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Review

Progress in Organic-Inorganic Hybrid Perovskite Solar Cells: Architecture, Efficiency and Stability

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In recent years, it has been established that solar cells based on organic-inorganic hybrid perovskite materials have substantial potential for the development of highly efficient photovoltaic devices and offers robust opportunities for research to the scientific community and industry. Power conversion efficiency (PCE) of perovskite solar cells (PSCs) have already surpassed 24.8 % within a decade, which is now third highest efficiency among single-junction photovoltaic materials. This report briefly introduces hybrid-halide perovskite materials, their structural properties, various possible device architectures and a comparative study of photo-voltaic performance. For commercialization, high stability of devices is must and here we have thoroughly discussed possible degradation mechanisms of PSCs, that is, moisture; oxygen; heat; structural stability; UV-light effect; defect-states, ion-migration and various approaches to passivity based upon recent reports. A proper encapsulation with optimized chemical composition (enhanced interaction between organic/inorganic cation and BX_6 octahedron) PSCs could possess superior stability for long-run while maintaining optoelectronic properties.

Keywords: Perovskite solar cells; Stability; Architecture; Efficiency; Degradation

1 Introduction

Global energy consumption is rapidly increasing with the increasing human population and modernization of society which has resulted in faster depletion of non-renewable energy sources. Moreover hazardous environmental effect of conventional energy sources like ozone depletion, increasing global warming, rise in sea level *etc*. are major concern these days, therefore, researchers and scientists are continuously working on the techniques to use renewable energy sources in most possible ways in context of long term sustainable development. Solar energy is the most potential energy source with 36000 TW extractable energy per year, among all renewable energy sources. After the discovery of silicon wafer based solar cell in 1953 at Bell Laboratories, new way to harvest sunlight has been unlocked. Thereafter various types of solar cells have been technologically advanced to convert solar energy into electrical energy. Silicon wafer based solar cells which come under the category of first generation solar cells and which still dominates the solar market with high efficiency (19-25%) and stability[1] are quite expensive due to high temperature processing and cumbersome fabrication techniques. The second generation solar cells which are based on thin films of inorganic semiconductor materials such as amorphous silicon, copper indium gallium selenide (CIGS), cadmium telluride (CdTe), copper indium selenide (CIS) etc. are of low cost due to lower consumption of material but still involves high processing cost. To obtain the best performance from these devices, high vacuum thin film deposition and high-temperature annealing is required which further increases the cost. These problems with inorganic solar cells enforced scientists to move on to third generation solar cells which can be fabricated using low cost techniques. Third generation solar cells includes tandem structured solar cells like organic dye sensitized solar cells (DSSCs), quantum dot solar cells (QDSCs) and perovskite solar cells (PSC's). Best obtained efficiency for DSSCs and QDSCs are 14.14%[2] and 13.43%[3], respectively, which is quite low compared to silicon solar cells.

Among the third generation solar cells, PSC's have been intensively studied around the globe and achieved an efficiency of 24.8% in short time period[4]. The main benefit of PSCs is their capability

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to form high quality crystalline structure by low temperature solution processing. Some other advantages of these solar cells are their cost effective fabrication, higher versatility of material, high charge transfer and tunable band gap over the visible range. Apart from these major advantages these devices also have some serious problems like instability, short lifetime in ambient environment and poor performance in intense irradiation. In this article we review the progress in perovskite based solar cells. First of all, the basic structures and fundamental processes behind PSCs are briefly summarized. Then the main focus is in the progress made so far in the improvement of efficiency in PSCs since the time of its inception. We also review the various schemes/ strategies adopted for improvement in efficiency, stability and lifetime. Finally future prospects of the PSCs are provided.

2 Basic structure of perovskites

The very first perovskite mineral calcium titanate ($CaTiO_3$, an inorganic compound) was discovered by Gustav Rose in 1839 and named after Russian mineralogist Lev Perovski[5]. All materials with same crystal structure and composition ABX_3 (where A and B are monovalent and divalent cations, and X could be O, C, N or any halogen) are known as perovskites. Recently, hybrid organic-inorganic perovskite materials have been rigorously studied due to their suitable properties for advance solar cell applications. In hybrid structure of perovskites inorganic monovalent cation A is replaced by an organic compound such as methyl-ammonium (MA), formamidinium (FA) and X is generally a halide anion (Cl^-, Br^- or I^-). The basic structural arrangement of hybrid perovskites is presented in Fig. 1, where A is an organic cation (MA) occupies cubo-octahedral site shared with 12X anions (made up of with 8 triangular and 6 square faces), and B is also a cation (e.g. Pb or Sn) stabilized in an octahedral site shared with 6X anions[6].

