**Review Article**

**Synthesis of Novel Perovskite-Organic Hybrid Materials for High-Efficiency Photovoltaic Devices**

**Abstract**

Herein, we reviewed the synthesis methods of perovskite organic hybrid materials for high-efficiency photovoltaic devices. Perovskite material is a material having a chemical structure of ABX3 which resembles that of CaTiO3. In this type of material, A is an organic cation, B represents a metal cation species and X represents a halide ion. The devices are widely applied due to a number of factors such as long charge carrier diffusion lifetimes and length, high absorption coefficients, and good optical absorption band edge. The power conversion efficiency of the perovskite organic-inorganic hybrid is about 25 % which illustrates the rapid increase and the need for commercialization. To improve the performance of the perovskite materials synthesis techniques such as gas phase synthesis, solid phase synthesis, and liquid phase synthesis are applied. The X-ray diffraction technique is discussed as a tool for determining the crystal structure of the materials but also scanning electron microscopy for morphology. This review summarizes the common synthesis techniques for perovskite solar cells and how the morphology and structural properties influence device performance.

**Key words.** Perovskite, organic cation, inorganic metal cation, halide, X-ray diffraction

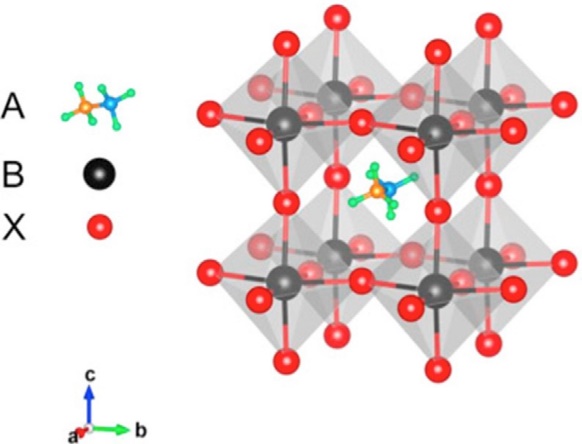
**1. Introduction**

Solar-generated electricity is the world’s fastest growing renewable energy with lots of technological advancements over the past years. The highest growth rates have been noted in China, followed by Japan, and the USA in second and third place, followed by three European countries such as United Kingdom (fourth), Germany (fifth), and France (sixth) [1].

To increase the market share, alternative technologies have to provide a desirable combination of high-power conversion efficiency, low manufacturing costs, and excellent stability. Recently developed hybrid organic-inorganic metal halide perovskite, methylammonium halide perovskite CH3NH3MX3 or MAMX3(MA = CH3NH3, M = Pb or Sn, X = Cl, Br, and I) or simply perovskite, solar cells have a great potential to become one of the leading technologies in PV industry due to their high efficiency and low manufacturing costs. As a result of intensive research efforts across the world over the past 8 years, perovskite-based solar cell performances are now comparable to silicon-based solar cells, at least at the laboratory scale [2,3,4]. A German mineralogist Gustav Rose discovered calcium titanate, also known as calcium titanium oxide (CaTiO3), in 1839. As a mineral, it is called perovskite, named after Russian mineralogist, Lev A. Perovskite (1792–856) [5]. In hybrid organic-inorganic metal halide perovskite (CH3NH3MX3), CH3NH3+ is an organic cation, M is a divalent metal cation (Pb2+ or Sn2+), and X is a monovalent halide anion (Cl−1, Br−1, or I−1). Because of their excellent optoelectronic properties and potential solution-processed synthesis [6,7,8], these materials have been studied to develop new materials for organic light-emitting diodes [9] and field effect transistors [8]

Since 2009, Kojima and his coworkers used CH3NH3PbBr3and CH3NH3PbI3as sensitizers in solar cells; great progress has been made for such kind of solar cells not only due to the fact that the power conversion efficiency (PCE) is increased from 3.8 to 20.8%, but also that it has high absorption characteristics, appropriate direct band gaps, high carrier mobility, long charge carrier diffusion length, low cost, and easy fabrication processes [10,11]. All these excellent performances mostly originated from the organic-inorganic perovskite film. The formula of perovskite is usually written as ABX3, where A is an organic cation, e.g., CH3NH3+, B is a metal cation, e.g., Pb2+, and X is a halide anion,

The A position contains an organic cation (CH3NH3+), B is a metal cation (Pb2+ or Sn2+), and X is a halide anion (Cl− or Br− or I−) as shown in Figure 1.



