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A COMPREHENSIVE REVIEW OF PHOTOVOLTAIC DEVICES BASED ON PEROVSKITES

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ABSTRACT

Perovskite solar cells (PSCs) though in its development stage, has been of interest to Scientists receiving considerable attention in recent years as a promising material capable of developing high performance photovoltaic devices at low cost. Owing to their solution processability, broad spectrum solar absorption, low non-radiative recombination losses, etc., PSCs provide numerous advantages over most thin film absorber materials. Due to the substantial improvement of Power Conversion Efficiency (PCE) of these materials, photovoltaic efficiency has reached prestigious position (approx. 20.1 %) within the last 5 years. In this review article, we discuss the current state of the Art for photovoltaic devices based on Perovskites, highlighting the underlying phenomenon, synthesis, challenges, comparison to other technologies and future outlook. We emphasized the importance of Perovskite film formation and qualities in achieving highly efficient photovoltaic devices. The flexibility and simplicity of Perovskite fabrication methods allows the use of mesoporous and planar device architectures. A variety of processing techniques are currently employed to form the highest quality $\text{CH}_3\text{NH}_3\text{PbX}_3$ films resulting to high performance PSC devices which include stoichiometry, thermal annealing, solvent engineering, additives and environmental control. In this review, we outlined and discussed the challenges of PSCs including its stability issues, hysteresis effects, and ion migration effects. Possible ways overcoming these challenges and improvement on the stability of PSCs so far were also addressed.

Keywords: cell, device, efficiency, film, materials, Perovskites, phase, photovoltaic, solution, structure.

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INTRODUCTION

World Energy resources 2016 reported that 1.3 billion people globally and 93 million in Nigeria have no access to electricity (world energy resources, 2016). Yet, every hour the sun beams more energy onto the Earth than it requires to satisfy the global energy needs for an entire year (National Geographic Report, 2017). Thereby offering a solution to the increasing concern of energy shortage, global warming, and greenhouse gases by fossil fuels (oil, natural gas and coal). Solar energy is the most abundant and cleanest form of energy for our energy-starved planet (Mohammed *et al.*, 2015). It remains a foremost energy resource with unlimited capacity to solve man's numerous energy needs (Abodunrin *et al.*, 2015). Surprisingly, most major solar installation has been in regions with relatively less solar resources (Europe and China) while potential in high resources regions (Africa and Middle East) remain untapped (World Energy resources, 2016). However, in regions other than Africa (like south-western United States, Central and South America, Middle East, the desert plains of India, Pakistan, Australia, etc.), such potential is only limited to generate 125 Gigawatt hours (GWh) from a 1 km² land area (Adaramola, 2014). A deliberate transition from conventional sources of electricity energy to renewable and environmentally friendly sources is critical for national development, though recent developments show the Nigerian government backsliding in adopting renewable energy technologies (Akuru, *et al.*, 2017).

The Energy Information Administration (EIA) of the United States government has quoted that, about 10% of the world's marketed energy consumption is from renewable energy. This 10% comprises of solar, geothermal, hydropower, wind, nuclear, biomass, and biofuel with the remaining 90% from fossil fuels (Chang *et al.*, 2010). With the world energy consumption expected to increase by 71% from 2003 to 2030, it becomes a fact that for the next two to four decades, fossil fuels are likely to remain the primary sources of energy in the world. Currently, the world's fossil fuels are being consumed more rapidly than they are being created, thus, there is a pressing need for alternative energy sources that are both renewable and environmentally benign (Mao *et al.*, 2007, Chang *et al.*, 2010; Elano *et al.*, 2009). Projected increase in global energy demand, predicted to be as high as 1Gw/day, will place significant strains on current energy infrastructure (Espinosa *et al.*, 2012). This looming challenge, coupled with depleting traditional fossil fuel-based energy sources with the threat of climate change, require the development of renewable energy technologies (Wang *et al.*, 2016). Among the renewable energy approaches, photovoltaic (PV) presents a promising route. The current photovoltaics landscape is dominated by silicon solar cells, though these cells are constrained by fundamental cost barriers, such as high temperature processing. However, Green *et al.*, 2012 reported that silicon solar cells have advanced tremendously both in terms of cost of production and efficiency over the past four decades. An alternative to these cells is the third-generation photovoltaic devices (a technology that promises a combination of lower cost and ease of synthesis with a better energy payback matrix) developed from various dye sensitizers, organic and hybrid (organic and inorganic) materials (Seelam and Lingamaller, 2016). Ever since the discovery of the photovoltaic effect by the French Physicist Edmond Becquerel in 1839, a myriad of emerging solar technologies has been developed, with three of the most highly researched being organic photovoltaics (OPVs), dye-sensitized solar cells (DSSCs), and recently, Perovskite solar cells (Ugwoke, 2014). Among these materials, organometallic halide Perovskites offer captivating prospects owing to their solution processability, broad solar absorption spectrum, low non-radiative recombination losses, etc. Due to the substantial improvement of Power Conversion Efficiency (PCE) of these materials, photovoltaic efficiency has reached prestigious position (approx. 20.1 %) within 5 years.

Though in its development stage, Perovskite solar cells (PSC) has been of much interest to

Scientists. The “Science” magazine touted it as one of the top scientific breakthroughs of 2013 (Dawn, 2016). However, there are issues which need to be resolved in the commercialization of Perovskites and limits in application. (Seelam and Lingamellm, 2016). Hence, this comprehensive review presents the current state of the Art of photovoltaic devices based on Perovskites, highlighting the underlying phenomenon, synthesis, challenges, comparison to other technologies and future outlook.

PHENOMENA

Though a detailed overview of the historical evolution of PSC performance, occurring over a short time period, can be found in several review articles (Snaith 2013; Leijtens *et al.*, 2015; Yu and Sun, 2015, and Rong *et al.*, 2015), Perovskites have been known over a century ago (Green *et al.*, 2014), they received attention only when Miyasaka *et al.* used methylammonium lead halide (Perovskite) as a light harvesting material in excitonic solar cells (Kojima *et al.*, 2009). This group utilized Perovskite as sensitizers in dye sensitized solar cells (DSSC) and achieved the solar-to-power conversion efficiency of 3.2% for $(\text{CH}_3\text{NH}_3)\text{PbBr}_3$ and 3.8% $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ (Kojima *et al.*, 2009). However, instability of these devices due to the degradation of Perovskites in liquid electrolyte containing lithium halide prompted Park *et al.* in 2011 to develop the quantum-dot sensitized solar cells using Perovskite $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ sensitizers (Im *et al.*, 2011). But these devices reduced the performance of solar cell in a short span of time due to the dissolution of halides in liquid electrolyte (Im *et al.*, 2011). In order to avoid corrosive liquid electrolyte in Perovskite DSSC, Kim *et al.*, developed the solid-state electrolyte, spiro-OMeTAD (2,2',7,7'-tetrakis (N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene), which can act as a hole transporting material (HTM) (Kim *et al.*, 2012).

The architecture of Perovskite solar cells was derived from the dye sensitized solar cell (DSSC) technology (Wang *et al.*, 2016). The traditional architecture of DSSCs consisted of a porous TiO_2 scaffold, sensitized by a dye and infiltrated by a liquid electrolyte. As regards the dye, Kojima *et al.* (2009) investigated $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ as an alternative to replace it. This however yielded moderate success (Kojima *et al.*, 2009; Kojima *et al.*, 2006). Based on the inherent instability of these devices, Lee *et al.* in 2012 attempted to replace the TiO_2 scaffold, used to transport electrons, with an insulator (Al_2O_3) (Lee *et al.*, 2012). This demonstrated for the very first time that Perovskite material could effectively transport electrons without the underlying TiO_2 layer. With this insight, the demonstration of a planar geometry solar cell with a Perovskite thin film as the absorber layer evolved (Liu *et al.*, 2013). A high efficiency with this device structure was however achieved.

WHAT ARE PEROVSKITES?

Perovskite is a type of mineral that is chemically found on the earth crust. It was first discovered in the Ural Mountains and was named after a Russian noble man and mineralogist, Lev Perovski (founder of the Russian Geographical Society) (Dawn, 2016). The Perovskite solar cells have the same structure of the Perovskite mineral, hence named Perovskite solar cells. A Perovskite structure is anything that has the generic form ABX_3 and the crystallographic structure as Perovskite (the mineral).

Depending on the atoms or molecules used in the structure, Perovskites may obtain a set of interesting properties like superconductivity, spintronics and catalytic properties. Hence, scientists and researchers find Perovskites as exciting playground for physicists, chemists and material scientists.

