. Semiconducting tin and lead iodide perovskites with organic cations: Phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorganic Chemistry*. 2013;**52**:9019-9038
- [25] Mitzi DB, Feild CA, Harrison WT, Guloy AM. Conducting tin halides with a layered organic-based perovskite structure. *Nature*. 1994;**369**:467-469
- [26] Kim H-S, Im SH, Park N-G. Organolead halide Perovskite: New horizons in solar cell research. *Journal of Physical Chemistry C*. 2014;**118**:5615-5625
- [27] Weber D. $\text{CH}_3\text{NH}_3\text{SnBr}_x\text{I}_{3-x}$ ($x = 0-3$), a Sn(II)-system with the cubic perovskite structure. *Zeitschrift für Naturforschung Part B*. 1978;**33**:1443-1445
- [28] Mashiyama H, Kurihara Y. Disordered cubic Perovskite structure of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{Cl, Br, I}$). *Journal of the Korean Physical Society*. 1998;**32**:156-158
- [29] Kitazawa N, Watanabe Y, Nakamura Y. Optical properties of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{halogen}$) and their mixed-halide crystals. *Journal of Materials Science*. 2002;**37**:3585-3587
- [30] Condeles JF, Lofrano RCZ, Rosolen JM, Mulato M. Stoichiometry, surface and structural characterization of lead iodide thin films. *Brazilian Journal of Physics*. 2006;**36**:320-323
- [31] Snaith HJ. Estimating the maximum attainable efficiency in dye-sensitized solar cells. *Advanced Functional Materials*. 2010;**20**:13-19
- [32] Snaith H, Grätzel M. Enhanced charge mobility in a molecular hole transporter via addition of redox inactive ionic dopant: Implication to dye-sensitized solar cells. *Applied Physics Letters*. 2006;**89**:262114
- [33] Im J-H, Lee C-R, Lee J-W, Park S-W, Park N-G. 6.5% efficient Perovskite quantum-dot-sensitized solar cell. *Nanoscale*. 2011;**3**:4088-4093
- [34] Kim H-S et al. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Scientific Reports*. 2012;**2**:591
- [35] Koutselas IB, Ducasse L, Papavassiliou GC. Electronic properties of three- and low-dimensional semiconducting materials with Pb halide and Sn halide units. *Journal of Physics. Condensed Matter*. 1996;**8**:1217-1227
- [36] Gao P, Grätzel M, Nazeeruddin MK. Organohalide lead perovskites for photovoltaic applications. *Energy & Environmental Science*. 2014;**7**:2448-2463
- [37] Stranks SD et al. Electron-hole diffusion lengths exceeding

- 1 micrometer in an Organometal Trihalide Perovskite absorber. *Science*. 2013;**342**:341-344
- [38] Ponseca CS et al. Organometal halide perovskite solar cell materials rationalized: Ultrafast charge generation, high and microsecond-long balanced mobilities, and slow recombination. *Journal of the American Chemical Society*. 2014;**136**:5189-5192
- [39] De Wolf S et al. Organometallic halide Perovskites: Sharp optical absorption edge and its relation to photovoltaic performance. *Journal of Physical Chemistry Letters*. 2014;**5**:1035-1039
- [40] Kazim S, Nazeeruddin MK, Grätzel M, Ahmad S. Perovskite as light harvester: A game changer in photovoltaics. *Angewandte Chemie (International Ed. in English)*. 2014;**53**:2812-2824
- [41] Zhao Y, Zhu K. Organic-inorganic hybrid lead halide perovskites for optoelectronic and electronic applications. *Chemical Society Reviews*. 2016;**45**:655-689
- [42] Yongping F et al. Solution growth of single crystal Methylammonium Lead halide Perovskite nanostructures for optoelectronic and photovoltaic applications. *Journal of the American Chemical Society*. 2015;**137**:5810-5818
- [43] Shi D et al. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science*. 2015;**347**:519-522
- [44] Dong Q et al. Electron-hole diffusion lengths > 175 um in solution-grown CH₃NH₃PbI₃ single crystals. *Science*. 2015;**347**:967-970
- [45] Saidaminov MI et al. High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization. *Nature Communications*. 2015;**6**:7586
- [46] Maculan G et al. CH₃NH₃PbCl₃ single crystals: Inverse temperature crystallization and visible-blind UV-Photodetector. *Journal of Physical Chemistry Letters*. 2015;**6**:3781-3786
- [47] Yang WS et al. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*. 2015;**348**:1234-1237
- [48] Heo JH et al. Efficient inorganic-organic hybrid heterojunction solar cells containing perovskite compound and polymeric hole conductors. *Nature Photonics*. 2013;**7**:486-491
- [49] Calado P et al. Evidence for ion migration in hybrid perovskite solar cells with minimal hysteresis. *Nature Communications*. 2016;**7**:1-40
- [50] Chen B, Yang M, Priya S, Zhu K. Origin of J-V hysteresis in Perovskite solar cells. *Journal of Physical Chemistry Letters*. 2016;**7**:905-917
- [51] Unger EL et al. Hysteresis and transient behavior in current-voltage measurements of hybrid-perovskite absorber solar cells. *Energy & Environmental Science*. 2014;**7**:3690-3698
- [52] Miyano K, Yanagida M, Tripathi N, Shirai Y. Hysteresis, stability, and ion migration in Lead halide Perovskite Photovoltaics. *Journal of Physical Chemistry Letters*. 2016;**7**:2240-2245
- [53] Frost JM, Butler KT, Walsh A. Molecular ferroelectric contributions to anomalous hysteresis in hybrid perovskite solar cells. *APL Materials*. 2014;**2**:081506
- [54] Snaith HJ et al. Anomalous hysteresis in Perovskite solar cells. *Journal of Physical Chemistry Letters*. 2014;**5**:1511-1515
- [55] Kim HS, Park N-G. Parameters affecting I-V hysteresis of CH₃NH₃

