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Recent Progresses in Perovskite Solar Cells

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Additional information is available at the end of the chapter

Abstract

Perovskite solar cell (PSC) can be regarded as a continuation of dye sensitized solar cell (DSSC) in terms of the sensitization phenomena that occurred in the functioning molecules. In 2012, a breakthrough propose has been made for the sensitization of PSCs, in which a solid-state structure is offered as an equivalent sensitizer used in DSSC. The power conversion efficiency (PCE) of those solid-state cells reached about twofold of its initial value during the past several years. Immediately after, the researchers followed this propose worldwide. They have introduced an improved efficiency of as much as 20%, which was originally started from its initial value of 4%, just in 4 years. Thus, the new concept, solid perovskite molecules, has eliminated the need for the liquid electrolyte in DSSC while still carrying the advantages of organic solar cells (OSCs). Therefore, the distinctive material of PSC—the organometallic halide molecules (also known as OMH or organic-inorganic trihalides)—inclined an unexpected reputation for solar cell (SC) researches. Hence, it seems that we will witness a new age for solar conversion devices depending on the recent hopeful progresses on PSCs. The high rate of photovoltaic (PV) conversion capacity in PSC is generally expressed by the basic properties possessed by the organic-inorganic perovskite crystal, such as better optical properties and well diffused charges along huge distances during the charge transport. In addition, a low temperature processing is applicable during its production. Moreover, the perovskite layer provides a tunable band gap. Therefore, depending on better developments on designed molecules, PSC may gain extreme performances compared to the other competitors, such as OSC or DSSC devices. This chapter starts with a general discussion on the need for an affordable clean energy conversion device that is urgent for the future of humanity, due to publicly well-known global warming issue. In Section 2, basic properties of PSC are mentioned together with their structure and working principles. Section 3 continues with an overview on organometallic perovskite molecules after a brief introductory history is presented. The absorption and band gap properties are also discussed. Since most perovskite materials need a hole transporting material (HTMs) within the PSC, the kinds of HTMs that are designed for PSCs are described in Section 3. The rendering of long-term stabilization has special importance

for PSCs since the instability issue remained idle in spite of those recent increased efficiency values attained by various research groups. Therefore, the stability issues are discussed in a separate part in Section 4. We finally close the chapter discussing the challenges and opportunities relying on the chapter content. We note that the recent investigations on PSCs have special importance for its large-scale realization in order to make them ready for the photovoltaic industry of the future. Hence, there are various announced meetings focusing on its mass production due to the unexpected sharp rise of the perovskite efficiency in the last 6 years. Hence, all the new cutting-edge scientific findings are also dealt with commercialization issues now, in order to attain the desired low cost fabrication, including the yield of high purity and the formation of smooth films during the continual manufacture of perovskite layers.

Keywords: perovskite solar cells, hole transport materials, spiro-OMeTAD

1. Introduction: the need for new and affordable power converters

The novelties in solar cell (SC) technology may be attracting the widest human attention in the world due to its significance on its effectiveness on electricity production from free and abundant sunlight [1–3]. Namely, petroleum is the main source of energy in the world by a percentage of 40, where most of the petroleum is produced just by a few oil exporting countries. The other countries are the consumers. They exist with increasing petroleum dependency, which means that the most of the countries rely on exporters. Unfortunately, the petroleum consumption accelerates quickly because of energy needs due to expanding industrial zones. It is expected to grow further unless an affordable novel clean energy technology becomes available.

To make a continuous delivery of the energy by means of an environmentally friendly manner, it is mandatory for governments to make immediate precautions against fuel consumption, particularly by strictly improving their alternative energy themes. Among a variety of energy sources, electricity is known as "clean energy". The best quality of electricity is its ease of transformation in other energy forms; thereby, it is crucial for the human society. Accordingly, half of the energy consumption is made by electricity using machinery, for that, conversion of energy into electric energy from other resources is related to fuel saving. This property directed countries to invest on renewable energy transformers (e.g., Germany has already announced that much of the country's consumption is fulfilled through renewables). Hence, many researchers from various institutions worldwide developed new types of alternative energy conversion devices in order to condense their capability more and more. Among them, SCs are the most promising devices since sun energy is accepted to be almost infinite for human needs.

Many new types of SCs in photovoltaic (PV) panels are used in new existing investments for meeting the residential and commercial energy needs. Maximizing efficiency is a must to satisfy those huge consumption needs. Hence, a majority of the investments obliged to use silicon-based PV panels, which have high conversion rates. Whereas for their production

processes, we need to use huge amount of water and energy and to release lots of pollutants to the environment as well. At this point, organic solar cell (OSC) technology attracts attention especially for the utilization of environmentally friendly production procedures. By means of this favorable property, in the last two decades, many new usages of organic materials in electric energy producing devices are proposed and applied. These novel devices are basically expected to satisfy low cost criteria and high efficiency; thereby, recent SC researches are especially shaped around these related topics.

Among SCs, many efficient types of organic materials and devices are present today. For example, commercial dye sensitized solar cells (DSSCs) are in the marketplace for a decade. However, this type of SCs is weak for its possible leaking in electrolyte liquid and imperfect encapsulation. The consistent and cutting-edge studies on this challenge give the fruit of a DSSC like but a novel SC: named, Perovskite Solar Cell (PSC). Relatedly, this chapter mainly deals with the main issues of PSC, i.e., its ideal phenomena, device structure, materials, and manufacturing challenges [4–17].
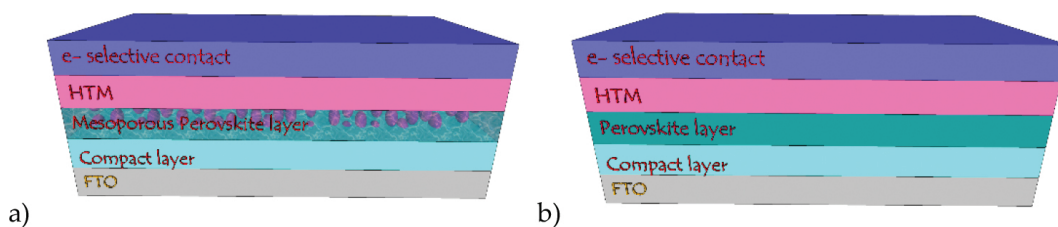
2. Operating principle and structural layout of PSC

As for the operating principle of PSCs, the present information obtained on "how they operate" is rather insufficient for now. Moreover, the whole working principle is not even well explained [18, 19]. There have already been many different approaches to point out a well-defined PSC operation mechanism. Nevertheless, the proficient working of methylammonium lead iodide (corresponding chemical formula is $CH_3NH_3PbI_3$ and the methylammonium inside the formulas are also introduced as MA or $CH_3NH_3^+$ in the related literature)-based PSC has not yet been completely understood. Accordingly, this confusion raises the necessity for deriving novel clues on (1) light absorption, (2) charge separation, (3) charge transport, and (4) charge collection. This is because these are general SC parameters that are used to express the principal working process during conversion of sunlight into electricity.