**Figure 1.**Crystal structure of hybrid organic-inorganic metal halide perovskites with the generic chemical formula ABX3; Organic cations occupy position A [light gray/dark gray/gray (green/blue/orange in the web version)] and the metal cations and halides occupy the B (black) and X [(purple in the web version)] positions, respectively[12].

The hybrid organic-inorganic lead halide perovskite compound was first used as a visible-light sensitizer for photovoltaic cells in 2009 with the efficiency of 3.8 % for X = Br and 3.1 % for X = I, respectively at one sun illumination [10]. Perovskite was also used as a sensitizer in quantum dot-sensitized solar cells in 2011 with an efficiency of 6.5 % [13]. These two performances indicated the potential of using perovskite for solar cells even though they were not very stable due to the presence of a liquid electrolyte. The first stable and solid-state perovskite was reported in 2012 with an efficiency of 9.7 % [14] and in the same year, another report on solid-state perovskite was published in science recording an efficiency of 10.9% [15]. Since then, perovskite-based solar cell performance has rapidly progressed with a best efficiency record of 22.1 % in 2015. Progress in the perovskite solar cells has been remarkable within a short time period and is considered the biggest scientific breakthrough in the PV industry [16,17,18]. Solution-based and vapor-based depositions are the two main deposition methods for the fabrication of high-quality perovskite thin films. The solution-based deposition technique is cost-effective and compatible with the fabrication process, which includes flexible substrates [19,20,21]. On the other hand, the vapor-based deposition technique is an industrial production technique with a potential for the commercialization of perovskite solar cells [22,23]. In either case, the deposition methods are relatively rapid and also consume a very small amount of materials. These are some of the reasons why scientific communities are attracted to the perovskite solar cells industry. The hybrid organic-inorganic metal halide perovskite-based materials exhibit several outstanding optical and electrical properties, which are ideal for photovoltaic applications.

**2. Synthesis inorganic-organic perovskite devices.**

Recently, hybrid halide perovskite was discovered to possess a photoelectric effect. This means that it can be used to harvest solar energy for man's use. Hybrid perovskite solar cell was introduced by Miyasaka et al in 2009 with a power conversion efficiency (PCE) of 3.8 %. A few years later, the PCE) of PSCs has reached 25.7 % [24]. This competitive increase in its efficiency has been made possible due to the unique optoelectronic properties of the hybrid perovskites [25,26,27,28,29]. Minemoto et al. [30] such as direct band gap, high absorption coefficient, and charge transport properties. However, this remarkable improvement in the power conversion efficiency of hybrid halide perovskite is deterred by the poor air stability of perovskite absorbers. This is basically true for polycrystalline thin films perovskite solar cells because their performance is drastically affected by the shorter diffusion length and high trap state densities [25,30]. In contrast, perovskite single crystals exhibit low trap state density (about six times less than that of polycrystalline thin films) and high diffusion length (in the order of micrometers) [30]. An improvement in the efficiency of solar cells was recorded when single crystal or large grain-sized perovskite material was used [28]. This remarkable improvement of the efficiency of perovskite is due to increased carrier mobility and diffusion length that arise because of the reduction of charge trapping by narrowing the interfacial area that is associated with large grains that eliminate hysteresis, and the reduction in magnitude of bulk defects [29] in the large grains. Therefore, highly crystalline perovskite material is needed for the improvement of solar cells. Despite the drastic increase in the efficiency of PSCs, the issue of stability and environmental friendliness is still at stake. It has been unfolded that the organic molecules in the organic-inorganic hybrid perovskite have poor thermal and light stability [30,31]. Bello et al. [32] highlighted the superiority of single-crystal synthesis over polycrystalline counterpart. Their studies identified the absence of grain boundary in single crystal structure which accounts for its stability in adverse weather conditions. During the last few years, a lot of research effort has been devoted to this end [33,34]. The Structural stability of a material is an indication of its ability to sustain a certain crystalline phase to be stable at different conditions of temperature, and pressure and characterized by the absence of polymorphism [34]. The factors contributing to the poor stability of perovskites can be classified into two broad categories: extrinsic and intrinsic. Extrinsic factors are related to the environment such as oxygen and moisture, while the intrinsic factors include thermal instability, hygroscopicity, and ion migration [35]. The inherent instability of the organo-inorganic halide perovskite solar cells on exposure to moisture, air, or oxygen, and thermal and UV illumination contributes to the degradation of the perovskite absorber layer. Frost et al. [36] showed that MAPbI3 would bind with a water molecule, and a proton in the methylamine ion would be captured, and finally leads to decomposing into a hydrate of methylamine and HI. It was inferred that replacing the organic ions of perovskite with proton-free ion groups, such as (CH3)4N+, would improve the stability of perovskite. Also, the presence of heavy metal in the most trending cluster (MAPbI3) has deterred its commercialization in addition to its instability in moist air. Hence, this work explores the assertion of Frost and his co-worker to model a novel lead-free organo-inorganic halide perovskite and characterize it for environmental friendliness and moisture stability and its potential application in photovoltaic cells.

