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2D Organic-Inorganic Hybrid Perovskite Light-Absorbing Layer in Solar Cells

Meng Wang, Qunliang Song and Sam Zhang

Abstract

With the rapid development of high-performance perovskite solar cell, its instability has become an urgent problem to be solved. 2D perovskite is considered as a potential light absorbing material for perovskite solar cells due to its excellent stability. However, the preparation of high quality 2D perovskite films suitable for photovoltaic devices remains a challenge. In this chapter, based on the structural and photophysical properties of 2D perovskite thin film materials, the latest progress in 2D perovskite cells in recent years and the strategy of controlling the film quality of 2D perovskite are summarized, which is of great significance for the further development of 2D perovskite photovoltaic devices.

Keywords: perovskite solar cell, stability, 2D perovskite, material property, film quality

1. Introduction

To solve the energy crisis coming with the rapid development of the society, solar energy is a promising renewable energy source which can convert light to electricity in the photovoltaic devices [1]. Among all the photovoltaic devices, perovskite solar cell (PSC) attracts researchers' attention most for its power conversion efficiency (PCE) has been increased from 3.8 to 25.2% in just 10 years [2–6]. With strong optical absorption, high carrier mobility and small exciton binding energy, organic-inorganic perovskite materials are semiconductors with remarkable optical and electrical properties [7–9]. The advantages of solution manufacturing and processing are widely used by researchers in solar cells with various structures [10]. However, one of the major reasons why high-performance perovskite solar cells have not been applied to practical application is the instability of the materials.

The instability of organic-inorganic hybrid perovskite is caused by many intrinsic and extrinsic factors. The external environmental factors include moisture, heat, oxygen and many other factors. Moisture is considered to be an important factor for the instability of perovskite materials, while the presence of light and oxygen accelerates the degradation process [11–13]. In addition to the influence of these external environmental factors, some intrinsic properties of the perovskite material itself also directly lead to its instability, such as composition and ion migration [14]. The perovskite materials with excellent photoelectric properties have a strong ionic property, indicating that the activation energy of ion migration inside the crystal

is low, and molecular dissociation and ion migration are prone to occur within the structure, which limits the structural stability of these materials [15].

In recent years, the two-dimensional (2D) perovskite structure formed by introducing large-size organic cations is proved to be more stable than its three-dimensional (3D) counterpart and it has become a potential light-absorber in the PSCs. There are many reasons for the 2D perovskite to exhibit higher stability. The 2D perovskite has higher formation energy and it is more difficult to be oxidized than the 3D structure [16]. Compared with 3D perovskite crystals, the bonding forces between organic ions and $[\text{PbI}_6]$ octahedral units such as van der Waals forces and hydrogen bonds are stronger [17]. Due to the presence of large size organic cations, ion migration is blocked [18]. Meanwhile, the 2D perovskite layer can work as passivation layer and blocking layer of moisture and oxygen to enhance the stability of perovskite [19, 20].

Although 2D perovskite materials show great potential in terms of stability, the relatively lower PCE needs to be improved. In this chapter, based on the structural and photophysical properties of 2D perovskite, the latest progress made in 2D PSCs in recent years and strategies to improve the performance of 2D PSCs are summarized, which is of great significance for the further development of PSCs based on 2D perovskite materials. Finally, a brief conclusion and outlook is promoted.

2. Material properties of 2D perovskite materials

2.1 Structural properties of 2D perovskite

The stability of perovskite structure can be described by tolerance factor- t , whose calculation formula is: $t = \frac{Ra + Rx}{\sqrt{2}(Rb + Rx)}$, where R_a , R_b and R_x are the radius

of the atom located at A, B, X site respectively [20]. The perovskite structure with tolerance factor in the range of 0.8–1.01 is stable and can form an ideal 3D cubic structure [21]. In the stable 3D structure, the octahedrons formed by lead ions and halogen ions are infinitely connected, and organic cations are located between the spaces formed by the octahedrons [22]. When the size of the organic cation at the A site increases, the tolerance factor will exceed the above range finally. Then the infinitely connected octahedral structure is broken, and a conductive inorganic layer and an insulating organic layer are alternately connected to each other [23]. The 2D layered perovskite film can be regarded as the infinitely connected octahedron structure separating by the large-size organic cations, and the thickness of the octahedron contained in each layer is n . The value of n is closely related to the ratio of large organic spacer cations, and represents the periodicity in the crystal structure. The perovskite crystal structure with n value ranging from $n = 1$ to $n = \infty$ is shown in **Figure 1**. The L -value there denotes the thickness of the inorganic layer in each compound [25].

