

Recent Progress and state-of art applications of Perovskite Solar Cells

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Abstract. Contemporarily, perovskite solar cells have become one of the hot topics among new energy. Currently, the highest photovoltaic conversion efficiency of perovskite tandem cells has reached 29.8%. Compared with silicon-based solar cells, which currently occupy most of the market share, they have a wider absorption band gap, and lower manufacturing cost and simpler manufacturing process, making them a strong candidate to replace silicon-based cells in the future. However, the commercialization of it is still hampered by its poor stability. This paper reviewed the state-of-art results from literatures, including the selection of materials for transport layers and the performance of different types, and summarize the limitations from the perspective of the working principle the cells. Finally, the current status of perovskite solar cells is summarized and the outlooks are put forward. These results offer suggestions for further studies focusing on perovskite solar cells.

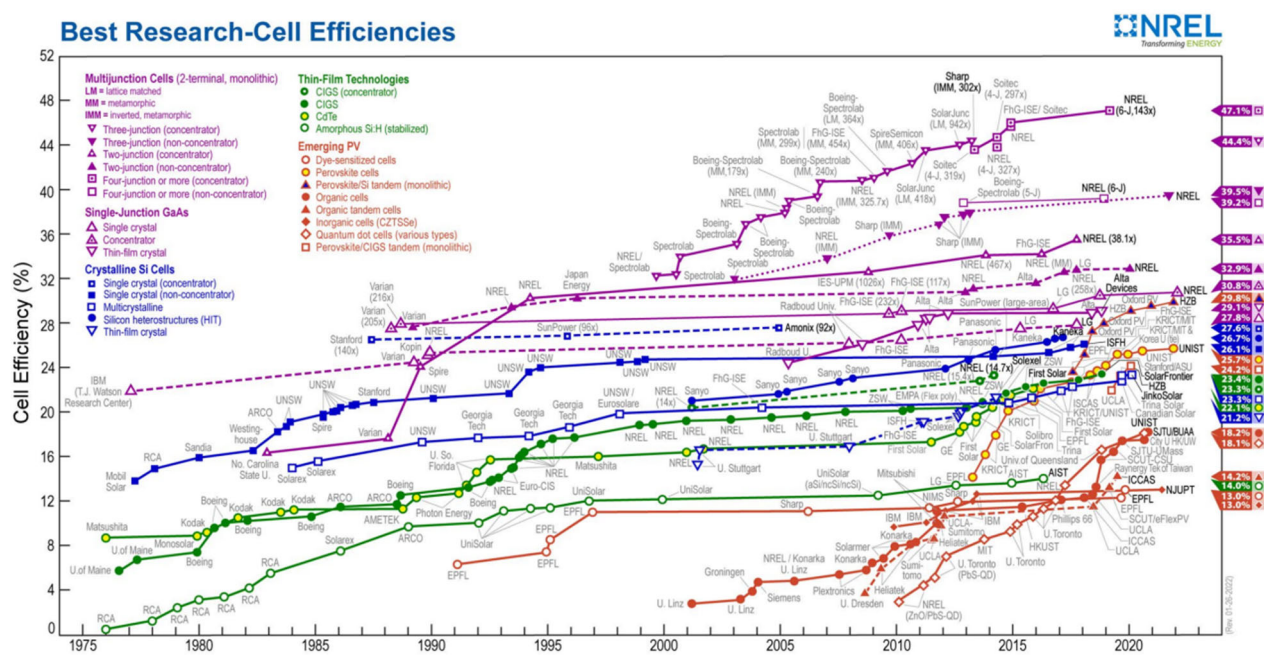
Keywords: Third generation solar cells, all-inorganic perovskite solar cells, hybrid perovskite solar cells.

