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Perovskite solar cells: A new class of photovoltaics

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Abstract
In this century, consumption of fossil fuels for energy demand is at peak with more than 80 % consumption for today's world energy related demands. Moreover, they are promoter of global warming and have deteriorating effect on our environment. As they are non-replenishable, their reservoirs will be dried up shortly at this consumption rate. So, there is a dire need of an alternate source of energy, which is renewable, cheaper and clean. There are many potential candiadates such as wind energy, solar power and hydro energy, but solar energy is the one of the most desired one as it is available free of cost, never exhausting and carries energy ~100 times the earth's energy demand. Photovoltaics is one of the technology to harness this abundant source of energy. Perovskites (ABO_3) is one of the class of compounds which utilise this energy by acting as light absorber in perovskite solar cells for ergy generation. Here, we reviewed, the recent progress of perovskite based solar cells with description of basic principles and emphasis on design and strategies to ehnance their efficiency. The motive of this review is provide current summary of recent progress and to some important gudelines for future development in this field.

Keywords: perovskite solar cells, pphotovoltaic, solar power

1. Introduction
High consumption of fossil fuels generating enormous CO_2 which is causing greenhouse effect. So, sustainable energy supply is one of the most sought after issue for our future world. Due to non-renewability of these fossil fuels, they cannot withstand for long at such a consumption rate. Solar power is the best alternative with approximately 3,850,000 exajoules (EJ) of solar power irradiating the Earth each year. If we can able to utilise only 1% of the solar energy, it would be sufficient for energy requirement of the entire human race at current consumption rate of energy. This can remarkably reduce dependence on fossil fuels, lower down pollution and cost. However, up to date, we consume 539 EJ globally per year, approximately 0.014% of the total solar energy reaching the Earth [1]. Development of new compounds which can directly harness this solar energy is the urgent need of the hour. Perovskite Solar Cells (PSCs) is a class of solar cells reaching conversion efficiencies ~21% within a short span of time just behind the crystalline silicone solar cells. They are also called "third generation solar cells" as silicon solar cells are first generation solar cells with highest conversion efficiencies but expensive due to higher manufacturing costs, then comes organic solar cells with low and cost effective production but limited efficiencies, reaching only up to 10-11%. And the third generation solar cells aim at both low cost of fabrication with efficiency increasing day by day.
In PSCs, well defined perovskite structure compounds are used as light absorber for utilizing the abundant solar energy available. Perovskite is a compound with the formula ABX_3 (X = oxygen, halogen). Mostly oxide perovskites studied for their ferroelectric properties. Halide Perovskites under noticed until layered hybrid organic-inorganic perovskites were reported by Mitzi *et al.* to exhibit semiconductor to metal transition on increasing layer thickness [2]. Miyasaka *et al* in 2009, first ever applied perovskite as light sensitizer in solar cells by replacing dye pigment in Dye sensitized solar cells (DSSCs). They achieved efficiencies of 3.1% for X = Br and 3.8% for X = I [3]. Further in 2011, efficiencies are increased up to 6% by Park *et al* [4].But due to their poor stability and lower efficiencies they did not garner much attention. In 2012, efficiencies of these solar cells reached to 10-11% by utilizing solid-state perovskites [56]. Since then hybrid organic-inorganic perovskite solar cells become hot topic of research with focus on material development, enhancement of properties and understanding device principles.
In this review, we here summarize studies on chemical and crystal structure of hybrid perovskites, their synthesis by various routes to understand their optoelectronic properties and effect on efficiencies of different transporting materials. Then we review the methods of fabrication of these devices by various vapor and solution phase deposition and their device operations. We also discuss the role various transporting materials on the efficiencies of these PSCs as they are very essential for better e^--h^+ separation and for future developments in this field.

2. Structure of Hybrid Inorganic-Organic Perovskites
Each unit cell of these halide perovskites have formula ABX_3, where each B cation with six nearest-neighbour anions X and each A cation has twelve nearest neighbours (Figure 1a). Tolerance factor, t ($t = (R_A + R_B)/[\sqrt{2}(R_X + R_B)]$) of the perovskite should be close to 1, to form highly symmetric cubic structure and should be between 0.8 to 1.1, where R_A, R_B, and R_X are the ionic radii of the respective ions.[7] In the

organic-inorganic hybrid perovskites, the B site is usually occupied by a large atom of Pb or Sn, so the A site must be large enough to satisfy the tolerance factor. Otherwise, the cubic structure will be distorted and crystal symmetry is reduced. Currently, mostly organic-inorganic hybrid perovskites generally have MA^+ (methyl ammonium) and/or $CH(NH_2)_2^+$ (formamidinium, or FA) cations at the A site.