All organic cations capable of forming a 2D perovskite structure have groups that can interact with the inorganic layer at their ends and can stably exist in the crystal structure. According to the structural characteristics of large-size organic cations, the obtained 2D perovskites can be divided into different types. And the corresponding PSCs have different performances accordingly. The 2D perovskite formed by organic cation similar to BA^+ and PEA^+ , which have only one amino group at the end, is called the RP phase, which was first applied to 2D PSCs in 2014 [19]. According to the characteristics of the crystal structure and the chemical ratio of each ion, the chemical formula of the 2D RP phase perovskite is $\text{AA}_n - 1\text{B}_n\text{X}_{3n + 1}$. [26]

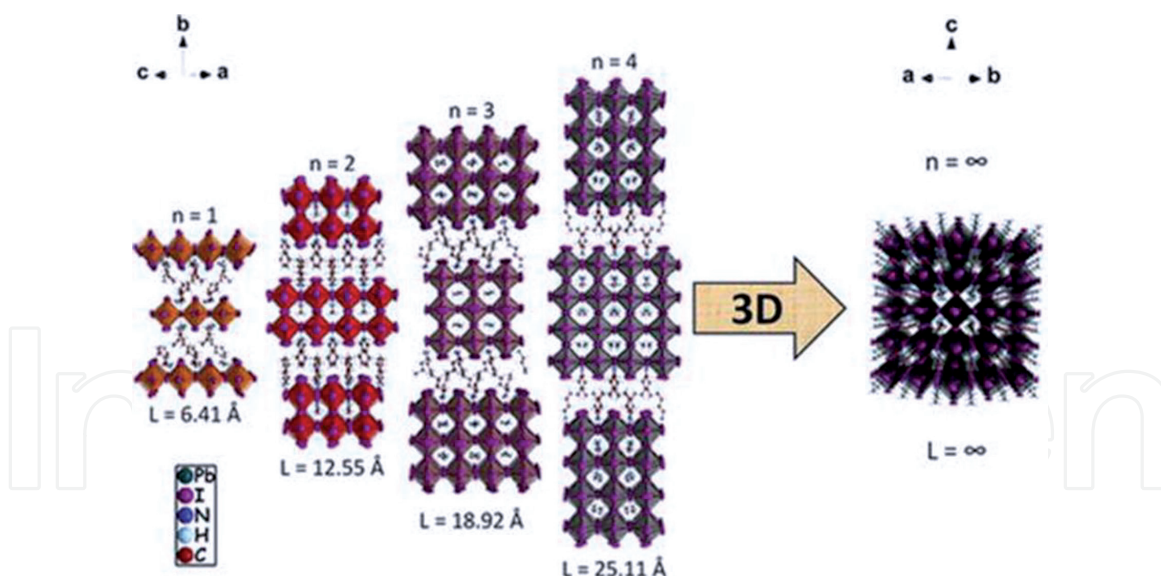


Figure 1.
 Crystal structures of the 2D lead iodide perovskites, $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, ranging from $n = 1$ to $n = \infty$. The L-value denotes the thickness of the inorganic layer in each compound [24]. Copyright 2016, American Chemical Society.