1. Introduction

While scientific development drives the progress of the times, energy shortage and uneven distribution have become the biggest obstacle limiting the further development of human society. Besides, the decline of non-renewable energies and the damage to the natural environment caused by energy extraction has aroused worldwide concern and worries. Human beings are looking for green and clean renewable energy sources to solve this problem, photovoltaic power generation has become one of the most important. The light and heat radiated by the sun to the earth contains enormous energy up to 1.75×10^{14} J per second. If this energy can be harnessed efficiently, it will become an important supplier of energy reserves for the world. Solar cell technology is a simple and effective way to harness photo-energy by directly converting inexhaustible solar energy into electricity.

Becquere, a French physicist, discovered in 1839 that light may create a potential difference between distinct portions of a semiconductor material. The photovoltaic effect was later named after the phenomena. In 1954, American researchers Chapin et al. created the first viable monocrystalline silicon solar cell in Bell Labs, paving the way for photovoltaic technology to become a reality. After more than 170 years of development, solar cells have experienced plenty of milestones.

The power conversion efficiency (PCE) of current product is generally around 20%, which have been in service for over twenty years in various industries with very stable performance. The first generation of solar cells represented by single-crystalline silicon and multi-crystalline silicon, their highest record efficiency reached 26.1% and 26.7% respectively. The conversion efficiency of second-generation products has been further improved, Gallium Arsenic thin-film solar cell, for example, reaching a maximum efficiency of 28.1% [1]. Nowadays, crystalline silicon type possesses about 90% of the whole PV market, but problems still exist among these cells. The first-generation cells are generally more expensive to produce and have a bottleneck in the conversion efficiency. Second-generation cells have improved efficiency, but mass production of these metal-based cells poses environmental problems. Therefore, perovskite solar cells, as a new type of third-generation solar cells, are receiving extensive attention and research. The advantages include a relatively simple preparation process, inexpensive and easily available raw materials, wide tunable band gap and high photoelectric conversion efficiency.



In 2009, Japanese scholars Tsutomu Miyasaka pioneered the use of perovskite materials and obtained a photovoltaic conversion efficiency of 3.8% using $\text{CH}_3\text{NH}_3\text{PbI}_3$ -sensitized TiO_2 sunlight electrodes and liquid I^-/T electrolytes. In 2012, Henry Snaith of Oxford University replaced the TiO_2 in the cell with Al_2O_3 , i.e., the perovskite is not only an absorber of light in the cell, but also serves as a semiconductor material for charge transfer. As a result, the PCE of the calcium-titanium oxide cell climbed to 15%. In 2018, scholars stated an approach of organic salt passivation of perovskite surface defects and developed a conversion efficiency of 23.3% and 23.7%. As shown in Fig.1, Helmholtz-Zentrum Berlin (HZB) developed a perovskite/Si tandem photovoltaic(monolithic) with the efficiency up to 29.8% recorded as the best performance in 2021. The current research progress is mainly focused on these hybrid organic-inorganic metal halide perovskites (HOMH perovskites). This paper will discuss the natural advantages of perovskite solar cells from the characteristics of perovskite structure, show the great performance of perovskites and compare with previous generations of solar cells, the current problems and limitations of and conclude the paper. The rest part of the paper is organized as follows. The Sec. 2 will introduce the working principles and properties of PSCs. The Sec. 3 will show the current selection of transport layer materials in and comparing the operating performance of two types of PSCs. The Sec. 4 will summarize the limitations that prevent the widespread dissemination of PSCs. Finally, a summary and an outlook are put forward.

2. Principle of perovskite solar cells

2.1. Photovoltaic effect

Since Becquerel discovered the photovoltaic effect in 1839, it has been implemented in photovoltaic power industry, which serves as the basis for solar cells. When a PN junction is irradiated by sunlight, the photosensitive material absorbs the energy of photons to produce electron-hole pairs. The electron-hole movement in the space charge region and the charge separation through the interface layer results in voltages on both sides of the PN junction, i.e., photogenerated voltages. If the PN junction is connected in a circuit, a current is formed. PCE is calculated as follows

$$\text{PCE} = \frac{P_{\text{max}}}{P_{\text{in}}} = \text{FF} \times J_{\text{sc}} \times \frac{V_{\text{oc}}}{P_{\text{in}}} \times 100\% \quad (1)$$

Here, $P_{\max}$ is maximum output power, P_{in} is maximum input power, V_{oc} is open circuit voltage, J_{sc} is current density proportional to maximum short-circuit current I_{sc} , FF is fill factor. Based on Eq. (1), it can be concluded that FF, I_{sc} and V_{oc} should all be maximized to maximize the efficiency of the solar cell.

