

Prediction of the future challenge and development direction for perovskite cell

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Abstract: New clean energy is an important topic of energy development, while solar cells have always been an important branch of clean energy, and perovskite solar cells have been the focus of researchers because of their simple process, low cost, and flexible preparation. In this paper, we will introduce the background, structure, fabrication methods, superiority, and downside of perovskite cells, and predict possible future challenges and directions for the development of perovskite cells.

Keywords: Perovskite, solar cell, challenge, advantage.

1. Introduction

The creation and use of green, renewable, and environmentally friendly new energy has grown significantly in importance in the modern world due to the diminishing global supply of non-renewable fossil resources like oil, coal, and natural gas. Solar energy is the source of most human energy, and the most direct use of it is solar cells. Solar cells have undergone three generations of development in total. the first-generation photovoltaic cells represented by silicon-based solar cells have disadvantages such as high-power generation cost, high energy consumption, and fixed component positions. The second-generation thin-film solar cells have the disadvantages of high toxicity and little reserve of component elements. the third generation of new solar cells bred from this has both a simple preparation process, Low cost, and flexible fabrication, including quantum dot solar cells, dye-sensitized solar cells, and novel perovskite solar cells (PSCs). Perovskite solar cells have a very high energy conversion efficiency and show great potential in the energy field. To promote the development and commercialization of perovskite solar cells, numerous researchers have made efforts. In 1991, Gratzel's group at the Swiss Federal Institute of Technology in Lausanne made dye-sensitized nano-TiO₂ solar cells; in 2006 and 2008, Miyasaka's group at Toin Yokohama University in Japan used $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ to make dye-sensitized solar cells, respectively. The conversion efficiency obtained 0.4% and 2%, respectively; the first lead-halide perovskite battery was produced by the Miyasaka research group in 2009, and the prepared device efficiency was 3.8%; 2014, University of California, Los Angeles by optimizing the perovskite structure and electrodes, Yang Yang's group at UCLA produced a planar perovskite cell with an average efficiency of more than 16%. Zhou et al. improved the perovskite structure layer and transport materials, and produced an efficiency as high as 19.3% solar cells [1]. This article will introduce the background, preparation method, structure, principle, advantages and disadvantages, application and future development direction of perovskite solar cells

2. Background

2.1 Development of perovskite solar cells

Organic-inorganic metal halide perovskite solar cells have become a research hotspot in academia and industry due to their excellent radio and television performance, inexpensive preparation materials, and simple fabrication processes. In recent years, the power conversion efficiency of PSCs

has rapidly increased from 3.8% at the beginning to 25.7%. Because PSCs have strong absorption coefficients in the visible and near-infrared parts of the solar spectrum, their photoelectric conversion efficiency increases faster than other types of solar cells. Both electrons and holes of PSCs have high mobility and long diffusion length. PSCs have low exciton ionization energy and good transportability. At the same time, researchers tried to passivate the interface of perovskite to improve the quality of interface film, use additive engineering to promote better crystallization of perovskite, adjust element composition to achieve better photoelectric conversion efficiency, and change the performance of battery devices. electrode materials to reduce manufacturing costs. The commercialization of perovskite solar cells is promoted through the various methods described above.

2.2 The general formula of perovskites

The general formula of perovskites is ABX_3 . For organic oxide perovskites, A is a divalent ion, B is usually a tetravalent ion, and X represents an oxygen atom; for alkali metal halide perovskites, A is an alkali metal ion, and B Usually a divalent ion, X is a halogen element; for organometallic halide perovskites, A represents an organic cation such as methylamine and ethyl acetate, and B and X combine to form a regular structure [2]. The figure 1 show the general structure of the perovskites.

