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Organic Inorganic Perovskites: A Low-Cost-Efficient Photovoltaic Material

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Abstract

Organic-inorganic perovskite materials, due to the simultaneous possession of various properties like optical, electronic and magnetic beside with their structural tunability and good processability, has concerned the attention of researchers from the field of science and technology since long back. Recently, the emergence of efficient solar cells based on organic-inorganic perovskite absorbers promises to alter the fields of thin film, dye-sensitized and organic solar cells. Solution processed photovoltaics based on organic-inorganic perovskite absorbers $\text{CH}_3\text{NH}_3\text{PbI}_3$ have attained efficiencies of over 25%. The increase in popularity and considerable enhancement in the efficiency of perovskites since their discovery in 2009 is determined by over 6000 publications in 2018. However, although there are broad development prospects for perovskite solar cells (PSCs), but the use of $\text{CH}_3\text{NH}_3\text{PbI}_3$ results in lead toxicity and instability which limit their application. Therefore, the development of environmental-friendly, stable and efficient perovskite materials for future photovoltaic applications has long-term practical significance, which can eventually be commercialized.

Keywords: organic-inorganic, Perovskite, photovoltaic material, optical properties, solar cells

1. Introduction

Organic-inorganic perovskites materials have emerged as a promising material for high-efficiency nanostructured devices such as light-emitting diodes (LEDs), detectors, field-effect transistors, and photovoltaic devices etc. [1, 2]. Organic-inorganic perovskites have attracted extensive attention due to their promising optical and electronic properties, excellent crystallinity, adjustable bandgap, long charge diffusion length, electroluminescence, and conductivity [3, 4]. As the most fascinating new-generation photovoltaic materials, organic-inorganic perovskite due to their facile synthesis, low temperature deposition, and capability to make flexible devices has been considered as a vigorous component of the efficient, low-cost, lightweight and flexible Perovskite solar cells [3, 4]. Perovskite solar cells (PSCs) have rapidly become the leading edge of third generation 3G photovoltaic technologies [5, 6]. PSCs based on the organic inorganic perovskite materials have fascinated great consideration, with their power conversion efficiencies (PCEs) reaching 25.2% certified [7, 8]. Over the past several months, it has been observed

a surprising revolution and rapid progress in the field of emerging photovoltaic, with the understanding of highly efficient solar cells based on organic inorganic perovskite materials. This perovskite technology is now well-matched with the 1G and 2G technologies and is thus probably be embraced by the conventional photovoltaic community and industry [9, 10].

1.1 Organic inorganic perovskite materials in solar cells

The advent of organic inorganic perovskite based solar cells has resulted in rapid growth in photovoltaic history. Organic inorganic perovskite materials have recently, fascinated greater attention due to its outstanding light-harvesting features [7].

Organic-inorganic perovskite absorbers have appeared in the field of DSSCs since 2009. The first perovskite-sensitized DSSCs were developed by Kojima et al. [11] which obtained PCE of 3.13% using liquid electrolytes. However, continuous irradiation produced a photocurrent decay in an open cell when exposed to air. Later, the electron transporting layer (Titania) surface and perovskite processing were optimized, and in 2011, Im et al. [12] developed first stable PSC, using $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based iodide liquid electrolyte offered a PCE of 6.5%. However, the perovskite nanocrystals dissolved in the liquid iodide electrolyte solution, and the cell degraded within 10 minutes. To avoid the problem of perovskite dissolution in an electrolytic solution, the liquid electrolyte was replaced by a solid in 2012, and a PCE of 9% was achieved showing good stability up to 500 h without significant losses [13, 14]. Afterward, Al_2O_3 an insulating network was used to substitute conducting nano porous TiO_2 . By using mixed $\text{MAPbI}_{3-x}\text{Cl}_x$ as the sensitizer, an enhanced open-circuit voltage (V_{OC}) and PCE (10.9%) was achieved [15]. In 2013, a successive deposition method for the perovskite layer within the porous metal oxide film was developed. The fabrication technique for solid-state mesoscopic solar cells greatly improved the reproducibility of cell performance and produced a high PCE of 15%. Many PSC devices are now attaining PCE > 20% since 2015 and 25% in 2019 [4, 16]. National Renewable Energy Laboratory (NREL), on 3rd August 2019 declared a new world record PCE of 25.2% for PSCs. This PCE value is improved up to ~28% for perovskite-silicon tandem structures [4].

1.2 Device architecture of perovskite solar cells

PSC consists of a perovskite absorbing material sandwiched between electron transporting layer (ETL) and hole-transporting layer (HTL) along with the transparent conducting oxide substrate (FTO) and a top electrode such as gold, silver [17]. In PSCs, the effective charge separation and the light harvesting efficiency are significantly affected by the properties like particle size, porosity, surface area, surface morphology, band gap, thickness of semiconductor materials, and the nature of organometal halide perovskites [18].

The primary function of an ETL is to extract a photo generated electron from perovskite and then transfer to electrodes. The basic criterion for an ideal ETL is high optical transmittance, excellent electron mobility, high conductivity, and an appropriate work function. ETL also performs as hole-blocking layer (HBL) [19]. The configuration and the choice of ETL are essential factors to understand the electronic mechanisms in PSCs, which control processes such as carrier separation, extraction, transport, and the recombination. Hence, the configuration of device structure is critical to alter different materials for ETL, electrode contacts, and the barrier layer of insight these processes and mechanisms [18]. TiO_2 , which has a wide band gap, has been extensively studied as an efficient electron transport material

(ETM). Moreover, ZnO and other *n*-type semiconductors such as SnO₂, Nb₂O₅ and BaSnO₃ are frequently used as ETMs and are used in flexible perovskite solar cells [20, 21].

