



## Full Length Review Article

### PEROVSKITE SOLAR CELLS: A QUANTUM LEAP IN SOLAR RESEARCH

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#### ABSTRACT

Organic-inorganic metal halide perovskites are recently proved to be suitable candidates for application in solar cells. Devices made of perovskite show efficiencies from 3.8% in 2009 to National Renewable Energy Laboratory (NREL) certified efficiency of 22.1% in 2016 making this the fastest-advancing solar technology to date.  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  are currently the front-and-center materials for high efficiency perovskite solar cell. They are used as absorber materials, in combination with electron (electron transport layer (ETL)- $\text{TiO}_2$ , ZnO etc.) and hole (hole transport material (HTM) - spiro-OMeTad, P3HT etc.) selective contacts. The structural stability of perovskite solar cells depends on organic cation  $\text{CH}_3\text{NH}_3$ , while the electronic properties are largely influenced by metal and halide hybridized orbitals. Different device architectures are possible due to flexibility and simplicity of perovskite fabrication methods. In this review, the current status of perovskite materials is highlighted along with mention on the issues and future challenges.

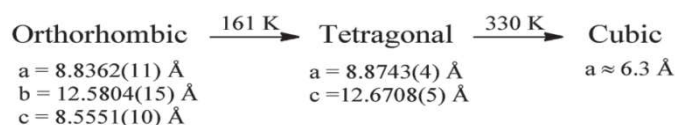
#### INTRODUCTION

Perovskite solar cell technology is often introduced as breath of fresh air in the emerging photovoltaic technology landscape (Photovoltaics, 2015). It was selected as one of the biggest scientific breakthroughs of 2013. Perovskites (PSC) are an old class of materials, first discovered by Gustav Rose in 1839 & named after mineralogist Lew A. Perovski (Henry Snaith and Lukas Schmidt-Mende, 2014). At the first instance, the 'perovskite' was used as new kind of dye for dye-sensitized solar cell (DSSC) application to boost its efficiency but the drawback was perovskite dissolved in liquid electrolyte used in DSSC. Thus different device architectures were attempted using perovskite (Conings *et al.*, 2014).

##### Crystal structure

The  $\text{ABX}_3$  crystal structure of the absorber material is referred to as perovskite structure, where the A cations are organic (typically  $\text{CH}_3\text{NH}_3^+$ ,  $\text{C}_2\text{H}_5\text{NH}_3^+$ ) the metal cations (B) are typically divalent metal ions such as  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cu}^{2+}$  while and X anions are halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ).  $\text{ABX}_3$  contains octahedral  $\text{BX}_6$  and cubo-octahedral  $\text{AX}_{12}$  unit. As shown in Figure 1 an ideal cubic-symmetry of perovskite crystal structure contains B cation surrounded by an octahedron of anions

(6-fold coordination) and the A cation in 12-fold cuboctahedral coordination with X anions. Perovskite can exist as single crystal or polycrystalline material (Park, 2016). Tolerance factor 't' determines crystal stability where,  $t = (r_A + r_X) / \{\sqrt{2}(r_B + r_X)\}$ ,  $r_A$ ,  $r_B$ , and  $r_X$  are the ionic radii & octahedral factor  $\mu$  which is the ratio  $r_B/r_X$  helps in structure determination of perovskite. Typical values of t and  $\mu$  are  $0.81 < t < 1.11$  and  $0.44 < \mu < 0.90$  for halide perovskites (X = F, Cl, Br, and I). Value of tolerance factor in range of 0.89 to 1.0 dictates cubic structure of perovskite crystal, while lower values stabilize less symmetric tetragonal and orthorhombic structures. Phase transition occurs as a function of temperature during the nucleation/evaporation processes which are the main steps in perovskite crystal growth as shown below (Martin, 2014).



##### Progress in perovskite solar cells

The progress in efficiency over time for various related technologies is shown in Figure 2. The first incorporation of perovskite materials into solar cell was made by Miyasaka *et al.* in 2009. This was based on dye sensitized solar cell architecture and it generated only 3.8% power conversion

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efficiency (PCE) with a thin layer of perovskite on mesoporous  $\text{TiO}_2$  as electron-collector. Perovskite was regarded as quantum dots (QD) deposited on  $\text{TiO}_2$ . Moreover, the cell was stable only for few minutes with the liquid corrosive electrolyte (Kojima *et al.*, 2009). Using the same dye-sensitized concept, Park *et al.* achieved a PCE of 6.5% in a later work (Jeong-Hyeok *et al.*, 2011). Snaith *et al.* proposed a non-sensitization type perovskite solar cell in which the mixed halide perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ -coated  $\text{Al}_2\text{O}_3$  film demonstrated PCE of 10.9% (10).