Most commonly used hybrid perovskite materials for solar cell applications are methylammonium lead halides such as $CH_3NH_3PbI_3$ ($MAPbI_3$), $CH_3NH_3PbBr_3$ ($MAPbBr_3$)[7,8] etc. Some mixed halide perovskites (e. g. $CH_3NH_3PbI_{3-x}Br_x$) are also used by other researchers[9,10]. A defect free single crystalline or polycrystalline layer with perovskite crystals of large grain size and negligible hysteresis result in higher durability of devices. Using perovskite as active material in solar cell promises several excellent advantages to solar cells like higher absorption coefficient and excellent tunable optical properties; low exciton binding energy, long carrier diffusion lengths leading to efficient charge collection and multiple choices for organic and inorganic cation and multiple halides[11-14]. Such advantages have made the scientific community to work intensively on perovskite solar cells in the last decade. Among existing photovoltaic materials perovskite now stands at third position in term of PCE after non-concentrated single junction GaAs and Si solar cells according to National Research Cell Efficiencies [4].

3 Architectures of perovskite solar cells

To extract best efficiency various architectures of perovskite solar cells have been developed such as - perovskite solar cells with liquid electrolyte or DSSC or mesoporous structured solar cells; meso-super structured solar cells and planar architectures.

3.1 Mesoporous DSSC Configuration

Perovskite solar cell was first fabricated by replacing dye pigment in DSSCs with organic-

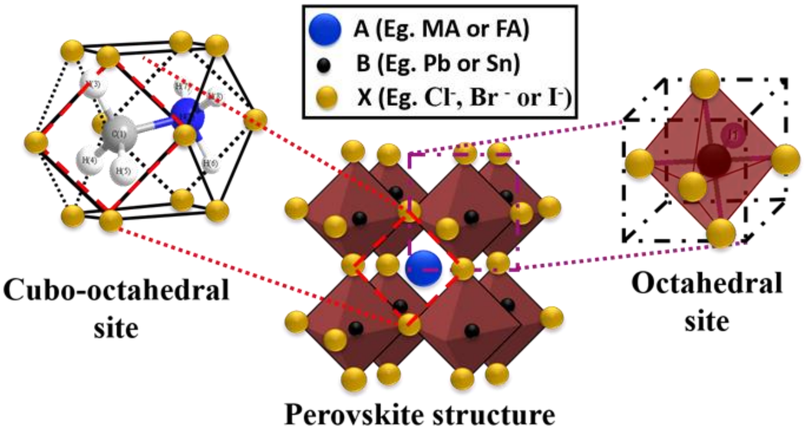

Fig. 1 — Cubo-octahedral site (left), perovskite crystal structure (center) and octahedral site (right).

inorganic hybrid perovskite compound by Kojima *et al.*[15]. It was used as an alternative to sensitizer in DSSC configuration and resulted into a nano-structured TiO_2 Perovskite-sensitized solar cell as shown in Fig. 2. $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ deposited on nano-crystalline-TiO_2 coated substrates were used as an active material to absorb the light and PCE of 3.81 and 3.13% was demonstrated using $MAPbI_3$ and $MAPbBr_3$, respectively[15]. In 2011, Im *et al*.[16] produced perovskite quantum-dots (QD) of size 2-3 nm and covered the nanocrystalline TiO_2 pores with a specific concentration of QD solution. In these devices, liquid redox electrolytes based on $LiBr/Br_2$/acetonitrile and LiI/I_2/methoxy-acetonitrile was used which resulted in low power conversion efficiency of 6.54% and very poor stability due to corrosive nature of perovskite towards the liquid. In order to enhance stability, Kim *et al*.[17] replaced liquid redox electrolyte with solid-state electrolyte and used spiro-MeOTAD as hole transport layer and achieved PCE of 9.74% with V_{oc} of 0.888 V. They also have successfully demonstrated charge carrier separation from light excited hybrid perovskite ($CH_3NH_3PbI_3$) using femto-second laser spectroscopy where holes injected to p-type organic spiro-MeOTAD and electrons towards n-type inorganic TiO_2.

To increase the absorption of perovskite on the TiO_2 structure, Burschka *et al*.[18] used sequential deposition method. Using this technique for the fabrication of solid-state mesoscopic solar cells, they reported a power conversion efficiency of approximately 15%.