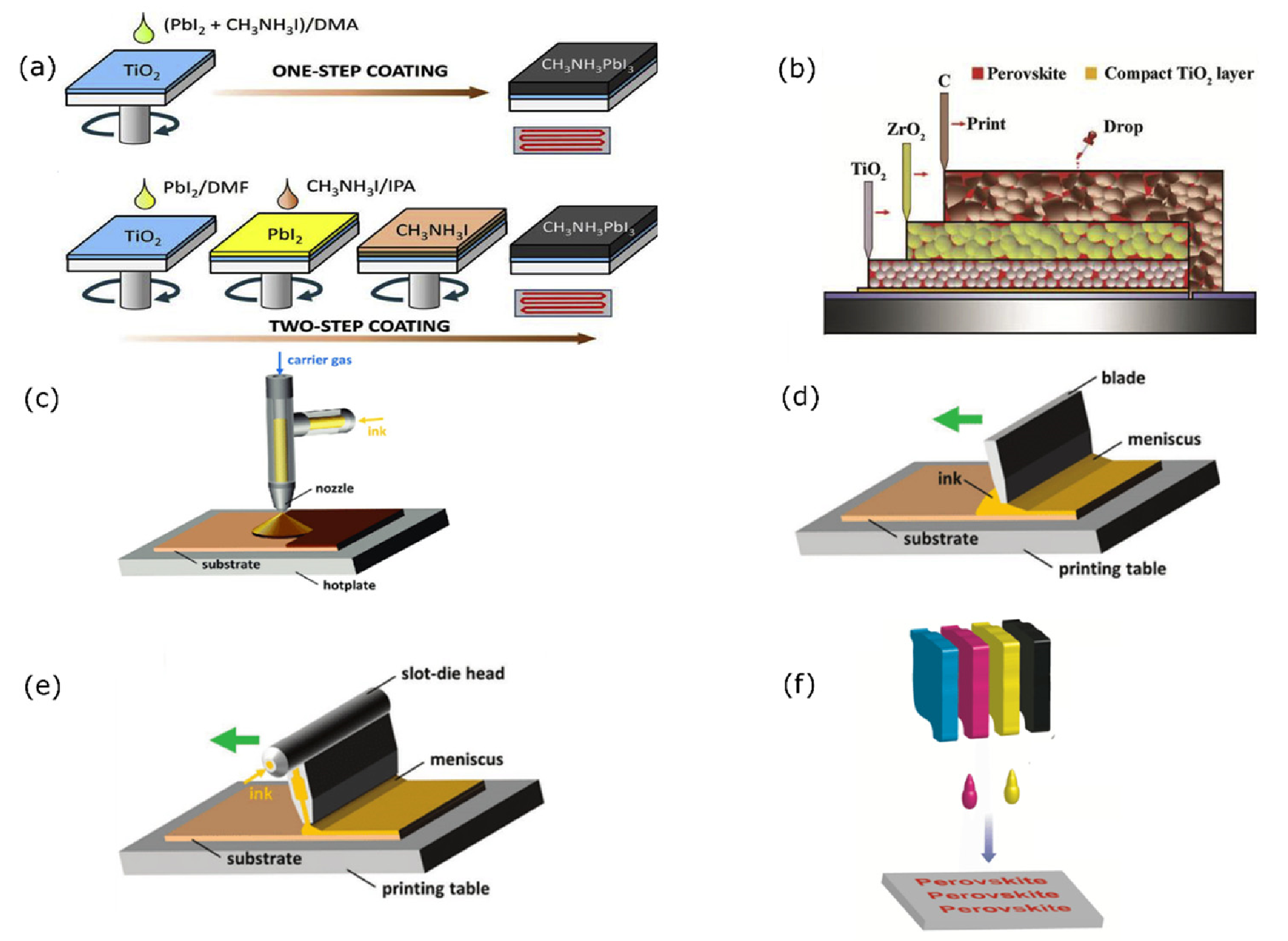
**2.1 Solution Processing-Based Method**