First example of solid-state dye-sensitized solar cells (ss-DSSCs) emerged in 1998, by using a solid hole-transporting material (HTM) spiro-OMeTAD instead of the conventional liquid redox electrolyte. In 2012, the real breakthrough in ss-DSSCs came when Gratzel *et al.* and Snaith *et al.* independently employed  $\text{CH}_3\text{NH}_3\text{PbI}_3$  ( $\text{MAPbI}_3$ ) and  $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$  ( $\text{MAPbI}_2\text{Cl}$ ) perovskite nanocrystals as light harvesters using submicron thick mesoporous  $\text{TiO}_2$  film and spiro-MeOTAD as an electron- and hole-transporting layer. Under AM1.5G illumination PCEs of 9.7% and 7.6% were achieved using devices with excellent long term stability (Shaowei Shi *et al.*, 2015). Moreover, by replacing the n-type mesoporous  $\text{TiO}_2$  with insulating mesoporous  $\text{Al}_2\text{O}_3$ , evolution of the ss-DSSC, which is termed as the meso-superstructured solar cell (MSSC) was developed by Snaith *et al.* which showed a PCE of 10.9% (10). Etgar and coworkers also fabricated a HTM free solar cell (FTO/bl- $\text{TiO}_2$ /mp- $\text{TiO}_2$ /MAPbI<sub>3</sub>/Au) and achieved a PCE of 5.5%. The above mentioned study proved that organometal halide perovskite can not only act as an absorber (dye) but also as an ambipolar charge transporter, which can transfer both electrons and holes (11). Mitzi & coworkers used a sequential deposition process for perovskite solar cell fabrication which showed a remarkable PCE of 15% in a FTO/bl- $\text{TiO}_2$ /mp- $\text{TiO}_2$ /MAPbI<sub>3</sub>/spiro-OMeTAD/Au-based device (Shaowei Shi *et al.*, 2015).

Subsequently, Snaith and coworkers deposited a high quality  $\text{MAPbI}_{3-x}\text{Cl}_x$  film via dual source vacuum deposition in a planar heterojunction perovskite solar cell and achieved a PCE of 15.4%. (11). Seok and coworkers also obtained a PCE of 12% in a FTO/bl- $\text{TiO}_2$ /mp- $\text{TiO}_2$ /MAPbI<sub>3</sub>/PTAA/Au-based device by replacing the conventional spiro-OMeTAD HTM with poly (triarylamine) (PTAA) (Shaowei Shi *et al.*, 2015). In 2013 both the planar and sensitized architectures saw a number of developments. By using a two-step solution deposition method, Burschka *et al.* fabricated a cell exceeding 15% efficiency and at a similar time Liu *et al.* fabricated planar solar cells by thermal evaporation, also achieving more than 15% efficiency. A variety of new deposition techniques with higher efficiencies were reported in 2014. For example planar thin-film architecture by Yang Yang produced a reverse-scan efficiency of 19.3%. Thus different ways to improve the efficiency of perovskite cells such as reducing the trap density, improving interface of hole transporter or electron transporter with perovskite, and using better deposition techniques were reported. In November 2014, a device by researchers from Korea University of science and technology (KRICT) achieved a record with the NREL certification of a non-stabilized efficiency of 20.1%. In December 2015, a new record efficiency of 21.0% was achieved by researchers at EPFL and in March 2016, researchers from KRICT and Ulsan National Institute of Science & Technology (UNIST) reported the

highest certified efficiency of 22.1% using single-junction perovskite solar cell (Perovskite solar cell-Wikipedia).

## Device architecture

Morphology and crystal optimization, ETL/HTM (electron/hole transporting material) adjustment and interface/band-gap engineering are all opening up a new direction for developing highly efficient perovskite solar cell with different device architecture having low cost and better stability (Shaowei Shi *et al.*, 2015). The structural evolution of perovskite solar cells are shown in Fig 3. The main architectures discussed include mesostructured, meso-superstructured, pillar, planar, pin, pn device structures (Nam-GyuPark, 2015).

In the sensitization concept shown in Fig. 3a, perovskite was used as a sensitizer in Dye-sensitized solar cells in which molecular dye was replaced by perovskite. HTM should be fully infiltrated inside the mesoporous oxide layer to induce hetero-junction. In addition, oxide layers (mesoporous  $\text{TiO}_2$  layer) with electron accepting properties are required to separate the photo-excited electrons in perovskite. But femtosecond transient absorption spectroscopic study performed on cell proved that perovskite solar cells may work even without an electron injecting layer (mesoporous  $\text{TiO}_2$  layer). So a slightly modified meso-superstructured architecture as shown in Fig. 3b was used in which the  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  thin layer was coated on mesoporous  $\text{Al}_2\text{O}_3$  film which reported a PCE of 10.9%. The  $\text{Al}_2\text{O}_3$  served as a scaffold layer because electron injection from perovskite to  $\text{Al}_2\text{O}_3$  was not allowed. This result implies that electron transfer can occur within the perovskite layer and sensitization concept is not necessary for perovskite solar cell design. A pillared architecture was also tried where pores of a mesoporous  $\text{TiO}_2$  film (pillars) were filled with perovskite instead of a surface coating and a thin capping layer (over layer) was formed after infiltration with the perovskite as shown in Fig. 3c. The pillared device fabricated using  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and HTM polytriarylamine PTAA reported a PCE of 12%. A higher PCE of 15% was achieved from the pillared structure with a two-step coating procedure. In this method, the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  layer was prepared by dipping the  $\text{PbI}_2$  layer formed in mesoporous  $\text{TiO}_2$  film into a diluted  $\text{CH}_3\text{NH}_3\text{I}$  solution while the perovskite layer was in contact with spiro-MeOTAD (Nam-GyuPark, 2015).