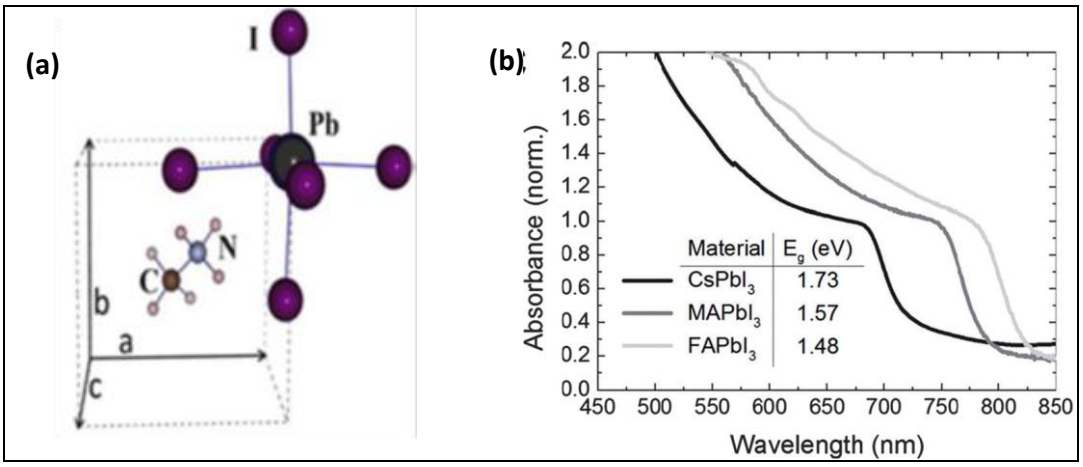

Fig 1: (a) $CH_3NH_3PbI_3$ perovskite structure showing PbI_6 octahedral and larger MA^+ cation occupied in cubo-octahedral site,[8] **(b)** absorption spectra for the $APbI_3$ perovskites formed, where A is either caesium (Cs), methylammonium (MA) or formamidinium (FA) [9].

The organic cation has a marked effect on optical properties of perovskites as it distorts the BX_6 octahedron. As effective radii of Cs^+, MA^+ and FA^+ increases in order, their band gap decreases causing red shift due to expansion of lattice as shown in Figure 1b [9].Thus, $FABX_3$ materials absorbs at longer wavelengths with efficiency as high as 14.2 % being achieved by $FAPbI_3$.

As toxicity of lead is of much concern, so it needed to be replaced by some better candidate in $CH_3NH_3PbI_3$ perovskite. There were several studies on replacement of lead by other cations[10] but Sn is the most viable of all for these hybrid perovskites. Sn based perovskites has stability issue due to their instability in lower oxidation states. Noel *et al.* synthesised a completely lead free perovskite with power conversion efficiency (PCE) of 6% [11], similarly a mixed metal perovskite of lead and tin, $CH_3NH_3Sn_xPb_{1-x}I_3$ was synthesised and extension in solar absorption spectrum was observed [12]. Moreover, doping of Sn in $CH_3NH_3PbI_3$ also affect morphology of thin film with complete homogeneity. In 2016, Sang *et al.* synthesized Formamidinium tin iodide ($FASnI_3$), with stability up to 100 days and observed PCE of 4.8 % with high J_{SC} due to absorption over a wide range spectrum [13]

Electronegativity of X-site elements has a striking effect on band gap E_g of Hybrid perovskites. On substitution of I with Br in $CH_3NH_3PbI_3$ increases it's band gap as conduction band position of Br is at higher position than I, which increases its V_{OC} with decrease in J_{SC} because of lower absorption ability. [2]. Aharon *et al.* observed that hybrid halide perovskites, $CH_3NH_3PbI_nBr_{3-n}$ conduct holes also in addition to acting as a light absorber material. They observed highest efficiency of 8.54% with n = 2 than with n = 3(7.2%) and n = 0(1.69%) [15].Organometal and mixed halide perovskites, were investigated for their electronic properties and formation energies for various mixed halide perovskites by Masconi *et al*. They observed absorption onset at ~800 nm wavelength for $CH_3NH_3PbI_3$ and the $CH_3NH_3PbI_{3-x}Cl_x$ perovskites, and below ~700 nm for $CH_3NH_3PbI_2Br$ perovskites, with formation energies in order Cl < Br < I indicating ease of formation of $CH_3NH_3Pb(I_{1-x}Br_x)_3$ with all intermediate compositions as compared to $CH_3NH_3Pb(I_{1-x}Cl_x)_3$ mixed perovskites by incorporation of Br and Cl in $CH_3NH_3PbI_3$ respectively [16].

