Research Progress on Structure and Property of Hybrid Organic-Inorganic Perovskite

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Abstract. This research briefly introduces the research background, structure, properties and application fields of perovskite, and reviews the research progress of hybrid organic-inorganic perovskite in recent years. The effects of crystal structure and organic cations on the stability, thermal conductivity, carrier mobility and optical and electrical properties of the hybrid perovskite are summarized, with which the importance of controlled crystal growth is highlighted and the current preparation methods and new preparation processes of perovskite materials are concluded. Finally, a prospection of perovskite materials and their applications is put forward, which provides a theoretical understanding for new perovskite materials with better crystal growth and crystal face control in the future, so as to promote the development of perovskite solar cells, light energy devices and other related fields.

Keywords: organic-inorganic perovskite; solar cell; anisotropy; stability; carrier mobility.

1. Introduction
At present, the most widely used resource on the earth is petroleum, but it is not renewable and its total amount is limited. In addition, the exploitation and use of oil will bring great damage to the environment. At this time, as a green and clean energy, solar energy enters people's field of vision [1]. Solar energy is the first choice for the development of new green energy because of its characteristics, including renewability, large reserves, cleanliness, and environmental protection [2-3]. At present, crystalline silicon solar cell is the most widely used solar cell, but its further development is restricted by its production cost.

Hybrid organic-inorganic perovskite has been used as light absorbing layer of solar cells due to its excellent optical properties such as adjustable optical band gap [4], high carrier mobility [5], and long carrier diffusion length [6]. Since its application, the efficiency of perovskite solar cells has increased from 3.81% to 25.2% in 2019 [7-10], which is several times faster than that of silicon solar cells. In addition, its low price makes it possible for solar energy to replace traditional energy.

However, there are still many problems in traditional titanium materials, such as the instability of humidity [11], which makes it unable to be commercialized on a large scale. At present, the preparation methods of perovskite include cooling crystallization, inversion crystallization and antisolvent steam crystallization. This paper mainly summarizes the stability, carrier migration rate, optical and electrical
properties of anisotropy of perovskite materials, with an exploration on its influencing factors. The importance of controllable crystal growth in the preparation of efficient and stable perovskite solar cells and optoelectronic devices is proposed innovatively, and the development of perovskite materials is prospected.

2. Hybrid Organic-Inorganic Perovskite

2.1. Crystal Structure

The general structural formula of perovskite is ABX₃. Inside it, A is a monovalent ion, and methylamine ion (MA) and formamidine ion (FA) are commonly used. B is a divalent metal cation, generally Pb²⁺ or Sn²⁺. X is a halogen ion, generally Cl⁻, Br⁻, and I⁻[12]. They form octahedral or cubic structures, as shown in Figure 1. Cation A is coordinated with 12 anion Xs, and cation B is coordinated with 6 anion Xs. It is a long-range ordered crystal.

![Fig. 1 Crystal Structure Model of Perovskite](image)

The stability and crystal structure of perovskite are determined by the tolerance factor (t) and octahedral factor (μ), where $t = \frac{R_A + R_x}{\sqrt{2}(R_B + R_x)}$, $\mu = \frac{R_B}{R_x}$, RA, RB, and RX are the radii of ion A, B and X respectively [13]. As shown in Table 1, when $0.9 < t < 1$, the cubic lattice with the highest symmetry and good stability is usually formed; when $0.7 < t < 0.9$, the crystal structure is distorted, and it is easy to form orthorhombic and rhombic crystal systems; when $t > 1$, the perovskite will transform from three-dimensional structure to two-dimensional structure [14]. In addition, chemical stability and bond valence also affect the stability of the crystal [15]. Due to the presence of easily decomposed organic ammonium ions, the formation energy of the system is low and the reaction activity is high. At the same time, the difference of components will cause component segregation, so the stability is poor [16].

| Tolerance Factor (t) | Crystal Structure | Notes |
|---------------------|------------------|-------|
| <0.7                | Ilmenite structure | Minimum radius A |
| 0.7-0.9             | Tetragonal, orthogonal or triangular structure | Smaller radius A or larger radius B |
| 0.9-1.0             | Cubic structure | Ideal configuration |
| >1.0                | Different types of layered structure | Larger radius A |

2.2. Preparation of Hybrid Organic-Inorganic Perovskite Crystals

At present, the main preparation methods of hybrid organic-inorganic perovskite are solution temperature-lowering, inverse temperature crystallization and anti-solvent vapor-assisted crystallization.

(1) Solution Temperature-Lowering (STL)

The solution temperature-lowering method was first invented by Weber [18]. The principle is that when the temperature decreases, the solubility of the solution decreases and the solute supersaturates, resulting in the precipitation of single crystals. In 2014, Dang et al. prepared large-size MAPbI₃ crystal by STL method for the first time, as shown in Fig. 2 [19]. In 2016, Dang et al. improved the STL method to prepare perovskite by bottom-seeded solution growth (BSSG), that is, putting the seed crystal at the
Dang et al. reacted SnO, SnCl₂·2H₂O, NH(CH₃)₃Cl, H₃PO₂ solution and acid HX (X is Cl or Br) by BSSG method to obtain NH(CH₃)₃SnX₃ (X=Cl, Br) crystal [20].