CRYSTAL STRUCTURE

Perovskite are a family of materials with the crystal structure of calcium titanate, that is, ABX_3 (Muhammad *et al.*, 2015). There are numerous materials which adopt this structure with exciting applications based on their thermoelectric, insulating, semi conducting, piezoelectric, conducting, antiferromagnetic and superconducting properties (Service, 2014). ABX_3 describes the crystal structure of Perovskite class of materials, where A and B are cations and X is an anion of different dimensions with A being larger than X. Crystal structure of Perovskites is illustrated in figure 2.1 below:

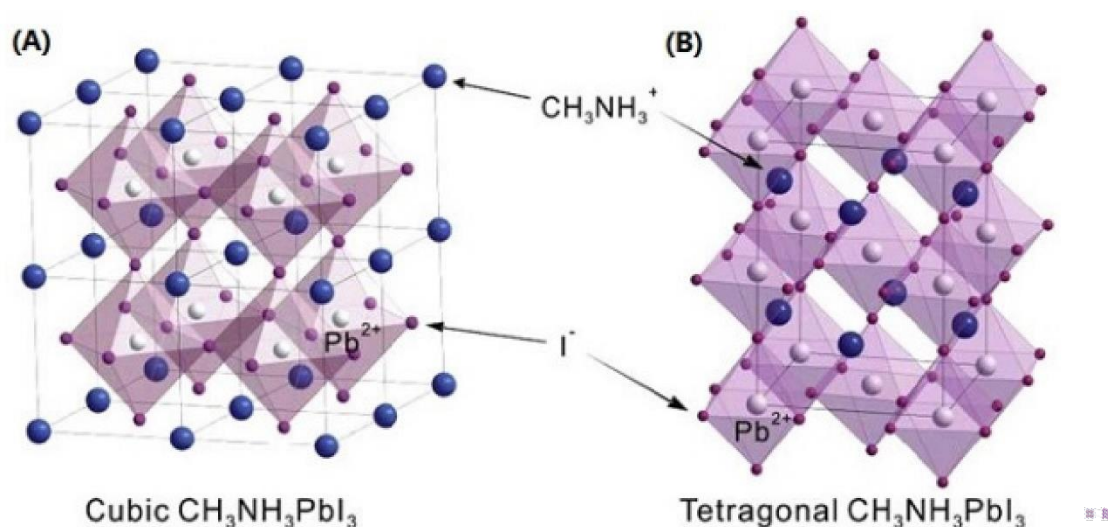


Figure 1: Crystal structure of Perovskite

Source: Shiqiang and Walid (2016).

The crystal structure of Perovskite can be alternatively viewed as corner-linked BX_6 octahedral with interstitial A cation. Its crystallographic stability and apparent structure can be deduced by considering a Goldschmidt tolerance factor t and an octahedral factor μ . The tolerance factor t is defined as the ratio of the distance $A-X$ to the distance $B-X$ in an idealized solid sphere model as shown in equation (1) below:

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

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

The octahedral factor μ is defined as the ratio R_B/R_X . For halide Perovskites ($X = F, Cl, Br$ and I), $0.81 < t < 1.11$ and $0.44 < \mu < 0.90$ are the typical values. Narrower range of t values from 0.89 to 1.0 dictates cubic structure, while lower values of t stabilizes as a less symmetric tetragonal and orthorhombic structure.

In case of ABX_3 , the larger cation A is considered as an organic cation typically methylammonium ($CH_3NH_3^+$) with $R_A = 0.18\text{nm}$ (Li *et al.*, 2008), though ethylammonium ($CH_3CH_2NH_3^+$, $R_A = 0.23\text{nm}$) and formamidinium ($NH_2CH=NH_2^+$, $R_A = 0.19-0.22\text{nm}$) also provide excellent results. Anion X is an halogen such as iodine with $R_X = 0.220\text{nm}$, Bromine (Br) and chlorine (Cl) used in Perovskites with $R_X = 0.196\text{nm}$ and 0.181nm respectively though in a mixed halide configuration. For cation B, Lead (Pb) with $R_B = 0.119\text{nm}$ and Tin (Sn) with $R_B = 0.110\text{nm}$ have been used for high efficiency in PSCs because of lower theoretical ideal band gaps (Pang

et al., 2014). Although Sn has similar band gap with Pb and in the same group, due to the ease of oxidation and lack of stability, it performs poorly compared to Pb in efficiency.

TYPES OF PEROVSKITE SENSITIZED SOLAR CELLS

PEROVSKITE SENSITIZED SOLAR CELLS

DSSCs are the forerunners of Perovskite solar cells. In search of a more efficient light sensitizers for DSSCs, Miyasaka *et al.* reported the first Perovskite sensitized solar cells between 2006 and 2008. $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ absorbers were employed with an iodide triiodide redox couple or a polypyrrole carbon black composite solid-state hole conductor. Full sun Power Conversion Efficiency (PCE) varying between 0.4 and 2% was measured for solid-state and liquid electrolyte cells, respectively (Kojima *et al.*, 2006).

Owing to the instability and degradation within minutes of these cells, due to the liquid electrolyte, the idea of adopting a solid-state hole transport medium was born. Kojima *et al.* in 2006 attempted this but success was only made when Murakami, Miyasaka and Park in collaboration with Gratzel *et al.* developed the first solid-state Perovskite solar cells employing Spirobifluorene (spiro-OMeTAD) as the hole transporter (Kojima *et al.*, 2006). This cell recorded maximum full sun PCE of between 8 and 10% employing mixed halide Perovskites of iodine and chlorine (Kojima *et al.*, 2009).

MESOPOROUS TiO_2 STRUCTURES

The first use of hybrid Perovskite absorbers in photovoltaic cells is based on the typical structure of a dye-sensitized solar cell, where the Perovskite absorber is self-assembled within the gaps of a porous TiO_2 layer formed by sintering nanoparticles (Song *et al.*, 2015). The typical configuration of this type of Perovskite based solar cells FTO / Mesoporous TiO_2 / Perovskite / (spiro-OMeTAD) / electrode is as shown below in figure 2

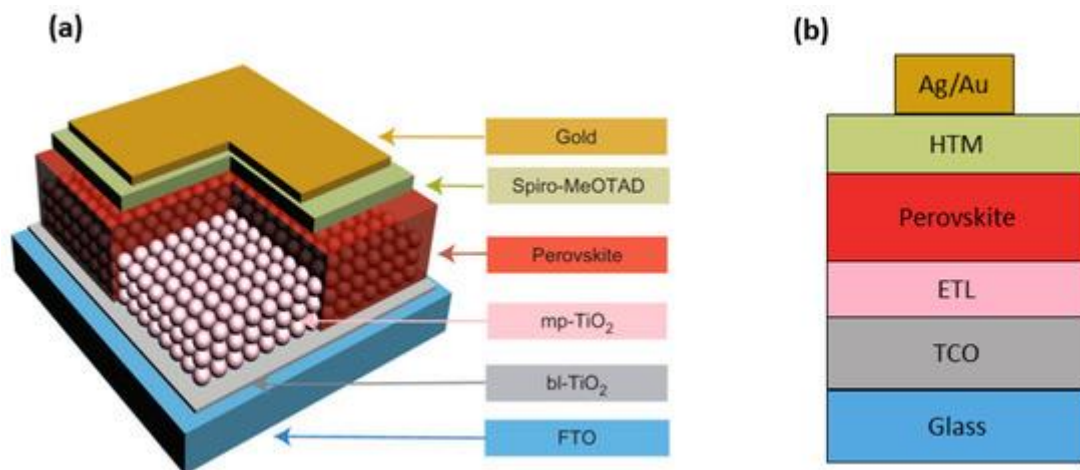


Figure 2: Schematic Diagram and Cross Section of the Mesoporous Structured PSC Device

Source: Paola *et al.* (2017).

In this structure, Perovskite materials are deposited onto Mesoporous TiO_2 , which is used to facilitate electron transport between the Perovskite absorber and the FTO (fluorine-doped Tin oxide) electrode. A subsequent work demonstrated the replacement of the relatively conductive porous TiO_2 with an insulating porous Al_2O_3 layer

(Song *et al.*, 2015). It is however important to note that successful pore-filling in these structures is necessary in order to prevent leakage via the device, which has been an issue for thick Mesoporous structures.

The use of Mesoporous structures as a scaffold to fabricate Perovskite solar cells has led to an increase in device performance from 3.8% to over 17% PCE within a few years (Kojima *et al.*, 2009). Just as these structures do not rely on long carrier diffusion length; it is also able to provide a compensation platform for the investigation of new Perovskite materials (Song *et al.*, 2015). While the use of a Mesoporous scaffold requires a comparatively complex device architecture and fabrication process in which many problems could arise, it has consistently delivered high efficiencies that made its use fully worthwhile for laboratory scale investigations (Song *et al.*, 2015).

PLANAR STRUCTURE

In a planar junction Perovskite solar cell, a several hundred nanometer thick absorber layer, is sandwiched between the electron transport layer (ETL) and hole transport layer (HTL) without a Mesoporous scaffold (Song *et al.*, 2015). These cells can deliver efficiency values of over 15% despite being under developed for an even shorter period than their Mesoporous counterparts. This architecture offers the advantages of a simplified device configuration and fabrication procedure, and thus, rapidly acquired the interest of the thin film research community. Planar structures are most commonly illuminated from the n-type side, resulting in the structure glass/TCO/ETL/Perovskite/HTL/metal or p-type side, resulting in the inverted structure glass/TCO/HTL/Perovskite/ETL/metal which functions in a superstrate configuration. Owing to its simplified fabrication and ease of deposition, the planar architecture provides a great promise in future applications, including high performance flexible and portable devices (Song *et al.*, 2015).