3. Fabrication of Organometal Halide Perovskites

There are various fabrication approaches for processing of perovskites focusing on their optical properties and device performance. These techniques include one-step (or) sequential solution deposition, vacuum deposition and vapour assisted solution processing.

In one-step (or) sequential solution deposition, fabrication of $MAPbI_3$ perovskite was processed by spin coating solution of CH_3NH_3I and PbI_2 or spin coating of PbI_2 after deposition of CH_3NH_3I as shown in Figure 2a and 2b. [17, 18, 19]Various solvents (DMF, DMSO, ɤ-butyrolactone or pyrazine) used for precursor solution also influence the device performance.[20] Lee *et al* fabricated solar cells on semi-transparent fluorine-doped tin oxide (FTO)–coated glass by spin coating precursor solution, then dried at 100°C and obtained 10.9% efficiency in single-junction cell [17]. Similarly, in 2013 PCE of15 % were attained by sequential deposition method. They first spin coated solution of PbI_2 in DMF on TiO_2 mesoporous layer and then dipped this film in solution CH_3NH_3I in propanol to $CH_3NH_3PbI_3$ [21].

Although solution processed fabrication is easy, vacuum deposition technique gives better results by giving uniform and crystalline layer of perovskite throughout by removing any possibility of pin holes [22, 23]. In this, precursor salts were evaporated simultaneously from separate sources as shown in Figure 2c under high vacuum leading to form uniform layer of perovskite instantly after evaporation [24, 25, 26]