Further, Heo *et al.*[19] have fabricated perovskite ($CH_3NH_3PbI_3$) solar cells using mp-TiO_2 and various polymeric hole transport materials (HTMs) namely P3HT, PCPDTBT, PCDTBT and PTAA. Maximum V_{oc} of 0.92 was observed in PCDTBT and highest PCE of 12% was produced using PTAA based HTM which facilitate higher surface coverage over top of $CH_3NH_3PbI_3$ layer due to stronger interaction of $CH_3NH_3PbI_3$ and PTAA compared to other thiophene-based HTMs[19]. Charge transport and recombination studies on mesoporous solar cells based on TiO_2 with PbI_2 and several perovskite compositions have been discussed in detail by Zhao *et al*.[20]. Best efficiency of 9.16% was achieved using $CH_3NH_3PbI_3$ followed by 6.75% with mixed halide composition $CH_3NH_3PbI_2Br$.

A large number of researchers were engaged in mesoporous perovskite solar cells using various materials and processing techniques[21-30]. Highly efficient and thermally stable PSC with mesoporous configuration was developed by Jeon *et al.* in 2018[31]. They synthesized a fluorene-terminated hole-transporting material with a modified energy level matching with perovskite and a high glass transition temperature and achieved steady-state efficiency of 22.85 and 21.7% for small-area of ~0.094 cm^2 and large-area of ~1 cm^2 cells, respectively. In the mesoporous configuration there are two structures: regular structure (n-i-p) and inverted structure (p-i-n) architectures. In n-i-p configuration the light moves from glass to transparent conducting oxide (TCO) to electron transporting layer (ETL), then absorbed by the perovskite layer and then moves to hole transporting layer (HTL) Fig. 2(b). In a p-i-n structure of a perovskite solar cell, the sequence is changed to Glass/TCO/HTL/Perovskite/ETL/Counter-electrode[32-33] Fig. 2(c). However, most of the work is carried out in the n-i-p mesoporous structure. The best efficiency recently reported till now is 24.8% in the mesoporous perovskite solar cells is by Jeong *et al.*[34] using Spiro-mF and Spiro-oF as HTMs in PSCs fabricated with the conventional n–i–p configuration.

3.2 Meso-super structured solar cells (MSSC) configuration

Further, a modified mesoporous device called as the meso-super structured solar cells (MSSC) was

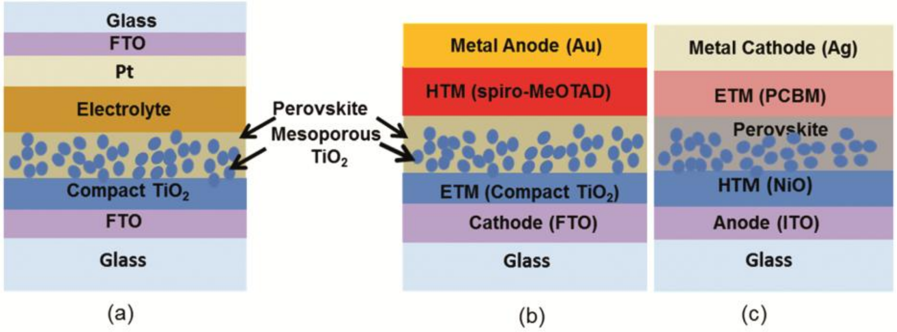

Fig. 2 — Mesoporous DSSC Configurations with liquid electrolyte (a), regular mesoporous structure with hole transport layer (n-i-p) (b), and inverted mesoporous structure (p-i-n) (c).