The HTL lies in the heart i.e. in between the metal electrode and perovskite of device. It plays a central-role in the PSC and extracts holes from the perovskite and transfer them to top-electrode. It avoids the direct contact of perovskite and top electrode [22]. For efficient hole transport, the highest occupied molecular orbit (HOMO) must match the valence band (VB) of perovskite materials. According to the chemical composition, HTMs in PSCs can be divided into two types: organic and inorganic HTMs. Spiro-OMeTAD is the most used organic HTM, which displays good penetration in perovskite and is an appropriate match with the VB energy of perovskite, though its hole mobility is not as superior as that of other organic HTMs. [21, 23]. Hence, in order to improve the hole mobility, polymers are doped with *p*-type (i.e., cobalt or Lithium salts) or some additives (i.e., bis(trifluoromethane) sulfonimide lithium, LiTFSI, and 4-tert-butyl pyridine, TBP) [21, 24]. Other organic materials reported as HTMs in PSCs are PTAA, PEDOT:PSS, P₃HT etc. [25]. Inorganic *p*-type semiconductor materials, due to their advantages such as high hole mobility, wide band gap, and easy solvent treatment process as compared with organic HTMs exhibit the possibility to replace organic HTMs. The reported inorganic HTMs for PSCs are NiO, CuSCN, CuI, CsSnI₃ etc. [21, 25].

A PSC includes an organic-inorganic perovskite material as the light-harvesting active layer. Amongst the component's PSCs, perovskite materials perform a key role. Perovskite is comprised of earth abundant and inexpensive materials. It is processed at lower temperature rather via the printing techniques [26]. The organic–inorganic perovskites can exhibit appropriately good ambipolar charge transport and the primary functions of photovoltaic operation comprising light absorption, generation of charges, and transport of both electrons and holes. They perform both as efficient light absorbers and charge carriers [21]. The commonly used perovskites are Methylammonium lead triiodide (CH₃NH₃PbI₃) and formamidinium lead triiodide (CH₃(NH₂)₂PbI₃) [27]. Moreover, The PSC architecture is represented in **Figure 1**.

The two main device architectures of PSC are

1. mesoscopic
2. planar

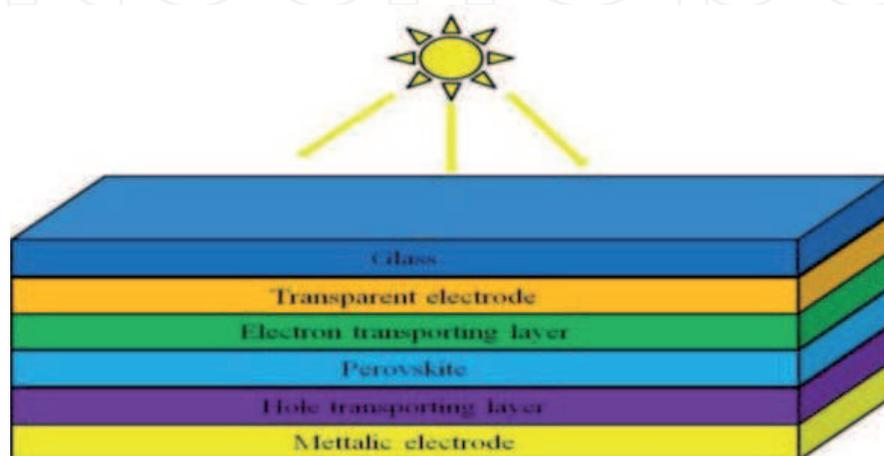


Figure 1.
Representative architecture of PSC.

The conventional PSC consists of mesoscopic n-i-p structure and is the novel architecture of PSC devices which consists of an FTO, an electron transport layer (ETL), a mesoporous oxide layer such as TiO₂, or SnO₂, perovskite (light absorbing) layer, a hole transport layer (HTL), and an electrode layer. The mesoporous TiO₂ layer played a significant role in the electron transfer process and as a scaffold providing mechanical support of the perovskite crystal. The use of mesoporous materials in PSC permit the perovskite material to adhere to the mesoporous metal oxide framework to increase the light-receiving area of the photosensitive material and results in improving the efficiency of the device. The mesoporous layer was usually less than 300 nm. The presently mesoporous structure of PSCs is one of the most common structures with a power conversion efficiency (PCE) greater than 20% [28]. The mesoscopic structure due to the fabrication ease and outstanding best efficiencies is the most extensively adopted in research labs. However, high temperature (>450°C) sintering is required for mesoporous layer-based devices, which prevents the use of plastic substrates [29–31]. To overcome this problem, the planar perovskite solar cell was developed that showed comparable performance for mesoporous perovskite solar cell. Planar heterojunction PSCs have been reported by several researchers in which only compact layers of ETM and HTM is used without a mesoporous layer at a temperature lower than 200°C [19, 21, 32]. Hence the planar structure turns out to be very attractive for basic research purposes. The mesoscopic and planar structures of PSC are represented in **Figure 2**.

1.3 Structure of perovskite materials

Perovskites materials are designated by the formula ABX₃, where A and B are cations of different sizes (A being larger than B) and X is an anion [7]. The crystal structure of perovskites is depicted in **Figure 3** and it has a cubic crystal structure with three-dimensional (3D) framework sharing BX₆ octahedron with the A ion placed at the octahedral interstices [33, 34]. In organic-inorganic materials, the A is organic cations generally methylammonium, ethylammonium and formamidinium and B is usually metal ions of group IV such as Pb²⁺, Sn²⁺ and Ge²⁺ whereas the X are VII group anions I⁻, Cl⁻ and Br⁻ [2, 7, 34].

The crystallographic stability and probable structure of perovskite can be inferred by studying a “tolerance factor” t and an “octahedral factor” μ . A “tolerance factor” is defined as the “ratio of the A-X distance to the B-X distance in an idealized solid-sphere model” and is represented by the formula:

$$t = \frac{(R_A + R_X)}{\left[\sqrt{2}(R_B + R_X) \right]} \quad (1)$$

where R_A , R_B and R_X are the ionic radii of the corresponding ions.

An “octahedral factor” is defined as “the ratio $\frac{R_B}{R_X}$ ”.