MESOSUPERSTRUCTURED PSCS (MSSC)

These are PSC device structures having $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$ mixed Perovskite, coated with alumina layer in a photovoltaic cell. Bi *et al.*, reported that the PCE of this type of structure reached 10.9% in 2013 (Bi *et al.*, 2013). They were so called because the photogenerated electrons are not transferred to alumina because of the difference in band edges of alumina and Perovskite active layer, which acts only as a scaffold for carrying the photoactive layer (Muhammed *et al.*, 2015). The scaffold layers afford processing at lower temperatures by excluding high temperatures annealing step as neither generated electron are injected into the Mesoporous layer nor transported. With the advantage of processing at lower temperatures, Lee *et al.* reported a MSSC/PCE value of 12.3% (Though Al_2O_3 Mesoporous layers was dried at 150°C) (Lee *et al.*, 2012).

HYBRID PEROVSKITE SOLAR CELLS

An example of a hybrid planar heterojunction solar cell is a device structure based on $\text{TiO}_2\text{CH}_3\text{NH}_3\text{PbI}_{3-x}$ / P3HT (poly (3-hexylthiophene)). Such device achieved a better photovoltaic performance when the ITO (indium-doped-Tin-oxide) substrate was treated with C60 self-assembled monolayer having an improved PCE of 6.7%. This was achieved with a significant increase in both J_{sc} (shunt current density) and V_{oc} (open circuit voltages) (Jeng *et al.*, 2013). The active layer of a hybrid planar heterojunction cell can be sandwich between poly (N,N¹-bis (4-butylphenyl) – N, N¹-bis (phenyl)- benzidine)(poly-TPD) as Hole transporting material layer and electron accepting PCBM layer (Abrusci *et al.*, 2013). A PCE of 12% was thus reported.

FLEXIBLE PEROVSKITE SOLAR CELLS

If the commercialization goal of PSCs must be achieved, further studies on the possibilities of fabricating cells and flexible substrate must be encouraged. However, several works have been done in this field owing to the low temperature solution processability of PSCs. Ability to conform to the contours of the platform holds obvious promises for incorporation of this technology in diverse application (Muhammad *et al.*, 2015). Docampo *et al.*, in 2013 achieved a higher PCE of 10.2% using device structure ITO / ZnO (25nm) / CH₃NH₃PbI₃ /Spiro- MeoTAD /Ag, fabricated using low temperature solution processing techniques (Docampo *et al.*, 2013).

HYBRID MULTI-JUNCTION SOLAR CELLS

Song *et al.*, concluded in the work saying it is anticipated that the demonstration of new solar technologies based on Perovskites, or the integration of an established manufacturing method that uses both Perovskite and existing technologies are particularly promising for the future photovoltaic market (Song *et al.*, 2015). They envisaged a tandem cell configuration where PSCs can be used effectively as a top cell with existing technologies and at very little optimization in terms of bandgap widening and Fill Factor (FF) enhancement (Mailoa *et al.*, 2015). With a reasonable estimate of achieving 20mAc^m-² and Voc of 1.1V at the top Perovskite cell, a silicon cell generating 0.75V Voc will lead to a FF of 0.8 and efficiency of 29.6% (Snaith, 2013). Tandem solar cells have attracted the attention of researchers around the world as it offers an alternative path towards higher efficiencies when compared to those obtained from single solar cell structures. For a good tandem solar cell structure, an optimized top and bottom cell structure must be used in order to achieve maximum conversion efficiency (Olopade *et al.*, 2015).

SYNTHETIC METHODS

Perovskite solar cells can be manufactured with simpler wet chemistry techniques in a traditional laboratory environment, unlike silicon solar cells that need expensive, multi-step processes requiring an extreme temperature and vacuum controlled system. Perovskites can be created using a variety of solvent techniques and vapour deposition methods (Dawn, 2016). Approaches reported for the synthesis of Perovskite active layers are: one-step precursor solution deposition; two-step sequential deposition; dual-source vapour deposition; vapour assisted solution process; and sequential vapour deposition (Liu *et al.*, 2013; Burschka *et al.*, 2013; Hu *et al.*, 2014). Categorically, we can put the synthesis methods of Perovskite under these broad heading: solvent techniques (solution processing); vapour assisted solution processing and vacuum deposition.

PEROVSKITE FILM FORMATION

Various processing techniques have been documented to fabricate hybrid Perovskite films. The major methods of fabricating Perovskite solar cells as suggested by Ezike *et al.* (2017) are Spin – coating, Vapour deposition and thermal evaporation methods. Spin-coating methods include one – step, two – step/ sequential deposition and vapour deposition method which include vapour - assisted deposition, and dual – source vapour deposition, and thermal evaporation technique (dual source approach) have been used to prepare CH₃NH₃PbX₃ materials (Ezike *et al.*, 2017).

It has also been suggested that the optoelectronic properties of Perovskite films are closely related to the

processing conditions, such as the starting material ratio and the atmospheric conditions during film growth, which lead to a substantial difference in the film quality and device performance (Wang *et al.*, 2014). Hybrid Perovskite materials form with crystallinity, even when processed at low temperatures, and the formation of the final Perovskite phase benefits from the relatively high reaction rates between the organic and inorganic species. These advantages substantially expand the choices of available processing methods such as thermal evaporation and solution processing, and facilitate the adoption of new and varied architecture (Song *et al.*, 2015).

In solution processing of Perovskite film, a mixture of MX_2 ($\text{M}=\text{Pb, Sn}$; $\text{X}=\text{Cl, Br, I}$) and AX ($\text{A}=\text{methylammonium, MA}$; Formamidinium, FA) is dissolved in an organic solvent and deposited directly to form a film and followed by thermal annealing to produce the final Perovskite phase (You *et al.*, 2014).

In thermal evaporation synthesis of Perovskite film, a dual source is employed for MX_2 and AX with different heat temperatures to form the Perovskite film (Liu *et al.*, 2013). Both solution processing and thermal evaporation methods described above are one-step processing methods. In one-step method, both the organic and inorganic halides are stoichiometrically prepared in a common solution and are then spin coated into a thin film. In sequential deposition synthesis of Perovskite films, MX_2 layer such as PbI_2 and an AX such as Methylammonium iodide (MAI) are deposited sequentially followed by heat treatment to form the completed Perovskite film (Xiao *et al.*, 2014). The deposition of the MX_2 is done by spin-coating while AX can be introduced by spin-coating the AX solution on top of the MX_2 layer or the AX solution can be immersed in MX_2 layer to induce a solid-liquid reaction or by exposing the MX_2 layer to AX vapour at elevated temperatures (Pang *et al.*, 2014). Spin-coating deposition processes allow metal halide and organic halide to be dissolved in organic solvents which is followed by deposition on a substrate from which the formation of the Perovskite is achieved through annealing around 100°C . This method is a low-cost approach but it wastes a lot of precursors.

Two-step sequentially deposition can be carried out in thermal evaporation, by sequential deposition the inorganic and organic components. Here, the PbI_2 is first spin-casted followed by solution processing or vacuum assisted deposition of MAI (Hu *et al.*, 2014). It is a heterophase reaction resulting in conversion to MAPbI_3 . A modification of two-step deposition method is the vapour assisted growth of MAI on the PbI_2 film. Compact and uniform PbI_2 film obtained by solution processing is exposed to MAI vapour under ambient conditions. In contrast to vapour depositing, this method does not require expensive vacuum equipment and environmental controls. Combining the advantages of solution processing and low temperature vapour deposition, the films grown are pinhole-free offering higher efficiencies (Hu *et al.*, 2014; Xiao *et al.*, 2014). In vapour deposition method, the substrate is exposed to one or more volatile precursors, which react with the substrate and/or decompose to produce the wanted deposit. It can be when the metal halide is deposited by spin-coating or other methods and volatile organic halide is deposited by ejecting it to give out vapour in the reaction chamber (Ezike *et al.*, 2017). The vapour process is argued to be better than the solution process in planar heterojunction layout because the former produces a flat and even surface (Kesiuro *et al.*, 2017).

Dual source vapour deposition method involves simultaneous evaporation of organic and inorganic salts from respective sources at high vacuum. PCE of $\sim 12\%$ was achieved using this method (Liu *et al.*, 2013). Dual source of organic and inorganic halide ejects the vapours to the substrate exposed in the chamber. It is a low-cost method, uniform step coverage, fast deposition, low processing temperature and high throughput.

Thermal evaporation is widely used as a technique for the preparation of thin films for deposition of

metals, alloys and many compounds. The requirement is to create vacuum environment where enough heat is given to the evaporants to attain the vapour pressure required for evaporation (Abbas *et al.*, 2015).

SYNTHESIS OF PEROVSKITE-SENSITIZED SOLAR CELLS

A typical DSSC is a Mesoporous n-type Titania sensitized with a light absorbing dye in a redox active electrolyte. It was in the process of finding a more efficient light sensitizer for DSSCs that Miyasaka *et al.* reported the first Perovskite-sensitized solar cells, which they formed employing $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ absorbers with an iodide triiodide redox couple (Kojima *et al.*, 2006).