Selection of light harvesters is the first step for the determination of the physical layout of a SC. Hence, investigation of perovskite's optoelectronic properties has priority during the design process. This is needed in order to theoretically construct the fundamental energy conversion process, and therefore, to decide the respective SC layout [1]. In this term, we know that organometallic perovskite —like $CH_3NH_3PbI_3$— may exhibit both electron and hole transport features, together. Hence, PSCs can be decided to be layered either using well-known *p-n* junction layout or *p-i-n* junction layout. The decision between the two layouts is made as follows: If the light harvester, perovskite, is an intrinsic semiconductor, a *p-i-n* junction is needed. Whereas a *p-n* junction is required if the light harvester, i.e. perovskite, has an *n*-type or *p*-type property. This is because both types are able to carry electrons or holes to the light harvester [1].

PSCs are fabricated depending on two typical structures of perovskites. These structures are called mesoporous and planar structures. These structures are unique to the perovskite crystal. **Figure 1** illustrates the consequent scheme for the device layout for both mesoporous- and

planar-type PSC. The former contains a mesoporous-type metal oxide layer (i.e., TiO_2 or Al_2O_3) coated with perovskite sensitizer. On the other hand, the latter includes a perovskite film sandwiched between electron and hole transporting layers. Here, in case of perovskite dots are stick to the surface of TiO_2 layer, charge is separated through electron injection. Namely, the charge certainly follows away from perovskite to the metal oxide (also known as transparent conductive oxide layer, TCO), such as TiO_2 [20]. Up to here, the operation principle is considered to be analogous to DSSCs. The remaining operation mechanism, however, is different from DSSCs for both mesoporous- and planar-type PSCs due to the charge accumulation and charge transport characteristics that occur in the PSCs [18, 19, 21]. Comparing these two architectures, it is evident that the charge transport rate is virtually the same for both of them, while mesoporous-type cell performs higher recombination rates [22]. The planar-type PSCs are found applicable to flexible solar cells since the typical high temperature rates are not mandatory in order to fabricate them.

Figure 1. (a) The model structure of mesoporous halide PSC and (b) the model structure of planar hetero-junction structured halide PSC.
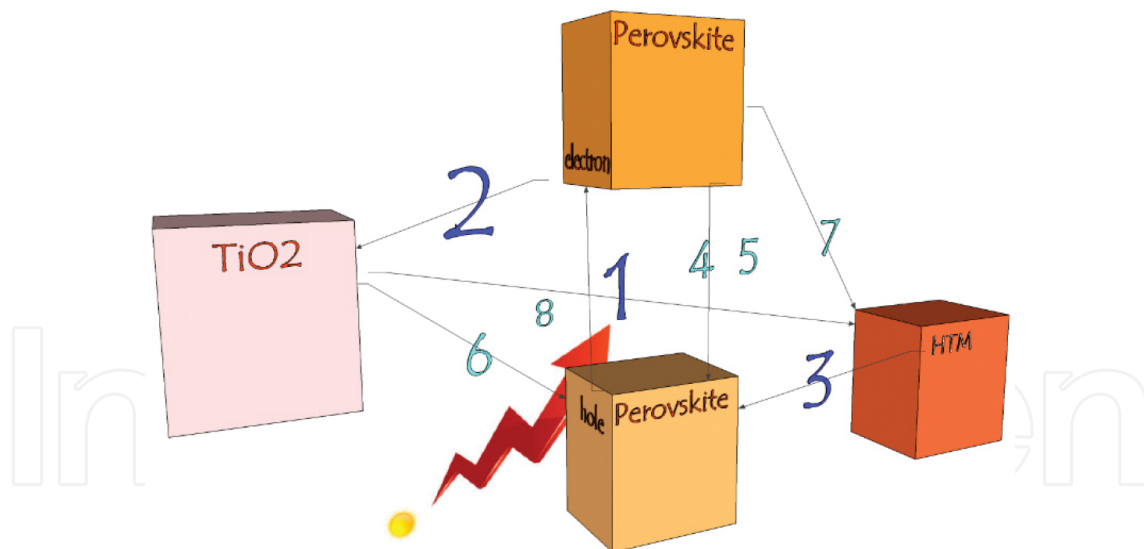
Besides these two structures, hole conductor-free (HTM-free) PSCs have also been investigated by many scientists. The first report on HTM-free $CH_3NH_3PbI_3/TiO_2$ hetero-junction SC was released by Etgar et al. [23]. In this study, the mesoporous TiO_2 was coated with a thick perovskite layer having large crystal functioning as both light harvester and hole transport material, simultaneously. In order to obtain highly efficient PSCs and to avoid building shunt pathways, a thick perovskite film having a smooth surface is required. The width of the depletion layer at the $CH_3NH_3PbI_3/TiO_2$ junction plays an important role on the performance of the HTM-free PSC. For instance, it is possible to enlarge the width by increasing the depleted part of TiO_2 according to this study. Such arrangement has given an increased power conversion efficiency (PCE) of almost 11% [24]. Another HTM-free PSC is the one that has tripled layers that is implemented by Han et al. The respective multilayer arrangement consists of simple layout from mesoporous $TiO_2/ZrO_2/C$ layers [25]. Here, the ZrO_2 film is especially used as blocking layer so that the photo-generated electrons could not flow back to the contact. Accordingly, electron hole recombination process occurring inside the device is delayed. With the help of such HTM-free PSC, researchers have already achieved a PCE of around 13% [25].

The charge transfer processes and the latest progresses in PSC are summarized in **Figure 2** and **Table 1** [26]. The explained photonic interaction matches well for a mesoporous-type PSC. Here, the energy level of the perovskite is designed in order to function in the following junction architecture: $TiO_2/CH_3NH_3PbI_3$/spiro-OMeTAD. The charge transfer process for analogous mesoporous architecture requires the steps specified in **Table 1** [26–28]. Here, the

general PCE of mesoporous-type PSC is controlled through the processes given in the table. Where the rate of charge generation as well as charge transport occurred from (1) to (3) should be much faster than the rate of undesired recombination occurred from (4) to (8) given in **Figure 2**. In this way, a high power conversion efficiency can be obtained.

Step no	Event	Occurrence
1	Photoexcitation of the Perovskite	$Perovskite + hv \rightarrow (e^-...h^+)_{Perovskite}$
2	Electron injection	$(e^-...h^+)_{Perovskite} \rightarrow e^-_{cb(TiO2)} + h^+{}_{(Perovskite)}, h^+{}_{(Perovskite)} \rightarrow h^+{}_{(HTM)}$ $h^+{}_{(Perovskite)}$
3	Hole injection	$(e^-...h^+)_{Perovskite} \rightarrow h^+{}_{(HTM)} + e^-{}_{Perovskite}, e^-{}_{(Perovskite)} \rightarrow e^-_{cb(TiO2)}$
4	Photoluminescence	$(e^-...h^+)_{Perovskite} \rightarrow hv$
5	Nonradiative recombination	$(e^-...h^+)_{Perovskite} \rightarrow \nabla$
6	Back electron transfer at TiO$_2$/Perovskite interface	$e^-_{cb(TiO2)} + h^+{}_{(Perovskite)} \rightarrow \nabla$
7	Back charge transfer at Perovskite/HTM interface	$h^+{}_{(HTM)} + e^-{}_{(Perovskite)} \rightarrow \nabla$
8	Charge recombination at TiO$_2$/HTM interface	$e^-_{cb(TiO2)} + h^+{}_{(HTM)} \rightarrow \nabla$

Table 1. The required charge transfer process for analogous mesoporous architecture [26–28].