A planar pin device architecture which is a simple structure consist of perovskite film as intrinsic layer, n-type thin  $\text{TiO}_2$  film, and p-type HTM film can be fabricated as electron accepting oxide layer is not important for design as perovskite layer can itself transport electrons. Using this planar pin concept, a 300 nm-thick  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  film was prepared by co-evaporation of  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbCl}_2$ , which exhibited a PCE of 15%. A pn junction structure is also developed in addition to the sensitization and planar pin junction concepts as shown in fig 4b. A pn junction structure with FTO/ $\text{TiO}_2$ / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /Au configuration proved that  $\text{CH}_3\text{NH}_3\text{PbI}_3$  exhibit ambipolar characteristics, transporting both electrons and holes thus act as both p-type and n-type semiconductor. With a 500 nm-thick nanosheet  $\text{TiO}_2$  film as the n-type layer PCE of 5.5% was shown but with a thinner nanoparticle  $\text{TiO}_2$  film PCE improved to 8% (Nam-GyuPark, 2015).

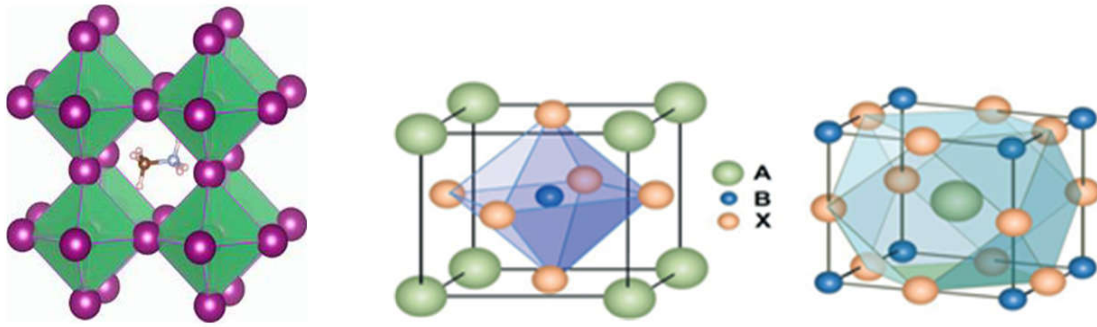


Fig. 1. Crystal structure of  $\text{CH}_3\text{NH}_3\text{PbX}_3$  perovskites ( $\text{X}=\text{I}, \text{Br}$  and/or  $\text{Cl}$ ). The methylammonium cation ( $\text{CH}_3\text{NH}_3^+$ ) is surrounded by  $\text{PbX}_6$  octahedra (4)

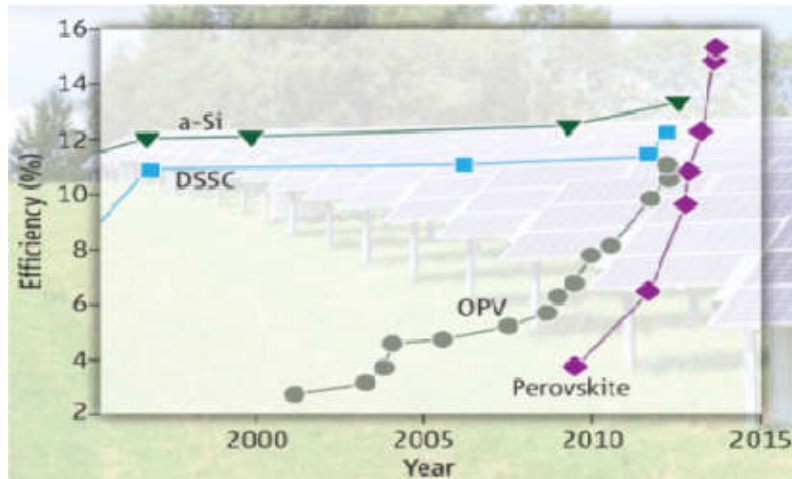


Fig. 2. The progress in efficiency over time for various related technologies. Perovskites have overtaken not only established technologies like a-Si (amorphous Silicon) and DSSC technology (which has undergone over 30 years of research) but also other emerging technologies such as organic PV (OPV) (7)