For halide (X = F, Cl, Br, I) perovskites, generally $0.81 < t < 1.11$ and $0.44 < \mu < 0.90$ [35]. If t value lies in the narrow range 0.89–1.0, the structure is cubic, but, if it is lower, symmetric tetragonal or orthorhombic structures is expected [2]. Regardless of these limitations, conversions between these structures are common on heating, at the high-temperature cubic phase is generally obtained.

For the organic–inorganic perovskites, organic cation A usually methylammonium (CH₃NH₃⁺) with $R_A = 0.18$ nm, ethylammonium (CH₃CH₂NH₃⁺) ($R_A = 0.23$ nm) and formamidinium (NH₂CHNH₂⁺) ($R_A = 0.19$ – 0.22 nm) are used. The cation B is commonly Pb ($R_B = 0.119$ nm); however, Sn ($R_B = 0.110$ nm) forms similar compounds with more ideal bandgap but exhibits lower stability

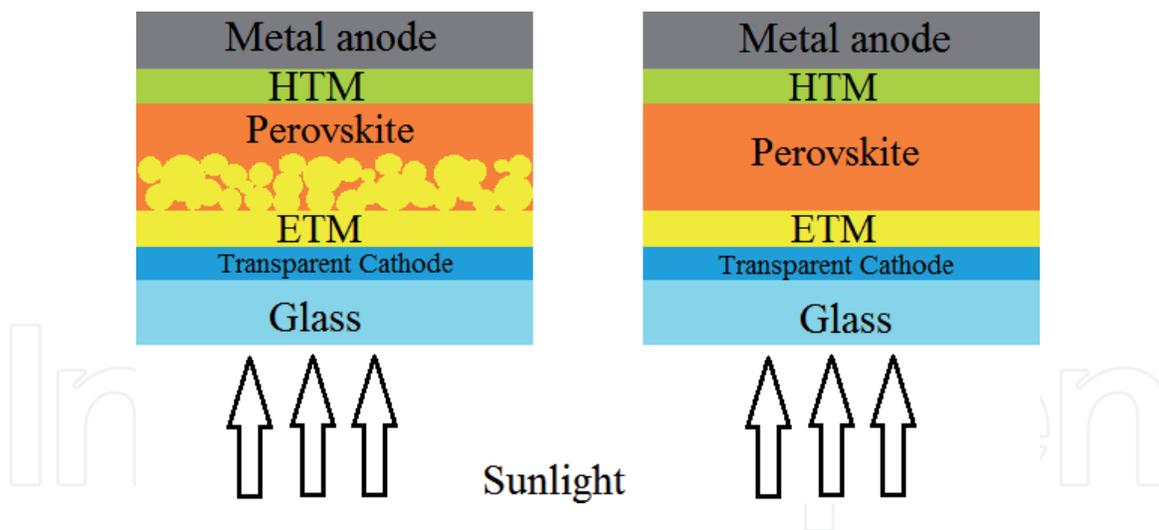


Figure 2.
Representative scheme of a mesoporous (right) and planar PSC (left).

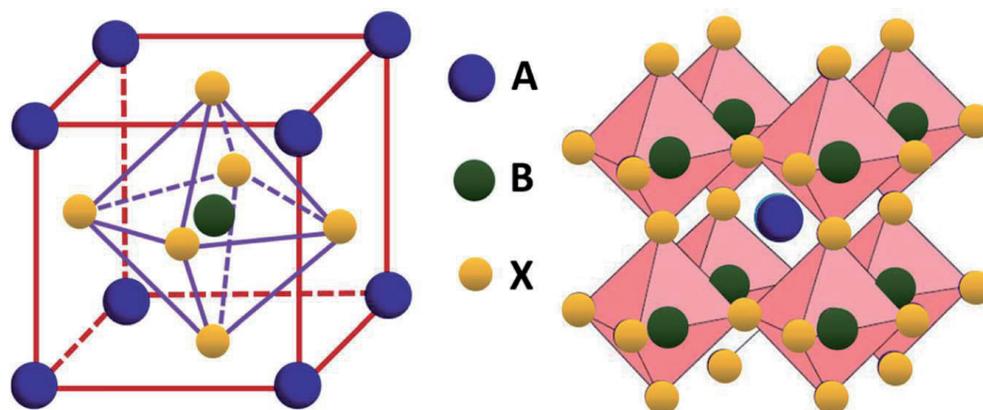


Figure 3.
Structure of perovskite.

(ascribed to the oxidation of Sn to SnI₄ in the iodide perovskite). The anion X is a halogen, generally iodine ($R_X = 0.220$ nm) is used, however Br and Cl are also used ($R_X = 0.196$ nm and 0.181 nm) [35, 36]. The commonly used organic inorganic perovskite material is methylammonium lead triiodide (CH₃NH₃PbI₃).

MAPbX₃ perovskite show multiple phases as a function of composition and temperature. These different phases have markedly different optical and electrical properties as well as stability. MAPbI₃ displayed α -phase, δ -phase, and γ -phases with transition temperatures of 400 K, 333 K, and 180 K, respectively. Generally, the δ -phase MAPbI₃ is used as absorber in solar cell due to its thermodynamically stable nature at room temperature and its increased conductivity and absorption coefficient (>26 mm⁻¹) in contrast to the α -phase. Though, a phase transition from δ -phase to α -phase may occur under continuous 1 sun illumination [15].

2. Synthesis of inorganic–organic solar cells materials

The deposition technique of organic-inorganic perovskites films is quite an important issue for perovskite studies, because the possible use of perovskite materials depends on the availability of simple and perfect thin film deposition method. As concerns the preparation methods of organometallic halide perovskite CH₃NH₃PbX₃ thin films, solution-based procedures have been proposed to manufacture thin films.

However, deposition of organic-inorganic perovskite materials is often challenging due to different physical and chemical properties of the organic and inorganic parts of perovskite materials [15]. Despite of this, several significant methods are used for thin film deposition of organic-inorganic hybrid perovskites. Various methods used for perovskite deposition are solution-processed (one-step and two-step) deposition, evaporation method, and vapor assisted solution process (VASP) are the typically adopted methods for film deposition [15, 37, 38].