SYNTHESIS OF MESOPOROUS TiO_2 STRUCTURES

A typical fabrication procedure for Mesoporous scaffold-based Perovskite solar cells involves the use of FTO substrates with a compact TiO_2 blocking layer and a Mesoporous oxide layer that have each undergone high temperature sintering steps (500°C). In solution processing, Dawn, 2016 gave an elaborate explanation of the procedures as follows: the FTO substrates are cleaned in an ultrasonic bath with a combination of methanol and acetone and finally dried with Nitrogen gas. After the preparation of FTO substrates, the 0.15M and 0.3M TiO_x precursor solutions are prepared from titanium diisopropoxide bis (acetyl acetone) (0.0055mL and 0.11mL) with 1-butanol (1 mL). The initial step is to spin-coat 0.15M TiO_x precursor solution on the FTO glass substrate at 3000rpm for 30 seconds, and annealed at 125°C for 5 minutes. This 0.30M solution process is performed twice, after which the FTO substrate is sintered at 500°C for 30 minutes to form a compact TiO_2 layer.

To prepare the Mesoporous TiO_2 layer, a TiO_2 paste is made using TiO_2 powder (100mg) and polyethylene glycol (10mg) in ultrapure water (0.5mL). This solution is then mixed with acetyl acetone (10.0 μL) and triton X-100 (5 μL) for 30 minutes and left for 12 hours. This helps in suppressing the formation of bubbles in the solution. The TiO_2 paste obtained is coated on the substrate by spin-coating at 5000rpm for 30 seconds. The cells are annealed at 120°C for 5 minutes and at 500°C for 30 minutes. To synthesize methyl ammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$), 23.2mL of methylamine (CH_3NH_2) is reacted with 25.0mL of hydroiodic acid at 0°C for 2 hours with stirring. The precipitate is collected by removing the solvents at 50°C for 1 hour. The product obtained is re-dissolved and stirred in diethyl ether for 30 minutes to remove any impurities and dried using a rotary evaporator at 60°C for 3 hours. The $\text{CH}_3\text{NH}_3\text{I}$ thus produced is finally dried in a vacuum.

To prepare Methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) with a Perovskite structure, a solution of $\text{CH}_3\text{NH}_3\text{I}$ (98.8mg) and PbI_2 (289.3mg) at a mole ratio of 1:1 in *n*-butyroactone (0.5mL) is mixed at 60°C . The $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution is then introduced into the TiO_2 Mesoporous using a spin-coating method and annealed at 100°C for 15 minutes. Next step is to prepare the Hole-transport layer (HTM) by spin-coating. A solution of spiro-OMeTAD (36.1mg) in chlorobenzene (0.5mL) is mixed with a solution of lithium bis (trifluoromethylsulfonyl) imide (260mg) in acetonitrile (0.5mL) for 12 hours. This solution and 4-tert-butylpyridine (4 μL) is then mixed with the Li-TFSL solution (8.8 μL) for 30 minutes at 70°C . All procedures are carried out in air. Finally, gold (Au) metal contacts is evaporated onto the sample as top electrodes. Figure 3 below shows the above detailed process.

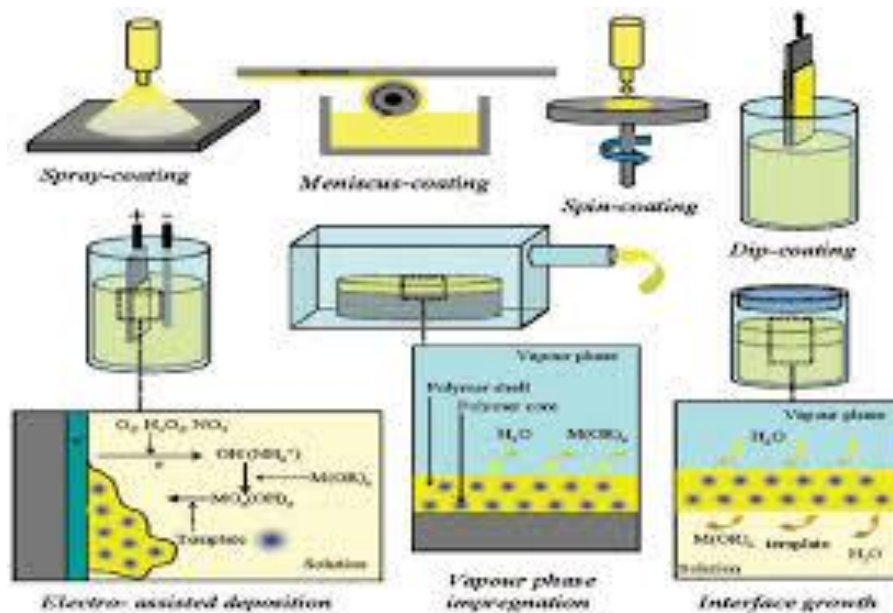


Figure 3: Synthesis of Mesoporous TiO₂ Structures

Source: Luther and Ranjit (2014).

SYNTHESIS OF PLANAR STRUCTURE

As earlier stated, planar junction PSCs have a several hundred nanometer thick absorber layer which is sandwiched between ETL and HTL without a Mesoporous scaffold. This architecture offers the advantages of a simplified device configuration and fabrication procedure. These structures are mostly commonly illuminated from the n-type side, resulting in the structure glass/TCO/ETL/Perovskite/ETL/metal (Jeng *et al.*, 2013; Chiang *et al.*, 2014).

The earliest attempts to fabricate planar Perovskite solar cells used single step deposition to deposit the Perovskite absorber layer. Compared to the Mesoporous scaffold, thermal evaporation can be more efficiently applied in a planar configuration, without worrying about the difficulty of Perovskite precursors penetrating into the Nanoporous scaffold. Bi *et al.*, 2013 attempted by thermal co-evaporation of CH₃NH₃I and PbCl₂ and deposited CH₃NH₃PbI_{3-x}Cl_x onto FTO with a thin TiO₂ layer resulting in a PCE of 15.4% (Bi *et al.*, 2013).

SYNTHESIS OF MESO PSCS (MSSC) SUPERS STRUCTURED

These devices are fabricated by spin-coating CH₃NH₃PbI₂Cl mixed Perovskite with alumina layer in a photovoltaic cell. A Mesosuperstructure concept was evaluated using ZrO₂ Mesoporous scaffold with CH₃NH₃PbI₃ light harvester which exhibited significant photovoltaic activity Voc of approximately 900mV through lower than titania (Kim *et al.*, 2013).

SYNTHESIS OF HYBRID PEROVSKITE SOLAR CELLS

This is a device structure based on TiO₂/ CH₃NH₃PbI_{3-x}Cl_x / P3HT, with the incorporation of self-assembled monolayer (e.g. C60). Here, the ITO substrate is treated with the C60 self-assembled monolayer (Jeng *et al.*, 2013). The concept of hybrid planar heterojunction cell incorporating 285nm thick layer of CH₃NH₃PbI₃ was investigated by Abrusci *et al.*, 2013. Active layer was sandwiched between hole-transporting poly (N,N¹- bis(4-butylphenyl)-N,N¹-bis (phenyl)-benzidine) (poly-TPD) layer (10nm) and electron accepting PCBM layer (10nm).

The charge collecting layers were solution-processed in spin-coated chlorobenzene while the active layer was vacuum-deposited by heating reagents $\text{CH}_3\text{NH}_3\text{I}$ to 70°C and PbI_2 to 250°C .

SYNTHESIS OF FLEXIBLE PEROVSKITE SOLAR CELLS

These PSCs consist of fabricating the cells on flexible substrates. Malinkiewicz *et al.*, 2014 investigated this using both regular and inverted device architecture on an ITO coated PET substrate. A $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ active layer with PEDOT: PSS and PCBM as hole-transporting and electronic selective contacts were used. A PCE of 6.4% was achieved (Malinkiewicz *et al.*, 2014). A higher PCE of 10.2% was achieved using device structure of ITO/ZnO (25nm)/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ / Spiro-OMeTAD/AG, fabricated using low temperature solution processing methods (Docampo *et al.*, 2013).

PEROVSKITE PHASE FORMATION

Depending on the relative sizes of the cation and the octahedron in a Perovskite structure, the Perovskite phase can be three dimensional (3D), two-dimensional (2D) or even one-dimensional (1D) in crystal structure (Stoumpos *et al.*, 2013).

Focusing on 3D organo-metal halide Perovskite phases, it is worth noting that the formation of Perovskite structures usually follows the overall reaction formula $\text{AX} + \text{BX}_2 \rightarrow \text{ABX}_3$. Using this reaction as a typical example, it has been observed that the reaction kinetics of Perovskite phase formation are very fast (Liu and Kelly, 2013). During the transformation into the Perovskite lattice, spaces are formed between the layered PbI_6 octahedral that share facets with PbI_2 to create PbI_6 octahedral that share only vertices in MAPbI_3 . Solution of PbI_2 is another important parameter that affects the intermediate reaction stage. Since it has been demonstrated that the soft Pb can easily coordinate with a variety of small molecules such as ethanolamine or dimethyl sulfoxide (DMSO), after which the original facet-sharing (PbI_6) octahedral are partially disintegrated and small ligands are inserted, it is therefore logical to conclude that during the dissolution of PbI_2 , solvent molecules partially replace iodine to ligate with lead, thus facilitating the subsequent reaction forming the Perovskite phase.