As shown in **Figure 2(a)**, the RP phase crystal is coupled by weak van der Waals forces. BA^+ and PEA^+ are the most widely studied organic spacer cations in 2D RP PSCs. In subsequent studies, organic cations such as AVA^+ , PEI^+ , PPA^+ have been extensively studied [27–29]. The development of new organic spacers cations is an important way to improve the performance of 2D perovskite solar cells. Recently, 2D RP PSCs with a record PCE more than 19% was prepared by using an organic-salt-assisted crystal growth (OACG) technique, which can induce the crystal growth and orientation, tune the surface energy levels, and suppress the losses caused by charge recombination [30]. The 2D perovskite formed by organic cation similar to EDA^{2+} , which have two amino groups that can interact with inorganic layers at both ends is called the DJ phase. Its chemical formula and crystal structure are shown in **Figure 2(b)** [31]. The DJ phase has better stability than RP perovskite (van der Waals interaction) because the spacer cations with two amino groups at both ends can form hydrogen bonds with inorganic plates without any gaps [32]. Ke et al. used 3-(amino methyl) piperidine (3-AMP^{2+}) as organic spacers. Compared with the single A-site cation, mixing cation (3AMP) $(\text{MA}_{0.75}\text{FA}_{0.25})_3\text{Pb}_4\text{I}_{13}$ perovskite has a narrower band gap, less inorganic skeleton distortion and the larger Pb-I-Pb angle [33]. Cohen used BDA^{2+} as an organic spacer cation and achieved 15.6% PCE

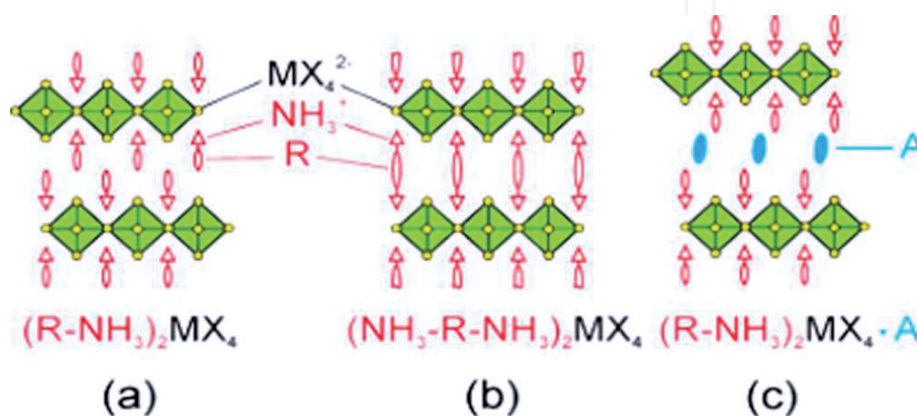


Figure 2.
 Schematic representation of (a) RP phase (b) DJ phase (c) ACI phase [26, 31, 35]. Copyright 2000, springer. Copyright 2018, American Chemical Society. Copyright 2017, American Chemical Society.

without additives and any additional treatment [34]. The 2D perovskite formed by organic cation similar to GA^+ , which can alternate interact with MA^+ in the organic layers, is called the ACI phase. Its chemical formula and crystal structure are shown in **Figure 2(c)** [35]. Due to its relatively small difference in ion size from MA^+ and FA^+ , it has smaller exciton binding energy and weaker quantum confined effect. So, it is expected to achieve higher efficiency. The perovskite solar cells with BEA^{2+} ligand achieved high efficiency of 14.48 and 17.39% when doped with and without Cs^+ respectively [36]. Zhao's team achieved a high PCE of 18.48% by adding methyl ammonium chloride as an additive to effectively control the film quality of ACI 2D perovskite $(\text{GA})(\text{MA})_n\text{PbI}_{3n+1}$ ($n = 3$), showing great potential of ACI perovskite with high stability and PCE [37].

2.2 Photophysical properties of 2D perovskite materials

Compared with 3D perovskites, 2D perovskite has a greater chemical and structural flexibility. The optical, electrical, and charge transfer properties can be regulated by controlling the width and composition of the potential well and barrier. In the 2D perovskite structure, a quantum well structure is formed between the insulating organic layer and the conductive inorganic layer, resulting in a quantum confinement effect [38]. The dielectric confinement effect is caused by the different dielectric constants of the potential well and the barrier, coupled with the quantum space limitation. The optical gap of 2D perovskites has a higher value than its 3D counterparts [39]. Zhang's work explored the inherent properties of 2D layered perovskites $(\text{PEA})_2\text{PbI}_4(\text{N})$ and $\text{Cs}_2\text{PbI}_4(\text{N})$, and demonstrated that their structure and properties vary with N . The results reveal that both $(\text{PEA})_2\text{PbI}_4(\text{N})$ and $\text{Cs}_2\text{PbI}_4(\text{N})$ are direct bandgap semiconductors. When $N \geq 3$, their band/optical gap and exciton binding energy vary linearly by $1/N$. This work shows that ultra-thin 2D materials can become potential candidates for nano-optoelectronic devices, and nanoplates with $N \geq 3$ can have similar properties to bulk materials in terms of carrier migration and exciton separation, so they can be effectively applied for photovoltaic devices [40].

