Advanced Perovskite Materials: Structure, Properties, And Applications in Solar Cells

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Abstract. Perovskite solar cells (PSCs) have developed rapidly in the past two decades. During this period, the energy conversion efficiency (PCE) of PSCs increased from 3.8% to 26%, indicating that PSCs is a promising candidate in the battery field. The low-cost fabrication process and excellent light-absorbing properties of perovskite materials have attracted the attention of researchers. Till now, PSCs have not been commercializated due to their instability and toxicity of the materials. Therefore, seeking for stable, long-lived, and environmentally friendly PSCs is of great significance for the commercial application of PSCs. So far, a large numbers of attempts have been made to achieve such goals. Lead-free PSCs, large-area PSCs, and more sophisticated encapsulation technologies were explored. This review discusses the photovoltaic properties of perovskite materials and introduces typical structures of PSCs along with their basic fabrication processes. In addition, the performance and commercialization progress of PSCs are also reviewed. Finally, potential research directions for commercialization of PSCs were pointed out. This work will contribute to a further understanding of PSCs.

Keywords: Perovskite solar cells; perovskite film; fabrication; application.

1. Introduction

Perovskite solar cells (PSCs) are a promising photovoltaic technology due to their high efficiency, easy-processing, and low-cost. The term 'perovskite' refers to a crystal structure with the formula ABX_3. This structure consists of the cation A, cation B and anion X. Perovskite materials have a unique crystal structure that allows for efficient light absorption and charge carrier transport, making them excellent candidates for use in solar cells. The rapid advancements in PSCs can be attributed to several key factors. The remarkable optoelectronic properties of perovskite materials are foremost among them, which include high carrier diffusion lengths, absorption coefficients, and tunable bandgaps. Due to these above-mentioned properties, PSCs can accomplish energy harvesting within a wide wavelength range, making PSCs competitive candidates even compare to traditional silicon-based solar cells. Additionally, the large-scale production of PSCs at reduced manufacturing costs are expected to be realized, because of the solution processability of perovskite precursors.

Furthermore, current research associated with PSCs is focused on improving long-term stability, reducing toxicity, and enhancing environmental sustainability. This paper presents a thorough review of the progress made in perovskite solar cell technology, covering materials development, device fabrication, characterization techniques, and performance optimization strategies. Additionally, the current challenges and future prospects for PSCs are highlighted.

2. Properties of Perovskite Materials

2.1. Crystal Structure of Perovskite

Perovskite is a calcium titanate ($CaTiO_3$) compound found in perovskite ores. It was first named after Lev Perovski, a Russian mineralogist, and has a fixed structure formula of ABX_3. The active layer of perovskite material in perovskite solar cells is generally composed of the following elements: A is an organic molecular cluster, which usually refers to $CH_3NH_3^+$ (MA^+), $NH_2CH{=}NH_2^+$ (FA^+), Cs^+; B are lead (Pb^{2+}) or tin (Sn^{2+}) ions; X refers to halogen ions, such as I^-, Cl^- and Br^- [1]. As it is

shown in Figure 1, the cation B is located in the octahedron formed by anions, while cation A is located at the center of a polyhedron of 12 anions in equal coordination positions. Most perovskites have distortion and are not a ideal cubic structure. The formability of perovskite can be calculated by geometric tolerance factor (t), as it is illustrated formula (1).

$$t = (r_A + r_X)/\sqrt{2}(r_A + r_B) \quad (1)$$

where, r_A, r_B, and r_X represent the effective ionic radii for A, B, and X ions, respectively. When t=1, it can form an ideal body-centered cubic structure. If t<1, the octahedral structure will be deformed. For alkali metal halide perovskite, 0.813<t<1.107 is expected in order to obtain the perovskite structure needed for solar cells [2]. Due to the crystal structure of perovskite, the bonds in perovskite materials are highly ionic. Therefore, it is easier to be degraded by oxygen, moisture and polar solvents compared to conventional semiconductor materials.

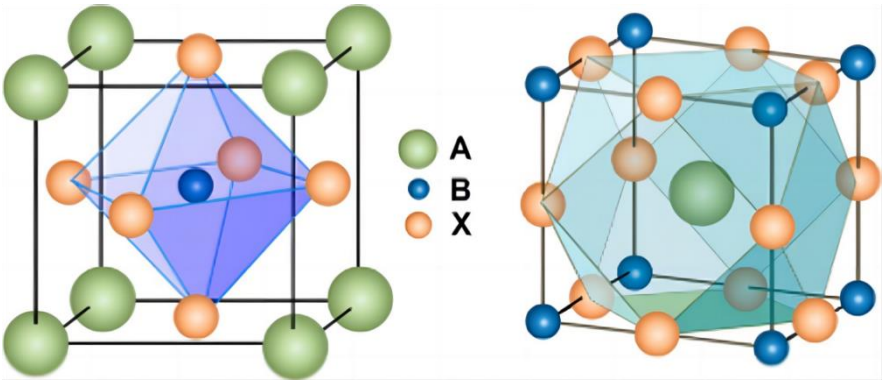

Fig 1. The perovskite structure of ABX_3 [3].