Figure 2. Electron and hole transport process for mesoporous PSC.

It is known that for a single-junction SC the ideal band gap should start from 1.1 and extend to 1.4 eV [27]. One of the most important characteristics related to perovskite material processes is that it is possible to vary this band gap by altering its composition. Fortunately, in PSC, the band gap may be arranged by changing from 1.2 and extend to 2.3 eV. This band gap control can be made by substituting halide composition of $CH_3NH_3Pb(I_{1-x}Br_x)_3$ as

described by Noh et al. [23]. Another way to alter the respective band gap is to increase the cation size, nevertheless it may also result in a decrease in the band gap, unfortunately [28].

The solid-state HTM was first implemented to DSSCs to substitute the undesired liquid electrolyte since it causes fast degradation of the cell if it is used with perovskite crystals. This advancement in structural layout has showed an increase in the open circuit voltage (V_{oc}) of the cell due to the high redox potential of the liquid. Within those cells, HTM layer gradually becomes a solid-state layer instead of a liquid one. Accordingly, the stability of PSC improves. Since after the development of solid-state DSSCs, the most common HTM utilized in PSCs is spiro-OMeTAD (*2,2′,7,7′*-tetrakis (*N,N*-di-*p*-methoxyphenylamine)-*9,9′*-spirobifluorene). This is a kind of small molecule which has improved the PCE of PSC up to 19% [29]. It was shown that an HTM with high conductivity decreases the series resistance and gives rise to improvement in the fill factor (FF) of the device [30]. For example, Seok et al. improved the V_{oc} and FF, just by substituting spiro-OMeTAD with polytriarylamine-type HTM [31]. The FF in turn can also be increased through improving the film quality by achieving enlarged grains and reduced grain boundaries [32].
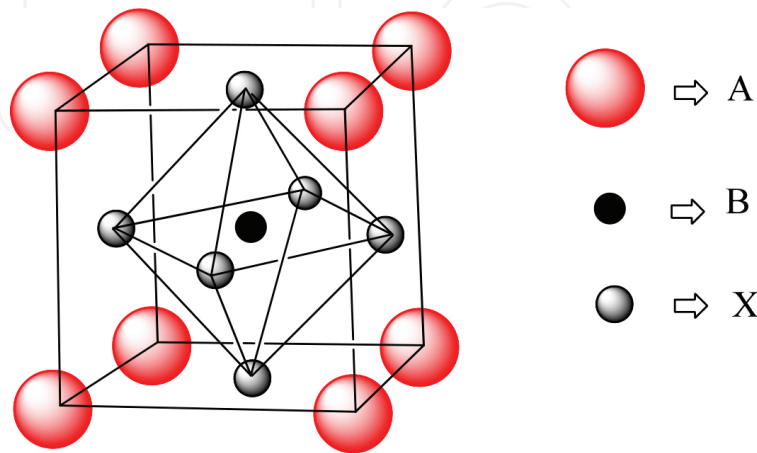
In addition to replacing organic HTMs with other organic HTMs for the purpose of increasing PCE of the PSCs, there are also some other studies on substitution of organic HTMs with inorganics in order to increase the stability of the PSCs. It is well known that perovskite used as light harvester are rather susceptible to moisture and air resulting in degradation of the cell because of perovskite's low energy of formation [14]. One of the most important reasons why HTM usage is necessary is to protect the photoactive perovskite layer from moisture and air exposure to achieve highly stable PSCs. It is also known that metal oxides have much higher mobility as well as good stability than the generally used organic HTMs mentioned above [33, 34]. In an attempt to increase the stability, therefore, You et al. replaced organic HTM with inorganic charge transport layers [14]. In this study, *p*-type (nickel oxide, NiO_x) and *n*-type (zinc oxide, ZnO) metal oxides were used as electron and hole transport layers, respectively. The device architecture was composed of glass/indium tin oxide/NiO_x/ $CH_3NH_3PbI_3$/ZnO/Al, where NiO_x was used to provide a perovskite layer with better crystallinity and ZnO acted as a coverage layer for perovskite layer, thus preventing degradation. According to the results of this study, the metal oxide-based PSCs demonstrated PCE of around 16% and higher stability compared to those fabricated with other common organic HTMs.

3. PSC materials

3.1. Perovskite as a solar device material: structure

Perovskite is a crystal with a special structure constituting ABX_3 formulation. It contains three same kind cationic ions and two different anionic ions. Here, A, B, and X represent large-dimension earth metal cation, rather smaller-dimension metal cation compared to A, and, either oxygen or halogen, respectively. The perovskite structure is symmetric. Within this structure, A is always larger than X (see **Figure 3**). Here, A-cations hold the octahedral corner coordinates while B-cations hold the octahedral holes; in 3-D structure. Within the composi-

tion, X can be substituted with numerous elements of O, Cl, Br, I, and S. The placements of atoms in 3-D structure are mainly regarded to be related with chemical charge neutralization process that is required for stability [8]. The crucial thing for the perovskite minerals is that, although the fundamental structure appears simple, they perform quite different characteristics under special circumstances, i.e., against structural distortion.

Figure 3. Crystal structure belonging to perovskite structure.

Gustav Rose, a German mineralogist, first recognized perovskite. Nevertheless, its entitlement is given after another mineralogist, Lew Perovskii, from Russia [35–37]. Perovskite is therefore originally a name for the mineral calcium TiO_2 ($CaTiO_3$) discovered by Perovskii, where it is basically used to refer a crystal structure that is the same as $CaTiO_3$. Starting from its discovery, perovskite structure has widely been used in diverse fields of research, such as superconductors, ferroelectricity, thermoelectric, dielectric, magnetoresistive, piezoelectric, conducting, electrooptic, semiconducting, [5, 8, 9, 38–47], etc. The wide range of their application carried out in scientific research is mostly due to their tunable behaviors within the crystal structure observed since its discovery [4]. In particular, researchers have focused on organometallic perovskites which must include anionic halogens (I, Cl, F, and Br) and cationic metals of carbon family like Ge, Pb, and Sn. The attention on them is basically due to their unique structure and their promising response to photovoltaic applications [5–7].