2.2. Crystal structure features

Fig. 2 presents a sketch of the structure [3]. The cubic perovskite structure generally exists in the Pm-3m space group and is prevalent in every octahedron reflecting every neighboring body, forming a three-dimensional straight chain.

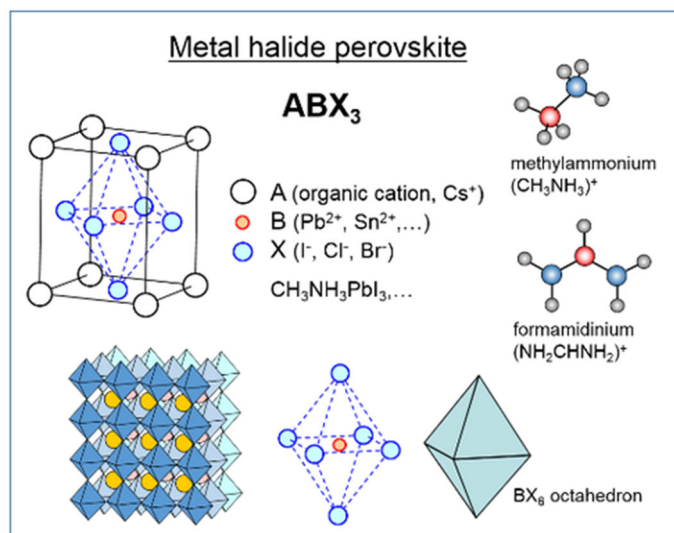


Figure 2. Crystal structure of perovskite materials [4].

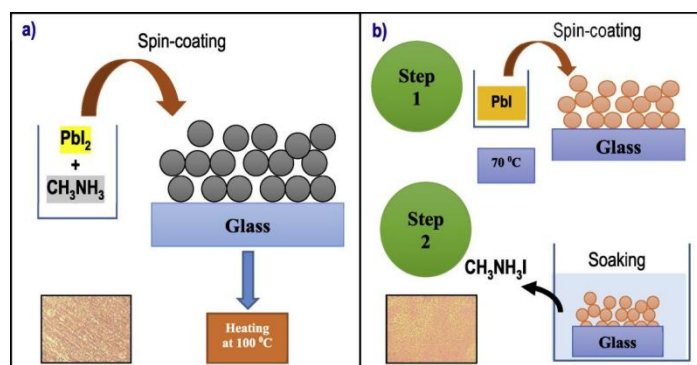


Figure 3. The sketch of a) single- and b) two-step deposition procedure [8].

2.3. Tunable band gap

As a matter of fact, tunable energy band width feature of perovskite solar cells is generally considered as the most crucial advantages. According to experiments, users can change the energy band width of PSCs in the range of 1.2 to 2.3 eV via controlling the composition of perovskite and varying the stoichiometry [5]. However, selecting the proper cation A and the matching BX_3 is not easy and requires consideration of many factors including matching of lattice constants, Shockley-Queisser limit and power conversion efficiency etc. The tunable energy band width of perovskite semiconductor materials is a double-edged sword. Its structural composition is very flexible, but it also poses a number of problems and the thermal stability is the most serious one, e.g., $\text{CH}_3\text{NH}_3\text{I}$ reacts and decomposes into CH_3I and NH_3 at temperatures as low as 80°C [6].