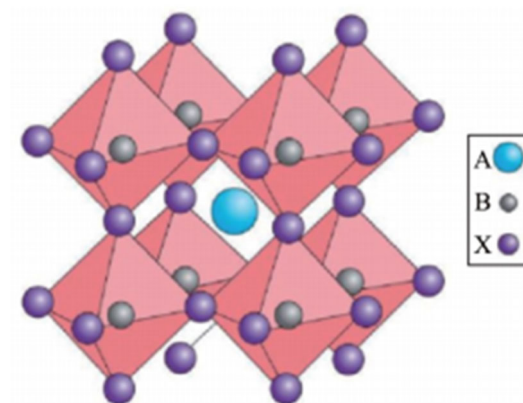


Figure 1. General structure of the perovskites

3. Preparation

The core part of perovskite solar cells is the solar absorption layer of the cell, that is, the preparation of composite perovskite materials. Under the continuous exploration of scientists, a simple, low-cost and non-polluting preparation method was summarized. The following will briefly introduce several commonly used methods for preparing perovskite layers.

3.1 Preparation steps

3.1.1 Solution synthesis

First, CH_3NH_2 was dissolved in methanol, and mixed with HI in an ice bath; then evaporated, dried, and washed to obtain crystalline CH_3NH_3I ; finally, crystalline CH_3NH_3I was mixed with powdered PbI_2 in an organic solvent, filtered, and filtered in titanium oxide. The thin film perovskite $CH_3NH_3PbI_3$; can be obtained by in-situ reaction on the layer. Although this method is difficult to control the appearance of perovskite crystals, the repeatability is poor. But at that time, it was a generally effective method.

3.1.2 Continuous precipitation

First, a saturated PbI_2 solution is deposited on the porous titanium oxide layer with a diameter of 20 nanometers; then it is dried; finally, the titanium oxide film immersed in the saturated PbI_2 solution

is invaded into the CH_3NH_3I solution for in-situ reaction, and the perovskite $CH_3NH_3PbI_3$ can be obtained after cleaning. film. This method can well control the morphology of perovskite thin films, improve the reproducibility of high-quality thin films, and make the reaction more sufficient and faster. However, this method cannot produce planar battery structures.

3.1.3 Dual-source meteorological evaporation method

The reactants CH_3NH_3I crystal and PbI_2 crystal is heated and evaporated at the same time, and the vapor reacts and condenses on the dense titanium oxide substrate, thereby forming a perovskite $CH_3NH_3PbI_3$ with good compactness, regular crystal morphology and high repeatability. The SEM image of the titanium ore thin film is shown in Figure 2 right. Although this method has high film quality, the process is too complicated, and the energy consumption is extremely high. The temperature needs to be above 400°C and the leakage of toxic steam must be strictly prevented, which will increase the cost of battery production [3].



Figure 2. SEM image of the titanium ore thin film

3.1.4 Vapor-assisted solution deposition

In order to solve the high-cost problem of the dual-source meteorological evaporation method, the Yang experimental group invented a preparation method of a mixed process, the gas-phase assisted solution deposition method shown in Figure 3 left. First, the PbI_2 solution is deposited on the titanium oxide substrate; then the CH_3NH_3I crystal is evaporated onto the titanium oxide substrate to fully reflect the PbI_2 , and a superior perovskite $CH_3NH_3PbI_3$ film can also be obtained. The SEM image is shown in Figure 3 right. In this method, since the high melting point PbI_2 crystal exists in the form of a solution, the reaction does not need to be carried out at a high temperature, which greatly reduces the preparation cost.