Besides the kinetics of phase formation, another issue is the formation of mixed-cation, mixed group IV metal, and mixed-halide Perovskite phases, allowing for the fine tuning of the optical and electronic properties of the final material (Song *et al.*, 2015). A Perovskite phase with mixed-group IV metals has recently been synthesized using MAI and a mixture of PbI_2 and SnI_2 (Hao *et al.*, 2014).

MAPbX_3 -based Perovskite have been found to exhibit multiple phases as a function of temperature and composition. These different phases possess dramatically different electrical/optical properties as well as stability. Stoumpos *et al.*, showed that MAPbI_3 exhibited an X-phase, δ -phase and γ -phase with transition temperature of 400°K , 333°K , and 180°K respectively (Stoumpos *et al.*, 2013). Phase transformation can also occur in mixed halide systems. A mixed halide $\text{MAPbI}_{3-x}\text{Br}_x$ ($0 \leq x \leq 3$) was used for band-gap tuning and it was observed that the crystal structure transformed from the tetragonal phase to a cubic phase when the percentage of Br present passed a threshold of approximately **X approx. 0.5** (Noh *et al.*, 2013). This phase transition has been presumed to explain the improved stability of $\text{MAPbI}_{3-x}\text{Br}_x$ materials in the air and humidity test, making it an interesting addition to our understanding of the specifics of the Perovskite lattice.

PEROVSKITE FILM QUALITY

Based on various processing approaches, Perovskite materials exhibit a wide range of film properties like grain size, morphology, crystallinity, surface coverage, etc. Several works have also shown that Perovskite films exhibit composition/structure dependent properties (Song *et al.*, 2015). Therefore, since it is essential to achieve fine control over the reaction between the inorganic and organic species so as to produce Perovskites within the required properties, various process parameters have to be incorporated. Paramount among these are: stoichiometry, thermal treatment, solvent engineering, additives and environmental control.

The stoichiometry, particularly the ratio of the organic to inorganic component, largely affects the resulting MAPbI_{3-x}Cl_x film quality in terms of film conformity and carrier behaviour. Generally, a solution of PbX₂ and MAX with a stoichiometry of 1:1 is used as the precursor to form a pure Perovskite phase (Song *et al.*, 2015). Further studies on film formation based on stoichiometry effects have also been conducted, in terms of the phase, the underlying reaction, and the possible byproducts. Details about this can be found in the works of Lee *et al.* (Lee *et al.*, 2012).

Thermal annealing is an essential step to initiate or accelerate the reaction between the molecules, as well as the film formation. A delicate control of heat treatment is needed due to the fast reaction rate between the organic-inorganic component and their various phase in the low temperature of hybrid Perovskite range materials. Eperon *et al.*, investigated the properties of mixed halide Perovskite MAPbI_{3-x}Cl_x planar films based on one-step solution processing at different annealing temperatures (Eperon *et al.*, 2013). The authors observed that the higher the annealing temperature, the lower the film surface coverage. Liang *et al.* added 1% of 1, 8, diiodooctane (Dio) into a Perovskite precursor solution and demonstrated an increase in device performance in contrast to devices based on precursors without additives (Liang *et al.*, 2014). The films exhibited improved surface coverage and crystallinity as observed using SEM and XRD, respectively. This result showed that the inclusion of small amounts of chemical additives in Perovskite precursor solutions can provide advantages in terms of crystallinity, film coverage, and the resulting device performance. It also showed that the film growth can be effectively controlled.

Generally, Perovskite films are deposited and annealed in nitrogen or dry air glove boxes with H₂O levels less than 5ppm, as the presence of moisture was deduced to deteriorate the Perovskite film. However, Zhou *et al.* found that Perovskite films annealed in a mild moisture environment of approximately 30% humidity. And could improve film properties significantly (Zhou *et al.*, 2014). The speculation is that the moisture could enhance film formation by partially dissolving the reaction species and accelerating mass transport within the film. It could also possibly promote the movement of organic species and accelerate the grain growth resulting in less pinholes in the films. This result indicates that a controlled atmosphere during the film formation will result in high performance Perovskite devices. The quality of hybrid Perovskite films can be determined by the critical role solvents play in all kind of solution processes. The selection of solvents with sufficient solubility for organic and inorganic precursor components is limited due to their distinct nature (Song *et al.*, 2015). Currently, DMF, DMSO, GBL and their mixtures are majorly used. These solvents have been shown to improve the film optoelectronic properties and device performance (Kim *et al.*, 2012; Zhan *et al.*; 2014). Kim *et al.*; reported that mixed solvents have improved the morphology of the Perovskite film (Kim *et al.*; 2014). Therefore, the solvents either from the precursor solution or induced during the processing, substantially influencing the molecule/species interaction within the system, and the subsequent film quality.

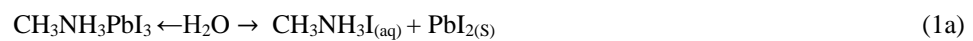
CHALLENGES

STABILITY ISSUES OF PEROVSKITE

Stability and efficiency are two factors important for the commercial application of Perovskite solar cells. For their commercial viability, it is imperative that studies be undertaken on issues of stability and reproducibility to enhance the lifetime of these devices (Muhammad *et al.*, 2015). Degradation in Perovskite solar cells is a synergetic effect of moisture, ultraviolet light, temperature, and the effects of hysteresis and ion migration.

MOISTURE

Niu *et al.* proposed a sequence of chemical reactions considered responsible for the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the presence of moisture (Niu *et al.*, 2014). By comparing XRD patterns before and after exposure to water, they were able to propose the following series of reactions (equations 4.1 to 4.4) for the moisture catalyzed decomposition of the Perovskite layer as follows:



Multiple reports have suggested that water is the catalyst required for the irreversible degradation of the Perovskite material (Wang *et al.*, 2016). Figure 4 below shows the proposed decomposition pathway of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the presence of a water molecule.

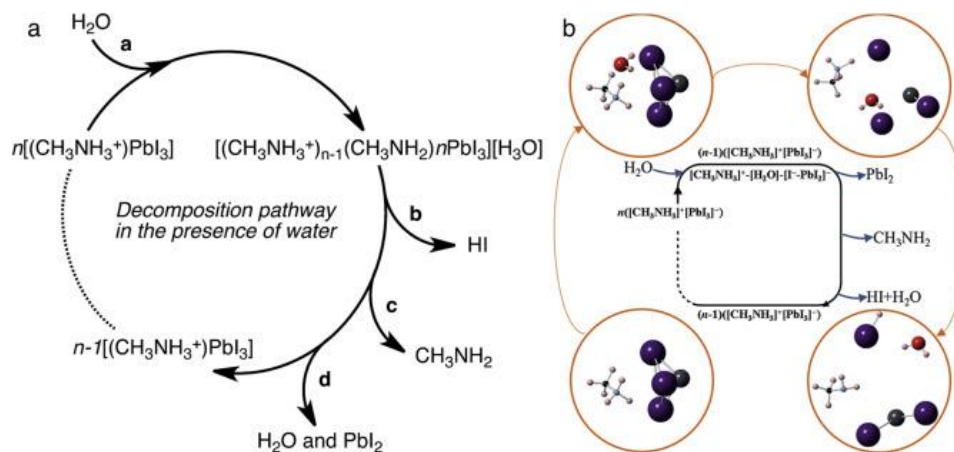


Figure 4: Proposed Decomposition Pathway of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the Presence of a Water Molecule

Source: Jianqing *et al.* (2017).

The irreversible degradation of the Perovskite layer is a challenge facing the lifetime of a photovoltaic cell. However, the challenge is compounded by the nature of the by-products. One of the by-products of this reaction

is PbI_2 (Eqn 1a) which itself is soluble in water (Yang *et al.*, 2015). The decomposition of PbI_2 in installed modules could cause significant eco-toxicological problems in the field.

In contrary to the findings of Niu *et al.* *In Situ* grazing incidence x-ray diffraction (GiXRD) measurements provided another insight into the decomposition reaction occurring in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film (Yang *et al.*, 2015). The authors discovered a new crystalline phase which they speculated as a hydrated compound $[(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot \text{H}_2\text{O}]$ when they exposed the Perovskite film to 80% relative humidity (RH) for 2.5 hours. The formation of this hydrated compound caused a significant reduction in the film absorption. However, $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ based absorbers retained good PCE on exposure to humidity of 55% for 20 days (Noh *et al.*, 2013).