developed in order to reduce the processing temperatures to less than 150 °C[35-39]. Meso-super structure comprises of thin porous Al_2O_3 layer to form a scaffold on which a perovskite absorber is deposited. Lee *et al.*[35] used a very thin layer (2-10 nm) of mixed-halide perovskite ($CH_3NH_3PbI_2Cl$) adsorbed on mp-TiO_2 and mp-Al_2O_3 and witnessed PCE up to 8% and 10.9%, respectively. Lee *et al.*[35] observed that due to unfavorable band mismatching electrons could not jump in the conduction band of mp-Al_2O_3 and concluded that mp-Al_2O_3 just delivers a scaffold structure for better coverage. Their key observation was confinement of photo-excited electrons within the perovskite phase which led to faster electron transfer along with improved open circuit voltage. This was the first time when ambipolar characteristic of perovskite material was observed and it was demonstrated that perovskite ($CH_3NH_3PbI_2Cl$) layer played dual role of light absorber and electron conductor. Later on ambipolar nature of perovskites ($CH_3NH_3PbI_3$) was confirmed by the experiments of Etger *et al.*[36]. They successfully fabricated hole conductor free perovskite ($CH_3NH_3PbI_3$)/TiO_2 hetero junction solar cell, where perovskite ($CH_3NH_3PbI_3$) behave as light absorber and hole conductor (p-type semiconductor properties) as well. The device with highest PCE of 5.5% at 1000 W/m^2 light intensity and a 7.3% at lower intensities at 100 W/m^2 has given a belief that perovskite can act both as n-type and p-type conductor. N-type and p-type behavior of perovskites depends upon the type of junction it has formed with the adjacent semiconductor junction. In 2013, Ball and coworkers[37] reported of perovskite solar cell with a compact TiO_2 layer (non-mesoporous, hole blocking layer), thin alumina layer (mp-Al_2O_3 scaffold) at low processing temperature of 150 °C, and the perovskite which can act as conventional thin-film absorber layer, charge carrier separation and transportation as well, the device showed higher PCE of 12.3%. Later on in 2014, Wang *et al.*[38] utilized graphene nanocomposites and TiO_2 nanoparticles as the electron absorption layers and demonstrated that the graphene nanoflakes provide higher charge-collection in the nanocomposites and therefore have potential towards fabrication of low-cost solar cell at temperatures about 150 °C with efficiencies up to 15.6%. Further, Wojciechowski *et al.*[39] proposed a new technique for the deposition of compact TiO_2 layer at low temperatures for MSSCs and reported efficiency of 15.9%. Highly crystalline nanoparticles of anatase TiO_2 of diameter <5 nm disseminated in an alcoholic solvent with titanium di-isopropoxide bis(acetylacetonate) (TiAcAc) was used to deposit compact and 100 fold higher conducting TiO_2 layer as compared to the TiO_2 produced from the high temperature route. Subsequently, the tuning of energy band gap was also employed using mixed halide perovskites.

Noh and group used mixed halide perovskite (CH_3NH_3Pb ($I_{1-x}Br_x)_3$), where x varied from (0-1) in order to understand physical properties like non-linear optical properties, magnetic properties, conductivity, *etc.*[23]. These studies resulted in tuning energy band gap of perovskite within 1.5 eV ($CH_3NH_3PbI_3$) -2.2 eV ($CH_3NH_3PbBr_3$). Gradual substitution of small atomic radii bromine (1.96 Å) with larger atomic radii iodine (2.2 Å) resulted in structural transition from tetragonal to cubic via pseudo-cubic of perovskite because of decreasing lattice spacing. Highest PCE with this composition as 12.3% could be achieved by utilizing polymeric HTM (PTAA)[23].

3.3. Planar PSC configurations

3.3.1 Planar n-i-p configuration

Previously investigated MSSC with an inert mp-Al_2O_3 oxide had significant energy losses at the electron acceptor and absorber layer interface. Moreover, the mesoporous DSSC configuration was recognized based on the assumption of short diffusion length of the charge carriers in perovskites. Later researchers realized the feasibility of planar structure of PSCs when they found diffusion length of perovskite is higher than 100 nm[22-27]. Further, on eliminating the mesoporous TiO_2 layer the processing of PSCs can be accomplished at low temperatures <150 °C. Thus planar structure of PSCs, comprising of only the perovskite absorber layer between the electron transport layer and hole transport layer Fig. 3 attracted attention to the researchers engaged in thin film photovoltaic devices. The conventional perovskite planar structure (n-i-p) Fig. 3(a) has electron transport layer (ETL) below the active layer,

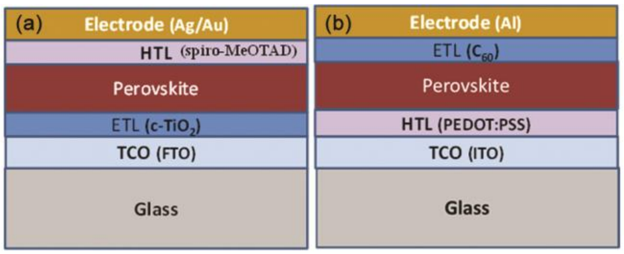

Fig. 3 — Planar (a) and inverted planar (b) PSC configurations.