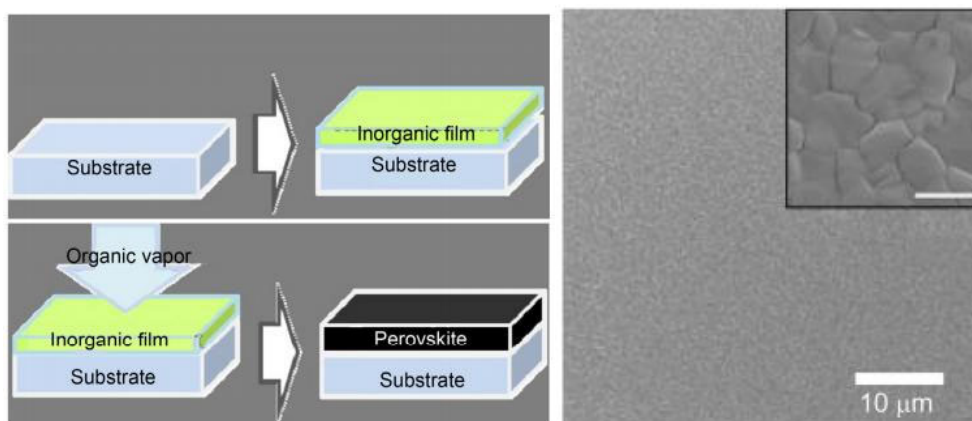


Figure 3. SEM image of superior perovskite

3.2 Perovskite solar cells' Preparation method

Although organic/inorganic hybrid lead halide perovskite solar cells have developed rapidly in recent years, and the photoelectric conversion efficiency has reached 19.3%, the light absorption layer of this type of solar cells is a lead-containing perovskite compound. Lead is a toxic metal element, and has extremely serious pollution to the environment. Some researchers tried to use Sr to partially replace Pb to prepare a lead-less perovskite compound $CH_3NH_3Sr_xPb_{(1-x)}I_3$, and used it in the light absorption layer to prepare perovskite solar cells, and to study the performance of the cells.

First, the methylamine solution and ethanol were mixed in an ice bath, and hydroiodic acid was slowly added to fully react; then the solvent was evaporated at 50 °C to remove the solvent to obtain the crude product monomethylamine; secondly, the monomethylamine was dissolved in ethanol, and added Diethyl ether makes it recrystallized, and after filtration, a white solid can be obtained, and this step is repeated; then the white solid is dried at 60 °C to obtain methyl iodide, and γ -butyrolactone is added in proportion with lead iodide and strontium iodide; Then heat and stir at 65°C, and fully react the $CH_3NH_3Sr_xPb_{(1-x)}I_3$ precursor solution to obtain $CH_3NH_3Sr_xPb_{(1-x)}I_3$ precursor solution. Assembled into a solar cell, the schematic diagram of the structure is shown in Figure 4

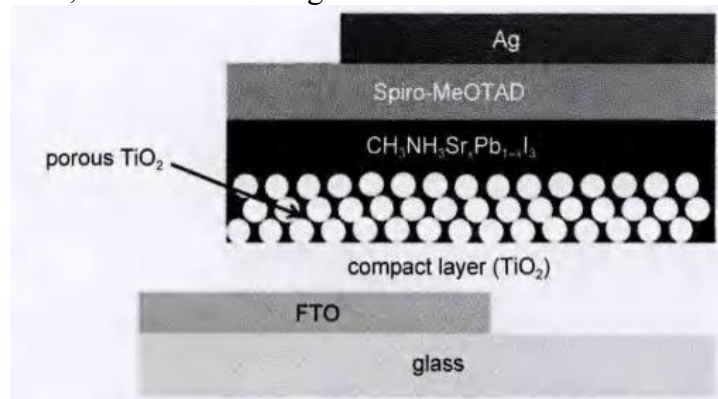


Figure 4. Schematic diagram of the structure

4. Structure

4.1 Crystal structure of perovskite

Perovskite, was given its name in honor of the Russian mineralogist L.A., general formula is ABX_3 with equiaxed crystal structure [4], space group is $P3M3$. According to the selection of X site cation in the general formula, Inorganic oxide perovskite ($X=O^{2-}$) and halide perovskite ($X=Br^-$, Cl^- , F^- , I^-) are the two main subtypes of perovskite. Furthermore, according to the a-site cation selection, halide perovskite may be split into alkali halide perovskite (Cs^+ etc.) and organo-metal halide perovskite (methylamine ion, methyl ether ion, etc.). For B site cation, due to their excellent optoelectronic characteristics and potential for low temperature device manufacturing, Sn^{2+} and Pb^{2+} are the most often used [5].

In perovskite crystal, A cation is in a cubo-octahedral site while B cation is in an octahedral position. BX_6 forms a regular octahedron and connected by a common vertex X to form a three-dimensional skeleton. The octahedral gap embedded by A provides the crystal structure stable. The optical active absorption materials present a certain ferroelectricity, photoelectric and nonlinear optic, imply that it has a wide range of applications in light-emitting diodes (LED), optical materials, solar cells, and photodetectors.