2.2. Absorption Coefficient of Perovskite

As a semiconductor with wide band gap, perovskite materials can absorb photons with energies greater than their band gap. A perovskite material with a thickness of 300nm has been reported to absorb most visible light, while ilicon materials require to be at least micrometer thick to reach the same effect. Figure 2 displays the absorption coefficient α(λ) of several materials as a function of wavelength. It is evident that $CH_3NH_3PbI_3$ with perovskite structure exhibits high absorption coefficient at wavelengths less than 780nm. This characteristic is contributed to the development of high-efficiency solid-state sensitized PSCs.

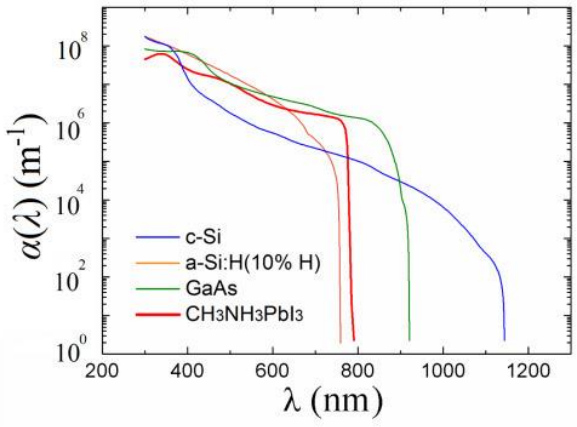

Fig 2. α(λ) of c-Si, a-Si:H(10%H), GaAs and $CH_3NH_3PbI_3$ [4].

2.3. Carrier Transport Properties of Perovskite

The bipolar transport of perovskite materials reflects their excellent carrier transport characteristics, which can be further improved by adjusting their composition, controlling their morphology, modifying their interfaces, and growing single crystals. In common semiconductor materials, the effective mass of holes and electrons differs greatly, resulting in distinct transport characteristics. The effective mass of holes in $MAPbI_3$ perovskite is similar to that of electrons. The bipolar transport characteristics of perovskite materials affect the performance of perovskite batteries during charge transport and collection by controlling the polarization of charge carriers in heterojunctions. It is widely recognized that the efficiency of solar cell is closely related to its absorption coefficient, direct bandgap transition, effective mass, diffusion length, and relatively carrier mobility [8].

3. Structure of Perovskite Soalr Cells

Mesoporous and planar structures are the most primary structures in PSCs. Mesoporous structures usually are regular, which means they have negative-intrinsic-positive arrangement (n-i-p type): compact ETL/mesoporous, ETL/perovskite/HTL/electrode. In this mesoporous structure, metal oxide (like TiO_2 and Al_2O_3) are also used as a scaffold layer to support perovskite layer. In addirion, it can also increase the contact area between the perovskite layer and the ETL to improve the charge transport efficiency. The perovskite layer is a light-absorbing layer. The excited carriers are then transported to the electrode through the ETL and the HTL. Figure 3 shows three common structures of n-i-p structure and p-i-n structure. The most common mesoporous structure has a FTO cathode. TiO_2 to be the n-type ETL, perovskite, doped Spiro-OMeTAD to be the p-type HTL and Au to be the metal anode. Here, Spiro-OMeTAD, an amorphous organic hole-transport material, has an excellent property in this area. However, this mesoporous thin film requires a high-temperature annealing process before perovskite was deposited onto it. At these temperatures, the flexible substrate can be damaged or even melted thus limit the further development of the device. PSCs with planar heterojunction structures are typically inverted. The structure of this type of solar cell consists of a transparent conducting layer, a hole transport layer, a light-absorbing layer, an electron transport layer, and an electrode. Common hole transport materials include PEDOT, PSS, and NiO. Due to the inherent characteristics of perovskite cells, the efficiency of flexible substrates is relatively high. This expands the applications of PSCs, making them suitable for applications in automobiles in the future.