1. one-step precursor solution deposition (Spin-coating technique)
2. two-step sequential deposition (including the vapor-assisted solution process)
3. thermal evaporation technique

2.1 One-step precursor solution deposition (spin-coating technique)

One-step processing (spin-coating) is a suitable technique extensively applied for uniform thin film deposition and is based on the co-deposition of both the inorganic and organic components either through solution processing or thermal evaporation. In solution processing, a mixture of both MX_2 ($\text{M} = \frac{1}{4} \text{Pb, Sn}$; $\text{X} = \frac{1}{4} \text{Cl}^-, \text{Br}^-, \text{I}^-$) and AX ($\text{A} = \frac{1}{4} \text{methylammonium MA}$); formamidinium, FA) is dissolved in an organic solvent and deposited through the spin coating to form a film (**Figure 4**), followed by annealing to produce the perovskite layer [15]. The post deposition annealing of the films at low temperature ($T < 250^\circ\text{C}$) is sometimes used to increase phase purity and crystallinity [6]. Spin-coating allows deposition of hybrid perovskites on various substrates, containing glass, quartz, plastic, and silicon. Selection of suitable parameters such as substrate, spin speed and the substrate temperature are essential for this technique and can be selected accordingly. The wetting properties of the solution on the chosen substrate can be improved by pre-treating the substrate with a suitable adhesion agent. The spin-coating technique does not involve cumbersome equipment and it gives high-quality films in quite short time at room temperature. It is considered as a distinct case of solution crystal growth, which results in the formation of highly oriented perovskites layer on a substrate. In order to obtain a layer with the desired thickness, optimization of various parameters such as concentration of perovskites solution, and spin-coating parameters (spin speed, acceleration and spin duration) can be carried out. Generally, 2D homogeneous perovskites films with a thickness ranging 10 nm to 100 nm can be obtained by carefully choosing the parameters. The selection of solvent is also important by considering the solubility for both the organic ammonium and the inorganic lead halide. The usually used solvents for spin coating technique are Dimethylformamide (DMF) or Dimethyl sulfoxide (DMSO) [39]. These spin-coated perovskites films are very reproducible, and this technique is suitable for all PSC structures (mesoporous vs. planar) [39].

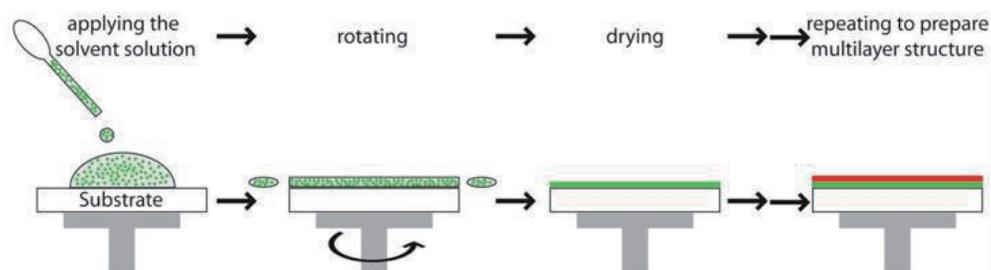


Figure 4. Schematic of the spin-coating process [4].

2.2 Two-step dip-coating

Mitzi [40] first time reported the two-step dipping technique in 1998, and later by Burschka et al. [41] in 2013. In a two-step dip-coating deposition process, a metal halide PbI_2 layer is first deposited by vacuum evaporation or spin-coated on a substrate. Then this coated film is altered into the perovskite by dipping into an organic MAI solution as it is shown in **Figure 4**. This method offered PCE of 15% and certified 14.14% [39]. Suitable selection of solvent is important for the dipping process. The solvent is selected such that can dissolve organic salt but cannot metal halide and the final organic-inorganic perovskite, toluene/2-propanol mixture is an appropriate solvent for the organic salt. The organic cations in solution intercalate into and react with metal halide on the substrate and form a crystalline film [6]. The dipping times are quite short: several seconds to minutes, depending on the system. This method is a suitable method for a variety of inorganic and organics, even if they have an incompatibility in solubility. This process effectively reduces the chemical reaction between the perovskite and the underlying ETL. The development of successive deposition methods has offered a variety of ETL options, though allowing for perovskite films to be prepared successfully at room temperature [15]. In addition, Chen et al. [42] developed a vapor assisted solution processing (VASP) method that used the reaction between MAI vapor and pre-deposited PbI_2 to form the completed perovskite film. The resulting MAPbI_3 exhibits excellent film quality.

2.3 Thermal evaporation technique

M. Era et al. [43] first used thermal evaporation method. They used the dual source vapor deposition by using ammonium iodide RNH_3I and lead iodide PbI_2 , organic and inorganic source were co-evaporated and deposited on quartz. The pressure of evaporation chamber was about 10^{-6} Torr. By using this method, it is possible to precisely control the smoothness and thickness of the films. However, it is often hard to balance the organic and inorganic rates, which is important in attaining the correct composition of the resultant perovskite films. Furthermore, Mitzi et al. [40] developed another method, by using a single evaporation source to deposit perovskites thin films called single source thermal ablation (SSTA) technique. This consists of a vacuum chamber, with an electrical feed-through to a thin tantalum sheet heater. A suspension of insoluble powders in a drying solvent is placed on the heater. Under a suitable vacuum, the temperature goes to approximately 1000°C in 1–2 second, the whole starting charge ablates from the heater. After ablation, the organic and inorganic parts reassemble on the substrates to yield films of the chosen product. Liu et al. [44] in 2013, improved this technique as a dual-source vapor deposition method for pinhole-free $\text{MAPbI}^{1-x}\text{Cl}_x$ perovskite films with a thickness of hundreds of nanometers for planar PSCs.

Later on, the chemical vapor deposition (CVD) method was reported by Leyden et al. [45], which precisely control the crystallization process. Vapor deposition methods are appropriate for multi-layered thin-film and a variety of substrates, though needs high vacuum [39]. However, this method has drawbacks of yield and therefore is not very effectively employed at industrial scale [46]. Though great achievements have been attained, researchers still meet some challenges, involving reproducibility and grain boundaries of perovskite films which are considered as a defect region initiates carrier recombination and accelerates device degradation. Hence, efforts to increasing grain size and reducing grain boundary of films are critical for stable and highly efficient PSCs.