The well-known perovskites are crystals of $MgSiO_3$, $SrFeO_3$, $SrZrO_3$, $BaTiO_3$, $LiNbO_3$, and $KMgO_3$. They originally give clear diffraction peaks at 110, 112, 220, 310, 224, and 314. In spite of its applicability to the mentioned diverse areas, the attention on the original molecules remained rather idle. Mostly, its actual fame has begun with the discovery of organometallic halide perovskite (OMH perovskite) related to the studies made for searching the interactions between the organic-inorganic materials. Namely, a research result claimed that a perovskite material shifts from the semiconducting state to the conduction region along with increased dimensionality [8, 9, 38]. In the mentioned and other related researches, A is exchanged by a cationic organic molecule, B is exchanged by an inorganic transition metal, and X is exchanged by an anionic halide. Hence, the new structure becomes inherently referred to as "OMH perovskite". Among many transition metal alternatives, Sn^{+2} and Pb^{+2} metals substituted for X

are the ones which have collected the scientific interest on the following formulas: "CH$_3$NH$_3$SnI$_3$"and "CH$_3$NH$_3$PbI$_3$." This attention increases day by day since the respective new molecules inherently carry significant optoelectrical properties and they are able to be processed in rather low temperatures compared to other OMH molecules with rather different formulas [47–49]. Even more, Pb^{+2} and Sn^{+2} cations are nonreactive, stand stable at room temperature, and their supply channels are wide due to being abundant, which makes them easily accessible cheap materials [50].

As for PV applications, Miyasaka et al. are the first group who used perovskite in SC panel production in 2009 [10]. They fabricated a SC with a liquid phase electrolyte based on meso-porous TiO$_2$ sensitized with CH$_3$NH$_3$X$_3$. Here, X is able to be substituted by I, Cl, or Br, depending on the application purpose. Similar to this first study on PSCs, the most prevalent organic compound used to fabricate PSCs are (1) CH$_3$NH$_3^+$ (methyl ammonium), (2) CH$_3$CH$_2$NH$_3^+$, (ethyl ammonium), and, (3) NH$_2$CH=NH$_2^+$ (form amidinium) [20, 51, 52]. Though, among all, the most common perovskite material implemented to the recent SC applications perhaps have been methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) with other lead halide structures (CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ or CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$) [37, 53].

3.2. Perovskite's absorption properties

It is beneficial to remind the absorbance of DSSC device here. Namely, the previous form of PSC, DSSCs, contains an n-type TiO$_2$ that has mesoporous structure. The dyes are stick to TiO$_2$ where the light is absorbed by dye molecules impregnated in a redox electrolyte sea, meantime. Here, the electrolyte regenerates the stable dye again and again by supplying electrons after having each excitation followed by charge transfer. The TiO$_2$ plays the role of helping the enlargement of the electrode surface as much as possible on behalf of the electrode's job. In this term, the soaring of incident photons become eased. In practice, an approximate 10 μm film thickness of TiO$_2$ is generally enough in DSSC to make a complete absorption of the visible light [9, 54, 55].

On the other hand, such broad thickness is not appropriate for the solid-state SCs. Because there are various factors that restrict the increase in film thickness. Due to these restrictions, the thickness is limited below 2 μm [9, 30]. In order to relieve these limiting effects, different active semiconducting layers are jointly coated with different thin film types in many research groups. Another approach to resolve this issue is the use of nano-sized quantum dots (QDs). These additional cares are taken in order to increase the sensitivity against the photons. As a result, the absorption band becomes carried to around near-infrared region (NIR) in several researches [30, 56–60].

Under the light of these facts expressed about improved absorption, more sensitization of DSSCs to the incident light worked in 2006 where CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$BrI$_3$ were used in the redox couple [9, 61, 62]. In some studies, on the other hand, they are applied as solid-state hole conductors. Nevertheless, those applications could only give efficiency as low as 0.2%. Whereas when they were applied to liquid-based DSSCs, it has reached as high as 10 times of this value escalating to around 2%. Therefore, the solid-state applications remained rather idle.

The first fascinating application on the absorbing sensitizer of perovskites is the one that is made with redox couple. Namely, one of the studies reached to around 3.5% efficiency level [9, 20]. Fortunately, improving the surface morphology and perovskite's processing carried the attained efficiency as high as 6.5% in the preceding years [9, 20, 63]. As may be easily guessed, the main obstacle to make a reasonable device was dissolution of the perovskite material inside the liquid electrolyte. Hence, its stability in the electrolyte sea has always remained questionable, since it is distorted after a while and eventually it is dissolved [9, 20, 63]. The removal of this problem needed realization of two ideas: (1) blocking the dissolution in any way, or (2) using them in a HTM that is insoluble in the liquid environment. The latter alternative idea has been applied to devices fabricated in 2006 [9, 64, 65]. Namely, researchers benefited from the insolubility of metilamonium trihalogenplumbate in nonpolar organic solvents. Hence, perovskites became used as sensitizer on TiO$_2$ as a target. These studies made up a ground for applying this idea to many different materials. Especially, different groups of spiro-OMeTAD have been tested as HTM [9, 11]. The results were surprising, because the use of perovskite molecules reached a respectable efficiency value of around 10% [9, 10, 66]. This result also emphasized the importance of usability of HTMs within the PSC. These records had been a jumping-of-point in terms of their use as alternative to classical dyes since the acquired advantages made PSC more visible among others [9, 67]. This advantage is particularly due to the fact that perovskite (1) makes a stronger absorption in a very wide range of visible colors and (2) realizes this strong absorption in rather small thicknesses compared to the liquid-type DSSCs, namely, a thickness of around 500 nm layer. This property emerged a reform in DSSCs, namely, the replacement of redox liquid with solid-state HTM materials found attractive for solid-state type SCs since the thickness issue become relieved for them. The gain of such property practically meant that the problem of limited thickness of 2 μm for solid-state type SCs has been overcome by use of perovskite. Till those dates, the perovskite material including solid-state type SCs have gained an advantage over other types of solid-state SCs in the scientific community.

Typically, the absorption properties of the PSC are related to the ABX$_3$-type crystal structure of the perovskite that is coated on the TiO$_2$ surface as a thin film. Technically, CH$_3$NH$_3$PbI$_3$ structure gives 1.5×10^{-4} cm^{-1} of absorption at 450 nm wavelength, whereas it only satisfies 0.3×10^{-4} cm^{-1} of absorption at 750 nm wavelength. Relatedly, the soared light is diffused to a depth starting from 0.7 to 2.2 μm. This typical property of CH$_3$NH$_3$PbI$_3$ specifically shows that the perovskite material in the form of a thin film is well enough to absorb the big part of the solar spectrum just being around 2 μm of thickness. This derived fact shows that the CH$_3$NH$_3$PbI$_3$ has enough capability in order to be easily used as a solid-state sensitizer material in SCs.

In order to identify the lack of interpretations about the photocarrier dynamics in lead iodide perovskites, the transient absorption should be characterized. These photophysical relations are observed where a quantitative work is presented in a recent paper [68]. Also, photon recycling has been investigated in the papers [69] where the energy transport is found out not to be restricted by diffusion of charge transport. It is figured out that this may occur at distant

intervals by means of several events including absorption, diffusion, and emission together. By means of all, high V_{oc} values are attained [69].