ULTRAVIOLET RADIATIONS

Illuminations with UV light can cause degradation in Perovskite solar cells. UV sensitivity is attributed to use of TiO_2 as photo anode in PSC. Proposed degradation mechanism for $\text{CH}_3\text{NH}_3\text{PbI}_3$ under UV illumination was given by (Ito *et al.*, 2014) and equations 2a to 2b shows:



At the interface between TiO_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$, we have:



Leijtens *et al.* showed that for Perovskite solar cells, this TiO_2 layer is susceptible to UV-induced degradation (Leijtens *et al.*, 2013). This was investigated by measuring a 5h efficiency decay curve, measured under 1 sun AM 1.5G illumination for devices with and without encapsulation and a UV filter. The results showed that, un-intuitively, the encapsulated device degrades more rapidly than the non-encapsulated device. These authors after several measurements to confirm the UV light degradation of PSCs proposed three methods to circumvent the problem viz: pacifying the trap states; avoiding UV light from reaching the TiO_2 layer and or; replacing the TiO_2 scaffold with another material.

The use of Sb_2S_3 blocking layer was investigated to reduce UV induced degradation by Ito *et al.* The technique involves depositing a Sb_2S_3 layer at the $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ interface (Ito *et al.*, 2014). The inclusion of this buffer layer improved the stability greatly. Without Sb_2S_3 , the $\text{CH}_3\text{NH}_3\text{PbI}_3$ decomposed to PbI_2 which correlates with the colour change to yellow. Whereas, $\text{CH}_3\text{NH}_3\text{PbI}_3$ maintains its crystalline structure with Sb_2S_3 buffer layer. The author reasoned that what happens when the Sb_2S_3 layer inserted at the interface blocks the UV induced photo catalysis in TiO_2 may be passivation.

TEMPERATURE

Thermal stability studies are very important as exposure to elevated temperatures causes degradation of the Perovskite layer. This is so because temperatures are expected to be over the phase transition temperature of $\text{CH}_3\text{NH}_3\text{PbI}_3$, changing from tetragonal to cubic structure at 56%. Phillippe *et al.* investigated the influence of elevated temperatures on both $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}$ films (Phillippe *et al.*, 2015). Here, the authors heated the films in an analysis chamber under an ultra-high vacuum. Removing the presence of water and air allowed for the isolation of the effect of temperature on the film degradation. The films were characterized using the I/Pb and N/Pb ratios, extracted from hard x-ray photoelectron spectroscopy (PES). A reduction of these ratios indicates the conversion of the Perovskite into PbI_2 . Heating at 100°C for 20 minutes led to a significant reduction of both ratios. Further heating at 200°C caused both ratios to drop to a minimum, 2 and 0, respectively. This is

indicative of a film consisting of 100% PbI₂. The author suggested the following reaction for the temperature induced decomposition as shown in equation 3 below:



Characterization results clearly shows the instability of the Perovskite material under elevated temperatures.

Thermal decomposition of Perovskite layer has also been reported to depend on the underlying layer (Yang *et al.*, 2015). Although initial reports used a TiO₂ scaffold, the requirement to reduce the fabrication temperature has been to replace TiO₂ with ZnO. These authors also reported that the ZnO/ CH₃NH₃PbI₃ interface appears to accelerate the thermal decomposition of the Perovskite layer. The film is less thermally stable, when compared to TiO₂. Yang *et al.* used *in situ* absorption measurements to uncover the mechanism causing this instability (Yang *et al.*, 2015).

STABILITY OF THE ELECTRON TRANSPORT LAYER (ETL)

Mesoporous Perovskite solar cells require an electron transport layer (ETL) and most commonly used is TiO₂. Pathak *et al.* reported that non-stoichiometry defects such as oxygen vacancies and titanium interstitials can form in this layer (Pathak *et al.*, 2014). These defects cause deep sub-band gap trap states, which reduce solar cell performance. Oxygen is required to passivate these traps; however, other layers in the device may require encapsulation to prevent moisture ingress. To solve this problem, Pathak *et al.* attempted aluminium-doping using TiO₂. The TiO₂ was doped using a sol-gel deposition process with an Al containing precursor. Low doping levels led to an increase in conductivity in the TiO₂ layer. PDS measurements showed that these low doping levels reduced the number of trap states while the Aluminium served to passivate the non-stoichiometry defects increasing the device stability and performance. Song *et al.* have also shown this by fabricating planar Perovskite solar cell replacing TiO₂ with SnO₂ as the electron selective contact which gave rise to a champion cell efficiency of 13% (Song *et al.*, 2015). Besides TiO₂, PCBM has also been used as a transporting layer. Just as TiO₂ layer is sensitive to ultraviolet light, PCBM is not stable in air (Song *et al.*; 2015).

STABILITY OF HOLE TRANSPORT LAYER (HTL)

Spirobifluorene (spiro-OMeTAD) and poly (triarylamine) PTAA are the most studied Hole transporting layer (HTL). The use of spiro-OMeTAD requires an additive, e.g., 4-tert-butylpyridine (tBP), which can react with the Perovskite materials causing instability. Other HTLs that have been used include PEDOT: PSS and P3HT (poly (3-hexylthiophene)). The acidic nature of PEDOT: PSS also becomes a concern for the long-term stability of solar cells (Song *et al.*, 2015). Yang *et al.* studied the ability for the hole transport layer to protect the underlying Perovskite film from moisture induced degradation (Yang *et al.*; 2015). Three HTLs were investigated viz; spiro-OMeTAD, PTAA [poly (bis (4-phenyl) (2, 4, 6-trimethylphenyl))] and P3HT. Both PTAA and P3HT caused a reduction in the degradation rate under the investigated relative humidities. P3HT served to reduce the degradation rate by a factor of 6 while spiro-OMeTAD layer caused an acceleration of the Perovskite decomposition. The difference in their degradation rates was explained by the discrepancies in the mechanical toughness of the layer. SEM images showed that spiro-OMeTAD layer underwent significant cracking, hence increased decomposition rate, while other HTL layers formed a conformal barrier layer which reduced the ingress of moisture to the Perovskite film.

In 2014, Habisrentingeer *et al.* investigated the influence of the HTL on the thermal and

moisture-induced degradation of Perovskite solar cells (Habisreutinger *et al.*; 2014). Spiro-OMeTAD, P3HT and PTAA HTLs yielded the highest efficiency results. One advantage of using P3HT is that the cost is reduced, due to both reduced material cost, and reduced layer thickness. The authors suggested that P3HT could be 10 times cheaper than spiro-OMeTAD (Zhang *et al.*, 2015). Yan *et al.* replaced PEDOT: PSS with a thin polythiophene (PT) film, deposited by electrochemical polymerization (Yan *et al.*, 2015). The optimized efficiency for PT/CH₃NH₃PbI₃ devices was higher than the reference devices using PEDOT: PSS. They proposed that the electrochemical polymerization employed to form the PT film is compatible with large-scale production. HTLs commonly used are organic materials. Kim *et al.* incorporated an inorganic HTL, NiO_x (Kim *et al.*; 2015). The authors observed that such inorganic oxide films display better environmental stability than their organic counterparts. However, organic HTLs gave higher device efficiency.

STABILITY OF PSCS VIA BUFFER LAYER

The addition of buffer layer was shown to improve the device efficiency and stability. (Guarnera *et al.*, 2015). They did this by incorporating Al₂O₃ Nano particles between the Perovskite absorber and the HTL. This improvement was due to an improved fill factor (FF). The buffer layer allows for a reduction in the thickness of the HTM layer causing a reduction in series resistance, thus improving fill factor. The author later propose that the degradation was not induced by moisture or UV radiation, but by the migration of metal from the top contact to the Perovskite layer. The buffer layer stopped the movement of metal to the Perovskite absorber which would otherwise cause shunt pathways (Guarnera *et al.*, 2015).

STABILITY OF THE ELECTRODE

High efficiency PSCs make use of Gold (Au) as the electrode material but this material is prohibitively expensive (Sheikh *et al.*, 2015). Michui *et al.* demonstrated in polymer solar cell modules how silver (Ag) paste can be alternative choice to Au (Machui *et al.*, 2014). But an issue which provides a barrier to the use of Ag as electrode for PSCs was uncovered by Kato *et al.* (Kato *et al.*, 2015). They found that PSC, using Ag as the electrode display worse environmental stability than those using Au electrode. Further investigation revealed that exposure to humidity (RH ~ 50%) caused a formation of AgI, making the electrode color to change from a reflective metal to a yellowish color. This however results to reduced efficiency. This environmental instability of the electrode is ultimately caused by the nature of the HTL, indicative of the inter-related nature of the degradation pathways within all layers in a PSC. Mei *et al.* fabricated a hole-conductor-free PSC with a printed carbon electrode (Mei *et al.*, 2014) and the device displayed excellent stability. This was as a result of the presence of the thick carbon layer providing excellent protection and the stability also enhanced with the elimination of the hole transport medium. They concluded that though the stability is impressive, the device architecture contains layers processed at elevated temperatures (400°C) which does not align with the desire of mass production.

Multiple novel applications of carbon electrodes have recently been reported (Li *et al.*, 2015). These were achieved by fabricating a flexible, fibre, supported PSC using nanotubes (CNT) fibres via a solution coating technique. They laminated a CNT network onto CH₃NH₃PbI₃ removing the need for the HTL and metal electrode (Li *et al.*, 2014).