3. Advances in perovskite solar cells

The possibility of merging the properties of inorganic with those of organic solids has inspired intensive research into the versatile properties. Organic-inorganic perovskite materials have been widely used in PSCs using different ETLs and HTLs. The optimization of materials and structures is one of the solutions to improve the PCE. **Table 1** shows some representative devices and their architectures and performance.

Methylammonium Lead halide perovskites (MAPbX_3) are mostly regarded as promising light absorbers owing their many advantages comprising high absorption coefficients, optimal bandgaps, and long-range exciton diffusion lengths. These perovskites have led to solar cells with PCEs upto 15% in combination with meso-structure metal oxides and deposition methods (such as sequential and vapor deposition) [34]. There were few attempts to synthesize new perovskites by changing halide anions (X) in the MAPbX_3 structure, but these materials did not result too much improvement in device efficiency. Optical and electronic properties of organo lead halide perovskites have been considered by replacing MA cation with other organic cations such as ethyl ammonium and formamidinium [55].

Dkhissi et al. [32] fabricated an efficiently $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based planar perovskite solar cells on polymer substrates at 150°C or below. The hole blocking layer employed is a TiO_2 layer. The devices showed an average efficiency of $10.6 \pm 1.2\%$, and a maximum efficiency of 12.3% for flexible perovskite solar cells, presenting great potential for further enhancement of the low-cost, low-temperature processing solar technology.

In 2014, Choi et al. [55] modified perovskite material with Cesium (Cs) by doping methyl ammonium lead iodide perovskites by Cesium to improve the performance of inverted-type perovskite/fullerene planar heterojunction hybrid solar cells. $\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$ perovskite devices achieved improvement in device efficiency from 5.51–6.8% with an optimized 10% Cs doping concentration. The devices exhibited an outstanding increase in efficiency due to increases in short-circuit current density and open-circuit voltage.

ETL	HTL	Perovskite	PCE	References
Gr/ZnO-QDs	Spiro-OMeTAD	$\text{CH}_3\text{NH}_3\text{PbI}_3$	9.73	[18]
$\text{TiO}_2\text{-Al}_2\text{O}_3$	Spiro-OMeTAD -Li-TFSI	—	10	[24]
ZnO-NPs	Spiro-OMeTAD	$\text{CH}_3\text{NH}_3\text{PbI}_3$	10.2	[34]
TiO_2	Spiro-OMeTAD	$\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$	11.7	[47]
TiO_2	Spiro-OMeTAD	$\text{CH}_3\text{NH}_3\text{PbI}_3$	15.4	[48]
TiO_2	—	$\text{CH}_3\text{NH}_3\text{PbBr}_{3-n}$	8.54	[49]
SnO_2 QD	Spiro-OMeTAD- Li-TFSI	$\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$	20.79	[50]
SnO_2 QD	Spiro-OMeTAD- Li-TFSI	$\text{CH}_3\text{NH}_3\text{PbI}_3$	19.73	[50]
SnO_2	Spiro-OMeTAD	Cs/MA/FA perovskite	20.7	[51]
SnO_2 QD	Spiro-OMeTAD	$\text{CH}_3\text{NH}_3\text{PbI}_3$	19.12	[52]
TiO_2	Spiro-OMeTAD	$(\text{FAI})_{0.81}(\text{PbI}_2)_{0.85}(\text{MAPbBr}_3)_{0.15}$	21.02	[53, 54]

Table 1. Comparison of different organic inorganic perovskite materials with different hole and electron TLs in PSCs.

$\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$, were used as sensitizers for TiO_2 in a liquid junction solar cell, with open-circuit voltages of 0.61 and 0.71 V were achieved. $\text{CH}_3\text{NH}_3\text{PbI}_3$ on mesoporous TiO_2 showed good charge transport properties, where the perovskite is both the absorber and the hole conductor. Further $\text{CH}_3\text{NH}_3\text{PbX}_3$ (X = Br, I), mixed perovskite lead halides i.e., $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$, $\text{CH}_3\text{NH}_3\text{PbBr}_3 - x\text{Cl}_x$, and $\text{CH}_3\text{NH}_3\text{PbI}_3 - x\text{Cl}_x$ were studied [27].

Giacomo et al. [47] fabricated PSCs using $\text{CH}_3\text{NH}_3\text{PbI}_3 - x\text{Cl}_x$ with different hole-transporting materials. The mostly used Spiro-OMeTAD has been compared to the P3HT. By changing the energy level of P3HT and optimizing the device fabrication, PCE reached to 9.3%. They showed that P3HT can be used a suitable low-cost hole transport material for efficient perovskite based solar cells.

NiO has been tried as a substitute for organic molecular or polymeric HTMs (spiro-MeOTAD), displaying encouraging results in the $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ configuration, a PCE of 9.5% was attained with nanocrystalline NiO layer. As the valence band edge (5.4 eV) for NiO is near to that of iodide perovskite (5.3 eV), so post-treatment of NiO film by means of UV light or oxygen plasma is vital to progress hole injection efficiency due to an increase in the work function of NiO by such post treatments. UV-ozone post-treated NiO usually has a greater photovoltaic performance than untreated NiO, due to change in work function and an enhancement in wettability indicating a better chemical interaction between perovskite and NiO [36].

The use of perovskites with mixed cations and halides has become significant for PV applications which are mainly MAPbX_3 , FAPbX_3 and CsPbX_3 (X = Br or I). on the introduction of MA into FA brings the crystallization of FA perovskite (because MA is slightly smaller than FA) which allows a large fraction of the yellow phase to continue. MA/FA compounds show notable PCEs and therefore the development of these compounds is an opportunity in the advancement of PSCs. Saliba et al. [56] introduces an innovative approach using a triple Cs/MA/FA cation mixture where Cs is used to progress MA/FA perovskite compounds. A small amount of Cs is enough to efficiently suppress yellow phase impurities allowing the preparation of pure, defect-free perovskite films.