(2) Inverse Temperature Crystallization (ITC)

The inverse temperature crystallization method was first proposed by Kadro et al. [21] in 2015, and its basic principle is that MAPbI₃ will show inversion solubility in butyrolactone. In this way, Bark et al. grew MAPbX₃ crystals (X is Br or I), as is shown in Fig. 4 [22].

(3) Anti-solvent Vapor-assisted Crystallization (AVC)

The anti-solvent vapor-assisted crystallization method is to make the antisolvent slowly diffuse to the solution containing crystal precursor for growth, which can grow the crystal without cracking and with regular boundary shape. Shi et al. [23] dissolved MAX and PbX₂ (X is Br, I) in DMF or GBA solution. Using DCM vapor as antisolvent, with the continuous diffusion of antisolvent into the solution, crystallization can be observed, and the results are shown in Fig. 4.
3. Anisotropy of Hybrid Organic-Inorganic Perovskite

The atoms in the crystal are arranged periodically, but, in different directions, the arrangement of atoms in the same lattice is different. So, the properties of the crystal are different in different directions, which are the anisotropy of the crystal. Anisotropy is one of the common properties of materials. The thermal and electrical properties of crystals are both anisotropic.

At present, the research on hybrid perovskite is usually based on polycrystalline film. However, the arrangement of single crystal molecules is more regular, and the orientation of each cell is the same, which has higher research value. Therefore, this research attempts to explore the anisotropy of the properties of single crystal hybrid perovskite, and provide research direction for the follow-up study of hybrid organic-inorganic perovskite.

3.1. Stability

When MAPbI$_3$ is exposed to the air, it will react with the moisture in the air, resulting in its degradation [24]. The reaction equation is as follows:

$$\text{MAPbI}_3 \rightarrow \text{MAI} + \text{PbI}_2$$

Hydrolysis reaction is one of the reasons for the instability of perovskite materials. In 2017, Yan et al. [25] studied the hydrolysis of single crystal MAPbI$_3$ with different crystal orientations. The (001) surface is obtained by wire-electrode cutting and no-water polishing. To control the variables, the (100) and (112) surfaces are treated in the same way, as shown in the left figure of Fig. 6 (A). The self-made water mist erosion instrument was used for 60s at 20 ℃ with water mist flow of 25 mL/H. The results are shown in the figure on the right. The results of XRD test before and after erosion are shown in (B).
Fig. 7 (A) is a laser scanning microscope image of the erosion process. The black is MAPbI$_3$ and the yellow is PbI$_2$. It can be seen that the erosion of the surface (001) is the most serious. Meanwhile, only a small amount of surface (100) and (112) were eroded, which was consistent with the XRD results. (B) is the UV Vis reflectance spectrum. There is an obvious inflection point on the crystal face (001) at 530 nm, corresponding to the band gap (2.32 eV) of PbI$_2$ [26]. Thus, it can be determined that the hydrolysis of crystal face (001) is the most serious.

Previous studies have shown that the first step of decomposition of MAPbI$_3$ perovskite is the formation of hydrate [27], and H$_2$O molecule will combine with H atom in CH$_3$NH$_3^+$. The smoother the combination of H$_2$O and H atom, the easier the hydrolysis of MAPbI$_3$. Fig. 8 is the structural diagram of MAPbI$_3$ in different crystal directions based on the research of Malliakas et al. [28]. There is a channel of 0.88 nm in the (001) crystal orientation, which can supply water molecules (0.4 nm), indicating that the (001) crystal orientation is easily eroded by water. While (100) is only 0.32 nm, there is no direct channel for water molecules to enter the (112) crystal orientation, and water molecules must bypass this crystal orientation to enter the intracell. Therefore, the hydrolysis reaction will not follow the crystal orientation (100) and (112), which well explains the previous experimental phenomenon.

3.2. Carrier Mobility

Carrier mobility anisotropy affects semiconductor performance, so it is necessary to match the electrode direction of the material with the optimal carrier transmission direction when designing electronic
devices [29]. Feng et al. [30] calculated the carrier mobility of MAPbI3 with different crystal faces by Marcus theory, and found that the optimal carrier transport directions were crystal orientation [001], [010] and [100]. Taking the crystal orientation (010) as an example, the maximum hole and electron mobility appears in the direction of θ=0° or 180°, that is, the maximum hole and electron mobility is in the crystal orientation [100]. The minimum values of hole and electron mobility are distributed on the crystal orientation [001] and [000]. Therefore, the crystal can be grown on the crystal face (010), (101) and (110) when preparing the battery.

