A Systematic Analysis of The Current 2D Perovskite Engineering Approach and Future Prospects

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Abstract. Perovskite solar cells (PSCs) have become a hot topic in the photovoltaic studies. Although perovskite has excellent photoelectric properties including adjustable bandgap, high power conversion efficiency (PCE) performance, high electron transport, the three-dimensional perovskite commonly studied is often unstable, short life, and subject to environmental interference especially heat and humidity. So two-dimensional perovskites have been studied and studied. This paper introduces the 2D materials and 2D perovskite solar cells. And then several new works of surface engineering on 2D perovskite solar cells including passivation strategies, interface engineering and orientation of crystallization on perovskite films are mentioned and concluded, thereby providing a future understanding to improve and balance the efficiency and stability of 2D PSCs. Even though the existing strategies for optimizing two-dimensional perovskite are abundant and have certain rules, more essential two-dimensional perovskite properties to improve efficiency and stability need to be studied, so that two-dimensional perovskite will have more possibilities in industrial production.

Keywords: 2D perovskite; solar cells; stability; surface engineering.

1. Introduction

Perovskite solar cells (PSCs) is now a hot research area for the great properties of perovskite, including high power conversion efficiency (PCE) performance, high electron transport, adjustable bandgap, etc. However, three-dimensional (3D) perovskite, which is often studied, is difficult to be implied in industrial area because of its instability including as failure under heat and humidity [1]. To reduce the instability, scientist have turned to two-dimensional perovskites, especially the research of 2D perovskite structures of Ruddlesden–Popper (RP) phases, which shows higher moisture and thermal stability, and a much lower ion migration and phase transition occurrence compared with 3D perovskites [2]. Although 2D perovskite show weaker PCE performance, through various work, it is approaching the efficiency achieved by 3D perovskite as well as maintaining its stability.

This paper first introduced solar cells and the specific impact on our lives, then mentioned the excellent properties of two-dimensional materials. Then an analysis of perovskite solar cells is given, pointing out that although the three-dimensional perovskite shows excellent performance, it is lack of stability, which affect its industrial appliance. Two-dimensional perovskites are more feasible, and the unique properties found also make two-dimensional perovskites have more potential applications in the field of solar cells. The existing engineering techniques for optimizing two-dimensional perovskite are summarized, including interface engineering, passivation strategies and orientation of crystallization. The PCE of different 2D perovskites can be improved to more than 20%, with great stability after thousand hours tests. Some excellent optimization strategies such as inducing growth and improving interlayer electronic properties are proposed, which give us a further understanding of improving the properties of 2D PSCs and make full use of the potential of 2D perovskites on the optoelectronic designs in the future.

2. Theoretical basis analysis

2.1. Photovoltaics and 2D materials

Photovoltaics, commonly referred to as solar panels, is a technology that converts sunlight into electricity. This innovative technology is becoming increasingly popular around the world as a sustainable energy. Photovoltaic are typically made of semiconductor materials that excite electrons and generate current by absorbing the photons mostly from visible light. The energy produced by photovoltaic systems can power homes, businesses, and even communities, which reduce the effects of climate change. In this way, photovoltaics brings a promising solution to the growing energy demands of the world while promoting a sustainable future. 2D materials refer to a unique class of materials with a few atomic or molecular layers. They are characterized by their unique optical and electronic properties, which are different from their bulk 3D composition. The properties of 2D materials make them widely used in a range of applications, including electronics, photonics, energy storage, and catalysis. Researchers are actively exploring the potential of 2D materials and developing new fabrication techniques to create high-quality 2D materials with tailored properties.

2.2. Advantages of 2D materials

Graphene, h-BN, TMDs-MoS2, WSe2, MXenes, BP, and Perovskite are among many atomically thin layered materials that have been developed recently in this area. 2D nanostructures performs good properties, such as high optical transparency, electrical conductivity, high photon absorption, tunable band gap, mobility, wide electronic band structure, charge carrier lifetimes, stable performance, sustainability and scalability [3]. 2D materials perform a high surface-to-volume ratio, which allows them to absorb a large amount of light. This property makes them ideal to be applied in thin-film solar cells. The bandgap can be tuned by changing the shape, or composition of 2D materials. This property allows them to absorb different wavelengths of light, making them useful for multi-junction solar cells [3]. 2D materials are suitable for use in flexible and lightweight solar cells due to their thinness and flexibility. For their chemical stability and ability to withstand harsh environments, 2D materials are an excellent choice for solar cells that need to operate in extreme conditions.