PbI₃ Perovskite solar cells: Effects of Perovskite crystal size and Mesoporous TiO₂ layer. *Journal of Physical Chemistry Letters*. 2014;5:2927-2934

[56] Shao Y, Xiao Z, Cheng B, Yongbo Y, Jinsong H. Origin and elimination of photocurrent hysteresis by fullerene passivation in CH₃NH₃PbI₃ planar heterojunction solar cells. *Nature Communications*. 2014;5

[57] You J et al. Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers. *Nature Nanotechnology*. 2015;11:75-81. DOI: 10.1038/nnano.2015.230

[58] Xiao Z et al. Efficient, high yield perovskite photovoltaic devices grown by interdiffusion of solution-processed precursor stacking layers. *Energy & Environmental Science*. 2014;7:2619

[59] Dou L et al. Solution-processed hybrid perovskite photodetectors with high detectivity. *Nature Communications*. 2014;5:5404

[60] Xu J et al. Perovskite–fullerene hybrid materials suppress hysteresis in planar diodes. *Nature Communications*. 2015;6:7081

[61] Schulz P et al. Charge transfer dynamics between carbon nanotubes and hybrid organic metal halide Perovskite films. *Journal of Physical Chemistry Letters*. 2016;7(3):418-425. DOI: 10.1021/acs.jpcllett.5b02721

[62] Ihly R et al. Efficient charge extraction and slow recombination in organic–inorganic perovskites capped with semiconducting single-walled carbon nanotubes. *Energy & Environmental Science*. 2016;9:1439-1449

[63] Hao F, Stoumpos CC, Cao DH, Chang RPH, Kanatzidis MG. Lead-free solid-state organic–inorganic halide perovskite solar cells. *Nature Photonics*. 2014;8:489-494

[64] Kumar MH et al. Lead-free halide Perovskite solar cells with high photocurrents realized through vacancy modulation. *Advanced Materials*. 2014;26:7122-7127

[65] Noel NK et al. Lead-free organic-inorganic tin halide Perovskites for photovoltaic applications. *Energy & Environmental Science*. 2014;7:3061-3068

[66] Ogomi Y et al. CH₃NH₃Sn_xPb(1-x)I₃ Perovskite solar cells covering up to 1060 nm. *Journal of Physical Chemistry Letters*. 2014;5:1004-1011

[67] Feng J, Xiao B. Effective masses and electronic and optical properties of nontoxic MASnX₃ (X = Cl, Br, and I) Perovskite structures as solar cell absorber: A theoretical study using HSE06. *Journal of Physical Chemistry C*. 2014;118:19655-19660

[68] Babayigit A et al. Assessing the toxicity of Pb- and Sn-based perovskite solar cells in model organism *Danio rerio*. *Nature Scientific Reports*. 2016;6:18721

[69] Volonakis G et al. Lead-free halide double Perovskites via Heterovalent substitution of Noble metals. *Journal of Physical Chemistry Letters*. 2016;7:1254-1259

[70] Chen Q et al. Under the spotlight: The organic-inorganic hybrid halide perovskite for optoelectronic applications. *Nano Today*. 2015;10:355-396

[71] Tang LC, Chang YC, Huang JY, Lee MH, Chang CS. First principles calculations of linear and second-order optical responses in rhombohedrally distorted perovskite ternary halides, CsGeX₃ (X = Cl, Br, and I). *Japanese Journal of Applied Physics*. 2009;48:112402:1-112402:9

[72] Tang LC, Huang JY, Chang CS, Lee MH, Liu LQ. New infrared nonlinear

optical crystal CsGeBr₃: Synthesis, structure and powder second-harmonic generation properties. *Journal of Physics. Condensed Matter*. 2005;**17**:7275-7286

[73] Krishnamoorthy T et al. Lead-free germanium iodide perovskite materials for photovoltaic applications. *Journal of Materials Chemistry A*. 2015;**3**:23829-23832

[74] Ganose AM, Savory CN, Scanlon DO. Beyond Methylammonium Lead iodide: Prospects for the emergent field of ns 2 containing solar absorbers. *Chemical Communications*. 2016;**53**(1):20-44. DOI: 10.1039/C6CC06475B