2.4. Crystallization processes of perovskite thin films

In 2019, a Chinese research team revealed that preparation procedures can alter the electrical characteristics of perovskite films. Carrier concentration, majority carrier type, and carrier mobility all are factors that will affect energy conversion efficiency [7]. According to previous literature, deposition is the main processing method for perovskite thin films. This approach can currently be carried out in vacuum or by solution processing. Although vacuum deposition produces more homogeneous films, solution-processing techniques have several advantages, including reduced costs and less scalability issues. Deposition methods are divided into two categories: single-step and two-step deposition. A related study indicated that two-step spin coating had greater absorbance than one-step spin coating due to superior morphology and interface, as depicted in Fig. 3, implying that management of coverage, pore filling, and morphology in perovskite films is crucial for high-quality perovskite films [8].

2.5. Structure of perovskite solar cells

As presented in Fig. 4, PSCs are mainly composed of five different layers [9]. Typical structures are mainly the following two types of structures, mesoporous structures and planar heterojunction structures. Normal and invert structures are used depending on the position of the electron transport layer (ETL) and hole transport layer (HTL).

Normal ones have the ETL on the top and are called n-i-p type, inverted ones are called p-i-n type. Electron transport layer transports electrons and blocks the transport of holes. Many factors need to be considered for the selection of ETL materials. For example, 1) the electron transport layer should have high density in order to avoid leakage currents and interfacial charge complexes generated by the presence of holes in the film; 2) the electron transport material also needs to have good chemical stability and cannot react with the perovskite layer or electrodes [10]. The hole transport layer mainly transports holes and blocks electrons. The selection of hole transport materials requires consideration of energy level matching, hole extraction and transport capability, chemical stability, etc. [11].

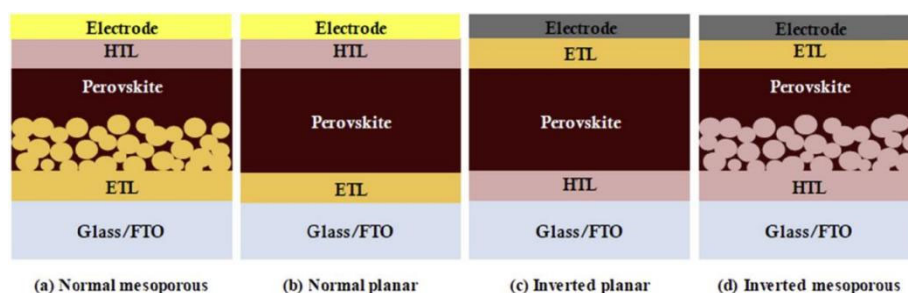


Figure 4. Four different schematic diagrams of perovskite solar cells [9].

3. Material for transport layers and Performance comparison

In the course of the development of PSCs, they are divided into two categories according to their different chemical compositions: all-inorganic PSCs and organic/inorganic hybrid PSCs. On account of the light weight, flexible device construction, and potential low cost, organic/inorganic hybrid perovskite, it has been extensively explored as viable alternatives for inorganic silicon solar cells over the last several years. This section will start with the material selection of ETL and HTL, two layers that can directly affect the photovoltaic PCE, and then discuss the latest research on the three types of PSCs and compare their performances.

3.1 Choice of ETL material

ETL is a component of PSC devices that is made up of a diverse of materials ranging from metal oxide semiconductors to fullerene-based polymers. Table. 1 lists the present best inorganic semiconductors that are used as ETLs in the PSCs [12]. Crystalline dense TiO₂ was the most common choice, and Mahmood et al. found that the higher average oxidation state of the amorphous TiO₂ surface significantly improved the performance of the PSC. In addition to TiO₂, tungsten oxide (WO_x) is a promising choice for efficient ETLs due to its chemical stability, strong electron mobility (10-20 cm²/Vs), and wide forbidden band width ranging from 2 eV to 3 eV [13]. Tin oxide (SnO₂) has also attracted great interest in PSCs in recent years due to its high forbidden band width (about 3.7 eV), high electron mobility (100-200 cm² V⁻¹ s⁻¹) and deeper valence band maximum as well as stability. The efficiency of PSCs in related studies is greater than 22% [14].