For the ideal perovskite crystalline structure, A site cation and cation is the same in the term of occupied space. Based on the octahedral close packed structure, geometrical relationship can be easily obtained:

$$R_A + R_X = \sqrt{2}(R_B + R_X) \quad (1)$$

Where R_A , R_B and R_X are the effective ionic radii for A, B and X ions, respectively.

For the practical perovskite structure in the solar cell utilization, the 3 site cations radius and occupied size are different, in the purpose of describing the perovskite crystal structure stability, geometric tolerance factor (t) and octahedral factor (μ) are applied.

$$t = \frac{R_A + R_X}{\sqrt{2}(R_X + R_B)} \quad (2)$$

$$\mu = \frac{R_M}{R_X} \quad (3)$$

Where R_A , R_B and R_X are the effective ionic radii for A, B and X ions, respectively.

The geometric tolerance factor can be used to determine perovskite's reliance on organic cations. The ABX_3 perovskite structure is classified as stable when the geometric tolerance factor is between 0.8 and 1.0 and octahedral factor is between 0.4 and 0.9 [6].

4.2 Perovskite cell structure

The common cell structures of perovskite cells are classified into five types: Mesoporous structure, regular planar structure and invert planar structure (which can be collectively referred to as flat planar structure), HTM-free (hole transport layer) structure and organic structure.

In general, the component structure of transparent conductive oxide substrate electrode /ETL/ perovskite absorption layer /HTL/ top electrode is called positive type (Figure 5); The structure of transparent conductive oxide substrate electrode /HTL/ perovskite absorption layer /ETL/ top electrode is called inverted type (Figure. 6). Although the carriers travel in different directions, the work principle is the same.

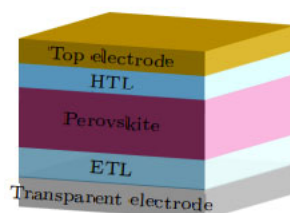


Figure5. Schematic illustration of normal planar.

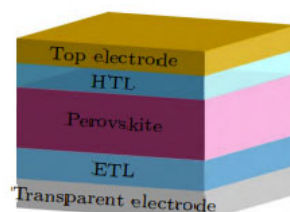


Figure 6. schematic illustration of inverted planar PSCs.

The device structure generally consists of the following six components: the electron transport layer (ETL), perovskite optical absorption layer (MAPbI_3 , FAPbI_3 etc.), hole transport layer (HTL), metal counter electrode, Transparent conductive oxide substrate electrode (FTO, ITO) [7].

Due to the inconsistency of fabrication processes and materials, different structures have different advantages and application directions. For example, since HTL is prepared first for the inverted structure, the transport layer sequence of the regular plane structure is exactly the opposite, and the preparation process of its structure is relatively low cost and simple. It is easy to be used in the preparation of perovskite laminated devices. Below, we only discuss 3 most common cell structures of perovskite solar cell.

4.3 Perovskite working principle

In general, the working principle of perovskite cells is shown in the figure, taking the flat heterojunction structure as an example: under the irradiation of sunlight, the perovskite dye sensitized layer can absorb photons and generate a large number of excitons, which become electron hole pairs and become free carriers (free electrons and positively charged holes). The electron transport layer

quickly removes electrons for FTO to absorb, the hole transport layer quickly removes holes, which metal electrode pairs then gather. Finally, by coupling the FTO to a metal electrode, a photocurrent is generated. For practical use of PSCs (perovskite solar cell), Charge recombination, which is intimately connected to efficiency, stability, and hysteresis, is frequently present during charge transit, extraction, and collection in the actual functioning of PSCs.

5. Challenge and advantages

5.1 Advantages

As one of fastest developed in last decade category of solar cell design, as well as one of the newest generation(3rd) of the entire solar cell tech-tree, advantages and challenges of the perovskite cell has been identified in the previous researches clearly. Compared to traditional other solar cells, lower fabrication cost, shorter preparation process and higher energy translation efficiency, High efficiency flexible device component are the main remarkable advantages. As the recent research provides the perovskite cell translation efficiency of laboratory validation has reached incredible 25.7% [8].