![Fig. 9 Anisotropy of Carrier Mobility in MAPbI3 Crystal [29]](image)

Therefore, when electronic devices is being designed, the crystal face with the same growth electron and hole transmission direction should be followed, in order to obtain better crystal growth and crystal face control, and, therefore, to optimize device performance.

### 3.3. Photoelectric Performance

The physical properties of MAPbI3 show significant differences between polycrystalline and single crystal [31-32]. One of the reasons is that polycrystalline films are usually composed of small particles, and the grain size and grain boundary are crucial to the optical properties of MAPbI3 [33-35]. Dong et al. [36] prepared vertical photodetectors, in which the single crystal structure of MAPbI3 reduces the recombination of stimulated carriers, which are more suitable for photoelectric applications [37]. In 2015, Sun et al. [37] prepared MAPbI3 single crystal planar photodetector based on crystal face (100) by BSSG method. The response spectrum of the photodetector to near infrared region is wider. Compared with polycrystalline film, its responsivity and EQE are about $10^2$ times higher, and the response speed is about $10^3$ times faster.

In 2017, Cui et al. [38] prepared large particle MAPbI3 single crystals with crystal face (100) and (220) by ITC method. It was found that crystal face (220) had better photoelectric properties than crystal face (100) under 405 nm, 15 MW illuminations and 10 V bias voltage. The highest responsivity and external quantum efficiency were 19.5 mA/W and 6.55%, and the maximum detectable value of crystal face (220) was $1.0 \times 10^{11}$ A. This is usually related to ion migration [39-41]. The ion concentration of I- on (220) is 0.037 atoms/Å$^2$, which is higher than that of (100). Therefore, I- ion migration on crystal face (220) will bring higher photocurrent and responsivity. The outline of [PbI$_6$] octahedron is zigzag on (220) [39-40], which provides ion migration channel perpendicular to (220) for I-, so crystal face (220) has stronger photoelectric surface than (100), which is more suitable for photodetectors.
Ding et al. [42] used ITC method to grow large-size MAPbI₃ single crystals with crystal face (100) and (112). Under the applied voltage of 405nm, 1-5mW and 5V, the dark currents at (100) and (112) are $1.41 \times 10^{-8}$A and $1.61 \times 10^{-7}$A respectively. The transport activity of (112) is stronger. When the irradiated power is 1mW and the bias voltage is 5V, the highest responsiveness and EQE of the device on face (100) are 0.023A/W and 7.2% respectively, and the numeric value on (112) is its 2.3 times. This may be helpful to choose oriented-grown thin film materials for solar cell device.

The difference in photoelectric properties of the crystal faces is mainly due to their different structures. There are eight [PbI₆] octahedrons surrounding MA⁺ on the crystal face (100), while only four on the crystal face (112). More octahedrons on (100) limit the rotation degree of freedom of MA⁺ in the inorganic cage, thus reducing the effective polar domain and impeding carrier motion [43]. Therefore, its photocurrent is lower than that of (112) face-based devices. It can be seen that the photoelectric anisotropy is helpful to the preparation of perovskite solar cells with higher performance.

**4. Prospects of Hybrid Organic-Inorganic Perovskite**

Hybrid organic-inorganic perovskite materials have excellent photovoltaic properties, so they have an important application prospect in solar cells and related fields. In this research, the structure and preparation methods of perovskite materials are briefly introduced, and the anisotropy of single crystal perovskite materials in stability, thermal conductivity, carrier mobility and photoelectric properties in recent years is summarized. Domestic and foreign existing researches indicate that factors including the organic cationic and crystal structure of single crystal perovskite materials effect on material properties of each crystal face. The importance of crystal controllable growth orientation is increasingly prominent, providing theoretical basis for the preparation of efficient perovskite solar cells. Moreover, it is helpful for getting a new perovskite materials with better crystal growth and crystal face control in the design of electronic devices.

However, there are still some work in need in the following three aspects.
(1) Compared with traditional perovskite, the structure and composition of two-dimensional hybrid perovskite are more flexible and adjustable. Through the reconstruction of the preparation process and the optimization of the device structure, it is of great research significance to improve the stability and photoelectric properties of two-dimensional hybrid perovskite, which can be applied to the large-scale commercial application of perovskite battery.

(2) Because of the biological toxicity of lead, it does great harm to the environment. However, the properties of lead-free materials do not work well enough, so it is urgent to develop better lead-free perovskite materials.

(3) Based on the organic-inorganic compound halide perovskite single crystal materials, a new design idea needs to be carried out to explore the synthesis of a variety of new perovskite materials, as well as their energy band engineering tuning. A systematical study can be conducted to figure out the intrinsic properties of this material, including its structure, photoelectricity, thermology, and stability. On this basis, the fabrication of single crystal devices can be realized, in order to expand the photoelectric application range of this kind of materials.

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