2.3. Perovskite solar cells

Among these two-dimensional photovoltaic cells being studied, perovskite solar cells (PSC) have become a high-profile research topic due to its high conversion efficiency. Before 2016, people mostly focused on 3D perovskite, especially 3D halide perovskite with the chemical formula of ABX_3, as shown in Fig 1 [2].

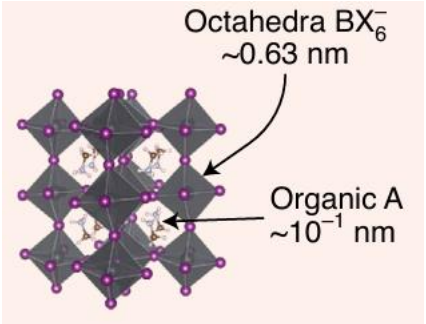

Fig.1 The 3D perovskite structure [2].

A can be Cs^+, $CH_3NH_3^+(MA^+)$, $HC(NH_2)_2^+(FA^+)$, B can be Ge^{2+}, Sn^{2+} or Pb^{2+} and X can be Cl^-, Br^- or I^-. This structure often has PB lead as a class B element, leading a $[PbX_6]^{4-}$ octahedra sharing 6 corners [4]. The structures created by the keys inside the materials are excellent, with wide conduction and valence bands to facilitate charge transport. 3D Perovskite is considered to be one of the great active layer materials, however, it can change its phase and properties quickly due to the change of environment (water, temperature, pressure, force etc). Usually, researches need to balance

between efficiency and stability. So that 2D perovskite is considered to be a way to greatly improve the stability, as lower dimensional perovskite has bigger binding energy.

Organic-inorganic(hybrid) 2D halide perovskite is self-assembled composite semiconductor materials made of nano-thick hybrid halide PVSKs stacked and separated from each other by spacing layers. 2DPKs presents a series of unique physical structural properties, including soft dynamic structure, high photoluminescence(yield), strong anisotropy, broadband luminescence, strongly bound excitons at room temperature (25°C), which is the result of incorporating additional bulky organic ligands (usually two kinds) [2]. As is shown in Fig 2 the formula of 2D perovskite is $A'_mA_{n-1}B_nX_{3n+1}$ [2].

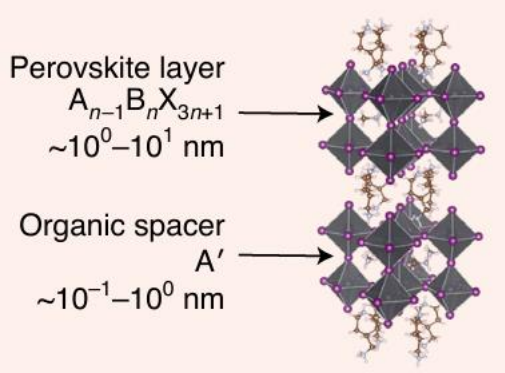

Fig.2 The 2D perovskite structure [2].

A' can be a monovalent (m=2) or divalent (m=1) cation which arranged between the octahedron [4]. And n is the inorganic layer number.2D PVSKs cab be divided into three types. The first one is Ruddlesden-Popper (RP) phase PVSK, which formed with divalent. The second one is Dion-Jacobson (DJ) phase PVSK, which formed with monovalent. The third one is called ACI (alternating cations in the interlayer), which is reported with guanidinium cation [4]. RP phase PVSK are more often used because the research of DJ began later. At current stage, there is a lack of effective means to regulate the orientation of crystallization of DJ PVSKs and control the kinetics of crystallization.2D perovskite changes phase and ferroelectricity when environment change. Disordering of dynamic organic cations and reducing distortions of PVSK octahedra can also create the ferroelectric-paraelectric phase transition, which is a way of understanding the interplay between ferroelectricity and semiconductor physics. Electron-phonon coupling, rashba-like effects are also studied in 2D PVSKs in order to improve its properties and widen its use in optoelectronic devices [2].

At the present, most 2D PSCs referred to as 2D/3D perovskite solar cells, because it is difficult to get pure 2D PVSK layer. Moreover, the 2D PVSKs grown on the surface of 3D PVSK can have advantages as filling grain boundaries and preventing non-radiative recombination etc.2D/3D perovskite is becoming a hot topic structure. Usually, 2D layer is prepare on the 3D PVSK and 2D layer is close to the ITO base. In order to improve the efficiency and other properties of 2D PSCs, several works have been made and now the PCEs have arrived at more than 20%, with great stability and other good performance of 2D PSCs.