Song et al. [57] reported that the combination of FA decreases the release of organic species but does not stop the formation of I/HI. Though, the addition of Cs successfully overcomes the release of all volatile gases. The best photostability is found with FA/Cs mixed perovskites, presenting the complete removal of MA from mixed-cation perovskite is favored for more photostable perovskites.

As $\text{CH}_3\text{NH}_3\text{PbI}_3$ has ambipolar properties and is slightly more p-type than n-type and is satisfactory to develop p-n junction-like devices without an HTM, known as HTM-free photovoltaic cells. $\text{CH}_3\text{NH}_3\text{PbI}_3$ could act both as light absorber and hole transporter in a $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{mesoporous TiO}_2$ heterojunction device with a PCE of 5.5%. It was observed that HTM-free perovskite solar cells had a poor FF and a low V_{oc} as compared to those with an HTM, which is related to the larger shunt current along with a lower IPCE for these devices [2].

Different proportions of inorganic (Pb, Sn) cations, organic cations and halide anions (I, Br, Cl) can be combined in mixed perovskites, permitting their properties to be fine-tuned [35]. Tuning of bandgap of MAPbX_3 has been attained through the substitution of I with Cl/Br ions, which occurs from a dependence of electronic energies on the effective exciton mass. The optical absorption can be tuned by bandgap engineering to comprise the whole visible spectrum. In the meantime, the combination of Cl/Br into iodide-based structure has markedly advanced the charge transport and the separation kinetics within the perovskite layer. Hence, by tuning the composition of perovskite resulted in improved efficiency and the stability of PSCs. It was observed that an increase in the size of perovskite cation materials

resulted in a reduction in the bandgap. A tunable bandgap can be obtained (between 1.48 and 2.23 eV) by replacing the methylammonium with a slightly larger formamidinium cation. Significantly, the reduced bandgap led to a PCE of up to 14.2% and high short circuit currents ($>23 \text{ mA cm}^{-2}$) [31].

$\text{CH}_3\text{NH}_3\text{SnI}_3$ is demanded to be a low-carrier-density p-type metal. Theoretical calculations on perovskite recommended that their electronic properties intensely depend on the structure of the inorganic cage and formation of the perovskite octahedral network. By changing the inorganic and organic components and their stoichiometric ratio, it is probable to control the system dimensionality and electronic and optical properties. Furthermore, the presence of weak bonds in the perovskite structures ensures malleability and flexibility that could permit the deposition of thin films on flexible substrates [26].

4. Toxicity and stability issue

4.1 Lead: the toxicity problem

Regardless of the excellent properties and high efficiencies, the poor stability of organic–inorganic perovskite materials are yet a serious challenge, inhibiting PSCs from being commercialized. To be marketable for commercial purposes, PSCs need to be capable of work constantly for over 20 years under outdoor conditions. Thus, large consideration has recently been centered to overcome barriers associated with stability and environmental compatibility of perovskite materials [10].

Presently there is a debate on the use of lead (main component) in PSCs, which causes toxicity problems during device manufacture, placement, and disposal. Hence, the toxicity of lead-based perovskites is an obvious problem due to leaching of lead into the environment [9]. Lead toxicity has been pointed out as one of the most challenging barriers towards the commercialization of solar cells, as compared to stability issues and cost-effective production ways. The environmental impact benefits of lead-free (or lead-reduced) solar cells have been analyzed by Life Cycle Assessment (LCA) [15].

4.1.1 Lead-free perovskite solar cells

Up to now, several research groups have ambiguously proven their solution to this challenge. Thus, it is critical to test alternatives to attain similar optical and photovoltaic performances for the commercialization of PSCs. Several research groups have tried to replace lead with other elements (Sn, Ge) and organic cations with inorganic cations to form new appropriate non-toxic and stable perovskite materials, which may be a long journey before the final commercialization of PSCs [9].

It is worth studying alternatives using lead-free PSCs, but Lead-free PSCs reached a PCE of only 6% at a time when lead-based PSCs produced efficiency of 17%. Moreover, the Sn-based solar cells display poorer stability than Pb-based solar cells. [14]. Bivalent Sn is the most favorable choice for replacing Pb as they both are in the same group and possess analogous lone-pair s orbitals [10]. Both Sn- and Pb-based materials have a tetragonal structure under ambient conditions; however, Sn-based perovskite have a higher symmetrized α phase as compared to the Pb-based materials lower symmetrized β phase [47]. Chung et al. [54] first demonstrated CsSnI_3 as a solid electrolyte in DSSCs. Afterward Chen et al. [58] fabricated a photovoltaic device, ITO/ CsSnI_3 /Au/Ti, attaining very low PCE of 0.88%. However, Sn^{2+} based perovskite undergoes oxidation from Sn^{2+} to Sn^{4+} , which is destructive

for the charge transport properties, and PCE. Recently, Lv 2019 [59] reported the replacement of spiro-OMeTAD by a Zn-derivative porphyrin in a lead-free solar cell has resulted in stability up to 60 h for water and 100 h for thermal stability.

There is another approach of mixed Pb/Sn perovskite Solar cell have also been reported. Lead and tin were revealed to be arbitrarily spread in the [MX₆] octahedra in the perovskite and percentage of tin could be altered from 0 to 1 [15]. These devices presented the best photocurrent at a 50% mixing ratio. SnO used as ETL has also resulted with good PCE of (13%) and stability (>700 h storage) [15, 60]. LCA showed the replacement of lead did not decrease the environmental impacts, meanwhile the loss of PCE and stability generates an environmental burden. However, those studies are also interesting because they draw consideration to other toxicity problems occurring from the solvent use during processing of charge transport layers (ETLs) [15].