Solution processing-based methods are the common methods for perovskite deposition. Various methods derived from solution processing include spin-coating, dip-coating, doctor blade, spray-coating, ink-jet printing, screen printing, drop-casting, and slot die coating [37].

**2.2 Vapor-Based Method**

The vapor-based method is an alternative method for fabricating perovskite PVs and it has better film uniformity compared to the solution-processing-based methods. This method is mostly used on an industrial scale for glazing, liquid crystal displays, and in the thin-film solar industry. The absorption efficiency of solar cells depends on the thickness of the perovskite layer. Thin layers absorb less sunlight, whereas thick films take a great deal of time to operate, as electrons and holes take significant time to reach their contacts. If the film is not uniform in the overall area, there will be direct contact with the electron transport material (ETM) and the hole transport material (HTM), resulting in a lower FF and Voc. Vapor-based deposition surpasses other techniques due to its ability to produce large-scale multi-stacked thin films with a uniform thickness. However, vapor-based deposition requires a vacuum to increase the mean free path between collisions to produce highly uniform and pure thin films. The vapor-based method is divided into two categories, physical and chemical [37].

**2.3 Vapor-Based Method**



**Figure 2.** Different solution processing-based methods for perovskite PV fabrication: (a) spin coating [38] (b) drop-casting [38] (c) Spray-coating, (d) doctor blade, and (e) slot-die coating [39] (f) Ink-jet printing [40].

#### 2.4 Chemical Vapor Deposition

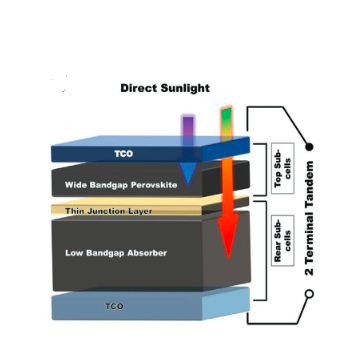
Chemical vapor deposition (CVD) is a deposition method that produces highly scalable and pinhole-free large-scale perovskite PVs. A co-evaporation technique is used to deposit the perovskite layers with the help of two different precursors. The precursors are heated, mixed, and then moved to another substrate at a lower temperature, using a carrier gas (argon) to form highly uniform films, which are pinhole-free and have larger grain sizes and long carrier lifetimes. CVD has been mostly deployed for fabricating perovskite layers to prevent the drawbacks of using low amounts of materials and the difficulty in controlling the flux deposition [41,22]. Moreover, while the use of CVD will produce a high material yield ratio and be highly scalable for perovskite layer depositions [42], it requires a vacuum and uniform co-evaporation of the sample material, which is a challenge at an industrial scale.

**3. Perovskite Tandem Photovoltaics**

Perovskite tandem PVs have been suggested as a method to improve the overall performance, stability, and lifetime of perovskite PVs. A perovskite tandem PV usually consists of a cell—either silicon, perovskite, or copper indium gallium selenide (CIGS)— overlaid by a perovskite PV [43], to increase the efficiencies beyond a single junction limit [44] without adding a substantial cost during production [45,31]. Typical single junction PV cells do not make use of 67% of the solar energy they receive, because of the weak absorbance capabilities of the semiconductors. Semiconductors can only absorb photons with energy above their bandgap energy (Eg) and they generate energy equal to Eg, where the rest of the energy is lost through thermalization as heat. This will severely affect the PCE of a PV because it corresponds to the Voc and Jsc of the PVs. As one of the solutions, tandem photovoltaics can address this problem [46].