[75] Lyu M et al. Organic–inorganic bismuth (III)-based material: A lead-free, air-stable and solution-processable light-absorber beyond organolead perovskites. *Nano Research*. 2016;**9**:692-702

[76] Li C et al. Formability of ABX₃ (X = F, Cl, Br, I) halide perovskites. *Acta Crystallographica*. 2008;**64**:702-707

[77] Brandt RE, Stevanović V, Ginley DS, Buonassisi T. Identifying defect-tolerant semiconductors with high minority-carrier lifetimes: Beyond hybrid lead halide perovskites. *MRS Communications*. 2015;**5**:1-11

[78] Mitzi DB, Brock P. Structure and optical properties of several organic–inorganic hybrids containing corner-sharing chains of bismuth iodide Octahedra. *Inorganic Chemistry*. 2001;**40**:2096-2104

[79] Kawai T, Ishii A, Kitamura T, Shimanuki S, Iwata M, Ishibashi Y. Optical absorption in band-edge region of (CH₃NH₃)₃Bi₂I₉ single crystals. *Journal of the Physical Society of Japan*. 1996;**65**:1464-1468

[80] Kawai T, Shimanuki S. Optical studies of (CH₃NH₃)₃Bi₂I₉ single

crystals. *Physica Status Solidi B: Basic Solid State Physics*. 1993;**177**:K43-K45

[81] Jakubas R, Zaleski J, Sobczyk L. Phase transitions in (CH₃NH₃)₃Bi₂I₉ (MAIB). *Ferroelectrics*. 1990;**108**:109-114

[82] Eckhardt K et al. Crystallographic insights into (CH₃NH₃)₃(Bi₂I₉): A new lead-free hybrid organic–inorganic material as a potential absorber for photovoltaics. *Chemical Communications*. 2016;**52**:3058-3060

[83] Park B-W et al. Bismuth based hybrid Perovskites A₃Bi₂I₉ (a: Methylammonium or Cesium) for solar cell application. *Advanced Materials*. 2015;**27**:6806-6813

[84] Hoyer RLZ et al. Methylammonium bismuth iodide as a Lead-free, stable hybrid organic-inorganic solar absorber. *Chemistry: A European Journal*. 2016;**22**:2605-2610

[85] Hamdeh UH et al. Solution-processed BiI₃ thin films for photovoltaic applications: Improved carrier collection via solvent annealing. *Chemistry of Materials*. 2016;**28**:6567-6574

[86] Benabdallah I et al. Lead-free perovskite based bismuth for solar cells absorbers. *Journal of Alloys and Compounds*. 2019;**773**:796-801

[87] Sanders S et al. Chemical vapor deposition of organic-inorganic bismuth-based Perovskite films for solar cell application. *Scientific Reports*. 2019;**9**:9774

[88] Ruddlesden SN, Popper P. New compounds of the K₂NiF₄ type. *Acta Crystallographica*. 1957;**10**:538-539

[89] Spanopoulos I et al. Uniaxial expansion of the 2D Ruddlesden-Popper Perovskite family for improved environmental stability. *Journal of*

the American Chemical Society. 2019;**141**(13):5518-5534. DOI: 10.1021/jacs.9b01327

[90] Boyd CC, Cheacharoen R, Leijtens T, McGehee MD. Understanding degradation mechanisms and improving stability of perovskite photovoltaics. *Chemical Reviews*. 2018;**119**:3418-3451

[91] Gao Y et al. Two-dimensional halide perovskite nanomaterials and heterostructures. *Chemical Society Reviews*. 2018;**47**:6046-6072

[92] Lan C, Zhou Z, Wei R, Ho JC. Two-dimensional perovskite materials: From synthesis to energy-related applications. *Materials Today Energy*. 2019;**11**:61-82

[93] Fu Y et al. Broad wavelength Tunable robust lasing from single-crystal nanowires of Cesium Lead halide Perovskites (CsPbX₃, X = Cl, Br, I). *ACS Nano*. 2016;**10**:7963-7972

[94] Zhang Q et al. High-quality whispering-gallery-mode lasing from cesium lead halide perovskite nanoplatelets. *Advanced Functional Materials*. 2016;**26**:6238-6245

[95] Grancini G, Nazeeruddin MK. Dimensional tailoring of hybrid perovskites for photovoltaics. *Nature Reviews Materials*. 2019;**4**:4-22

[96] De Bastiani M et al. Ion migration and the role of preconditioning cycles in the stabilization of the J–V characteristics of inverted hybrid perovskite solar cells. *Advanced Energy Materials*. 2016;**6**:1501453

[97] Sanghadasa M et al. Ultrahigh durability Perovskite solar cells. *Nano Letters*. 2019;**19**:1251-1259

[98] Asghar MI, Zhang J, Wang H, Lund PD. Device stability of perovskite solar cells—A review. *Renewable and Sustainable Energy Reviews*. 2017;**77**:131-146

[99] Tsai H et al. High-efficiency two-dimensional ruddlesden-popper perovskite solar cells. *Nature*. 2016;**536**:312-316. DOI: 10.1038/nature18306