In general, the advantages are drained from many unique photoelectric properties of perovskite material and cell structure. For example, a perovskite cell with an $AM(II)X_3$ crystal structure possesses solution processing, an adjustable band gap, a low exciton binding energy, a high absorption coefficient, and extended carrier diffusion length and lifespan. It ultimately results in excellent electricity production efficiency.

To improve the transform efficiency of the PSCS device, the research that focuses on material selection, fabrication processes, structure reconstruction of device fabrications have been suggested. One of them is 2D and 3D combination of perovskite solar cell, a new strategy for the search of potential stable PSCs fabrication. 2D/3D mixed dimensional perovskite thin layer has the high efficiency of 3D perovskite and the hydrophobicity of 2D perovskite, which greatly improves the stability of the equipment. However, a critical challenge is the contradiction between hydrophobicity and charge transport properties 2D/3D mixed perovskite weaken the high optical properties.

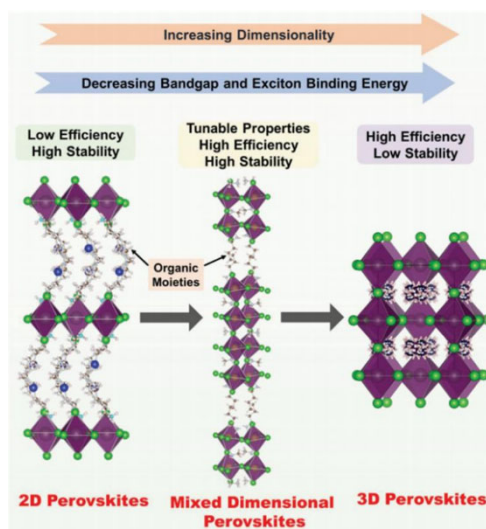


Figure 7 2D and 3D perovskites and mixed dimensional perovskites crystal structure

5.2 Challenges

5.2.1 Durability

In contrast, the critical problems and challenges of perovskite cell utilization is also obviously. One of them is cell durability. In the comparison of the silicon solar cell, PSCs is less stable in various environments and has a low lifetime (about 1 year) [9]. For 3D perovskite solar cell, due to the basic structure of the device and material selection, temperature, environment humidity, oxidation, illustration, External bias can damage the structure in different dimension.

In general, solar cell operation environment, Perovskite crystals are easy to combine with water molecules in the environment through hydrogen bonding, which changes the properties of perovskite and thus affects the efficiency of equipment. Oxygen can adsorb onto perovskite films and passivate the deep surface trap state to enhance luminescence and eventually inactivate the trap state. Under high temperature conditions, perovskite crystal will produce thermal decomposition, crystal structure changes, grain boundary changes. These are extremely detrimental to solar cell working factors [1].

One of the biggest obstacles to the commercialization of perovskites in recent years has been the inability to produce an upscaling perovskite cell with high efficiency and stability. At present, the usually effective way is to optimize the manufacturing process to achieve the purpose of improving stability. According to a 2021 report, N-methyl-2-pyrrolidone was firstly added to the perovskite precursors to provide a 23% efficiency and strong thermal stability at 85°C and the result support the formation of black α -phase [10].

5.2.2 Perovskite material

In the recent research, due to their superior photoelectric performance, organic-inorganic metal halide perovskite solar cells have become a popular topic in current research, including MAPbI₃ and FAPbI₃, which are widely understood. However, in the non-polar metal is often used Pb²⁺ to obtain higher operation incident photon-to-electron conversion efficiency, as a result, solar cell devices may cause large-scale pollution and harm to the environment without effective treatment measures and cannot be further commercialized. In recent years, the strategy of using other inorganic metal ions to replace Pb²⁺ in non-lead perovskite batteries has developed rapidly. Non-lead perovskite cells show the same high performance under special processing. According to recent research, chemo-thermal Surface DE Doping can remove self-dopants from FAMASnI₃ Perovskite Thin Film provides high performance for Tin Perovskite solar cell, it includes 3-fold enhancement in lifetime, 2-fold reduction in trap density, and ensures the photoelectric conversion efficiency of 14.7. Previously, tin-based perovskite cells are far less efficient than lead-based perovskite, and lack sufficient stability compared to lead-based perovskite due to Sn²⁺ is easily oxidized to Sn⁴⁺.