3.3. Optical band gap

Among different atoms, Pb and Sn included in perovskite materials are fair due to that they yield higher efficiency levels due to their tunable band gap values and improved absorption. The main contribution to the tunable band gap comes from the orbitals of additive metals and halides [70–73]. Hence, the metals which will make the electronic contribution should be carefully selected from among numerous metals. Yet, the band gap harmony and proper valence arrangement requires watching the outermost orbital of the metal and one can see that there are highly less metals constituting mentioned configuration. With that, there is no specific procedure or sharp method to eliminate this hardness. Hence, these theoretical issues should be carried along with the observations and some experimental works.

The intrinsic properties of OMH led them to be used in many diverse engineering applications till now, including thin film diode-based devices, such as SCs, transistors, and light-emitting diodes (LEDs). Moreover, it has also been reported that the band gap of OMH perovskite is decreased when the structure is shifted from 2-D to 3-D [9]. The less spaced band gap intervals are especially found applicative for constructing SC devices. Hence, the developed 3-D structure of $CH_3NH_3PbX_3$ is initially tested as an inorganic semiconducting sensitizer in 2009 in DSSCs. Nevertheless, the researchers got unsatisfactory amounts of PCE from the test results compared to those most efficient DSSCs performed till that time (~3.5% versus ~11%) [74]. With that, the testing groups reached a PCE efficiency of 6.5% [10, 11] later on.

The interest on the perovskite material remained poor until a research is exhibited in 2012. The corresponding research results reported 500 hours of stable lifetime of a perovskite thin film coated on TiO_2. The distinguishing specialty of this kind perovskite was its 10 times enlarged absorbing coefficient compared to that of the widely known ruthenium-based sensitizers. The new molecule has been recognized as a breakthrough discovery. In addition to all, the band gap intervals could be reduced more along with the processing of perovskite materials. And more, they can even be processed more to make them gain highly absorbing structure. Together with these improving arrangements, the optical adsorption can become tunable and recombination properties can also become enhanced [50, 75]. Consequently, as a cation for B, Pb is exclusively preferred for SC applications for the assumed reasons when they are put into perovskite molecule. Neatly, Pb including PSC are found to be theoretically ideal. They practically constitute small spaced band gap intervals as well [8–11].

Through the characterization work, the satisfaction of band gap values can be attained through ultraviolet photoelectron spectroscopy and UV-Vis spectral measurements for any kind of material. Namely, the research [8] made for $CH_3NH_3PbI_3$ has revealed that the minimum and maximum valance values are between –5.5 and –3.95 eV interval, giving out approximately 1.5 eV of band gap for this structure [8, 20]. Through looking at the given typical valence-band and conduction-band values, we infer that perovskite material satisfies enough hole and electron separation. The separation gives a band gap value of 1.5 eV that reveals us enough absorption is made using an onset wavelength of 830 nm.

Shortly, the fundamental request for a SC is its strong and wide absorption range. In these terms, OMH perovskite is suitable for its tunable crystal sizes. Namely, with that condition, the band gap value of the absorber material may be arranged by differently utilized cations and anions [23, 28, 76, 77] within the crystal arrangement, as well. As an example, PbI_yBrI_{3-y} crystal structure can be modified to derive different absorption levels through varying the "y" value here. Derivation of varied absorption levels is generally referred as "tuning band gap." This is essential for perovskite's future, because the development of various types of advanced molecules is allowed by means of such procedure that makes perovskite attain a tunable band gap [23, 78, 79]. Here, the usability of this strategy is shown for $CH_3NH_3PbBr_{3-x}Cl_x$ SCs, where V_{oc} of 1.5 V is derived. This shows the availability of this idea as a method. One more parameter for getting high power values is reaching high photocurrent values. Namely, this can be made through an engineering on n-type and p-type materials in order to match wider band gap perovskites. Also, the widened band gap of perovskite may require synthesizing new hole transport materials since valence band is shifted [78–81]. Therefore, engineering for deriving appropriate hole transporters is especially important for PSCs, too.
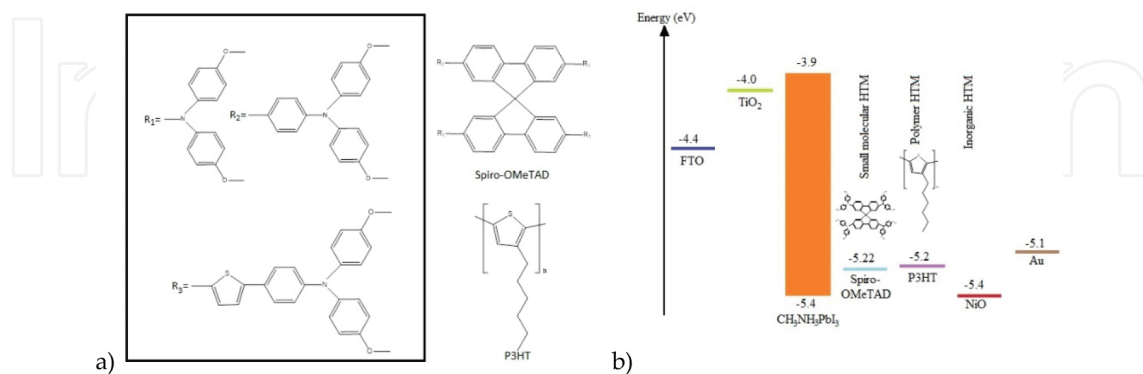
4. Hole transport materials

The HTMs for PSCs are similar to that of solid-state DSSCs, in view of the general structure. The main distinction between them is that the HTM layers do not fill the pores of TiO_2, and it is because they are currently coated by the perovskite material in a PSC. Fortunately, during the practical selection of the materials, this property eases the determination of HTM molecules for PSC devices for us. This is because it becomes more possible to choose them from a large range of materials—compared to the selections that are made for solid-state DSSCs. Once decided to be used for PSC, the produced HTM layer from chosen molecules should meet the similar requirements as requested for solid-state DSSCs, as follows:

1. The molecules should maintain better hole mobility.

2. They should be good soluble in terms of better film formation.

3. In order to supply a good hole transfer they should carry appropriate HOMO energy level with that of OMH perovskites.

4. They have to be produced by eased synthesis procedure and be low cost molecules.

Among them, spiro-OMeTAD has been the most used HTM as small-molecules in PSCs till now. Because it has already been tested and evaluated as a HTM layer in solid-state DSSCs and OLED devices [67, 74, 82, 83]. Therefore, its interlayer functioning is well known by researchers. Namely, use of hybrid lead halide with spiro-OMeTAD-based HTM has given an efficiency of around 15% PCE [82, 84]. On the other hand, the biggest obstacle yielding spiro-OMeTAD in wide range of applications is its high cost that still remains high due to its difficult synthesis process. This obstacle has been a hindrance for further improvements of PSCs in terms of maintaining high efficiency and low cost production together [74]. At this point, new HTMs that are alternative to spiro-OMeTAD have been an issue for improving cost-effective

designs in recent years. These new molecule designs are generally separated to organic and inorganic HTMs as for PSC applications. Organic molecules can either be polymers or other small molecules. Different types of HTM structures that are already used are given in **Figure 4** with their corresponding HOMO values within the cell.