For lead-free inorganic perovskites Tetravalent cations have also been thought to replace Pb. A new chemical formula of A₂BX₆ structure is designed by eliminating half of the B-site ions in the ABX₃ perovskite for adjusting the heterovalent cation substitution as shown in **Figure 1**. Due to the lack of connectivity in the [BX₆] octahedral structure, the A₂BX₆ can be considered as a 0D non-perovskite which results in different optical and optoelectronic properties of the A₂BX₆ from those of the ABX₃. [3, 9, 10]. Amongst the A₂BX₆ perovskites, Cs₂SnI₆, Cs₂TiBr₆ and Cs₂PdBr₆ have been employed in photovoltaic devices [9, 10]. Chung et al. [54] first utilized this material as a solid hole transport material in DSSCs.

Furthermore, a special concern for toxicity must be upraised during experimental work in the laboratory, since hazards arise primarily by the absorption of the toxic lead when used in solution, which is significantly higher, particularly through the dermal and respiratory routes; some of the lead derivatives are soluble both in water and fat, posing a high risk. Solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO) are not only toxic, but also raise the risk of bio incorporation as they are miscible in all ratios with water. Thus, these solvents have also been considered as a major contributor to environmental impact [61].

4.2 Stability

Perovskite solar cells (PSCs) have been established with promising PCEs. Regardless of the great potential as PV material in terms PCE, the instability of the PSCs is one of the core barriers for larger scale applications [8, 9, 39]. At present, PSCs can only perform for several months under active conditions, whereas traditional silicon cells can operate for more than 25 years. Therefore, stability issues must be reasonably dealt with before its actual use and commercialization [62]. Poor stability of PSCs is due to several affiliated factors resulting from exposure to moisture, oxygen, light, and heat [63, 64].

Nevertheless, the importance of stability has been highlighted and recognized as the foremost problem, in the past five years to solve for the perovskite solar cells (PSCs) to be able to challenge in the market arena. So, how to increase the stability of perovskite solar cells is the most significant issue in this field [15].

In this section, the effect of environmental factors will be discussed on PSCs along with approaches developed to improve stability of perovskite solar cells.

4.2.1 Moisture

The first environmental factor observed to degrade perovskites was Moisture/water. The instability of perovskite at high humidity is the serious issue that needs to be focused. Solar cells when exposed to moisture (water), due to the hygroscopic

nature of the organic components of perovskite materials are spontaneously affected by moisture access and then degrade [62]. It has basically been supposed that moisture-induced degradation is the leading issue, imitating MNH_3PbI_3 stability under ambient conditions.

Prolonged exposure of perovskite material to water vapor activates an irreversible degradation which eventually leads to transformation of the perovskite back to the initial precursors (such as PbI_2). In detail, perovskite forms hydrate complexes with water such as $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ and leaves out PbI_2 , which tend to crystallize, forcing the forward reaction. Moreover, MA^+ is slightly acidic and reacts with water to form volatile methylamine (CH_3NH_3) and hydroiodic acid (HI), according to the following reaction (1): [63].



Some researchers have reported that the compositions, microstructures (such as grain size) also affected the moisture stability of perovskite devices and concluded that larger grains resulted in a smaller area density of grain boundaries, which can be correlated with the improved stability [65].

In demand to progress the chemical stability of MAPbI_3 -based PSCs against moisture, scientists have proposed replacing the organic cation MA^+ with alternative components at the A position. For example, FAPbI_3 has been presented to be further thermally stable than MAPbI_3 because of its larger tolerance factor. Though, FAPbI_3 suffers a phase transition from the a- FAPbI_3 (black triangular) phase to the d- FAPbI_3 (yellow hexagonal) phase due to the presence of moisture. Furthermore, degradation of $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$ is prevented by adding a small amount of cesium (Cs) into orbital lead-iodine to form $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$ in high humidity environment [33].

Smith et al. [66] discussed that Low-dimensional 2-D perovskites exhibited better moisture stability than 3D perovskites due to the hydrophobic nature of organic cations. Though, the insulating aspect of the organic cations with poorer charge transport resulted in lower PCE as compared to 3D perovskites. Therefore, various efforts have been made to form a quasi-2D (or 2D–3D mixture) and 2D on top of 3D (2D@3D) to use the benefits of both 2D and 3D perovskites. The use of 2D perovskite is mostly to improve the moisture stability, a thin 2D layer was deposited on top of 3D MAPbI_3 perovskite to cover it fully and shield the 3D perovskite from moisture. The highest PCE for 2D@3D perovskite solar cell was observed to be of 18.0%, with an enhanced device stability under both inert (90% of initial PCE for 32 d) and ambient conditions (72% of initial PCE for 20 d) without encapsulation.

Polymers, such as poly(4-vinylpyridine) (PVP), poly (methyl methacrylate) (PMMA) covering p-type and n-type semiconductors, or insulators, were also reported to improve stability. These long chain polymer acts as defect passivator and a moisture blocker by forming a network along perovskite grains and resulted in improved device efficiency and stability [58, 60, 64].

4.2.2 Light

Light-induced perovskite solar cell degradation and environmental stability are the most frequently cited villains. Early on, stability of PSC was a big issue. But just as there were quick improvements in efficiency of PSCs, there has also been similar quick progresses in stability. Ultraviolet light (UV) can also cause the degradation of MAPbI_3 perovskite. For e.g. the commonly used TiO_2 electron transport layer

(ETL) for these PSCs is responsible for UV-induced degradation. According to the international standards for climate chamber tests (IEC 61646), solar cells need to tolerate long-term stability at 85°C.

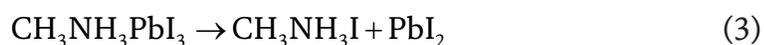
Bryant et al. [67] demonstrated that contact of MeNH₃PbI₃ films to both light and molecular oxygen can initiate quick degradation. Particularly, this reaction is started by the deprotonation of the methylammonium cation of the perovskite by a photogenerated reactive oxygen species (superoxide, O₂⁻). The stability of MeNH₃PbI₃ based devices was checked under different operating (e.g. light and dark) and environmental conditions and infer that oxygen induced degradation, is relatively dominant than moisture induced degradation and limits the working stability of MeNH₃PbI₃ containing devices under ambient conditions. Moreover, they pointed out that this fall in device performance can be reduced by the addition of electron acceptor layers within device architecture. Such layers are exposed to augment electron extraction from the absorber (perovskite material) before they react with oxygen, hence decreasing the amount of superoxide O₂⁻ and increasing the device stability.