HYSTERESIS EFFECTS

The origin of hysteresis and its mechanism is a highly debated topic and has become an area of intense research. Understanding the ferroelectric behaviour of Perovskite solar cell materials may be critical in increasing its

efficiency and stability. Ferroelectricity may affect the photo excited electron hole pairing and separation (Liu *et al.*, 2015). This behaviour of PSC material came under focus on the report of the hysteresis in current voltage scans, dependent on the scan rate and direction, light soaking history and contact material and interfaces (Unger *et al.*, 2017). Recent reports on hysteresis have attributed the following to its causes: grain boundaries and size; charge trapping at the interface; ion migration within the crystal structure of Perovskites; defects states and surface imperfections of Perovskites (Stephan *et al.*, 2015). Though the frontiers of understanding the intricacies causing hysteresis are evolving, its impact on operating stability of the device remains quite unclear (Wang *et al.*, 2016). Snaith *et al.* have proposed capacitive effects, ferroelectric behaviour of absorber, and defect densities to be the sources of hysteresis behaviour (Snaith *et al.*, 2014).

In organic-inorganic halide Perovskites, grain boundaries and imperfection on its surface may introduce localized states, which will serve as trap centres for photogenerated carriers. Because of its susceptibility to defect formation arising from low thermal stability of these PSC materials, these trap centres could induce a field across that can counteract with the overall photo voltage of the device. Hence, hindering its efficiency (Shao *et al.*, 2014). Reports have shown C₆₀/fullerene passivation eliminates this kind of photocurrent hysteresis (Xu *et al.*, 2015; Shao *et al.*, 2014). The fullerene is found to interact with halide rich defective regions at the grain boundaries; leading to the passivation of localized trap states. Baena *et al.* reported a reduction in hysteresis by replacing TiO₂ with SnO₂ as the electron transport layer (ETL) (Baena *et al.*, 2015). A 15nm SnO₂ layer was deposited by low temperature atomic layer deposition (ALD). Planar Perovskite devices with SnO₂ ETL thereby achieved efficiencies greater than 18%. This reduction in hysteresis the authors attributed to a more favourable band alignment at the SnO₂/Perovskite interface.

ION MIGRATION EFFECTS ON THE STABILITY OF PSCS

The process of ion migration within the crystal structure of Perovskite is another issue that could potentially have an impact on device stability (Eames *et al.*, 2015). Ion migration is sought to be a major reason for hysteresis observed in PSCs (Pellet *et al.*, 2014). The diffusion of intrinsic ionic defects in organic-inorganic halide Perovskites has implications in terms of their long-term stability and performance efficiency. However, recent studies have revealed that the migration iodide ion vacancies under the influence of either electric field or light illumination could alter the collection of efficiency of the photogenerated carriers, causing hysteresis in PSCs (Zhao *et al.*, 2015). Eames *et al.* also reported that the ionic conductivity in the PSCs depend on the intrinsic iodide ion vacancies, which is found to be dependent on the synthesis conditions and thermal processing techniques (Eames *et al.*, 2015).

Tress *et al.* also reported that hysteresis was found to increase with aging of the device (Tress *et al.*, 2015). The authors gave several reasons behind this anomalous behaviour to include: degradation of CH₃NH₃I and the formation of PbI₂; and mobile iodide vacancies. Eames *et al.* concluded their work by portraying a picture of hybrid halide Perovskite to look like a mixed ionic-electronic conductor and this behaviour is expected to have major repercussions for unravelling the degradation pathways and for the design of future device architectures (Eames *et al.*, 2015).

OVERCOMING THESE CHALLENGES

ATTEMPTS TO IMPROVE INTRINSIC STABILITY OF PSCS AND ITS GROWTH

Variations on the most commonly used Perovskite material ($\text{CH}_3\text{NH}_3\text{PbI}_3$) structure may lead to improved environmental stability. Noh *et al.* tuned the stoichiometry of $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ of Perovskites by substituting I ions with Br ions (Noh *et al.*, 2013). The author concluded that the stability of PSCs devices incorporating Br was found to be significantly improved. This improvement they attributed to a reduced lattice constant and a transition from tetragonal to cubic phase. The desire for non-toxic, solution processable solar cells has led a few researchers to consider alternatives to lead (Pb) within the Perovskite structure (Wang *et al.*, 2016). The most appropriate element to replace Pb is tin (Sn), as it is also a group 14 metal having four electrons in its outer shell. Noel *et al.* formed a device by spin-coating $\text{CH}_3\text{NH}_3\text{SnI}_3$ on TiO_2 . The authors observed a decolouration/degradation of both the non-encapsulated and encapsulated devices they tested (Noel *et al.*, 2014). Hao *et al.* also reported PSCs incorporating Sn halides and stability investigation was formed by encapsulating the device with surlyn films. They concluded that advances in encapsulation techniques are paramount if this material is to be suitable for future applications (Hao *et al.*, 2014).

Espinosa *et al.* reported an initial life cycle assessment (LCA) and environmental impact analysis (EIA) for PSCs and concluded that the component contributing the most to environmental impact was the Perovskite layer, however, the PbCl_2 contributed very little to this. The problem they said lay largely with MAI (Espinosa *et al.*, 2014).

Smith *et al.* decided to investigate a two-dimensional (2D) layered Perovskite structure with the aim of improving the device stability (Smith *et al.*, 2014). They reported better efficiencies with the use of the 2D layered synthesized Perovskite material as the absorber in PSC devices. The layered Perovskite also did not decompose after samples were exposed to RH of 52% in 46 days.

Ternary halide $\text{Cs}_3\text{Sb}_2\text{I}_9$ was also investigated (Saparov *et al.*, 2015). The lead-free material does not consist of a hydrophobic layer to protect the film. The authors recorded an enhanced stability which they attributed to the inorganic crystal structure or film grain size. MAPbI_3 band gap value is 1.55eV. This reported a higher value than the ideal value for a simple junction solar cell. By replacing the organic cation, it is possible to tune the band gap (Eperon *et al.*, 2014). Eperon *et al.* showed that replacing the MAI cation with the larger FAI results in a reduction of the band gap to 1.48eV. The narrower band gap allows FAI-based Perovskites to generate photocurrent over a larger spectral region, resulting in an increase in J_{sc} (shunt current density). Additionally, the author also showed that FAI Perovskite exhibit improved charge transport characteristics compared to MAI Perovskite, allowing for easy integration into planar geometry devices. When exposed to temperatures of about 150°C in air, the FAI Perovskite films were stable. The authors then suggested that just unlike MAI, FAI films did not undergo discolouration. Further studies done by Lee *et al.* later showed that this stability was related to the crystal structure (Lee *et al.*, 2014). Stoumpos *et al.* carried out Differential Scanning Calorimetry (DSC) measurements and found that FAI does not undergo a phase transition within the temperature range of 25 to 125°C. This is unlike MAPbI_3 , which was shown to undergo a structural phase change at approximately 55°C (Stoumpos *et al.*, 2013).

Li *et al.* in 2015 employed chemical Engineering to alter the stability of the commonly used $\text{CH}_3\text{NH}_3\text{PbI}_3$. They achieved this by incorporating an additive (butylphosphonic acid 4-ammonium chloride (4-ABPACl)) into a one-step spin coating method to modify the $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface (Li *et al.*, 2015). XRD and TEM revealed that

these additive molecules bond to the surface of $\text{CH}_3\text{NH}_3\text{PbI}_3$, rather than becoming integrated into the Perovskite crystal structure. This has the effect of cross-linking adjacent Perovskite grains leading to the formation of a smoother capping layer, with improved infiltration into the underlying TiO_2 . Devices fabricated using the 4-ABPACl cross-linked Perovskite film achieved efficiencies higher than 16%.

Xu *et al.* (2016) reported a new approach to obtain a high quality $\text{MAPbI}_{3-x}\text{Cl}_x$ Perovskite layer, by pumping away the solvent of the precursor film before annealing to decrease the influence of solvent evaporation rate on the growth of $\text{MAPbI}_{3-x}\text{Cl}_x$ Perovskite film. This approach was proved to be effective as a compact and uniform Perovskite film with stronger absorption, fewer crystal defects, and smaller charge transfer resistance was formed. Devices based on this high-quality Perovskite film showed enhanced performance compared with the reference device. The averaged efficiency increased from 10.61 to 12.56 % and a champion PCE of 14.0 % was achieved.

Figure 5 below summarizes the growth of PSC since 2009 to 2016, while Figure 6 shows the reported efficiency of PSCs between the same period.

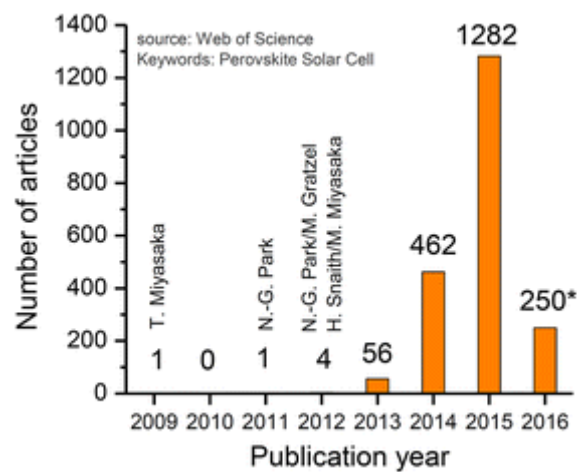


Figure 5: Summary of the Growth of PSC Since 2009 to 2016

Source: Nam-Gyu, 2016.