Figure 3 shows the absorption and emission spectra of a series of ultra-thin $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1-5$) crystal layers mechanically peeled off from the pure phase (fixed n) single crystal by Blancon et al. In the exfoliated crystal, as n decreases from 5 to 1 (quantum well thickness varies from 3.139 to 0.641 nm), the band edge absorption and emission peaks monotonically increase from 1.85 to 2.42 eV. Due to the quantum and dielectric confinement effect, exciton binding

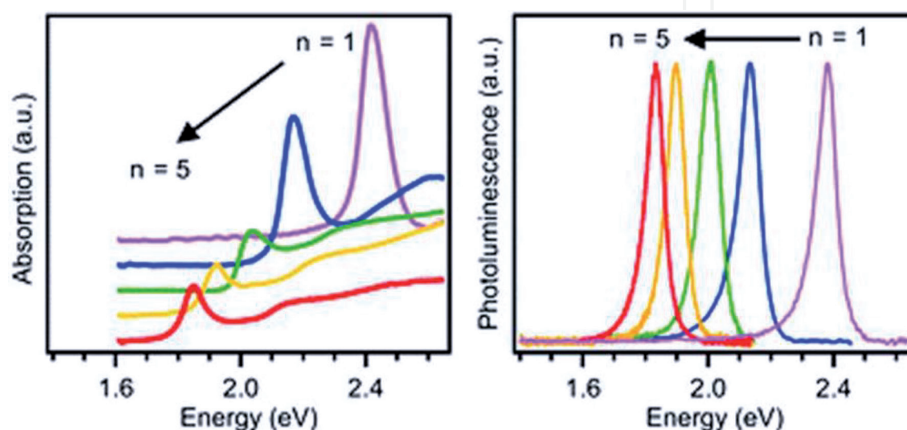


Figure 3. (Left) absorption and (right) PL Spectrum of the exfoliated $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ crystals (from $n = 1$ to 5) [41]. Copyright 2017, American Association for the Advancement of Science (AAAS).

energies are approximately one order of magnitude higher than the values found in 3D perovskites. Their results also show that in the film, the optical band gap is consistent with that of the exfoliated crystal at $n = 1$ and $n = 2$, but the red shifts about 200–300 meV at $n = 3-5$ [41].

3. Film quality control of 2D perovskite

Consistent with the situation in the 3D PSCs, it is of vital importance to control the film quality of absorption layer for a high-performance 2D PSC. For the synthesis of the light-absorption layer, the most-commonly used spin-coating method is applied. However, things become more difficult when it comes to the crystallization process of the 2D perovskite films. To improve the film quality of the 2D perovskite, many strategies are used to optimize the film quality, mainly focusing on adjusting the crystal orientation and the phase distribution, as summarized below.

3.1 Vertical orientation

The precursor solution of 2D perovskite is prepared by mixing and dissolving ammonium salt of the organic cation spacers, ammonium salt of the A-site organic cations and metal halide according to a certain proportion (depending on n value). During the crystallization process, competition was confirmed to occur between the large organic cations and A-site organic cations [18]. To be more specific, the large organic spacers tend to form a low-dimensional perovskite while the A-site cations tend to form a 3D structure. The low- n phases are prone to have a horizontal orientation instead of vertical orientation, which is unfavorable to the charge transfer. Since the presence of insulating large-size organic cations will hinder the charge transport out-of-plane, Tsai, H. et al. used a hot-casting technology in 2016 to prepare high-quality films, which means that the substrate is preheated before spin-coating the perovskite precursor solution. With this method, a more beneficial crystal growth along (111) and (202) planes is observed instead of random orientation [42]. The application of the hot-casting method has promoted the efficiency of 2D PSCs and confirmed the importance of the crystal orientation perpendicular to the substrate for the performance improvement. At present, hot-casting method is widely used for better performance of the 2D PSCs. However, it is hard to keep temperature accurate and uniform when transferring the substrate from the hot-plate to the spin-coater. To solve this problem, Li et al. partially replaced the BA^+ with MA^+ in the BAMA quasi-2D perovskite, reducing the dependence on the preheating of the substrate. After being replaced, the quantum confinement effect of the perovskite film is weakened, the crystallization barrier is reduced, and higher quality perovskite film crystals and fewer defect states are obtained [43]. Beyond ion replacement, the morphology of the 2D DJ perovskite film with rigid piperidine ring was adjusted by MASCN additive at room temperature. By optimizing the amount of added MASCN, the perovskite film deposited on the substrate has good crystallinity, preferred orientation, reduced defects and better energy level alignment with the transport layer. The device had an inverted planar structure with a maximum PCE of 16.25%, which is the highest PCE of 2D DJ PVSCs without hot casting. After being exposed to air for 35 days, the unencapsulated device maintains about 80% of its initial efficiency ($Hr 45 \pm 5\%$). It provides a possibly practical way for the development of high-performance 2D DJ PSCs [44].