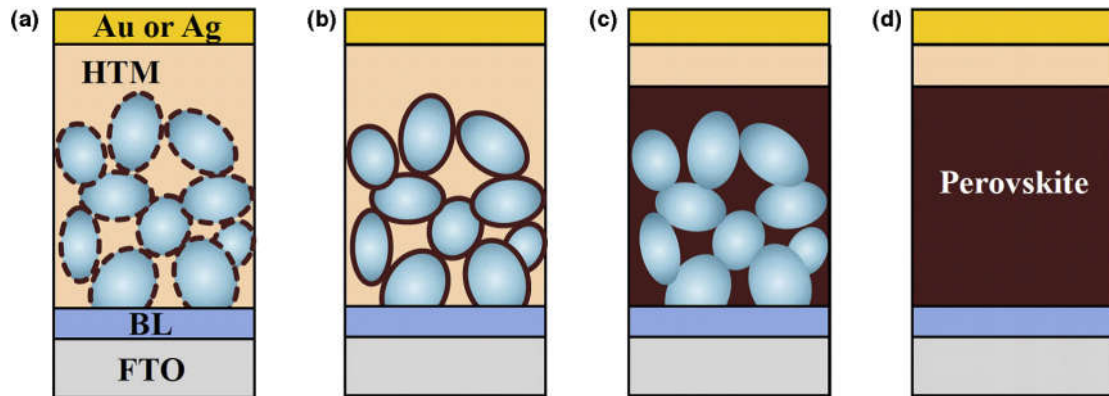


Fig. 3. Structural evolution of perovskite solar cells: (a) sensitization concept with surface adsorption of nano dot perovskite (Mesostructured), (b) meso-superstructure concept with non-injecting scaffold layer, (c) pillared structure with a nano oxide building block, and (d) planar pin heterojunction concept. Spheres represent  $\text{TiO}_2$  in (a) and (c) and  $\text{Al}_2\text{O}_3$  in (b) (10)

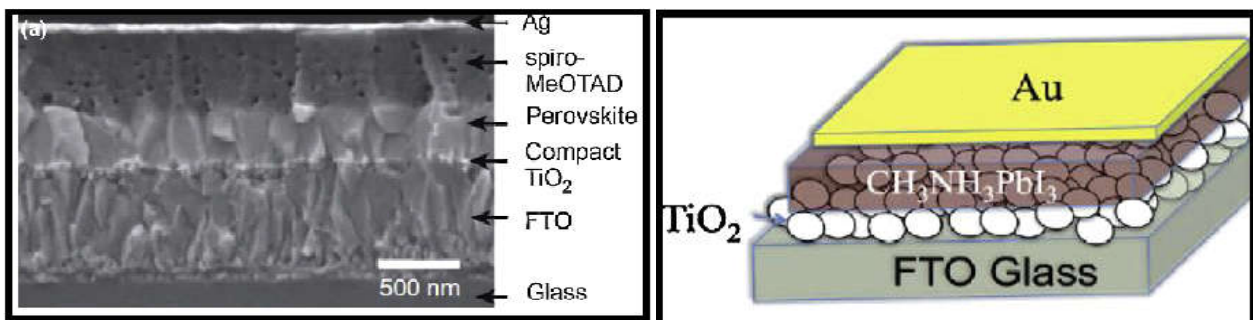


Fig. 4. (a) Cross-sectional SEM image of planar pin junction structure with vapor-deposited  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ . (b) Schematic illustration of pn junction structure with p-type  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and n-type  $\text{TiO}_2$

## Device operation

With an absorption onset of 800 nm and bandgap energy of 1.5 eV,  $\text{CH}_3\text{NH}_3\text{PbX}_3$  is a semiconducting pigment which exhibits good light absorption over the whole range of visible solar emission spectrum. The Wannier-Mott excitons produced by light absorption have a weak binding energy of range 20-50 meV and dissociate very rapidly into free carriers (electrons and holes) at room temperature.

device operation are 4) recombination of photo generated species 5) back charge transfer at the interface of  $\text{TiO}_2$  with the perovskite 6) back charge transfer at the interfaces of HTM with the perovskite 7) charge transfer between  $\text{TiO}_2$  and the HTM as shown in Figure 5a. The undesirable processes 4 to 7 can happen when nanoparticles or voids are present due to absence of perovskite film coating in some areas. So processes 1 to 3 must occur at faster rate when compared to processes 4 to 7 for good device performance (Refer Fig. 5a).

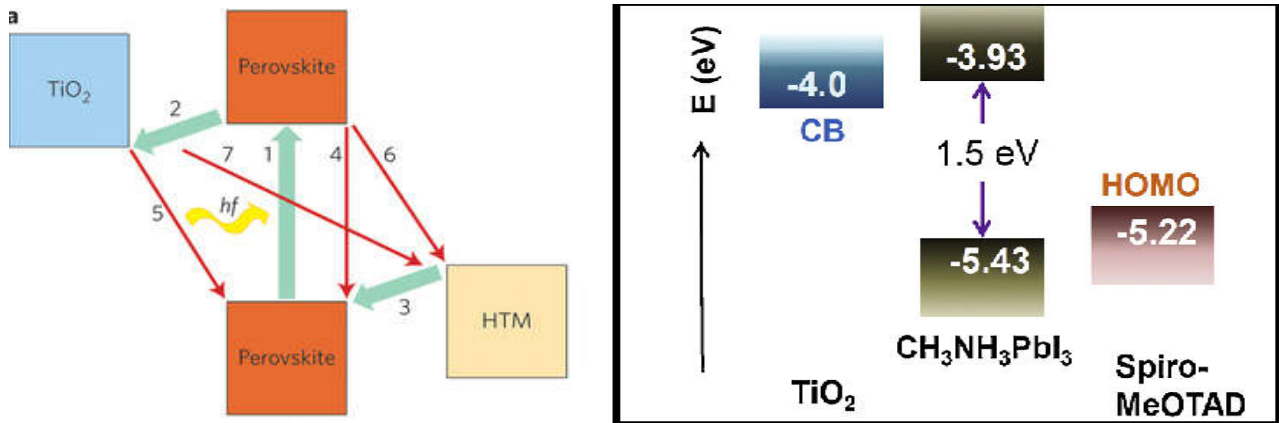


Fig. 5. (a) Desirable process of electron transfer (b) Schematic energy level diagram of  $\text{TiO}_2$ ,  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and spiro-MeOTAD