Figure 4. (a) Recently used HTM materials used for PSCs and (b) their corresponding HOMO values.

Spiro-OMeTAD and other small molecule type HTMs have more availability compared to the organic and inorganic HTMs [74] due to its ease of design where the triarylamine is an essential part of the molecule. Here, nitrogen is used as a doping site and can be stabilized through aromatic rings. The nonplanar triarylamine leads to have longer distances between molecules and thus reduces the hole mobility, here. Nevertheless, this makes the molecules more applicable as HTMs for SCs fortunately. Due to the advantages among different molecules, spiro-OMeTAD has been a standard HTM for researchers, where the new small molecules are comparable to that of the standard HTM for this reason. During the application of new types of spiro-OMeTAD and other small molecules some key issues for increasing the efficiency levels are (1) thickness optimization and (2) inclusion of additives, such as making composites [74]. There are also some works done for searching the device's physics on the interface between HTM layer and perovskite layer, as well.
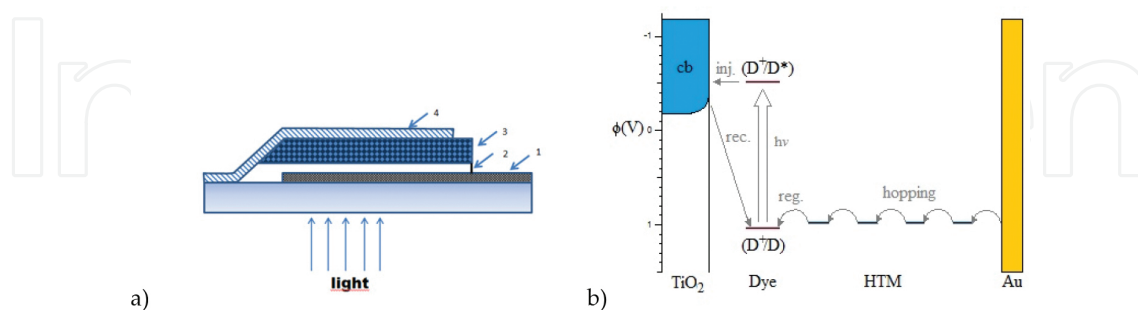
4.1. Early device materials as hole transporters

A HTM layer is needed for sensitizing the TiO_2 layer to satisfy the working of PSCs. The working principle of HTM-based PSC originally depends on DSSCs developed in 1991 by O'Regan and Gratzel based on a liquid electrolyte layer. These cells are photoelectro-chemical cells with a wide surface area of TiO_2 film layer that is sensitized by molecular dyes [54]. The same principle is valid for solid-state sensitized SCs and PSCs, as well. In Gratzel's works, a final efficiency of 12% has been reached. Nevertheless, a leakage is always possible within the corresponding device structure. Shortly, the liquid may leak from the bordered edges. Therefore, the same structure for that of DSSC has been protected in solid-state SCs in principle, on the other side, the electrolyte is altered by a solid hole conductor material instead.

Figure 5 represents the general structure of such solid-state SC and its electron transfer properties. Here, the layered device structure benefits from the TiO_2 layer for blocking the

direct touch of TiO$_2$ layer to HTM. The working principle of the solid-state SC is the same as that of DSSC, where the only distinction stems from the difference in electron transmission processes occurred inside the liquid electrolyte and solid HTM. Namely, the electron is hopped through the solid HTM instead of reducing in the liquid electrolyte.

Figure 5. (a) General structure of solid-state solar cells and (b) working principle.

In order to satisfy the HTM's working within the other film layers, the corresponding layer should fill the pores of the mesoporous TiO$_2$ film layer. With that a heterojunction is produced. For filling process, a molecular HTM structure may be determined. This molecule may be selected from various types of structures, such as small molecule HTM (mostly spiro-OMeTAD is used), and an inorganic or organic HTM. During the layer design, the hole diffusion length and conductivity of HTM is selected at the meantime, because these are parameters directly affecting the layer thickness of the mesoporous TiO$_2$. Namely, the TiO$_2$ film layer thickness is inversely proportional to the absorption coefficient. In other words, the less TiO$_2$ layer thickness, the more the absorption coefficient value. Here, unfortunately, the mesoporous film thickness can only be stretched up to 2 μm, i.e., when spiro-OMeTAD is used [85]. Hence, a breakthrough development in a solid-state DSSC is not expected with typical molecular dyes that constitute ~10^3 cm^{-1} of absorption coefficient. Neatly, in order to wholly collect the incident light arrays using those dyes, a TiO$_2$ layer with a thickness of 10 μm is needed.

The main problem in the early HTMs leads researchers to think that they may achieve a high efficiency solid-state sensitizer for SCs by means of a stronger light absorbing material. This becomes realized by means of the perovskites' property that has superiority against traditional dyes in terms of absorption. Namely, it has a stronger adsorption over a broad range and therefore full coverage absorption becomes realized within a very low thickness of 500 nm. This property of Perovskite becomes a real advantage for solid-state SCs. Because the previous obstacle for them were that a mesoporous TiO$_2$ film thickness restricted at around 2 μm length is needed in order to generate photocurrent with the given light absorption [30].

4.2. New small molecules as hole conductors: spiro-OMeTAD

The perovskite basically yield high series and shunt resistances which results in lower FF for SC devices. This is mainly because of the perovskite layer with higher conductivity in contact with the thicker layer of HTM that has lower conductivity. Hence, reduced thickness and better conducting HTM layer is a must to develop more efficient PSC devices [50].

Recently, some efforts on spiro-OMeTAD molecules used as HTM are under attention of researchers in view of their increased hole conductivities [86, 87]. For example, lithium bistrifluoromethanesulfonimide (Li-TFSI) has been found out to increase the hole conductivity when doped to spiro-OMeTAD, within some researches [87]. Using various techniques, spiro-OMeTAD has widely been used for enhancements in conductivity through increasing the hole mobility and charge density in HTM layers [88, 89].

Within the cell, the holes are injected from the perovskite into the spiro-OMeTAD and electrons are passed from perovskite to the mesoporous TiO_2 layer. Here, therefore, the TiO_2 is an active counterpart of the photovoltaic conversion event which makes it a main element of the PSC. Lately, it was fortunately shown that TiO_2 scaffold has leaded a PCE of up to almost 10% [20, 74]. In some studies, spiro-OMeTAD has also been used while coupled with other scaffolds (i.e., Al_2O_3). Where it is mixed with perovskites and good PCE has been attained in [30, 74]. These are famed as meso-super-structured SCs where the $CH_3NH_3PbX_3$ is served as an electron transport material (ETM) in addition to its basic sensitizer duty. Besides with all that, the metal oxide only acts as an insulator with a wide band gap and therefore do not take part in charge transport. Hence, the metal oxide becomes an inactive scaffold here. For that, these are referred as passive scaffolds in the PSC literature. It is good to say that a more uniform perovskite layer formation is applicable with a wide thickness in both of the scaffolds which improves the light absorption of PSCs, thus lead an increase in efficiency [74].