3. 2D PSCs Engineering:

3.1. Interface engineering:

Generally, 2D PSCs synthesize thin 2D perovskite film on 3D perovskite surface, which can be influenced by the concentration, type of ligand solution etc, resulting in different surface structures. The grain size and surface defects have become the key factors of the efficiency of solar cells. It is a study direction to improve the grain size and reduce the recombination caused by defects through engineering work.

Dongqin Bi and his team used guanidinium bromide (GABr) on the top of the 2D $GA_2MA_4Pb5I_{16}$, processing a smooth film with great optoelectronic properties. The PCE arrived at 19.3% under AM

1.5G illumination, after 3000h ambient condition storage, the PCE still retain 94% [5]. The work shows that 10 mM GABr concentration is optimized because this proportion form larger bulk materials on the film and means fewer grain boundaries and defection which suppress the is the upper limit of incorporation of GA^+ in the PVSK lattice and it will not affect bandgap of PVSK [5]. The SCLC method was employed by them to confirm that GABr has the ability to lower the defect density of perovskite films and prevent non-radiative recombination triggered by non-radiative recombination. For the suppressing of charge traps, GABr added 2D films also shows longer photovoltage and shorter photocurrent decay.

According to the work of Ming Shao, Xinliang Zhang and their team in 2022 [6]. The Pure FA based 2D PSC $(4FPEA)_2(FA)_4Pb5I_{16}$ shows better PCE of 21.07%, compared to Pure MA $(4FPEA)_2(MA)_4Pb_5I_{16}$ with 17.05% and FA/MA mixed $(4FPEA)_2(FA_{0.3}MA_{0.7})_4Pb5I_{16}$ PSC with 20.07% [6]. FA PSC shows strong stability which retain 97% efficiency after 1500h thermal test, compared to MA of 78% and MA/FA of 92%. It also shows better humidity resistance, which still has 90% efficiency after 1000h 80 ± 5 RH moist environment tests, compared to 3D PSC with 60% after 400h tests [6]. It was founded that increase FA ratio can wide the absorption range and enhance light absorption. Pure FA performs smooth and dense film surface, and the crystal size also becomes larger, which have a same benefit as the passage above [6]. The XRD shows an oblique crystal orientation of FA-based PSC. Results shows 2D/3D mixed phase distribution shows nonorientation in the 2D material. However, TA test proved that it facilitates ultrafast energy/charge transfer from 2D layer to 3D layer, which greatly benefits the PCE.

Theoretical simulation experiments on perovskite are also carried out.Jaya Madan and his team use SCAPS-1D simulator to simulate a 2D MXene contact 1.4-butanediamine ((BDA)-based) DJ 2D PVSKs in 2024 [7]. According to their data, the PCE of $(BDA)(MA)_{n-1}Pb_nI_{3n+1}$ (n=1 to 6) can get to a maximum of 24.58%. According to the work done by Zheng et al in 2019, the PCE of (BDA)-based PCEs showed no change after 20 days in ambient air with 45% relative humidity environment, which showed excellent stability [8]. MXene/$(BDA)(MA)_{n-1}Pb_nI_{3n+1}$/MXene structure was designed to test the relation between PCE and n (of material). Result showed that when the composition of active layer, which can be represented by n becomes bigger, PCE goes upper, because energy band bending was founded in n=5 devices, while n=1 devices only found electric field in back electrode.

3.2. Orientation of Crystallization

2D perovskites are usually arranged in layers so that the carrier mobility depends on the direction of charge transport between layers as shown in Fig.3 [4]. Transport efficiency increase when paralleled to the inorganic layer, leading to studies focusing on the orientation of crystallization in 2D perovskites.