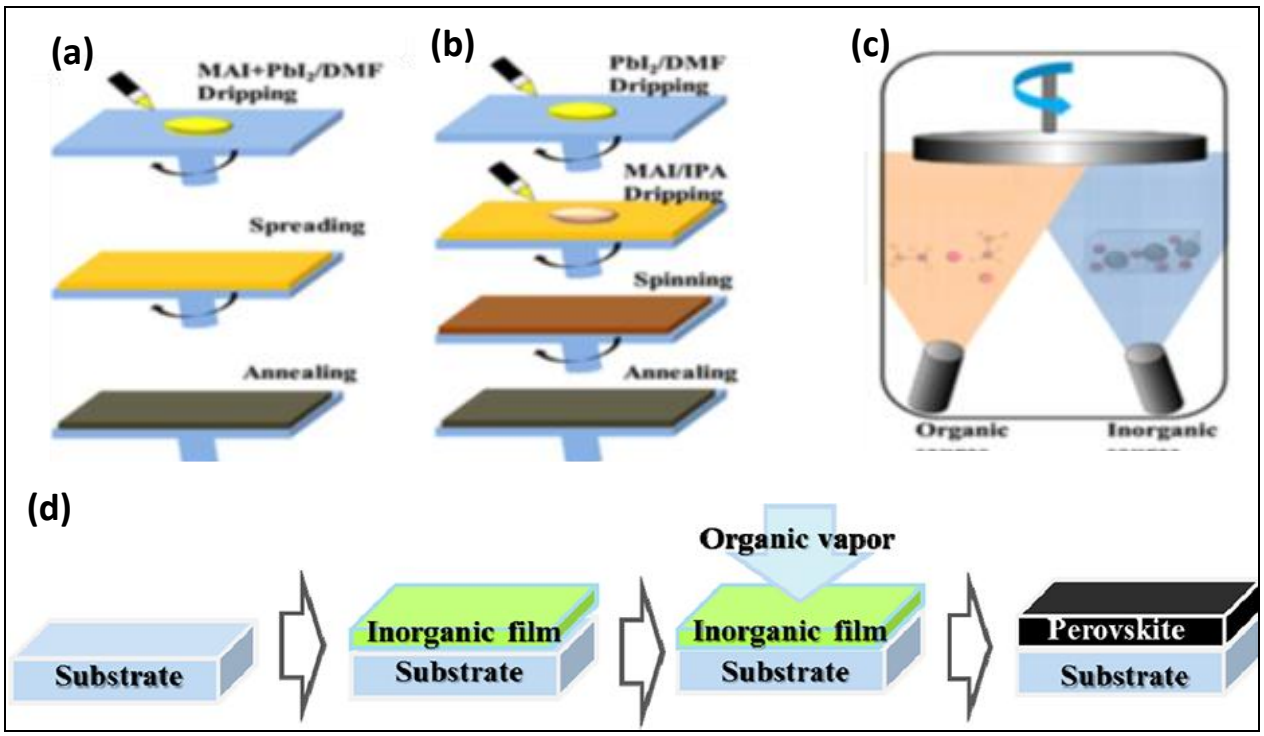

Fig 2: Perovskite material formation by **(a)** precursor solution deposition in One-step, **(b)** sequential solution deposition in two-step, **(c)** vacuum deposition by dual-source and **(d)** Vapour-assisted solution process (VASP).

In solution processed devices, pin holes formation hampers device performance, while in sequential solution processed devices, greater roughness instigates perovskite film to peel off from substrate and high temperature and vacuum cannot withstand in vacuum deposition technique. So, vapor-assisted solution process (VASP) technique (shown in Figure 2d) was introduced to fabricate perovskite thin films. The crucial step is in situ reaction of the as-deposited film of PbI_2 with With day by day increasing efficiencies of perovskite solar cells develops interest of researchers in this field. The first ever PSC was a typical sensitized solar cell using the liquid electrolyte. In contrast to this earlier PSC have a mesoporous metal-oxide layer (e.g., TiO_2 and Al_2O_3) as the scaffold for perovskites active layer [5, 16, 29] (shown in Figure 3a). These CH_3NH_3I to form perovskite film [27].It differs from solution and vacuum deposition by evading from co-deposition of organic and inorganic species and produces films with small surface roughness, well-defined grain structure with sizes ranging up to micro scale, because of thermodynamic stability and kinetic reactivity in the course of in situ reactions.

4. Device Architectures

mesoporous configurations helped reaching high efficiencies when other techniques to develop high quality perovskite films were not well known. The mesoporous configurations show low open circuit voltage (V_{OC}) and weak absorptions at > 700 nm due to limitations in charge-collection efficiency, thickness of these layers is generally greater than 500 nm.[29]

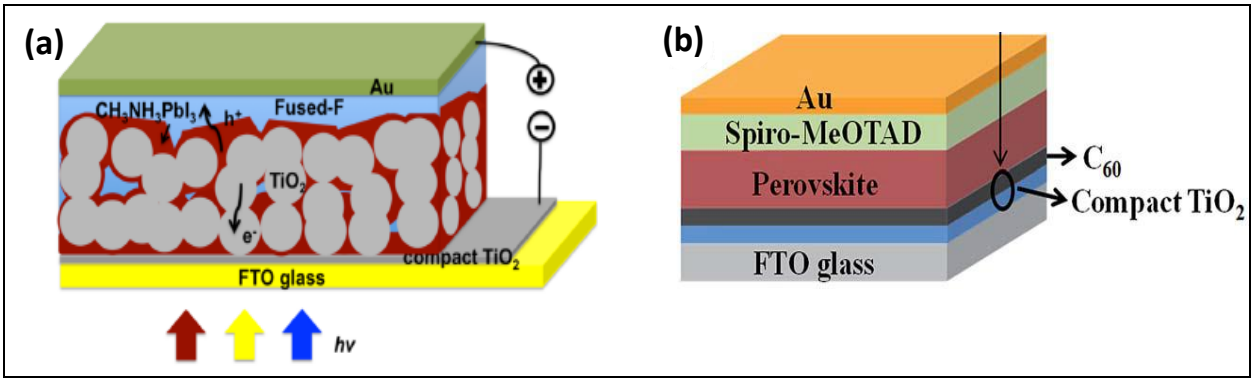

Fig 3: Schematic device architectutre of **(a)** mesoporous (FTO glass/compact TiO2 layer/mesoporous TiO_2 with $CH_3NH_3PbI_3$/HTM/Au) [30] and **(b)** bilayer (FTO/TiO_2/C_{60}/$CH_3NH_3PbI_3$/spiro-MeOTAD/Au) [31] hybrid perovskite solar cells.