5.2.3 Crystal structure defects

In the actual process of perovskite film preparation, many complex polycrystalline materials with grain boundaries are prone to form dislocation and crystal structure defects during the growth process. When the transition level is near to the valence band or conduction band, these defects can inject shallow level defects and transition levels into the band gap. Carriers trapped by shallow level traps are easy to de trap, so shallow level defects have little impact on carrier recombination. When the transition energy level is reaching 1/3 of the gap band, deep level defects form. They trap electrons or holes that are destroyed by oppositely charged charge carriers through the NRR because they are unable to escape due to thermal activation.

The Defects could Eventually damage the Extraction of Carriers, Affect the photovoltaic performance parameters of PSCs, such as Perovskite material conductivity, Carrier Mobility fill factor (FF), open circuit voltage (VOC), short circuit current density (JSC), and photoelectric conversion efficiency, and reduce Carrier Lifetime seriously.

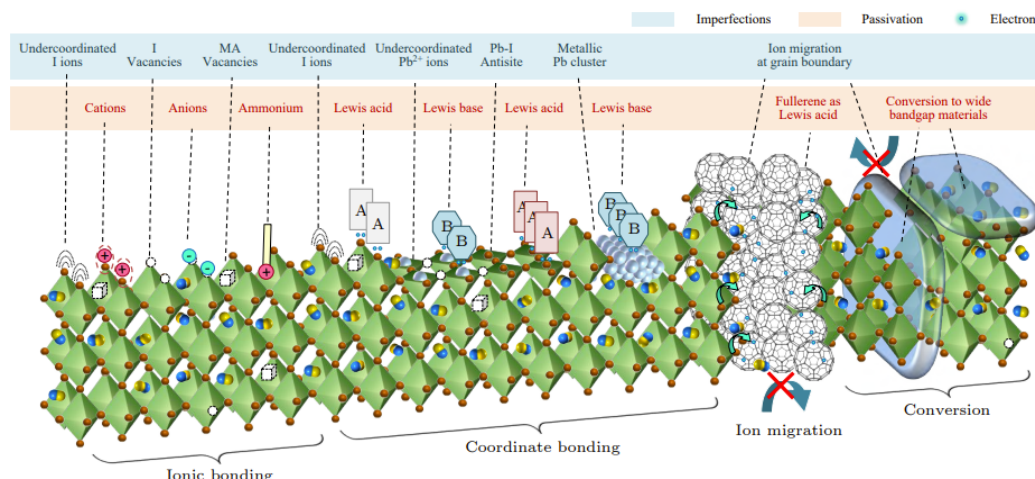


Figure 8. Schematic illustration of defect passivation mechanism

Defect passivation, a mature strategy to reduce the negative impact of defects on equipment is very common in manufacturing processes. One of them is Lewis base passivation in the Lewis acid-base concept, An acid is an electron acceptor, whereas a base is an electron donor. The addition of a Lewis acid or Lewis's base additive could form a Lewis adduct that matches the defect site. The Lewis base atom's two shared bonding electrons form a coordination bond (also known as a coordinated covalent bond) that holds this compound together.

Defect passivation of PSCs can provide PSCs with higher performance and efficiency, nevertheless, passivation of the surface treatment can also seriously affect the heterointerface energetic by accumulation of electrons (negative work function shift) in the device according to recent research. Furthermore, Accumulation of electrons in special area could affect the halide migration destroy the PSCs stability. Therefore, Detrimental side effect and the defect passivation benefits should be considered equally.