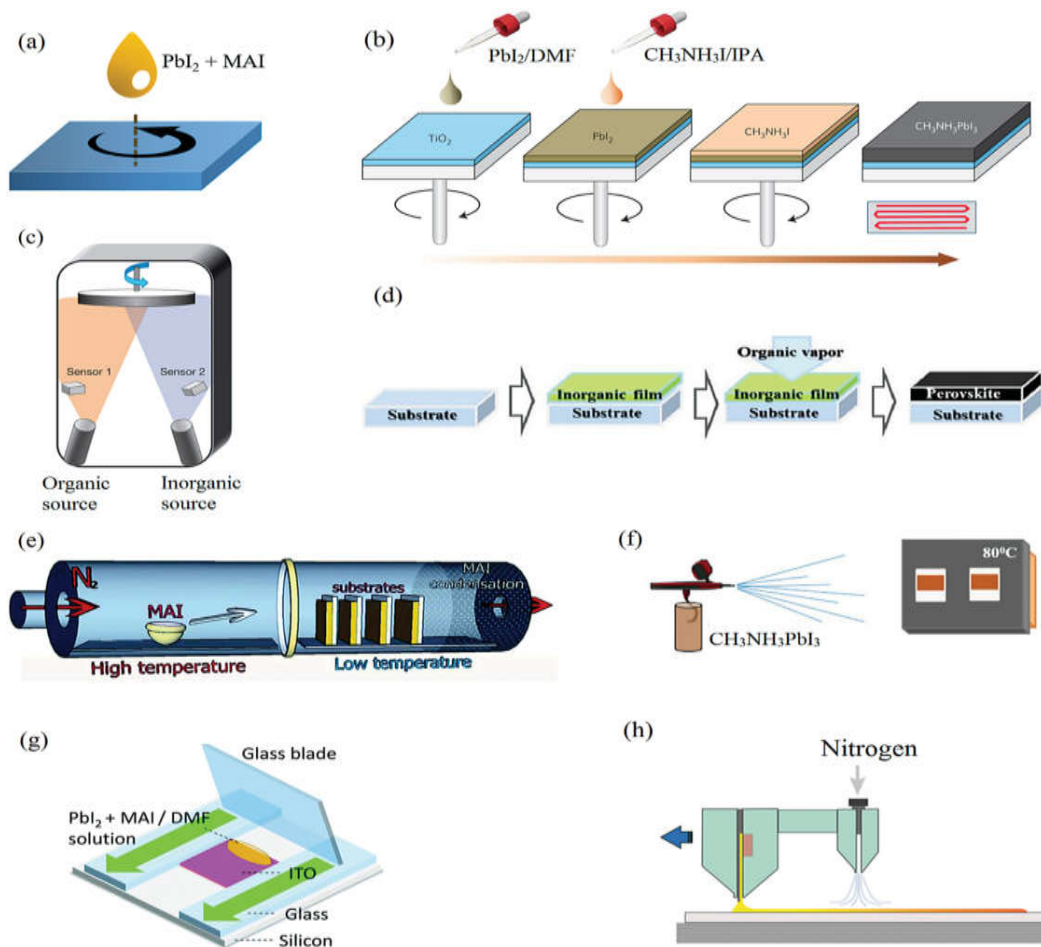


Fig. 6. The different film deposition techniques

The electrons and holes produced in this material exhibit a small effective mass resulting in high charge carrier mobility (Michael Grätzel, 2012). The device operation involves mainly three steps 1) photoexcitation in perovskite 2) transfer of electrons to titania 3) electron transfer from the HTM to the perovskite. But some process which are undesirable during

The rate of reactions that occur can be obtained by time-resolved transient techniques (Martin, 2014). The HOMO-LUMO levels of titania, perovskite and spiro-MeOTAD is also shown Fig. 5b which are favorable for charge transfer processes.

## Significant properties

Many extraordinary properties of metal halide perovskites are now being unraveled as a result of recent intense research efforts. High optical absorption, tunable band gap, lasing properties, high dielectric constant, high electron and hole mobility's, long diffusion length, low exciton binding energy, ambipolar behavior, high open circuit voltage (typical value 1.1V), low surface recombination velocity etc which makes them suitable for photovoltaic applications but hysteresis, use of toxic lead, low reproducibility & stability are the some of the major issues. Perovskite has a sharp photon absorption edge and an absorption coefficient as high as  $10^5 \text{cm}^{-1}$ , both of which contribute to effective utilization of solar radiation. Band gap of  $\text{CH}_3\text{NH}_3\text{PbX}_3$  is of order of 1.5eV which is tunable by changing the halide ion (Sarah Brittan *et al.*, 2015). Optical band gap and absorption coefficient of  $\text{CH}_3\text{NH}_3\text{PbX}_3$  which are suitable for photovoltaic applications can be obtained from UV- visible spectrophotometer studies. Band gap can be calculated using either Kubelka-Munk relation or Tauc's relation as given below.