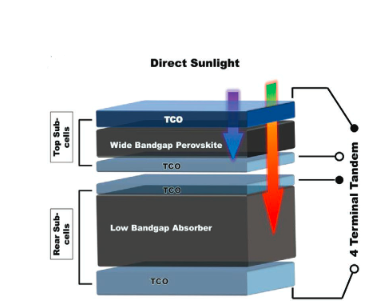
Tandem PVs use stacks of materials with different bandgaps, where materials with larger bandgaps are put at the top of a cell and those with small bandgaps are at the bottom. High-energy photons are absorbed by the upper materials, while low-energy photons are not lost, in this case, but rather are absorbed by the lower stack materials, making use of most of the incident energy. One of the most known structures of tandem cells is the double-junction tandem device. They have two different configurations: two-terminal (2-T) and four-terminal (4-T) tandem, according to the stacking method used [46].

The 2-T tandem cells are synthesized by stacking a transparent front electrode, with a front cell and an opaque rear electrode, with the rear cell being one substrate where an interconnection layer (ICL) separates them as shown in the Figure 3. below [47].



**Figure 3**. A schematic representation of 2T tandem solar cell [47].

The recombination of the photogenerated carriers from either sub-cell takes place in the ICL. On the other hand, 4-T tandem cells are made of two separate devices with two separate electrodes, linked together through a dichromatic mirror as shown in Figure 4 [47].



**Figure 4.** A schematic representation of a 4T tandem solar cell [47].

However, due to the additional electrodes, the optical loss will result in a more expensive cost compared to 2-T tandem PVs. Moreover, 2-T tandem PVs are cheaper to fabricate, though it is harder to fabricate 2-T or monolithic tandem PVs compared to 4-T tandem PVs for general applications [46]

**4. Ink-Jet Printing**

Ink-jet printing is a common method used in the manufacturing of optoelectronic devices, field-effect transistors, and PVs. It is a non-contact technique that uses additive patterning. It is based on the selective ejection of ink from a chamber through a nozzle onto a substrate. A liquid droplet is ejected when an external bias is applied. This bias causes the chambers containing the liquid to contract, creating a shock wave in the liquid, and therefore ejection occurs. The technique is considered fast, consumes less material, and can be used for large-scale production. However, the main drawback is the possibility of a blocked nozzle because the used materials are poor solvents [48,49]

**5. Synthesis of hybrid perovskite crystals**

Much effort has been devoted by researchers to obtain high-quality organometal halide perovskite films for PV applications. However, the synthesis of high-quality large perovskite single crystals as well as a variety of nanostructures are still of great importance to the fundamental research about the physical properties of these materials and a better understanding of the crystal growth process [50]

**5.1 Bulk Crystal Growth**

The growth of organometal halide perovskite bulk crystals is generally similar to the traditional solution-based crystal-growth methods. In most cases, the oversaturated perovskite precursor solution with organic halide salts and inorganic lead halide salts is slowly cooled to evaporate the solvents and form the hybrid perovskite single crystals. So far, many researchers have reported the successful synthesis of large hybrid perovskite single crystals up to centimeter scale [28,25,51,52,53]. Bakr et al. reported an antisolvent vapor-assisted crystallization (AVC) process to grow high-quality, millimeter-sized MAPbBr3 and MAPbI3 single crystals with ultra-low trap densities (109 ~ 1010 cm-3) and high charge carrier diffusion lengths (> 10 µm). In this method, the antisolvent dichloromethane (DCM) is slowly diffused into the perovskite solution to promote the growth of perovskite crystals of high quality and controllable crystal size. This concept of the antisolvent method has also been widely used to fabricate high-quality perovskite thin films through a fast-crystallization process. Bakr and co-workers also developed an inverse temperature crystallization (ITC) method to grow MAPbBr3 and MAPbI3 crystals at a rate much faster than the previously reported methods [51]. This method is based on the phenomenon that the solubility of MAPbBr3 or MAPbI3 in DMF drops dramatically with the increase of solution temperature from room temperature to 80 ºC. This inverse solubility phenomenon was utilized to grow MAPbX3 crystals rapidly from hot precursor solutions by carefully controlling the solution temperature and concentrations. By using a top-seeded solution-growth (TSSG) method, Huang and co-workers grew large-sized MAPbI3 single crystals (the largest size is around 10 mm) with electron-hole diffusion lengths larger than 175 µm under 1 sun illumination [25]

In this process, small MAPbI3 crystals at the bottom of the solution in a container were used to help maintain a saturated solution while the cooler top half of the solution was supersaturated. Thus, a crystal seed put in the top region of the solution can grow to a larger size by consumption of small crystals in the bottom. Recently, Liu et al. [52] also developed a facile method to prepare inch-sized MAPbX3 (X = Cl, Br, I) perovskite crystals (the largest one is 71 mm \* 54 mm \* 39 mm) based on a seed-induced heterogeneous nucleation mechanism.