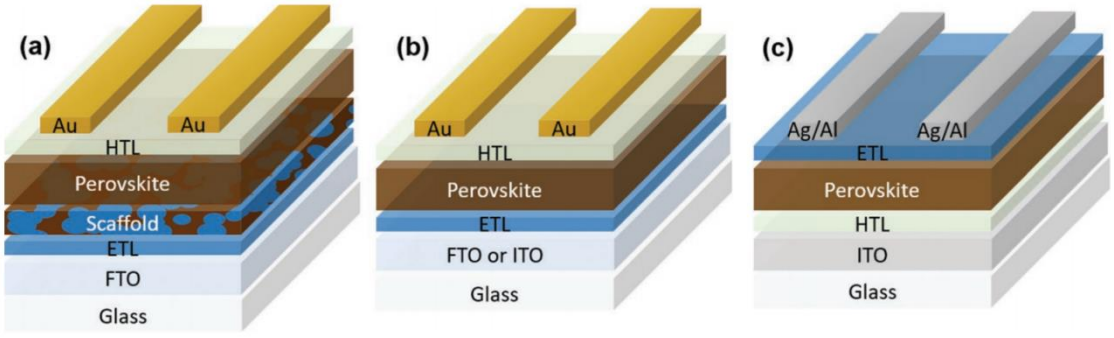

Fig 3. Structures of PSCs:(a) mesoporous NIP, (b) planar NIP, and (c) inverted planar PIN [5].

4. Fabrication Techniques of Perovskite Solar Cells

Qualities of the films can determine the performance of PSCs. Thus, there is need to develop better fabrication technologies which can accomplish thorough coverage, no voids, and high degree of crystallinity. Numerous techniques at low temperatures can generate perovskite layers owing to their minimal activation energy. One-Step and Two-Step processes are often used to fabricate the perovskite film. Both of them belong to the spin coating process, which is widely used in the

laboratory, as it is shown in Figure 4(a). It can be used to manufacture films with high uniformity and high performance. It can also be used to obtain films of different thickness more accurately by changing parameters such as time and speed. For the one-step method, all the precursors are usually dissolved in a solvent, and the mixed solution is spin-coated directly onto the substrate to obtain a perovskite film. As for the two-step method, taking $CH_3NH_3PbI_2$ as an example, PbI_2 is spin-coated onto the substrate firstly, and then organic ions are released in solution or vapor to obtain a perovskite film. The morphology and surface state of the prepared thin film have an impact on its performance. Therefore, a large number of studies on post-processing have been reported concerning with the morphology of thin films. Vapor-assisted solution method is another film preparation method that has been widely used in the semiconductor industry, which can accurately control the crystallization process, as it is shown in Figure 4(b). For this method, high vacuum assistance is needed [6].

4.1. One-step Method

This technique was most widely used because of its low-cost and easy processing comparing to other methods. In this perovskite film fabricating technique, all the precursors including PbI_2 and methylammonium iodide (MAI) are dissolved in an aprotic polar solvent, such as DMF, DMSO, GBL, DMAc, and NMP. Then the mixture can be coated onto the substrate directly. During the spin-coating process, evaporation of solvent and convective self-assembly occurred thereby lead to the supersaturation of dissolved precursor. Then uniform and crystallized perovskite layer can be formed. Afterwards, the film would then be annealled at a temperature of 80-150^{o}C [7]. However, the imprecise operation and slow film formation rate lead to the poor quality of films. For instance, the formed film is difficult to cover the substrate completely, which leads to inhomogeneous and poor crystallization of the film. The primary reason of sluggish nucleation is the elevated boiling points and minimal vapor pressure of solvents at ambient temperature, thus generating nonuniform perovskite film. Therefore, much research is developed to evaporate the solvent rapidly and control the nucleation of films accurately. Gas blowing, substrate heating, solvent engineering and vacuum treatment are reported to be the effective means.

4.2. Two-step Method

The two-step method was reported to fabricate $MAPbI_3$ films initially. The PbI_2 was deposited on substrate, and then perovskite film was obtained by reacting with MAI solution. There are two methods to add the MAI solution: (i) dip coating the PbI_2 film over MAI solution (ii) spin-coating the MAI solution onto the PbI_2 layer. To get high quality films, speed and time of spinning the MAI solution need to be accurately controlled. Moreover, dipping time and concentration are also significant factors to affect the consistency and crystallinity of perovskite films. Though the two-step method, the nucleation process can be controled. In addition, films with better quality can be obtained. It is worth noting that the roughness of the film surface increases as the grain size increases during crystallization. This led to elevated leakage current and heightened surface recombination losses. Furthermore, residual PbI_2 during treatment would hinder carrier transport and thus reduce the efficiency of PSCs.