- Kubelka-Munk relation:  $\alpha/S = (1-R^2)/2R$  where  $\alpha$  is the absorption coefficient, S is the scattering coefficient and R is the percentage of reflected light
- Tauc's relation:  $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$  where h is Planck's constant, n is the photon's frequency,  $\alpha$  is the absorption coefficient,  $E_g$  is the band gap, and A is a proportionality constant. For perovskite  $n = 1/2$  as it is a direct bandgap semiconductor.

Photothermal deflection spectroscopy (PDS) is also used to measure the optical absorption of the perovskite films near the band edge with high sensitivity & for  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , we observe sharp band edges with an exponential decay of the density of states at the band edge, known as the Urbach tail (Wei Zhang *et al.*, 2015).

- Urbach rule:  $\alpha = \alpha_0 \exp [(h\nu - E_0)/\Delta E]$  where  $\alpha_0$  &  $E_0$  are material dependent constants and  $\Delta E$  is called Urbach width is also a material dependent constant.

$\text{CH}_3\text{NH}_3\text{PbI}_3$  films also exhibit lasing at low optical pumping thresholds which indicates high level of crystalline nature and small concentration of bulk impurities or defects in the perovskite material (Michael Grätzel, 2014). The X-ray diffraction pattern of powder  $\text{CH}_3\text{NH}_3\text{PbI}_3$  helps to get lattice parameters a, b and c of tetragonal crystal phase (Shaowei Shi *et al.*, 2015). High dielectric constant of perovskite material suggests a very strong polarization of the perovskite lattice in response to the electric field (photovoltage, which is generated under illumination). Perovskite structure produces high charge carrier mobility, longer diffusion lengths (100-1000nm) and life time (100ns) allowing photo-generated electron-hole pairs (EHPs) to travel long distance without any energy loss. High electron- hole mobility can be obtained from Density functional theory (DFT) and using one-dimensional diffusion model diffusion coefficient D can be obtained.

- Diffusion length:  $L_n = \text{Sqrt}(D_e \times \tau_R)$  where diffusion length  $D_e \sim 10^{-6} \text{cm}^2/\text{sec}$  and  $\tau_R$  relaxation time. Longer lengths of electron and hole diffusion were obtained for  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  when compared to  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .

In  $\text{CH}_3\text{NH}_3\text{PbI}_3$  the incoming photons generate electron-hole pair that belongs to Mott-Wannier exciton with low binding energies of order of 20 to 50meV (Pablo *et al.*, 2014). Perovskite exhibit ambipolar behavior (balanced electron and hole transporting) eliminating the need for electron and hole transport layer which was proved by transient spectroscopic studies. The value of open circuit voltage ( $V_{OC}$ ) obtained for perovskite is high when compared to other photovoltaic (PV) technology. A graph between  $V_{OC}$  and  $E_g$  shows that perovskite solar cell attains fourth position in PV technology.

- $V_{OC}$  formula:  $V_{OC} = V_{OC\text{-ideal}} + (kT/q) \ln(\eta_{\text{ext}})$  where k is the Boltzmann constant, T temperature, q charge,  $\eta_{\text{ext}}$  is the external quantum efficiency.

External quantum efficiency (EQE) is the measure of fraction of photons incident on the solar cell that create electron-hole pairs in the absorber and  $V_{OC\text{-ideal}}$ , is reached only  $\eta_{\text{ext}}$  measured at  $V_{OC}$  is 100% (10). Due to combined influence of charge, spin and structural properties, perovskite also exhibit exciting properties like piezoelectric, thermoelectric, magneto-resistance, ferro-electricity, superconductivity etc. They also have superior structural defect tolerance and shallow point defects, benign grain boundary effects which all support the stability of crystal. Perovskite also has a charge accumulation property that was identified by impedance measurement (Shaowei Shi *et al.*, 2015).

## Perovskite film deposition techniques

Ease of fabrication and variety of methods for fabrication, abundant and low cost of material constituents is an important characteristic of perovskite material. As shown in Figure 6, perovskite films can be prepared by chemical and physical deposition techniques as described below (Chen *et al.*, 2016).

- **One-step solution processing method-** One-step solution processing is the simplest among all the deposition methods. As shown in figure 6a, in this method precursor solution of a mixture of  $\text{PbX}_2$  and  $\text{CH}_3\text{NH}_3\text{X}$  (X = Cl, Br, I) in a polar solvent such as  $\gamma$ -butyrolactone (GBL), N, N -dimethylformamide (DMF) or dimethylsulfoxide (DMSO) is spin coated on top of substrate.
- **Two-step spin-coating procedure-** In this method,  $\text{PbX}_2$  is firstly spin-coated onto the substrate and subsequently transformed into  $\text{CH}_3\text{NH}_3\text{PbI}_3$  by dipping or spin-coating of a solution of  $\text{CH}_3\text{NH}_3\text{I}$  in 2-propanol (IPA) above the first layer (Fig. 6 b).
- **Dual-source thermal evaporation system-** The Snaith group first employed this fabrication technique and obtained extremely dense films with crystal size of hundreds of nanometers and PCE exceeding 15%. As shown in Fig. 6c, a dual source evaporation system (i.e., separate  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbCl}_2$  sources) is used to deposit  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  film.
- **Vapor-assisted solution process (VASP) -** A novel low-temperature method by combining solution process and vacuum deposition method was applied to fabricate perovskite films. The key step was in-situ reaction of  $\text{PbI}_2$  film with  $\text{CH}_3\text{NH}_3\text{I}$  vapor, resulting in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films. These devices have planar architecture with full surface coverage and grain size up to micro scale (Fig. 6d) and also exhibited an impressive PCE of 12.1%.