**5.2 Nanocrystal Synthesis**

In the early work on the synthesis of hybrid perovskite nanocrystals, mesoporous TiO2 or Al2O3 films were normally used the control the perovskite nanocrystals’ growth [13,54]

In these reports, the regular perovskite precursor solution for solar cell fabrication was used and no surfactant ligands were adopted, thus the crystal size was controlled by the pore size of this mesoporous scaffold. Later, a series of hybrid perovskite nanostructures with different sizes and morphologies were synthesized through various solution processes without using templates. Jin et al. successfully fabricated single crystalline nanowires, nanorods, nanobelts, and nanoplates of MAPbI3 and MAPbBr3 perovskites through a dissolution-recrystallization conversion from lead halide films coated on substrates to perovskites [55]. These perovskite nanocrystals show stronger room-temperature photoluminescence and longer carrier lifetimes than the bulk crystals and thin films.

Galian et al. reported the non-template synthesis of monodispersed 6 nm-sized hybrid MAPbBr3 perovskite nanoparticles for the first time [5]. The medium-sized chain alkyl ammonium bromide was used to react with PbBr2 in the presence of oleic acid and octadecene. These nanoparticles can be dispersed and kept stable in a variety of solvents for more than three months. By using similar methods mentioned above, all-inorganic lead halide nanocrystals (e.g., CsPbX3) can also be obtained from inexpensive commercial raw materials [56]. Through compositional modulations, the emission spectra are widely tunable from 410 nm to 700 nm, which makes them appealing for many optoelectronic applications. In addition to the three-dimensional organic-inorganic hybrid perovskites, the two-dimensional counterparts are also fairly appealing for their special novel features and wide applications. Two-dimensional MAPbX3 (X = Cl, Br or I) perovskite nanosheets with the thickness of a single unit cell were synthesized by Bao and co-workers using a hybrid method that combines the solution and vapor-phase processes [57]. The high-quality two-dimensional nanocrystals exhibit high photoluminescence with broad wavelength tunability. Yang’s group reported the direct growth of atomically thin single-crystalline two-dimensional hybrid (C4H9NH3)2PbBr4 perovskites from solution-phase growth [58]. Much larger organic cations are needed for the fabrication of this kind of layered two-dimensional perovskites.

**5.3 Two-step Solution Process**

For the two-step solution process in very early stages [19], PbI2 is normally dissolved in DMF and spin-coated on the substrate to form a PbI2 layer, and the as-deposited film is kept at a low temperature (e.g., 70 ºC) for a certain time. After drying, the film is immersed into a 2-propanol solution of MAI (e.g., 10 mg/ml) for an appropriate time and is then rinsed in pure 2-propanol to wash away the residual MAI. Normally, a further thermal annealing process is also required for crystallization. Gratzel et al. firstly adopted this two-step solution process and successfully achieved a certified efficiency of 14.1 % [19]. Later, a thermal annealing-induced inter-diffusion method was developed by Huang’s group to fabricate pin-hole-free perovskite films [59]. the stacked PbI2/MAI bilayer structure will convert to perovskites upon thermal annealing. A lot of groups later adopted this approach for the fabrication of PSCs with relatively high efficiencies [2,11,60,25]

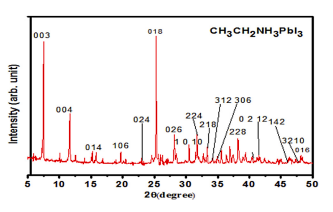
**6. Working Mechanisms and Device Architectures**

The operation of a solar cell requires four basic processes, i.e., light absorption and generation of excitons, charge separation, charge transport, and charge collection. For light absorbers with different optoelectronic properties, diverse device structures are selected. For example, an n-i-p (or p-i-n) structure is needed if the light-absorbing material is an intrinsic semiconductor, while only a p-n structure is needed when the active material itself has a p-type (or n-type) property. Thus, the organic-inorganic hybrid perovskite materials are suitable for either p-i-n or p-n structures owing to their long-range balanced ambipolar charge transport nature [26]. The original perovskite solar cells employed a mesoporous structure with a thick mesoporous layer (mp-Al2O3 or mp-TiO2) as a scaffold, which evolved from the typical DSSCs. In this structure, the mesoporous scaffold is filled with perovskites and located between ETLs (mostly TiO2) and HTLs layers. The mesoporous structure is proven to be able to increase the charge collection efficiency by decreasing the charge transport distance. In the very early stage, the thickness of the mesoporous layer was generally larger than 500 nm (or even several micrometers), to absorb enough sunlight [10,14,13,15,19]