It was noticed that by replacing MA with Cs and FA resulted in improved photostability of the PSCs. By systematically monitoring the development of PL intensity of perovskites, light-induced formation and annihilation of defects were reported to induce photo-instability [68]. Photostability can be improved through defect control by passivating which acted as a defect reservoir on the surface and grain boundaries. To stabilize surface defects, polyethylene oxide was applied and thus improved photostability was achieved. By substituting MA with FA, the degradation became slow with small pores forming on the surface after exposure to light. Moreover, Addition of Cs into the MAFA (forming CsMAFA) further lessen the degradation. XPS, XRD, Fourier transform infrared (FT-IR) spectrometry, and ultraviolet-visible absorption spectrometry were used to investigate the variation of MAPbI₃ films under illumination. The result showed that light induced degradation is the main cause of degradation. Using polymer such as PTAA (Poly(triarylamine)) as the HTM, it was observed that pure MAPbI₃ devices retained nearly 100% of their initial efficiency after 1000 h aging under constant illumination at room temperature. PTAA which act as a protection layer, inhibited the discharge of gaseous degradation products enhanced stability. However, for devices using Spiro as the HTM, their stability under illumination was lesser than that using PTAA [69, 70].

4.2.3 Heat

Heat is also another factor that influences stability due to the inherent matter with low formation energies, and perovskites thus have a great response to a small increase in external temperature [71]. Organic-inorganic perovskites tend to decompose due to the instability of organic A⁺ cations under thermal atmosphere. Commercial solar cells should be able to work efficiently above 85°C, to have any influence in the market.

MAPbI₃ is basically unstable upon thermal stress which produces a discharge of I₂ and the presence of metallic Pb at 40°C in the dark [63]. This is produced by the decomposition reactions (2) and (3):



Although reaction (3) is reversible at just 80–85°C, methylammonium iodide decomposes into more volatile compounds as represented by reactions (4) and (5):



It was found that HI(g) and CH₃NH₂(g) were dominant products during the decomposition of MAPbI₃ and only trace amounts of CH₃I and NH₃ were found. Though, the ratio of CH₃I and NH₃ increased at higher temperature and lesser than HI(g) and CH₃NH₂(g). In short, HI(g) and CH₃NH₂(g) were the dominant decomposition products at ambient temperature under vacuum while CH₃I and NH₃ gases were obtained at high temperature. Both processes occurred simultaneously near ambient temperature in vacuum and the later was favored at high temperature.

To find out the decomposition temperature of perovskites, Thermogravimetric analysis (TGA) was used. From the mass loss of TGA curve for MAPbI₃, the decomposition onset temperature was found to be 234°C [62]. This indicates that as the practical application temperature usually is less than 100°C, so this high decomposition temperature made the stability of MAPbI₃ not a big issue. The as prepared film did not show any changes in XRD patterns when stayed inside the vacuum for up to three days. This might be owing to the purer perovskite films without any exposure to the ambient atmosphere. Though, the commonly degradation of the perovskite solar cell was apparent even with encapsulation. This could be inadequate to estimate the long-term stability of a photovoltaic material, which is essential to work for a long time at temperatures lower than the decomposition temperature [72]. The fact that inert condition and encapsulation cannot completely avoid MAPbI₃ perovskite degradation. At low temperature, the degradation of MAPbBr₃ was found by only releasing HBr and CH₃NH₂ gases [69]. The encapsulation of devices is essential not only to prevent exposure to oxygen and moisture, but also to avoid leakage of volatile decomposition products. Photostability can also be increased by replacing MA cation with more stable Cs/FA combination.

Substituting organic cations with inorganic Cs⁺ or Rb⁺ cations is also valuable to stabilize perovskite solar cells [73, 74]. Grancini et al. [74] stated an ultra-stable 2D/3D (HOOC(CH₂)₄NH₃)₂PbI₄/CH₃NH₃PbI₃ perovskite, presenting a PCE of 12.9% with carbon electrodes and 14.6% with the normal mesoporous structure and stability of one-year.

By introducing n-butylammonium iodide (BAI) to MAPbI₃ perovskite, a mixed 2D (BA)₂PbI₄ structure is formed, which probably provide an improved protection for the 3D perovskite against heat stress [75]. Octylammonium (OA) cation has also been reported to enhance the thermal stability of perovskites and keep 80% of their initial efficiency for 760 h aged at 85°C in ambient atmosphere without encapsulation [76]. Other additives, such as π-conjugated polymer, nonvolatile ionic liquids, bifunctional hydroxylamine hydrochloride guanidinium isothiocyanate, have also been reported to improve the thermal stability of various perovskites [77–79].

5. Conclusion and perspective

The discovery and development of organic inorganic perovskite materials have become a hot research topic in the field of photovoltaics. This chapter deals with a comprehensive discussion on the properties and applications of organic inorganic perovskites materials in PSCs. The extraordinarily outstanding performances of organic inorganic perovskites result of their excellent properties. Solar cells based

on organic inorganic perovskite materials have achieved much advancement, both in PCE and stability, in a short very time. To PSCs, though great progress has been attained, there are still various obstacles in terms of stability and toxicity until its practical usage in the PV market. However, for large-scale performance, are required to be overcome. So far, great research has been made to overcome these issues by changing the composition of organic inorganic perovskite material either by replacing Pb with Sn or Ge or organic methyl with other organic or inorganic cations. However, commercialization of an organic inorganic perovskite solar cell needs further development in both efficiency and long-term stability, with low-cost photovoltaic materials and ease of printability. To increase stability, various methods such as the use of buffer layers, varying the composition of organic inorganic perovskite materials, and better techniques of encapsulation. In inference, the research which has been enduring for the past five years has attained significant results. Future research needs to endeavor for longer stability with high efficiency.

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