Many other fabrication methods besides hot-casting have also been applied to obtain a vertical crystal orientation. Ke et al. used a two-step method of spin-coating a stoichiometric precursor containing PEAI and PbI_2 , then performing FAI,

and then dropping the solution and spin-coating it on the substrate to prepare 2D perovskite film [45]. Koh et al. also obtained preferential oriented growth of 2D perovskite perpendicular to the substrate through the immersion method, greatly improving the charge transport and extraction [46].

Adding additives was also proved to be an effective method to modify the crystal orientation. The role of additives in the 3D perovskite includes improving the morphology of the film, adjusting the energy level alignment, inhibiting the non-radiative recombination inside the film, eliminating the hysteresis of the device and so on [47–50]. Additives play the same roles in 2D PSCs. However, due to the different crystallization process, they have some other effects. Xinqian Zhang and his colleagues improved the PCE of $(\text{PEA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 5$) PSC from the initial 0.56% (without NH_4SCN) to 11.01% through optimized NH_4SCN addition. The performance improvement was attributed to the vertically oriented highly crystalline 2D perovskite film and balanced electron/hole transport [51]. NH_4SCN additives was also proved to be a simple and effective method to induce the growth direction of 2D DJ phase perovskite crystals perpendicular to the substrate, and at the same time the phase distribution in the perovskite crystals can be concentrated near the phases of $n = 3$ and $n = 4$. The quasi 2D DJ phase $(\text{BDA})(\text{MA})_4\text{Pb}_5\text{I}_{16}$ perovskite film based on NH_4SCN treatment has a PCE of 14.53%. In addition, after storing under an environmental condition of $50 \pm 5\%$ humidity for 900 hours, the device retained 85% of its initial PCE [52]. Xu Zhang and his colleagues demonstrated in their work that a 2D $\text{BA}_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ PSC doped with cesium cation (Cs^+) had a PCE of up to 13.7%. The efficiency increased from 12.3% (without Cs^+) to 13.7% (with 5% Cs^+) due to perfectly controlled crystal orientation, increased grain size, excellent surface quality, reduced density of trap states, and enhanced carrier mobility [53].

3.2 Phase distribution

The coexistence of 2D perovskite phase and 3D perovskite phase lead to a phase impurity inside the low-dimensional films. Though hot-casting method has become an effective way to improve the efficiency of 2D PSCs, the impurity and phase distribution in 2D perovskite films were ignored at the early stage of studying 2D PSCs. Jin's work also shows that multiple phases of $n = 2, 3, 4$, and $n \approx \infty$ coexist in a 2D perovskite film with a nominal n value of 4. And they are naturally arranged perpendicular to the substrate. Through transient absorption spectroscopy analysis, they successfully observed continuous light-induced electron transfer from small n -phase to large n -phase driven by the band offset. And hole transfer in the opposite direction within hundreds of picoseconds was also observed. Exciton absorption peaks corresponding to different phases appear on the absorption spectrum, which is a strong evidence for the coexistence of mixed phases with different n values in the thin film. The strength of emission peaks corresponding to different n values was different when excited from the perovskite film side and the glass side, which confirmed the gradient distribution from small n value to large n value in the film [54]. Therefore, the mixed phases with multiple n values affect performance of 2D PSC from two aspects. One is phase purity, and the other is the arrangement of those phases. Besides gradient distribution in the vertical direction, other phase distributions may occur in low-dimensional perovskite films prepared by solution method. To realize high-performance low-dimensional perovskite cells, it is necessary to deliberately regulate the phase distribution inside the film.