6. Conclusion

As a new generation of solar cells, perovskite cells have many advantages, however, in the terms of the comparable poor durability (short lifetime) and potential heavy metal pollution are the huge obstacle to the commercialization of perovskite cells. In essence, most of these shortcomings come from the crystal characteristics of perovskite crystal itself. This paper mainly analyzes the current perovskite cell structure, PSCs material selection, and provides the recent accessible strategies to improve the shortcomings of perovskite solar cell. Such as Defect passivation, non Pb base perovskite cell, Chemo-thermal Surface DE Doping strategy and so on. By the review of sufficient recent research about material selection, device structure improvement and fabrication procedure assessment, the possible future research direction is provided finding the balance between conversion efficiency and performance of PSCs is the most fundamental in the future.

References

- [1] Pan Ying, Zhang Fan, Gao Hua. Technical Development and Economic Analysis of Solar Perovskite Battery [J]. Sino Foreign Energy, 2022,27 (07): 23-28
- [2] Jiang Ziheng, Zhang Xuan, Shen Qiuwan, Zhang Xingkai, Shi Baocheng. Preparation methods and research progress of perovskite solar cells [J]. Energy and Chemical Industry, 2018, 39 (03): 1-5
- [3] Liu Yangyang, Cao Hui, Liu Xuhao, Zhu Rongzhi, Tao Tao, Sun Jinwei. Fabricating Efficient and Stable Quasi-3D and 3D/2D Perovskite Solar Cells with 2D-Sheets Connected by Inorganic Type Ionic-Bond.[J]. Nanotechnology, 2021,32(35).

- [4] Yao Zhun,Xu Zhuo,Zhao Wangen,Zhang Jingru,Bian Hui,Fang Yuankun,Yang Yan,Liu Shengzhong (Frank). Enhanced Efficiency of Inorganic CsPbI₃-xBr_x Perovskite Solar Cell via Self-Regulation of Antisite Defects[J]. Advanced Energy Materials,2021,11(23).
- [5] Jin Zhenhang,Wu Yiman,Li Song,Wu Qingfeng,Chen Shanjun,Chen Yan,Zhang Weibin,Zhang Chuanzhao. Electronic structure, elastic, optical and thermodynamic properties of cubic perovskite NaBaF₃ with pressure effects: First-principles calculations[J]. Results in Physics,2021,22(prepublish).
- [6] Yangyang Cai,Lai Xie,Zongbao Zhang,Yang Zhou,Hui Liu,Xubing Lu,Xingsen Gao,Jinwei Gao,Lingling Shu i,Sujuan Wu,Junming Liu. Tuning the A-site cation and X-site anion composition of CH₃NH₃PbI₃ perovskite material for efficient planar perovskite solar cells[J]. Electrochimica Acta,2019,293.
- [7] Nam-Gyu Park. Perovskite solar cells: an emerging photovoltaic technology[J]. Materials Today,2015,18(2).
- [8] Tan Shaun,Huang Tianyi,Yavuz Ilhan,Wang Rui,Yoon Tae Woong,Xu Mingjie,Xing Qiyu,Park Keonwoo,Lee DoKyoung,Chen ChungHao,Zheng Ran,Yoon Taegeun,Zhao Yepin,Wang HaoCheng,Meng Dong,Xue Jingjing,Song Young Jae,Pan Xiaoqing,Park NamGyu,Lee JinWook,Yang Yang. Stability-limiting heterointerfaces of perovskite photovoltaics.[J]. Nature,2022,605(7909).
- [9] Wei Li,Zheming Wang,Felix Deschler,Song Gao,Richard H. Friend,Anthony K. Cheetham. Chemically diverse and multifunctional hybrid organic–inorganic perovskites[J]. Nature Reviews Materials,2017,2(3).
- [10] Bu Tongle,Li Jing,Li Hengyi,Tian Congcong,Su Jie,Tong Guoqing,Ono Luis K,Wang Chao,Lin Zhipeng,Chai Nian Yao,Zhang XiaoLi,Chang Jingjing,Lu Jianfeng,Zhong Jie,Huang Wenchao,Qi Yabing,Cheng YiBing,Huang Fuzhi. Lead halide-templated crystallization of methylamine-free perovskite for efficient photovoltaic modules.[J]. Science (New York, N.Y.),2021,372(6548).