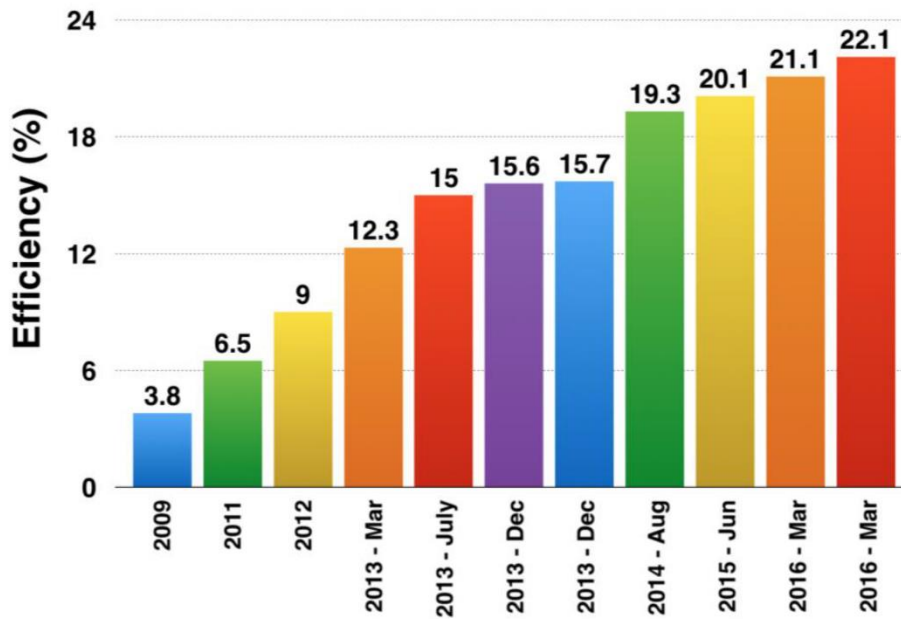


Figure 6: Reported Efficiencies of PSC Between 2009 and 2016

Source: Naveen et al. (2016).

COMPARISON TO OTHER TECHNOLOGIES

The advantage of Perovskite solar cells over existing solar technology lies within their excellent optical and electrical properties, low cost raw materials, facial film and device fabrication. It is anticipated that the demonstration of new solar technologies based on Perovskites, or the integration of an established manufacturing method that uses both Perovskite and existing technologies will be particularly promising for the future photovoltaic market (Song *et al.*, 2015).

Perovskite materials have the potential to disrupt the current photovoltaic landscape owing to their unique use as an active layer in PV modules. This is so because Perovskites can deliver high open circuit voltages (V_{OC}) under full sun illumination, leading to light harvesting from a broad spectrum of incident solar radiation. The fundamental loss in a solar cell which is the difference between V_{OC} and the potential of the lowest energy photon generating a charge has been studied (Snaith, 2010). Snaith reported that thermodynamic treatment limits this loss to the tune of 250-300meV, varying the band gap, based on Shockley-Queisser treatment. Onset of the IPCE spectrum determines the lowest energy absorbed photon. For $CH_3NH_3PbI_{3-x}Cl_x$ Perovskite, the onset is 1.55eV (800nm) with the best V_{oc} of 1.1 gives a loss in potential of 450meV which is lower than the reported loss of 0.59eV for best commercially available PV technology CdTe at an efficiency of 19.6% (Green *et al.*, 2013). Thus, Perovskite solar cell, with the current state of the art, is at par with commercial technologies like CIGS, GeAs, and crystalline silicon.

Film formation of the absorber layer is the lay factor that determines the eventual performance of a PSC. The successful demonstration of high-performance Perovskite solar cells based on Mesoporous oxide scaffolds has proven the importance of the film quality, e.g. surface coverage and roughness, loading percentage, and crystallinity. However, a high temperature annealing process is needed to fabricate the Mesoporous scaffold which may increase the processing complexity and cost, and decrease the compatibility of implementing a high-

performance flexible product, as well as integrating tandem cells into existing technologies; e.g. Si and CIGS modules.

Within a short span, Perovskites have demonstrated that they possess the right mix of properties to offer a solution to our energy needs (Muhammad *et al.*, 2015). Though they evolved out of liquid electrolyte DSSCs, they are now established as a class of their own with extensive focused research pushing the efficiency limit beyond 20%. Exploration of tandem cell configuration with Perovskite based cell as the top cell will push further the achievable efficacy limit. When the issues of stability and the use of lead is addressed, it can go a long way in maturing this technology for commercial application, though in the present legal framework, use of lead is not a problem as CdTe based solar cells has received wide acceptance despite Cd content (Muhammad *et al.*, 2015). The use of lead extensively in lead acid batteries and its content at comparable levels in CIGS and silicon modules to Perovskites suggest that in the short term, the concern may not be pressing, but these technologies are increasingly being phased out and alternatives are explored to minimize the environmental impacts of these heavy metals. Noel *et al.* reported that the replacement of lead with tin in Perovskite solar cell is already under investigation and may offer an environment friendly alternative (Noel *et al.*, 2014).

CONCLUSION AND FUTURE OUTLOOK

Advantages of PSCs which has captured tremendous attention are its; ability to fabricate large-scale transparent or semi-transparent flexible devices, simplicity of processing, easy optimization for structural design and material engineering; projected cost efficiency with superior PCE, longer electron / hole diffusion length, broad spectral absorption and high open circuit voltage, etc. With the amount of research effort underway, guided by the adherence to the issue of best practices, this technology holds great promise to addressing our energy needs in this present-day energy-starved nation, Nigeria. Balancing electron and hole transporting properties of PSCs, engineering its band gap, enhancing its fill factor either by doping or by improving its morphology, replacement of Pb with Sn, use of mixed halogen Perovskites, use of composite of TiO₂ and Sb₂S₃, use of TiO₂ free oxides, use of CNT polymer Nanocomposites, use of layered hybrid Perovskites, employing NiO as the p-type semiconductor, processability to improve HTL and ETL layer designs and the use of several different processing techniques such as Atomic layer deposition (ALD), high pressure pressing, chemical sintering, sol-gel and electro-deposition are known alternative optimization methods that can improve the efficiency and stability of PSCs devices. The solar industry should focus more on the quality and development of its technology.

Additionally, researchers should also focus on improving the competitiveness of solar power against both conventional and other renewable energy sources (Ehsanul *et al.*, 2017). Hopefully, more research efforts will be dedicated toward PV technologies in the near future to enhance their efficiency, stability, manufacturability, and availability, to reduce balance-of-system (BOS) costs and reduce the costs of modules. Just recently, scientists in Hong Kong reported that they have successfully developed Perovskite-silicon tandem solar cells with the world's highest power conversion efficiency of 25.5%.

It is recommended that the poor and incipient status of solar integration in the vastly populated Nigeria should be viewed in a positive light by potential foreign investors as such status is a guarantee that solar power and thermal industry is a firsthand investment opportunity (Ozoegwu *et al.*, 2017). Solar energy resource is available in all parts of the country with an average sunshine hour of 5.535KWh/m²/day. Adekunle *et al.* (2015) carried out an analysis of global solar irradiance over climatic zones in Nigeria for solar energy applications. The

authors found that generally, in all the climatic zones, coefficients of variation of solar radiation were high and mean values were low in July and August. Contour maps showed that high and low values of global solar irradiance and clearness index were observed in the Northern and Southern locations of Nigeria, respectively. The vast expanse of Sahel Savanna in the Northern region of Nigeria provides more than enough land space for this kind of project. According to Tunde *et al.* (2008), a yield of 5 – 20W/m² is estimated for solar power. Assuming an area of about 300Km² and at 10% solar panel efficiency; the power achievable:

$$\begin{aligned} &= (5\text{W/m}^2 \times 30 \times 10^6 \text{ m}^2) \text{ to } (20\text{W/m}^2 \times 30 \times 10^6 \text{ m}^2) \\ &= 150\text{MW} - 600\text{MW}. \end{aligned}$$

This land space accounts for only about 0.03% of Nigeria's total land mass. Multiplying this land space by a factor of 10 gives a geometric feasibility of up to 6000MW of power. In addition, if one million homes in Nigeria own a 1000W solar power system on their rooftops, the cumulative power production will be 7000MW of power which can add notably 45% to the present electricity consumption per capita.

In this review, we discuss the current state of the Art for photovoltaic devices based on Perovskites, highlighting the underlying phenomenon, synthesis, challenges, comparison to other technologies and future outlook. Accordingly, we conclude that despite a few drawbacks, solar energy technology is one of the most promising renewable energy sources to meet the future global energy demand.

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