- **Hybrid chemical vapor deposition based perovskite synthesis-** Chemical vapor deposition (CVD) is a method to synthesize perovskite films, where thermal evaporation of  $\text{PbCl}_2$  is done first, followed by vapor phase deposition of MAI as shown in Fig. 6e. This method is used in large scale in industries to deposit perovskite films as it is a cost effective technique.
- **Spray deposition technique-** Spray-coating is another viable processing technique to fabricate large-area, low-cost perovskite films. Figure 6f shows the schematic illustration of spray process. A mixture of  $\text{PbX}_2$  and  $\text{CH}_3\text{NH}_3\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) in a polar solvent such as  $\gamma$ -butyrolactone (GBL), N, N -dimethylformamide (DMF) or dimethylsulfoxide (DMSO) is sprayed from a nozzle onto a hot substrate, followed by swift evaporation of solvent, thereby creating the perovskite crystals. A flexible perovskite solar cell with a PCE of 8.1% was fabricated by Das *et al.* using ultrasonic spray-coating of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  on polyethylene terephthalate (PET) substrate.
- **Doctor-blading-** For the blade-coating process, the precursor solution was first dropped onto substrate, followed by a linear swipe using a glass blade with the relatively high speed (Fig. 6g).
- **Slot-die coating with a gas-quenching process-**  $\text{PbI}_2$  solution was first coated on substrate from one slot-die head and coated film was dried quickly using high-pressure nitrogen from another head (Fig. 6h). Using same procedure MAI solution was also coated sequentially and finally we get perovskite film. Under ambient conditions a PCE of 11.96% was achieved for slot-die devices (Chen *et al.*, 2016).

### Future direction and challenges

As the power of perovskite material for photovoltaic applications becoming quite clear, it is very important to discuss the future improvement required in this technology for widespread use of PSC. Some of them are mentioned below.

- **Stability-** It is found that  $\text{CH}_3\text{NH}_3\text{PbI}_3$  degrades in humid conditions and forms  $\text{PbI}_2$  at higher temperatures due to the loss of  $\text{CH}_3\text{NH}_3\text{I}$ . Also fabrication requires nitrogen atmosphere where humidity is low. Above facts may limit its outdoor applications (Michael Grätzel, 2014). Long-term light-soaking tests (1,000 h in full sunlight) as well as damp heat tests (1,000 h at 85% humidity and 85 °C) help to check the stability of fabricated devices. Future research must be focused to improve stability of PSC.
- **Toxicity-** Lead compounds are very toxic and harmful to the environment. When  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is kept in contact with water (polar solvents) it may produce  $\text{PbI}_2$ , a moderately water-soluble carcinogen whose use is banned in many countries. So identification of some non-toxic materials or pigments to replace lead from perovskite presents a scope for further research. Tin analogues  $\text{CH}_3\text{NH}_3\text{SnI}_3$  and  $\text{CsSnI}_3$  show promise, but their extreme sensitivity to oxygen limits its application (Michael Grätzel, 2014).
- **Better materials for transport layers and contacts-** To improve the efficiency and reducing cost of PSC, identification of better materials for charge transport layers and appropriate contacts which extract photo generated charges efficiently are important. For

transport layers the main features are 1) band alignment must be suitable for flow of one carrier and blocks the other, low lying HOMO for HTM and suitable LUMO level for ETL 2) charge mobility (electron and hole mobility must be high) that is comparable with that of the perovskite 3) Good contact with the perovskite layer which is achieved by conformal deposition technique 4) chemical stability of layers (HTM & ETL) during reaction with perovskite 5) Ease of synthesis, low cost, transparency to allow absorption of light (Michael Grätzel, 2014). But commonly used HTM spiro-oMeTAD suffers drawbacks like high cost, synthesis complexity, more hole mobility etc result in exploration for alternatives (Tze Chien Sum and Nripan Mathews, 2014). Similarly instead of conventionally used anode and cathode better materials can be used.