Table. 1. Photovoltaic parameters with ETLs of inorganic material [12].

ETLs	VOC (V)	JSC (mA/cm-2)	FF (%)	PCE (%)
TiO ₂ NPs	1.02	24.6	71.0	17.8
TiO ₂ NWs	0.96	20.7	74.0	14.7
Nd-Doped TiO ₂	1.08	23.9	74.0	19.0
WO _x	1.06	24.8	79.1	20.8
SnO ₂	1.17	23.9	76.5	21.4
ZnSnO ₄	1.04	24.7	78.0	20.0
NbOH	1.16	23.0	79.0	21.1

3.2 Choice of HTL material

The hole transport layer (HTL) is sandwiched between the perovskite film and the metal electrode, which helps to improve the selectivity of contact with the gold electrode and reduce carrier recombination by reducing the diffusion loss and increasing the open circuit voltage. The materials for HTLs can be divided into three types: organic material, inorganic material and carbon-based material. As summarized in Table. 2, Pitchaiya et al. have drawn the conclusion that organic hole transport materials (HTM) have advantages in terms of efficiency but do not guarantee long-term stability, while inorganic HTMs are better in terms of stability factors but less efficient [9]. The latest carbon-based HTM is a better material candidate in terms of device performance and stability. The reason is its low cost, good connectivity, good mechanical properties and adhesion to the film, which reduces the interfacial resistance in the solar cell [7].

Table. 2. Photovoltaic parameters of organic, inorganic and carbon-based HTLs in PSCs [9].

Device gestalt	VOC (V)	JSC (mA/cm-2)	FF (%)	PCE (%)	Structure
FTO/TiO ₂ /PSK/Pristine-spiro-OMeTAD/Ag	1.12	22.90	73	18.7	Planar p-i-n
ITO/ Cudoped NiOx/ PSK/ PCBM +C60-bis surfactant/Ag	1.11	18.75	72	14.98	Planar p-i-n
FTO/TiO ₂ /PSK/C/Al	1.00	21.02	63	13.53	Mesoporous n-i-p

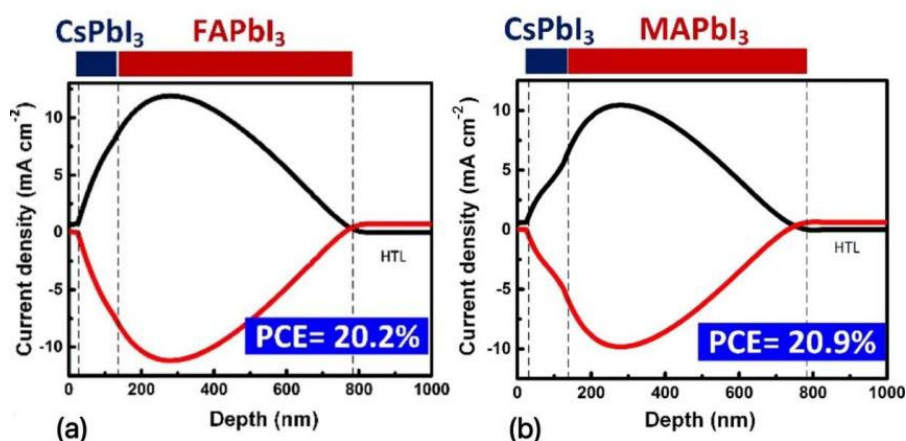


Figure 5. (a) CsPbI₃ 100 nm combined with FAPbI₃ 700 nm (b) CsPbI₃ 100 nm combined with MAPbI₃ 700 nm [15].