normally based on metal-oxides like TiO_2 and SnO_2, and an organic hole transporting layer (HTL), typically Spiro-OMeTAD on top side of the active layer. Snaith and his group (Lee *et al.*)[35] had developed the first planar heterojunction PSCs with compact TiO_2 as ETL, and the PCE of 1.8% was attained in 2012. Later, Liu *et al.* (Snaith's group) developed efficient planar heterojunction PSC by vapor deposition and succeeded with a PCE of over 15 per cent and demonstrated that the perovskite absorbers can work at the higher efficiency in basic device architectures, without requiring nanostructures and mesostructures[40]. Liu *et al.*[41] recognized that the low performance of planar structure was largely due to the poor coverage of perovskite crystal, and optimized solution-based film formation; power conversion efficiencies of up to 11.4%_was achieved with only compact TiO_2 used as ETL. Further, developing a more compact TiO_2/ZnO bilayer as electron transport layer, Xu *et al.*[42] could achieve a high efficiency upto 17% in planar perovskite solar cells. The compact TiO_2/ZnO bilayer assisted in the suppression of recombination at the front surface and also the elimination of the shunt between the FTO electrode and perovskite absorber. Huang *et al.*[43] reported a planar device with UV-ozone treated FTO substrates and without any ETL. They achieved a power conversion efficiency of over 10% in this ETL free planar solar cell.

Chen *et al.*[44] synthesized Al-doped SnO_2 at low temperatures (190 ^{o}C) by solution processing and them as ETL in n-i-p structure. They attained enhanced current density, FF and power conversion efficiency of 12.10% in planar solar cells.

In 2019, Akin[45] developed a planar PSC with a ruthenium (Ru) doped tin oxide (SnO_2) and Zn-TFSI2 doped spiro-OMeTAD as ETL and HTL, respectively. He achieved hysteresis-free planar PSCs with high efficiencies up to 22%. Thereafter, with further reforms in processing techniques highly efficient and stable planar perovskite solar cells have been realized[46]. Recently, Zhao *et al.*[47] reported rigid and flexible substrate PSCs with 0.2wt% Au−TiO_2/TiO_2 dual ETLs with PCE of 20.31% higher than that of the devices with TiO_2 as a sole ETL. They developed significant stability of PSCs with this plasmonic dual ETL in light soaking, and recognised it to improve light absorption, low charge recombination loss, and increased carrier transport, and extraction.

3.3.2 Planar (p-i-n) configuration

The inverted PSCs (*i.e.*, p-i-n device) Fig. 3(b) have their HTL at the bottom and ETL on the top of the perovskite active layer. Jeng *et al.*[48] demonstrated the first inverted structure planar heterojunction PSCs and attained a PCE of 3.9%. The inverted p-i-n structure has some advantages when compared to the regular planar (n-i-p) structure, like negligible device hysteresis and it does not need a high-temperature sintering. Therefore, many researchers are working to develop the performance of inverted PSCs[49-57]. Zheng *et al.*[57] achieved a high efficiency of 22.3% by ligand anchoring to handle grains and interfaces in inverted PSCs in 2020. Wang *et al.*[58] reported stable inverted planar solar cells towards humidity with efficiency > 21%.

4 Efficiency improvement trends

Researchers were not just limited to understand intrinsic properties of perovskite, but have also explored numerous possibilities of improving physical properties like non-linear optical properties, magnetic properties, conductivity, *etc.* as well as improving the cell configurations and processing techniques for the enhancement in efficiency in PSCs. Various processing techniques in each cell configurations have been employed by various researchers for efficiency enhancement. PSC fabrication techniques and efficiency improvement trends have been summarized in this section. Table 1 shows the efficiency improvement trends with corresponding device architecture, growth technique of perovskite crystals and the photovoltaic parameters.

Figure 4 shows the bar graph of efficiency improvement trend of PSCs. It can be seen that within 5 years after the demonstration of first device the efficiency of PSCs improved from 3.81 to 15.4% making it the fastest improvement in efficiency among all type of solar cells. After 2015 the efficiency of PSCs gradually increased and now reached to 24.82%[34]. Therefore within a span of one decade a huge improvement in the efficiency of PSCs. With this gradual increase within next 10 years the efficiency of PSCs may reach to 33% or more. Therefore, PSCs have great potential for future solar panels.