Besides all, new kinds of small molecules as for HTM are continuously introduced to the literature. For example, a Trux-OMeTAD small molecule is reported where an excellent hole mobility is achieved [90]. Here, the constructed PSC has given efficiency as close as to 19%.
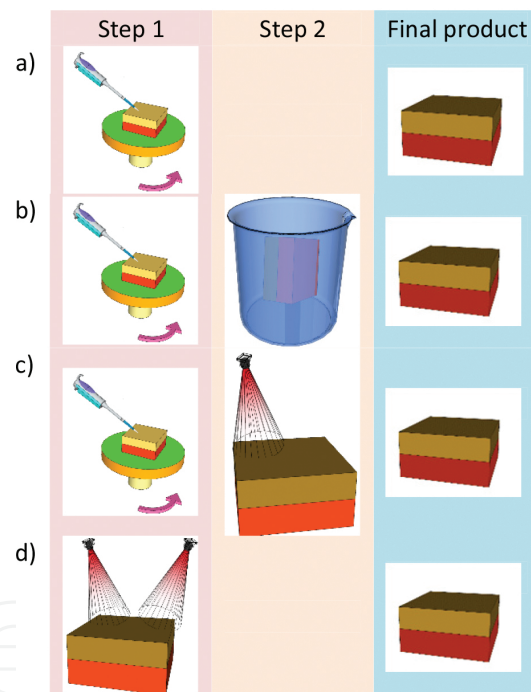
4.3. Inorganic and polymer HTM

Inorganic HTMs: The inorganic HTMs are rather low cost materials; on the other hand, they have progressed less in recent years due to the poor existence of such materials. The most known inorganic HTMs are listed as CuI, CuSCN, and NiO with respective PCEs of around 6, 12, and 11%. These inorganic HTMs are evaluated in mesoporous-type PSCs. The main advantage is their stability yielding property in ambient conditions compared to the organic HTMs. On the other hand, they yield a low-quality performance compared to the organic HTMs which makes them disadvantageous against others, as well.

Polymer HTMs: Compared to the inorganic counterparts, organic-based HTMs have tunable oxidization potentials and surface morphology. In addition, high V_{oc} values can be attained together with advanced HOMO levels [78, 91–93]. Basically, polymer HTMs have some drawbacks related to filling the pores which was tested in solid-state DSSCs before. Some kinds of polymer HTMs are known to be PTAA, P3HT, and PANI. It has been shown that they have generally good hole mobility and satisfies a better film formation. Among them, PTAA and P3HT have yielded an efficiency level of around 12 and 6%, respectively [31]. The efficiency of PTAA has later been reported to reach more than 16% using a mixed structure with perovskite material [31, 94, 95]. There has been a study where P3HT is used together with carbon nanotube and formed a novel composite [96] in which the conductivity of the new structure is increased

more. Besides PTAA and P3HT, PANI is also known to satisfy a long-term stable device, which is tested through characterizations.

5. Film formation and stability

The optical and electrical properties of perovskite films show varieties depending on the film formation conditions, such as atmospheric conditions and materials' ratios, which affect the device performance significantly. Up to the present time, several film techniques for fabrications of perovskite have been reported. Generally, these are grouped as (1) solution process and (2) vapor deposition process. The solution processes can be carried out either as a (a) one-step coating technique, or (b) sequential two-step coating technique. The vapor deposition processes are considered through two types of production as well, using (a) the dual-source evaporation process and (b) vapor-assisted solution process (see **Figure 6**).

Figure 6. Fabrication of perovskite cells through (a) one-step solution-based, (b) two-steps solution-based, (c) two-step solution and deposition-based, and (d) one-step deposition-based processes.

5.1. Solution processed methods

Two solution process methods have been developed in order to create perovskite film onto substrates: (1) one-step coating and (2) sequential (two-step) coating methods. The first deposition method is the most widespread film coating method for PSCs because of its ease of processing and low production cost. In general, the precursor solution contains the mixture of CH_3NH_3X (or other OMH perovskites) and PbX_2 (where X: I, Br, Cl) at 1:1 or 3:1 molar ratios.

This mixture is dissolved in a polar aprotic solvent, such as *N,N*-dimethylformamide (DMF), γ-butyrolactone (GBL), or dimethyl sulfoxide (DMSO). Nevertheless, it is still a challenging issue to form a homogeneous pinhole-free perovskite film using the one-step deposition process. Therefore, the device efficiency is significantly reduced by a poorly coated perovskite layer which causes decreased light absorption and also poor shunting path for charge recombination process [6, 97].

The second deposition method is another kind of solution-based coating process for PSCs. This is first introduced by Mitzi et al. [98], and first used by Burschka et al. [82] for PSC fabrication. In this method, PbX_2 is coated on TiO_2 layer under optimal conditions that is adjusted through spin-coating speed and solution concentration. The optimal coating conditions should yield full penetration of this material into the mesoporous layer. Subsequently, the perovskite layer is obtained either by dipping the substrate into a solution of CH_3NH_3X/isopropanol [82] or by spin-coating of CH_3NH_3X molecules on to the substrate [99]. Here, the perovskite films coated by using the two-step process have a cuboid-like crystal structure, while the one-step method provides a shapeless morphology. Among them the process can be much better controlled to form perovskite morphology by using the two-step method. Namely, better PbX_2 confinement into the nanoporous network of TiO_2 is obtained using this method. Moreover, the two-step sequential coating process provides more uniform and dense perovskite films compared to the single-step coating process. Hence, high efficiency perovskite devices can be fabricated using this process. In addition to all, the two-step process is both well controlled and provides a reproducible treatment.

In the two-step coating process, the perovskite grain size can be controlled by changing molar concentration of the CH_3NH_3X solution. Nevertheless, there are some drawbacks of this coating method related to the trade-off between surface smoothness and perovskite grain size. The perovskite films which have larger grain size also have poor surface morphology which may negatively affect the device efficiency.

The incomplete perovskite conversion is another challenging issue within the two-step coating process. This problem can be overwhelmed using some developed device engineering techniques expressed in the study performed by Song et al. [100]. Recently, the PCE of a perovskite SC has reached 20% through the second-coating method [101].

5.2. Vapor deposition methods

One of the vapor deposition methods consists of a dual-source evaporation process. The vapor deposition method through using dual evaporation sources of $PbCl_2$ and $CH_3NH_3PbI_3$ was first used by Snaith et al. These were realized for $CH_3NH_3PbI_{3-x}Cl_x$-based planar SCs. The manufactured PSCs attained an efficiency level of 15% [84]. In this process, the dual sources contain $PbCl_2$ and $CH_3NH_3PbI_3$. Here the two sources are simultaneously heated to about 120 and 325°C, respectively. Thereafter, the evaporated materials are codeposited onto the TiO_2/FTO substrate in a high vacuum chamber. The pinhole-free and extremely uniform perovskite films can be produced by using this method. However, since it is crucial to use high vacuum for this method, thermal evaporation method is limited because of high cost, low

thermal stability of sources, and unsuitability to mass production. Hence, only a few research groups have published high efficiency PSCs using this method [102, 103].