- **Multi-junction photovoltaic-** Multi-junction photovoltaic (tandem solar cell) is an arrangement obtained by stacking solar cells with decreasing band gaps and used widely to improve efficiency by minimizing the losses. When photons are incident on tandem solar cells, high energy photons are converted by high-band-gap solar cells on top while low energy photons are converted by the lower-band-gap solar cells on the bottom. Application of PSC in this tandem solar cells require further studies as multi-junction photovoltaic requires lattice mismatch between different layers and use of inexpensive techniques for fabrication instead of expensive epitaxial growth processes used presently (Sarah Brittman *et al.*, 2015). Higher efficiency is still possible through structural modification, along with band gap tuning (Michael Grätzel, 2014).
- **Achieving high Voc in perovskites with larger band gaps-** Using higher band gap perovskites like  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  (band gap ( $E_g$ ) ~2.2 eV), the highest  $V_{oc}$  obtained was only 1.51V which yields a loss-in-potential of 0.7 V compared to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (band gap ( $E_g$ ) ~1.5 eV) which loses only 0.5 V. Loss in potential is the difference between potential of lowest energy absorbed photon that generates charge and open circuit potential under full sunlight. For low band gap iodide perovskite loss in potential is smaller than bromide perovskite for achieving its maximum efficiency (Sarah Brittman *et al.*, 2015). In organo metal halide perovskite high  $V_{oc}$  is related to high internal photoluminescence quantum efficiency. So  $V_{oc}$  can be improved by controlling luminescent property of perovskite and there by getting higher power conversion efficiency in perovskites with larger band gaps (Nam-GyuPark, 2015).

### Conclusion and outlook

Due to large extent of electrical and optical properties, hybrid perovskites have shown tremendous potential for application in photovoltaic research. The devices fabricated using perovskite exhibit high efficiency and properties that compete favorably with other technologies. Although many details of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  are available, research activities are still continuing to explore further possibilities. By improving the way of synthesis, structure, understanding basic properties of perovskite, material scientists are taking lot of efforts to fulfill the challenges of cost, efficiency, and stability which are considered as “golden triangle” in solar technology

(Henry, 2013). To realize the full potential of hybrid perovskites, exciting research is going on around every corner of world (Sarah Brittman, 2015).

## REFERENCES

- Chen, Y., M. He, J. Peng, Y. Sun, and Z. Liang, 2016. "Structure and Growth Control of Organic-Inorganic Halide Perovskites for Optoelectronics: From Polycrystalline Films to Single Crystals," *Adv. Sci.*
- Conings, B., L. Baeten, T. Jacobs, R. Dera, J. D'Haen, J. Manca, and H.G. Boyen, 2014. "An easy-to-fabricate low-temperature TiO<sub>2</sub> electron collection layer for high efficiency planar heterojunction perovskite solar cells" *APL Mater.* 2, 081505.
- Henry J. Snaith, 2013. "Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells" *J. Phys. Chem. Lett.*, vol4, pp. 3623-3630
- Henry Snaith and Lukas Schmidt-Mende 2014. "Preface: Special Topic on Perovskite Solar Cells" *APL MATERIALS* 2, 081201.
- <http://www.idtechex.com/research/reports/perovskite>
- Jeong-Hyeok, I.M., Chang-Ryul Lee, Jin-Wook Lee, Sang-Won Park and Nam-Gyu Park, 2011. "6.5% efficient perovskite quantum-dot-sensitized solar cell" *Nanoscale*, 3 pp.4088-4093.
- Kojima, A., Teshima, K., Shirai, Y., Miyasaka, T. 2009 "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells" *J. Am. Chem. Soc.*, 131, pp.6050-6051.
- Martin A. Green, 2014. Anita Ho-Baillie and Henry J. Snaith "The emergence of perovskite solar cells" *Nature Photonics*, Vol 8, July.
- Michael Grätzel, 2014. "The light and shade of perovskite solar cells" *Nature materials*, Vol 13, pp.832-848, September.
- Nam-GyuPark, 2015. "Perovskite solar cells: an emerging photovoltaic technology" *MaterialsToday*, Volume18,no-2, March.
- Pablo P. Boix, Kazuteru Nonomura, Nripan Mathews and Subodh G. Mhaisalkar, 2014. "Current progress and future perspectives for organic/inorganic perovskite solar cells" *Materials Today* vol 17, No 1, January/February.
- Park, N. G. 2016. "Crystal Growth Engineering for High Efficiency Perovskite Solar Cells," *CrystEngComm*, vol. 3.
- Perovskite solar cell- Wikipedia.org
- Perovskite-The next PV revolution-Solar choice
- Photovoltaics-2015-2025-technologies-markets-players-000442.asp
- Sarah Brittman, Gede Widia Pratama Adhyaksa, and Erik Christian Garnett, 2015. "The expanding world of hybrid perovskites: materials properties and emerging applications" *MRS Communications*.
- Shaowei Shi, A.B., Yongfang Li, C., Xiaoyu Li and Haiqiao Wang, 2015. "Advancements in all-solid-state hybrid solar cells based on organometal halide perovskites" *Materials-horizons*.
- Tze Chien Sum and Nripan Mathews, 2014. "Advancements in perovskite solar cells: photophysics behind the photovoltaics," *Energy Environ. Sci.*, vol7, pp. 2518-2534
- Wei Zhang, Michael Saliba, David T. Moore, Sandeep K. Pathak, Maximilian T. Hörl, Antonietti, Thomas Stergiopoulos, Samuel D. Stranks, Giles E. Eperon, Jack A. Alexander-Webber, Antonio Abate Aditya Sadhanala, Shuhua Yao, Yulin Chen, Richard H. Friend, Lara A. Estroff, Ulrich Wiesner & Henry J. Snaith, "Ultrasoft organic-inorganic perovskite thin-film formation and crystallization for efficient planar heterojunction solar cells" *Nature Communication*, 6:6142

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