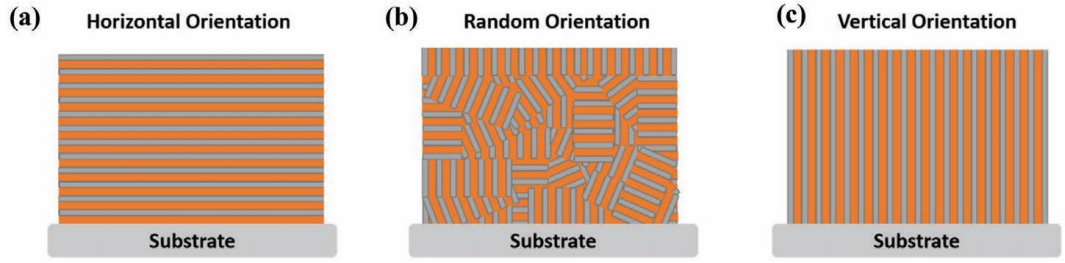

Fig.3 The orientation of thin films 2D perovskite films with organic and inorganic layers [4]

Where, a) Oriented parallel to the substrate preferentially, b) randomly oriented, and c) Oriented vertically to the substrate

In the work of Chang Liu and the group in 2023, a ferroelectric flexible 2D PVSK was founded. 3-pyridinylmethylammonium(3-PyA) was used to make this $(3\text{-}PyA)_2PbI_4$ 2D PVSKs as organic layer, which reached a PCE of 23.01% in inverted-structured f-PSC [9]. Moreover, this f-PSC showed bending endurance, its efficiency retained 93% after bending test. Tested in 30±5 RH room temperature environment for 1000h, its efficiency retained 82%, which means a good stability. It was

founded that 2D PVSK promoted the (110) orientation of 3D PVSKs. The 2D PVSK incorporation distribute homogeneous and compact in 2D/3D films. Although the component of 2D PVSK added to the 3D PVSK constrain the crystal growth, leading more grain boundaries, the 2D PVSKs formed can passivate the surface and suppress defects [9].

Zhike Liu et al. (2024) found a seed-mediated way to create a 2D PVSK layer, which can let 3D PVSK atop it grow epitaxially, which preferred (112) direction [10]. They used $FA_{0.85}MA_{0.15}PbI_3$ perovskite film and added unilateral N, N-Dimethyl-N-octyl-1-octanaminium bromide (DAB) modification. The DAB modified PVSK showed a PCE of 24.83%. Under strong in ambient air for 1650h, the PCE retained 95% [10]. The growth kinetics of crystal nucleus happens when the size is larger than r*(critical nucleus). 2D materials can be produced by DAB when the perovskite precursor solution is coated on top, and PbI2 and FAI react directly with it. For the fact that 2D PVSKs crystals exist at the bottom of the film, the single-side-film (SSM) can grow in directly phase. During the crystallization process that started at the bottom of the film, the surface can become saturated and nucleated, resulting in the appearance of the (002) oriented phase. The epitaxial growth template of 2D perovskite could be utilized to improve the oriented growth of perovskite grains in the (112) direction instead of (001) direction [10]. By modifying DAB, charge recombination can be effectively limited and charge transfer from perovskite to the hole-transport layer can be expedited, which can enhance FF and VOC of the PSCs.

Martin Kaltenbrunner et al. investigated the initial stages of crystallization and used methylammonium chloride (MACl) to grow preferential orientation of 2D perovskite on the monofluorinated 3-fluorobenzylammonium (3FBA) based $(3FBA)_2(MA)_{n-1}Pb_nI_{3n+1}$ active layer. When n=7, the PCE reached 18.5%. After up to 97% relative humidity (RH) test for more than 10h, the PCE showed no decrease [11]. Remarkably, they found a way of preparing high orientation crystallization film. Chloride-containing additives can improve the morphology of PVSK films, benefiting the transport properties and stability. It was proved that when MACl is heated and vapored, it left unstable inter mediary on the air-liquid interface. The evaporation of solvent leads to increase on saturation of solution and the reaction of MACl. As the clearly defined orientation of the liquid surface, the crystals form in the same preferential orientation of (220) [11].

3.3. Passivation Strategies

Passivation strategy is also a way to improve the efficiency of 2D PSCs. The interaction between functional groups of surface passivated molecules and selective defect states of films inhibits trap recombination of surface defects, which can increase efficiency.

Qiang Fu and his team used morpholine hydriodide (MORI) and thiomorpholine hydriodide (SMORI) on PVSK surface and create a passivation area of 2D hybrid perovskite structure on the 3D PVSK surface [12]. Although 2D perovskite orientated in parallel to the substrate, it is thin enough for the carrier to tunnel through and suppress the recombination of charge. It was proved that SMORI showed better passivation with PbI_2 than MORI and PI. Compared to 1D PVSK film surface, SMORI-treated 2D PVSK surface form better surface passivation and stronger n-N homotype 2D/3D heterojunctions, and shows a PCE of 24.55%. After 1500h MPPT test, the efficiency retained 87.6%, which is the fact of 2D quantum well structure of the PVSK capping layer [12]. And it also adds the thermal/humidity stability of the device.