In 2018, Liu's team used in situ time-resolved GIWAXS technology to track the transition process from precursor solution to solid film under different conditions of substrate temperatures and different solvents of precursor solutions. The results reveal that under lower temperature the intermediate phase formed by lead

iodide crystal and solvate complexes can cause multiple RP phases with random grain orientations. It is better for the disordered solvate to transform to perovskite directly [55]. The mixed phases in the low-dimensional perovskite thin film crystals are prone to energy transfer, resulting in large V_{oc} loss. To get a more vertically phase distribution, later Liu's team transferred the device to a hot plate at a suitable temperature for several hours after the 2D perovskite device was prepared, which is called a slow post-annealing (SPA) method. Such a device obtains an open circuit voltage as high as 1.24 V, which proves that the quantum well effect in the perovskite film is reduced to greatly improve the charge transfer and extraction efficiency in the device. They compared the phase distribution of the SPA films with the film prepared by the hot casting method and at room temperature respectively. Inside the thin film prepared at room temperature, the phases with different n values are randomly distributed. There is a sudden and uneven phase gradient inside the thin film prepared by the hot-casting method, resulting in the presence of 2D phase and 3D phase at the bottom and top respectively. After SPA treatment, the phase distribution inside the thin film appears more orderly [56]. Tiefeng Liu and his colleagues reported that the phase distribution of different n values in a 2D perovskite film deposited on a hole transport layer is different from that on a glass substrate. Due to the colloidal characteristics of the perovskite precursor, the vertical distribution can be explained by the sedimentation equilibrium. The addition of acid changes the precursor from colloid to solution, thereby changing the phase distribution. The self-assembled layer was used to modify the acidic surface properties of the hole transport layer, which can cause the vertical distribution required for charge transport. The surface-modified 2D PSC had a higher open circuit voltage and a higher efficiency than the control device [57].

Zhou and his colleagues proved that by controlling the crystal growth direction and growth rate, the phase distribution and carrier transport of quasi-2D perovskite films can be controlled. They found that using ethyl acetate as an anti-solvent can change the growth direction of quasi-2D perovskites by accelerating the formation of surface crystals. In addition, through the introduction of MACl and DMSO in the preparation process, the film with the phases of $n = 3$ and $n = 4$ was successfully obtained. With the addition of MACl and DMSO in the precursor solution, an intermediate phase is formed, which slows down the rate of crystallization in the solution. In addition, by correlating the phase distribution with the device characteristics, it was shown that the performance of the solar cell is sensitive to the phase purity and phase distribution [58].

Zhang Jia et.al confirmed that the phase distribution obtained in the film prepared by the vacuum-poling method is different from the traditional films that the phases with n value from small to large are arranged in a gradient distribution from the bottom to the top. The research result showed that the phases with different n values show a uniform distribution inside the film. The uniform phase distribution was confirmed by the PL results. When excited from the perovskite film side and from the glass side, and after the film is peeled off by the tape, the measured PL spectrum showed negligible differences, proving the uniform distribution of the mixed phase. In this case, the excellent PCE up to 18% can be ascribed to the shortest charge transfer path [59].

4. Conclusions

The high stability and relatively poor capability to convert light to electricity of low-dimensional perovskite films are the two aspects that need to be balanced. Based on the above analysis, we conclude that crystal growth direction and phase

distribution in the low-dimensional perovskite film determine the performance of the 2D PSCs. The crystal orientation in vertical direction and the proper phase distribution in favor of charge transfer are the targets for preparing high performance low-dimensional perovskite films. A few high-performance low-dimensional perovskite cells have emerged, showing high stability and efficiency comparable to 3D PSCs. Though the research on low-dimensional perovskite cells is far from enough and the crystal growth mechanism and carrier transport kinetics are still obscure, it is very promising to achieve efficient and stable photovoltaic devices using 2D perovskite materials as light absorbers.

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Conflict of interest

The authors declare no conflict of interest.

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