The other vapor deposition method is called vapor-assisted solution process. The vapor-assisted solution process is almost same as the two-step solution process except an additional modification. In this method, the first step of the two-step solution process is applied initially. Then, CH_3NH_3X is coated onto substrate by vapor deposition. This method provides better grain size and surface morphology control through gas-solid crystallization. In contrast, liquid-solid interactions, which occur in the two-step coating process, may result in delamination of the film. On the other hand, this deposition method allows uniform surface, large grains, and full conversion to the perovskite structure. Nevertheless, this method is restricted by its long processing time passed during the manufacture. For example, the gas-solid reaction takes tens of hours for the full conversion. With all that, the PSCs produced using this method could only attain device efficiencies of up to 12% [104, 105].

5.3. The impact of film composition

The surface morphology of the perovskite film has an important effect on the device performance. As mentioned above, high coverage and uniform crystallinity is required for high power efficiencies. One of the most important effects that influence the surface morphology is the composition of the perovskite films.

In order to increase PSC efficiency, mixed-halide perovskite films have been studied by modifying their film compositions [30]. For instance, a perovskite layer of $(NH_2CH = NH_2PbI_3)_{1-x}$ $(CH_3NH_3PbBr_3)_x$ was used in a SC device. Here, in order to examine the influence of the perovskite materials' composition on the device performance, the proportion of $MAPbBr_3$ in the $FAPbI_3$ was altered. When the composition value is kept at $x = 0.15$, an extremely smooth morphology with EQE > 80% is attained without any noticeable pinholes [106]. Another perovskite film material $MAPbI_{3-x}Cl_x$ was also studied to examine the effect of the chlorine composition on morphology and device performance. It is reported that chlorine allows lower temperature thermal annealing, therefore, it results in reduced pinholes and voids [107, 108].

5.4. The stability of perovskite solar cells

The stability of PSCs is the most critical issue to obtain high performance devices. The stability issues can be related to both perovskite material and SC devices. In order to resolve the related problems and to develop effective strategies, physicochemical processes occurred during the perovskite degradation should be understood. We note that the comparison of stability testing results taken from different studies generally become a challenging issue due to different experimental conditions, such as light intensities, humidity level, temperature, and atmospheric conditions [17].

Air stability: The two molecules in the air, H_2O and O_2, negatively affect the stability of PSCs. Perovskite film color can change from brown to yellow. In order to obtain air stable perovskite

devices, the degradation process should be clearly understood where there are few reports about the effects of O_2 on perovskite films. According to the study about the degradation mechanism of the perovskite under water [109], it is shown that the hydrolysis reaction of $CH_3NH_3PbI_3$ arises under humid condition.

Photo-stability: The mesoporous TiO_2 layer in the device is preferred in order to easily transport photo-generated electrons. On the other hand, TiO_2 is inherently sensitive to ultraviolet light, which may cause degradation in PSCs. The instability of encapsulated and nonencapsulated perovskite devices was investigated through considering the device efficiency by Snaith et al. [110], and it is showed that the degradation of the first-type device occurs faster than that of the second type. Nevertheless, the first device has given a more stable condition in the lack of UV light. In order to overcome this photo-instability due to the TiO_2 layer, the respective authors suggest some methods such as pacifying the trap states, replacing the TiO_2 layer with other materials, and avoiding UV light from the TiO_2 layer. For example, stability at over 1000 hours at 40°C is accomplished when mesoporous Al_2O_3 is used instead of TiO_2 layer in the PSC device. Nonetheless, the PCE was decreased to around by half of its first value after the first 200 hours. A continuing reduction is also observed in both V_{oc} and FF values.

Thermal stability: Thermal stability is an issue regarding both perovskite material and in HTM layer. The intrinsic thermal instability of a perovskite material was reported in the literature [111], and it is showed that even though the film was maintained in an inert condition, the degradation of perovskite is seen at 85°C. It means that the SCs may not be used properly in cases where the SC temperature exceeds this temperature level.

6. Summary

Perovskite has been the most initiative and promising material in terms of energy harvesting among organic, inorganic, and organic-inorganic SCs [8]. In case the difficulties, which are mainly about stability, are overcome, the humanity would face to a new and affordable solar energy harvester for future use. Therefore, the novelties in PSC technology attract a large amount of attention in our recent world due to its significance on its effectiveness on electricity production from free and abundant sunlight.

The main prospects for the future cover the strategies in terms of reducing the band gap, enhancing the light absorption capacity, and improving the conversion efficiency. In addition, exposing the charge transport properties and improving interfacial engineering methods in device fabrication are important. Especially, the chemistry work on chemical composition has great value. Hence, the lion's share for future work should be explaining the photo-physical mechanism of solid-state SCs with respect to different chemicals.

Unfortunately, the present information obtained on "how PSCs operate?" is rather insufficient at least for now. Because the complete working principle is not well explained [18, 19]. Therefore, deriving novel clues on (1) light absorption, (2) charge separation, (3) charge transport, and (4) charge collection are needed during research since these four key issues are general SC parameters to identify the principal working of solar conversion process.

The PSC is mostly accompanied with a HTM layer. In view of the available HTMs, the inorganic ones are rather less progressed reaching an applied efficiency of 11%. On the other hand, these applications are promising in view of their improved stability against ambient conditions. With respect to these, polymeric HTMs offer tunable oxidization potential and better surface morphology. In addition, the researchers also attained advanced HOMO levels [78, 91–93]. The efficiency of polymer HTMs-based SCs is reported to reach more than 16% [31, 94, 95]. The third kind of HTMs is small molecules. Among these, spiro-OMeTAD has been the most used HTM in PSCs till now since it has already been evaluated in solid-state DSSCs and OLED devices [67, 83, 112] (that is, spiro-OMeTAD has already been a standard HTM for researchers). The use of hybrid lead halide with spiro-OMeTAD-based HTM is reported to give an efficiency of around 15% PCE [82, 84]; however, the cost of spiro-OMeTAD remains high due to its difficult synthesis process. Therefore, novel small molecules should be designed and synthesized in order to develop cost-effective PSC devices.

We note that PSCs evolved rapidly and the semiconducting phenomena occurred within the cell remained shaded until now. Hence, the semiconducting behavior is continuously investigated benefitting from the current-voltage characteristics of SCs in some research groups [113]. Deriving an increased efficiency level in PSCs is also related to the way how deposition is carried out. The perfection within the selected coating method is also important [114, 115]. Besides all discussion presented here, we note that the use of completely wet processing method during the production of SCs is especially important for an easy fabrication. Therefore, studies made on "all-solution production process" are highly valuable since vacuum production is expensive and highly energy dependent [116].

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