According to the work of Heejoo Kim et al. 2023, a way was found to passivate the surface of 2D RP $PEA_2MA_4Pb_5I_{16}$ perovskite and Zwitterionic n-tert-butyl-α-phenylnitrone (PBN) act as the passivation material. The PCE of their work arrived at 20.05%, which the RP PVSK without PBN added only showed 17.53%. Under over 1000h 1-sun irradiation, the PCE retained 88%. Ionic defects are always considered as the problem of carrier trapping and the loss of recombination [13]. During their work, they used Fourier transform infrared (FTIR) analysis and found an interaction between PBN and the RP PVSK. When a thin layer of PBN locates on the RP PVSK, it can passivate the defects and some grain boundaries on the surface. The decomposition and dissolution of 3D halide PVSKs by PBN molecules can be achieved by using a low concentration solution, which has the most

effective passivation effect and it is similar to the research of pure FA research before [13]. Also, PBN can change the orientation of some RP PVSKs at the surface to (111), which is beneficial to the PCE too.

According to the work of Suman Kalyan Pal and his team in 2023.They found a strategy to passivate 3D $MA_{0.9}FA_{0.1}PbI_3$ PVSK surface with 2D $(TEA)_2PbI_4$ layers. The PCE of Sulfur-rich spacer cation2-thiopheneethylamine iodide (TEAI) treated device can reach 20.06%. Under heat treatment at 80°C for 2h, the PCE retained 79%, compared to 3D PVSK losing almost are efficiency [14]. It was found that TEAI can help growing a 2D layer on the 3D PVSK. An extended carrier lifetime and decreased non-radiative recombination were confirmed by TRPL and TA measurements after the incorporation of thiophene-based cations in the PVSK film, which resulted in a significant reduction in defects. The $(TEA)_2PbI_4$ perovskite is better suited for band alignment and higher hydrophobicity than the $(PEA)_2PbI_4$ perovskite used earlier [14].

4. Conclusion

The performance of 2D perovskite cells has been proved and greatly improved in PCE efficiency, heat resistance test, bending test and waterproof test through various engineering work. However, it is still in an early stage, and 2D perovskite solar cells are still a certain distance from 3D perovskite solar cells in terms of efficiency. In the engineering part, passivation strategies, interface engineering, and efforts to improve crystal orientation are mentioned. At present, the interface engineering is mainly to improve the ligand to make the surface more smooth, more large-scale grains can be generated, and reduce the grain boundary to achieve less recombination to improve the PCE value. In the passivation strategy, 2D perovskite covering layer is mainly introduced to improve surface defects of perovskite layer to reduce surface recombination. In order to improve crystal orientation, part of the reactants is usually preexisting on the interface during the ligand process, and objective orientation laws such as the direction of force on the surface are used to make use of crystal nucleation laws. The orientation of the crystal formation is improved.

However, we also found that sometimes these summarized rules and facts are not completely consistent, for instance, the crystal orientation of the 2D perovskite surface generated by passivation strategy is different from the orientation required to improve the crystal, but its performance is much improved compared with the untreated material; For example, the research focusing on improving crystal orientation makes the crystal size smaller and increases the number of grain boundaries, but from the result, it still improves the performance. Therefore, more 2D perovskite properties for improving performance need to be further studied, so as to truly find out that the properties of 2D perovskite can be balanced in crystal size, crystal orientation, ligand solute concentration, passivation thickness, etc. The relationship between factors related to performance improvement.

At the same time, many studies have also begun to combine these projects, making some 2D perovskite materials with very low performance greatly improved, which is a positive development direction. In the future, more detailed and more characterization studies should be encouraged to reveal the fundamental factors that enhance the performance of 2D perovskite solar cells, such as the study of the built-in electric field and work function. The tradeoff between efficiency and various types of stability should be thought about and studied in more detail. More industrial production technology of 2D perovskite should also be paid more attention, such as the research of large-scale production and packaging technology, so that 2D perovskite solar cells can truly move from the laboratory to the industrial production chain and enter people's lives.

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