3.3 Performance of inorganic PSC

The cesium-based all-inorganic halide chalcogenide CsPbI₃ has superior thermal stability than organic-inorganic hybrid chalcogenides in perovskite materials for solar cells. CsPbI₃ is commonly utilized as a substitute for organic MAPbI₃ in PSCs because it has better long-term stability in outdoor environments [15]. As shown in Fig. 5, PCE of devices increased to 20.2 % and 20.9 %, respectively, by converting CsPbI₃ perovskite solar cells with PCE of 13.1 % to CsPbI₃(100 nm) combined with 700 nm-thick FAPbI₃ and 100 nm-thick CsPbI₃ combined with 700 nm-thick MAPbI₃ heterostructures. [16].

3.4 Performance of hybrid organic/inorganic PSC

The general formula of perovskite is ABX₃ [a = methylammonium (MA), formamidinium (FA), cesium (Cs)]. Plenty of researchers are working on MA-free PSCs, e.g., Lei Yan et al. improve the efficiency and stability of MA-free PSCs, which mainly agglomerate along the grain boundaries of the perovskite films as the doping concentration increases [17]. After more than 300 hours of continuous light exposure, the efficient and stable FA_{0.9}Cs_{0.1}PbI₃ Zn-doped PSCs had a maximum PCE of 20.7 % and negligible deterioration.

4. Limitations

4.1 Perovskite structural defects

From a thermodynamic point of view, perovskite crystals have a low formation energy. Factors include gap, substitution and vacancy defects in perovskite crystals result in deep energy level defects resulting in non-radiative composite. Since the ionic radii of FA⁺ and Cs⁺ are larger or smaller than that of MA⁺, phase instability occurs in both pure FA-based and Cs-based PSCs, resulting in lattice distortion.

4.2 Crystalline surface defects

The existence of defects, as well as the perovskite structure's instability in moisture, UV light, and temperature, limit its further growth. Despite perovskites' remarkable charge mobility, non-radiative recombination of charges on the electrodes caused by surface imperfections prevents photoexcited charges from aggregating effectively on the electrodes. In order to increase their photoelectric capabilities, these surface imperfections must be passivated. Organohalide salts, among the available passivators, are a potential substance for passivating surface defects in perovskite films while also improving their stability.

4.3 Thermal stability

Solar panels made of silicon are typically guaranteed to last at least 25 years. Under the effect of weather fluctuations, excessive light levels, temperature, and humidity, PSCs currently only endure for months [18]. Because the thermal expansion coefficient of halide peroxide differs significantly from that of selective contact, thermal cycle stability is a concern. Despite its excellent performance, the thermally unstable and volatile nature of MA⁺ is a serious problem for organic–inorganic PSC commercialization.

4.4 Toxicity problems

Perovskite batteries hold a number of heavy components and are almost impossible to replace. The toxicity concerns and the safety dangers that result are grounds for worry. Potential lead leakage may be regarded as an environmental and public health danger during manufacturing [19].

5. Conclusions

In summary, this paper discusses recent progress and state-of art applications of perovskite solar cells from the perspective of working principle, materials chosen for layers in the solar cell and performance comparison and the limitations. As third-generation solar cells, PSCs are strong candidates to replace the current mainstream silicon-based solar cells due to their high PCE, tunable energy band width, and lower manufacturing costs. TiO₂ is the most common choice for ETL now and emerging materials include tungsten oxide and tin oxide are proved to have better stability and wider band width. For HTL, latest study demonstrates that carbon-based HTM is a better material candidate in terms of device performance and stability. Different kinds of perovskite solar cells have achieved a PCE of more than 20%, but they have many limitations including grain boundaries, thermal stability, toxicity and other problems. Further improvement of PCE and cell stability will be essential aspects in the commercialization of perovskite cells in the future. In addition, PSCs need to reduce manufacturing costs and improve environmental friendliness to further strengthen their competitiveness in the solar cell market. The average efficiency of PCE is currently higher than 20%, and some methods to improve cell stability, e.g., optimizing the crystal structure and improving the quality of film, are still in the laboratory stage. The research on perovskite is still inadequate and its potential is still immeasurable. Overall, these results offer a guideline for future development of perovskite solar cells.

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