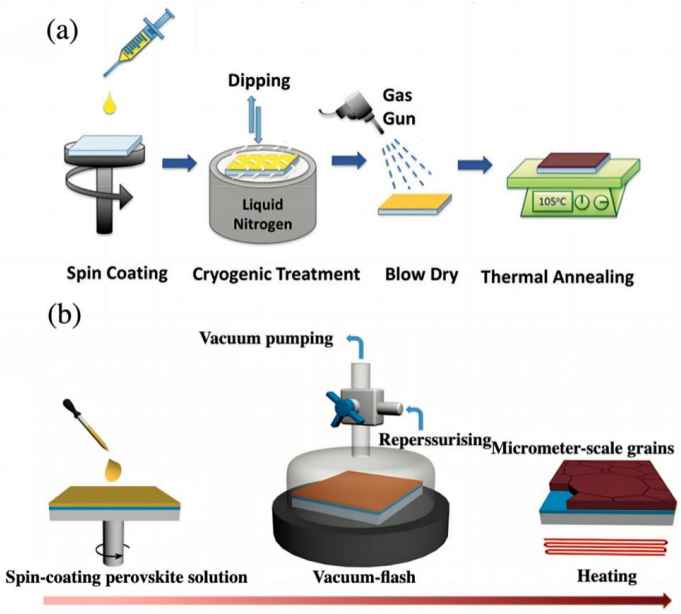

Fig. 4 (a) Diagram depicting cryocontrolled nucleation for perovskite synthesis and (b) Illustration outlining the nucleation and crystallization steps involved in the generation of a perovskite film using vacuum flash-assisted solution processing (VASP) [8]

5. Progress in Perovskite Solar Cells

$MAPbI_3$ solar cell is a kind of PSCs, but their thermal instability renders them from practical commercial applications. Therefore, scientists have replaced MA ions with FA with a stronger hydrogen to enhance the thermal stability of PSCs. Additionally, in order to attain the ideal bandgap of 1.34eV, many other structures have been explored as shown in Table 1. Three major classes of non-lead perovskite have been extensively researched, in addition to Pb-based PSCs, which currently exhibit the best performance. It can be seen that the PCE of some lead-free PSCs is already comparable to Pb-based PSCs.

Table 1. Performance of PSCs

Classfications	Device structure	PCE (%)	Ref.
Pb-based	TCO/ZnO/$CH_3NH_3PbI_3$/CuI/Pt	23.2	[11]
Sn-based	FTO/PEDOT-PSS/Sn/perovskite/SnO_x/C_{60}/BCP/Ag	14.31	[12]
	FTO/TiO_2/$CH_3NH_3SnI_3$/CZTS/Au	25.48	[13]
Ge-based	FTO/ $Cd_{0.5}Zn_{0.5}S$/ IDL_1/ $CsGeI_3$/ IDL_2/ CuI	20.19	[14]
Mixed halide	ITO/Neutral PEDOT/$Cs_{0.2}FA_{0.8}Pb_{0.5}Sn_{0.5}I_3$/BDA/$C_{60}$/BCP/Cu	23.7	[15]
	FTO/c-TiO_2/m-TiO_2/$CsPbBr_3$/carbon	9.72	[16]

5.1. Progress towards Commercialization of PSCs

Device performance, stability, cost are currently the three main factors influencing the commercialisation of PSCs. In terms of cost, the cost of PSCs currently is comparable with the cheapest crystalline silicon solar cells. It is estimated that perovskite solar panels have the potential to reach a cost of approximately $0.10 per watt in the future, making them one of the most economical photovoltaic technologies. Due to the extremely high photon absorption capacity of perovskite and the relatively simple preparation process, PSC also has good device performance. However, the lack

of stability and loss of high efficiency hinder its further development. Therefore, large-size devices (1 cm^2 or even larger) are urgently expected. Great commercialization prospects for PSCs attract significant financial support which would contribute the further development of PSCs [10].

6. Conclusion

PSCs are expected to be a significant innovation in photovoltaic power generation. Their low cost and simple fabrication process make them ideal for commercialization. This review provides a basic description of the structure, material properties, and fabrication process of PSCs. Due to some drawbacks of the perovskite material, further research is needed to improve device performance. Firstly, developing new perovskite materials that environmentally friendly is important for the further development of PSC. In addition, improving manufacturing and encapsulation processes is necessary to enhance the stability of PSCs for large-scale commercial cell production. Moreover, optimising device structure to improve carrier transport is also a topic worth further research.

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