Perovskite solar cells have attained higher PCE and gathered widespread scientific and industrial interest due to their low cost and excellent photovoltaic performance; however, their long-term stability in

Table 1 — Efficiency improvement trend for perovskite solar cell from 2009 to up to date

Device Architecture	Device Parameters				PCE (%)	Ref.	Year
	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	Active Area (cm^2)			
FTO / mp-TiO$_2$ (8-12um) / MAPbI$_3$ / 0.15 M LiI and 0.075 M I2 dissolved in methoxy acetonitrile / Pt-coated FTO glass	11.0	0.61	0.57	0.24	3.81	[15]	2009
FTO / mp-TiO$_2$ with Pb(NO$_3$)$_2$ / MAPbI$_3$ / iodide/iodine-based redox electrolyte / Pt-coated FTO glass	15.82	0.706	0.58	0.3	6.54	[16]	2011
FTO / mp-TiO$_2$ / MAPbI$_3$ / Spiro-MeOTAD / Au	17.6	0.888	0.62		9.7	[17]	2012
FTO / mp-Al$_2$O$_3$ / CH$_3$NH$_3$PbI$_2$Cl / Spiro-OMeTAD / Ag	17.8	0.98	0.63	0.09	10.9	[35]	2012
FTO / compact-TiO$_2$ / mp-Al$_2$O$_3$ (~20nm) / CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ / Spiro-OMeTAD / Ag	18.0	1.02	0.67	0.09	12.3	[37]	2013
FTO glass / mp-TiO$_2$ / MAPbI$_3$ / Spiro-OMeTAD / Au	20.0	0.993	0.73	0.285	14.14	[18]	2013
FTO glass / mp-TiO$_2$ / CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ / Spiro-MeOTAD / Ag	21.5	1.07	0.67	0.076	15.4	[40]	2013
FTO glass / Graphene nanocomposite / TiO$_2$ / mp-Al$_2$O$_3$ / CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ + capping layer / Spiro-OMeTAD / Au	21.9	1.04	0.73	0.0625	15.6	[38]	2014
ITO / ZnO / CH$_3$NH$_3$PbI$_3$ / Spiro-OMeTAD / Ag	20.4	1.03	0.749	0.07065	15.7	[41]	2013
FTO glass / anatase TiO$_2$ (with 20 mol% TiAcAc) / mp-Al$_2$O$_3$ / CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ / Spiro-OMeTAD / Ag	21.5	1.02	0.71	0.0625	15.9	[39]	2014
FTO glass/ bl-TiO$_2$ / mp-TiO$_2$ / HC(NH$_2$)$_2$ PbI$_3$ / CH$_3$NH$_3$PbI$_3$ (thin film) / Spiro-MeOTAD / Au	20.97	1.032	0.74	0.136	16.2	[21]	2014
FTO glass / bl-TiO$_2$ / mp-TiO$_2$ / bilayer-CH$_3$NH$_3$Pb (I$_{1-x}$Br$_x$)$_3$ (x=0.1-0.15) / PTAA / Au	19.64	1.11	0.742	0.0938	16.15	[22]	2014
FTO glass / bl-TiO$_2$ / mp-TiO$_2$ / MAPbI$_3$ / o-spiro-OMeTAD / Au	21.2	1.02	0.776	0.16	16.7	[24]	2014
FTO glass substrate / compact TiO$_2$ / mp-TiO$_2$ / MAPbI$_3$ / MAPbI$_3$ cuboid / Spiro-MeOTAD / Au	21.64	1.056	0.741	0.159	17.01	[25]	2014
ITO (PEIE) / Y:TiO$_2$ / Perovskite (CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$) / Spiro-OMeTAD / Au	22.75	1.13	0.750	0.1	19.3	[49]	2014
FTO glass substrate / blocking-layer TiO$_2$ / mp-TiO$_2$ / (FAPbI$_3$)$_{1-x}$ (MAPbBr$_3$)$_x$ / PTAA / Au	23.54	1.059	0.77	0.096	20.11	[26]	2015
FTO glass substrate / compact TiO$_2$ / mp-TiO$_2$ / MABr/PbBr$_2$ (5.67M) + PbI$_2$ /FAI (1.05M)] (500nm) / Spiro-OMeTAD / Au	24.6	1.16	0.73	0.16	20.8	[27]	2016
FTO glass / compact-TiO$_2$ / Li-doped mp-TiO$_2$ / Cs$_x$(MA$_{0.17}$FA$_{0.83}$)$_{(100-x)}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ / Spiro-OMeTAD / Au (70-80nm)	23.5	1.147	0.785	0.16	21.17	[28]	2016
FTO glass / bl-TiO$_2$ / La-doped BaSnO$_3$ (LBSO) / MAPbI$_3$ / PTAA / Au	23.4	1.12	0.813	0.096	21.2	[29]	2017
FTO glass / bl-TiO$_2$ (60nm) / mp-TiO$_2$ / Perovskite / PTAA (50nm) / Au (100nm)	25.0	1.1	0.803	0.0946	22.1	[30]	2017

(*Contd.*)