Shortly after these mesoporous architectures, comes the bilayer configuration (shown in Figure 3b) with a breakthrough in efficiency reaching 15%. These architectures have capping layer above the mesoporous scaffold layer.[3233]

Such bi-layer structure demonstrated high cell efficiency with very small J–V hysteresis [34]. Mesoporous scaffold layer in these bi-layered structures is generally thinner and this arrangement of mesoporous and capping layer is they key behind less hysteresis and high efficiencies of PSC.

In 2013, Snaith *et al* reported an efficient planar PSC [24] and key finding was that a mesoporous metal-oxide is not necessary for high-performance PSC. Planar PSCs fabricated at low temperatures which is the main advantage of planar PSCs over high temperature processed mesoporous TiO_2 layer. Planar solar cells are sandwich configurations like other OPV devices [35, 36] Morphology of perovskite surface is crucial to avoid shunting, as challenge to develop smooth perovskites film with higher surface coverage.

5. Perovskite Solar Cell Operational Principles

Any of the known device configurations can be employed to construct PSC with good device performance. This predominantly depends on the electron and hole separation with long diffusion lengths. Development of high class hybrid perovskite films is not enough to achieve high efficiencies in PSCs, rather it is equally required to develop or select suitable electron- and hole-transferring materials to achieve high-efficiency PSCs.

5.1 Hole-transfer materials (HTMs)

Hole transfer materials is one of the crucial constituent of PSCs, most commonly used HTM is doped Spiro-MeOTAD (2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenylamine) 9, 9′-spirobifluorene) which is used in generally in all solid state PSCs [37, 38]. Other frequently used HTMs in PSCs are poly-3-hexylthiophene (P3HT), poly-[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)4H-cyclopentab[2,1-b:3,4-b′]dithiophene-2,6-diyl]] (PCPDTBT), (poly-[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]) (PCDTBT) and poly triarylamine (PTAA) [6]. These organic HTMs easily decayed while in solution [39], which limits the long-term stability of PSCs. So, HTM-free solar cells such as $CH_3NH_3PbI_3/TiO_2$ heterojunction solar cells which acts as both light harvester and HTM and prevents unnecessary use of extra HTM were prepared [40]. Similarly, Mei *et al* reported mixed-cation perovskite, $(5\text{-}AVA)_x(MA)_{1-x}PbI_3$ having efficiency of 12.8% with longer lifetime of charge species and stability greater than 1000 hours [41]

5.2 Electron-transfer materials (ETMs)

Materials like TiO_2 (or) ZnO generally used as ETMs in various photovoltaic devices. Effect of various deposition techniques of depositing compact TiO_2 (spin coating, spray pyrolysis, and atomic layer deposition) on device performance was well studied by Han *et al*. [42] In addition to TiO_2 compact layer, ZnO and SnO_2 were also studied for hole-blocking layers or electron-transport layer for high-efficiency devices [19, 43]. In 2014, Zhu and his co-workers reported for the first time a compact layer free PSC, where they used an alkali solution for modification of ITO glass and observed 15.1% of efficiency [44]. Recently Liu *et al* demonstrated that ETL is not essential for high performing devices. They reported an ETL free bilayer PSC using P3HT and Spiro-MeOTAD as HTLs with efficiencies reaching up to 11.6% and 13.5% respectively [45].

5.3 Stablity

Perovskite Solar Cells reached up to a remarkable efficiency of 21.2% within a short span of time. But stability of these organic-inorganic hybrid perovskite is of much concern for commercialization of these solar devices. As perovskite films is very sensitive to moisture in atmosphere, and should be fabricated in controlled humidity conditions [21].[2] Al_2O_3 can be used in solid state PSCs and prevents perovskite layer from humidity in air and provides stability to device. Many researchers studied the effect of moisture, light, temperature and other things on device stability

6. Conclusion

Here we discuss the progress in the field of perovskite based solar cells, especially lead halide perovskite. The increase in their efficiency from ~ 3% to today's 21.2% was achieved by a various efforts made by researchers in this field. PSCs surpass DSSCs and OPVs in terms of efficiency and can obtain V_{OC} greater than 1.1 eV to exploit broader range of solar spectrum. Therefore they are viable contender to replace crystalline silicone solar cells (1.1 eV). As their excellent optoelectronic properties with continuous progress in efficiency is the reason behind thousands of publications every year on this topic. Ease of fabrication, low costs and higher efficiencies is the cause of 'perovskite fever' among researchers. For commercialization of these devices, stability related issues should be addressed. Replacement of Pb by some other metal cation for environment friendly perovskite solar cells without affecting their efficiency is desirable.

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