However, because the dimensions of the pores can confine the crystal growth of perovskites, a certain part of the material exists in amorphous phases with poor crystallinity [61] which will definitely deteriorate the device's performance. Interestingly, if the mesoporous layer thickness decreases to less than 300 nm, a dense perovskite capping layer with large grains will form on top of the porous layer [62,63,19,64] which is called a bilayer structure.

**7. Characterization**

This section describes the material characteristics that should be met for perovskite PVs, including the structural and morphological properties. XRD analysis can be used to detect a crystallite structure from the layer formation [65]. Based on synthesis conditions, there are three types of MAPbI3 structure. At T < 163 K, it is in an orthorhombic phase, at 163 K < T < 327.3 K, it is in a tetragonal phase, and beyond 327.3 K, it will begin to form a cubic phase [66]. Substantial changes occur at 60 ◦C, as it shifts from the tetragonal to the cubic phase, with better grain sizes, based on the XRD results from several research studies, as multiple new peaks are present compared to the tetragonal phase [67,68,69]. Rahul et al [70] designed a perovskite solar cell using a polymer electrolyte and determined the x-ray diffraction pattern of the material as shown in Figure 5.



**Figure 5**. X-ray diffraction pattern of CH3CH2NH3PbI3 [70].

The properties of HOIPs are also affected by organic monocation. Adding a bulky hydrophobic organic cation to the perovskite lattice can prevent moisture intrusion [71]. Because of this structure, the bandgap is large and tunable. Moreover, increasing the chain length of the organic mono-cation allows the prevention of oxidation of Sn2+ to Sn4+ [37].

Other than XRD characterization, with the different methods implemented for the fabrication of perovskite PVs, the resulting devices will also have different crystal structures relative to their fabrication methods [72]. The morphology of the perovskite is another factor to improve perovskite PV performance which is determined by scanning electron microscopy. Numerous works have been done on optimizing morphology by improving the fabrication methods [73] and by applying additional additives [74,75]

**8. Summary and Perspectives**

In summary, the inorganic-organic metal halide PSCs have experienced rapid development in the past decade and have revolutionized the prospects of next-generation photovoltaics. They turned a new leaf in solar cell research due to their high PCEs, easy processing, and low material and fabrication costs. The organic-inorganic hybrid perovskites have shown great potential for a variety of optoelectronic applications not just for photovoltaic devices. In the past decade, a lot of efforts have been devoted to producing high-quality perovskites and devices with great performances. Based on the fast development in the device performance of perovskite solar cells, further advancements will be promoted by some more fundamental investigations. It is of great importance to have a deeper understanding of the fundamental properties related to hybrid perovskite materials.

Despite the great development speed, the inorganic-organic hybrid perovskite solar cells are still in the early stages of lab research. In order to meet the requirements of mass production in the future, the PSCs must have a substantially higher solar module performance with much lower manufacturing costs than the other existing solar technologies. Thus, there is still much room for improvement. Also, some challenging issues, like large-area modules, reproducibility, long-term stability, I-V hysteresis, and toxicity of lead, should be carefully addressed through much more research before their real application.

**9. Conclusion**

Perovskite materials are discussed basing on the synthesis techniques and how they influence device performance due to thermal instability and structural distortions. The chemical structure of the material is illustrated where A represents the organic cation, B is the metal cation and X is the halide ion. The common synthesis techniques such as chemical vapor deposition, doctor blade, spin coating, spray coating, and sol-gel method have been introduced. The factors that influence device performance such as large-area modules, reproducibility, long-term stability, I-V hysteresis, and toxicity of lead. The characterization techniques such as X-ray diffraction for determining the crystalline structure and scanning electron microscopy for determination of the morphology are also addressed. In brief, this review discusses the synthesis techniques used in the fabrication of perovskite devices but also the characterization techniques that are employed to analyze device structural properties.

**Ethics approval and consent to participate**

Not applicable.

**Consent for publication**

Not applicable.

**Availability of data and materials**

Not applicable.

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