Table 1 — Efficiency improvement trend for perovskite solar cell from 2009 to up to date (*Contd.*)

Device Architecture	Device Parameters				PCE (%)	Ref.	Year
	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	Active Area (cm^2)			
FTO glass / c-TiO_2-mp-TiO_2/ $(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$/ DM with Li-TFSI/Au	24.9	1.14	0.81	0.094	23.2	[31]	2018
ITO/P3CT-N/$MAPbI_{3-x}Cl_x$/$PC_{61}BM$/BCP/Ag [38]	22.10	1.11	0.81		20.36	[50]	2019
ITO/poly(triarylamine) (PTAA)/$MAPbI_3$/C60/BCP/Cu	23.46	1.07	0.84		21.09	[55]	2019
ITO/PTAA/Cs0.05(FA0.92MA0.08)0.95Pb (I0.92Br0.08)3/C_{60}/BCP/Cu [40]	24.1	1.17	0.81	0.1	23	[57]	2020
FTO/C-TiO_2-mp-TiO_2/$FAPbI_3$/Spiro-mF/Au	26.35	1.16	0.80	0.1	24.82	[34]	2020

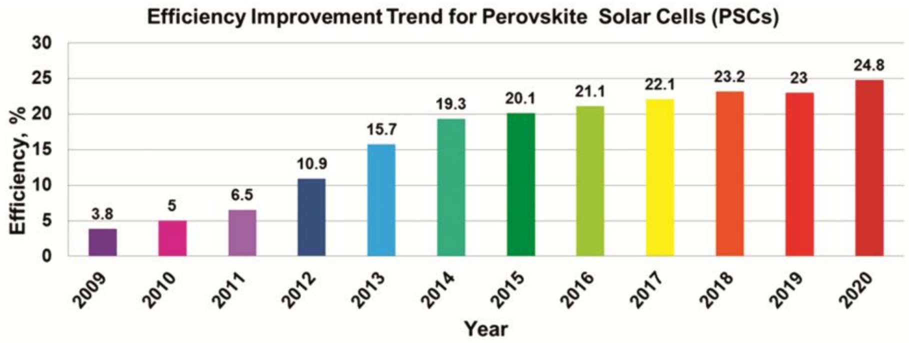

Fig. 4 — Efficiency improvement trend for perovskite solar cells.

ambient conditions is a big concern for the scientific community which is also inhibiting their commercialization. Degradation of PSCs due to moisture has been studied by many researchers and various approaches have been active to improve the stability due to moisture[23,58-66]. Formation of a hydrate product similar to $(CH_3NH_3)_4PbI_6{\cdot}2H_2O$ on exposure of $CH_3NH_3PbI_3$ to moisture has been reported by Christians *et al.*[60] which is responsible in the reduction of absorption in the visible region spectrum as well as distortion of the material's crystal structure. Halide substitution has been employed by a number of researchers[23,61-63] to improve the stability due to moisture. Jiang *et al.*[61] replaced two I^- ions with SCN^- to improve moisture stability of $CH_3NH_3PbI_3$ perovskite. Ke *et al.*[63] observed that by adding a slight amount of $Pb(SCN)_2$ in the perovskite precursor considerably increased the grain size and of perovskite crystalline quality. They also found significant reduction in the hysteresis and increased FF of PSCs[63]. Introduction of hydrophobic layer such as polytetrafluoroethylene (PTFE), fluoroalkyl silane (C_{13}-FAS), etc. and other multi-dimensional approach have been used to enhance the stability due to moisture[64-69].

Aristidou *et al.*[70] demonstrated the part of oxygen in the degradation of PSCs. They observed the formation of superoxides (O_2^-) by withdrawing excited electrons from the conduction band of perovskite when it is irradiated to light. These superoxides start degrading perovskite by deprotonating methylammonium cation which further leads to the formation of PbI_2 and I_2 as confirmed via NMR, XRD, Raman spectroscopy and UV-VIS spectroscopy. The authors also proposed that utilization of non-inert mp-oxide where electrons can easily jump from perovskite conduction band to metal-oxide degrade much slower rate, and alternate less acidic organic cation which has higher resistance to deprotonate can survive for longer[70]. Further, it has been found that the temperature increase from 25 to 250 °C, the MA-perovskite decomposed into PbI_2 which reduces the efficiency of the solar cells[71]. The migration of iodine and lead at elevated temperature with ageing is a serious concern while long-run. Thermal instability in perovskite solar cells has been studied by a number of researchers and various techniques have been employed to improve the thermal stability of PSCs[72-75]. Afroz *et al.*[74] engaged oxalic acid (OA) with two bifacial carboxylic acid groups as an additive into the perovskite precursor solution which enabled in larger grain size, lesser grain boundaries and trap states and showed a better thermal stability and power conversion efficiency as compared to control device. To improve thermal stability, Jodlowski *et al.*[75] introduced an alternative cation guanidinium ($CH_6N_3^+$, ionic radii ~278pm) combined with methylammonium $MA_{0.75}Gua_{0.25}PbI_3$ based stable 3D tetragonal perovskite structure composition which enabled a high thermal stability with no significant decay in PCE. Saliba *et al.*[28] found that with addition of inorganic cation Cs was found to have larger impact on device thermal stability. Photo-stability remains a key challenge especially for 3rd generation device since long time[76-80]. The formation of meta-stable deep defect state is largely responsible for photocurrent degradation and role of superoxide formation especially with TiO_x ETL in device performance reduction can't be neglected. Conventionally, used ARC is good approach in device protection against UV-light. It was observed that UV-light mainly create large defects at the interface, so improved surface roughness reduced the defects in significant number; while use of quantum dots and other down-conversion approaches have been employed[81-85].

For the stable performance of perovskite-based solar cells (PSCs) under ambient conditions, the most crucial factor is the structural stability of perovskite phase. Doping of the alkali metals raised the concern about full crystallization within perovskite crystal lattice. This is because the higher concentration can lead to incomplete conversion and produce higher impurity grains. This probably reduces the structural stability of non-perovskite phase, which is inefficient for the photovoltaic operation and change of phase, while operating temperature slowly reduces the performance of the device. One way to predict about the structure possessed with given materials is Goldschmidt tolerance factor (t) mathematically[70].

$$t = \frac{\mathrm{r(a)} + r(\mathrm{x})}{\sqrt{2}(\mathrm{r(b)} + r(\mathrm{x}))} \quad \ldots (2)$$

Where r(a), r(b) and r(x) are the ionic radii of cation A, cation B and anion X, respectively. Tolerance factor in the range of 0.9-1.1 forms cubic structure which is highly suitable for photovoltaics applications. Tolerance factor > 1.1 and < 0.9 results in distorted perovskite structure which is highly undesired for photovoltaic operation[70]. Hence to promote the commercialization of PSCs, and to extend the operational stability of the devices both the materials processing and fabrication technology need attention.

5 Conclusion

High-performance perovskite solar cell (PSCs) has proven itself a potential candidate for the photovoltaic applications. PSCs have reached up to 24.8% power conversion efficiency and acquired 3rd highest efficiency for the single-junction solar cell as per NREL, USA. However, their ambient stability remains a key challenge for their large-scale commercialization. Although, there are very good reports around the globe which proves higher potential of this PV technology, here in, we have discussed various perovskite solar cell architectures, efficiency improvement trends since 2009 to 2021 and key degradation mechanisms and stability issues and how to overcome them based upon recent reports. The best way we observed against environmental protection (moisture and oxygen) so far is proper encapsulation of the device; along with utilization of appropriate halides; multi-dimensional approach; hydrophobic passivation layer *etc.*, yet encapsulated material cannot be protected from the heat produced at photovoltaic operating temperature.

From this study we concluded is that by combining the efforts against degradation mechanism together with use of appropriate active layer chemical composition and proper encapsulated device may result a high performance device. Many researchers are still not highly convinced that perovskite-based modules will be able to replace conventional Si-based modules. They are quite true at this stage because if we compare it with long-term stability of Si solar cell which is very high, typically 20~25 years. There are more than 700 laboratories and many industries working in the development of perovskite based single-junction / multi-junction devices and other applications of perovskite materials. Global industries are coming up the prototypes like – Poland's Saule Technologies[76] utilizing inkjet printing technique for fabrication of flexible A4 size solar cells and announced to be commercialized this year for green building application; Solliance[76] used roll-to-roll process and proved 13.4% PCE with 4 cm^2; Chinese Microquanta Semiconductors[78] hold the world record with 15.24% PCE for an active area of above 15 cm^2 and many more. So far, China is dominating the market for conventional silicon solar cells and at the moment it is equal opportunity for everyone to gain the market for upcoming perovskite solar cells. The most recent development in PSCs is the silicon perovskite tandem solar cell architecture[86-90]. By means of using tandem structure more than 29% efficiency has been achieved[88-90]. Thus, to summarize, hybrid perovskites have great potential for harvesting solar energy with high efficiency at low cost.

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