The Exploration and Outlook of Two-Dimensional Perovskites

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Abstract. Owing to the low cost and high efficiency in power conversion, perovskites have become a popular material for solar cells. Different from three-dimensional (3D) perovskites, two-dimensional (2D) perovskites tend to acquire high stability and high resistance to moisture. In addition, while lead is a commonly used B cation in 2D perovskites, it brings serious environmental damage. Therefore, people have been trying to replace lead (Pb) with tin (Sn), which is an almost harmless metal, in perovskites. This paper talks about the latest developments of 2D perovskites, as well as their prospect and future research directions.

1. INTRODUCTION

The majority of the world’s energy has been produced by burning oil, coal, and natural gas, which leads to scarcity of energy resources and deterioration of some environmental issues, such as global warming. Therefore, various kinds of environmental friendly energy resources have been discovered and created as substitutes, such as wind energy[1], tidal energy[2] and solar energy[3]. In terms of solar energy, solar energy is converted into electrical energy via solar cells according to the theory of photovoltaic effect. They are usually classified into three generations. The first generation is silicon-based solar cells, including monocrystalline silicon cells, polycrystalline silicon cells, amorphous silicon cells, and hybrid silicon cells. The second generation is thin film solar cells. A typical type of thin film solar cells is a copper indium gallium selenide (CIGS) solar cell. Due to their high costs and complex preparation processes, people have shifted their focus on researching and developing the third generation solar cells.[4] Among many new materials, perovskite, a calcium titanium oxide mineral composed of calcium titanate (CaTiO3), has been proven to be an excellent candidate for the third generation solar cells and now refers to any material that has the same crystal structure type as CaTiO3.[5] A three-dimensional (3D) perovskite has the general formula ABX3, where central ion B, is located at the center, connecting the X ions, the six halides, forming an octahedral structure, and organic cation A is distributed on the eight vertices of the circumscribed cube of regular octahedron BX6, forming a closely packed cubic structure. With such a unique structure, the perovskite solar cell has the following advantageous photoelectric properties:

1. Its energy band structure can be modulated by substituting similar ions. For instance, replacing part or all of iodide ions with bromide or chloride ions makes its energy band match the energy level of the Hole Transport Material (HTM) and the Electron Transport Material (ETM), improving its power conversion efficiency (PCE).[6]

2. Perovskite has a much higher optical absorption coefficient than silica, meaning that perovskite solar cells require thinner materials (around 300 nm) than silicon solar ones (3-5 µm).[7]

3. Its excitons have such low binding energy (37 emV to 50 emV) as is close to KBT (where KB is the Boltzmann’s constant and T is the temperature), making separation between electrons and holes possible at ambient temperature.[8]
4. Its charge carriers have high mobility. It is reported that the hole mobility and electron mobility in a perovskite-based solar cell have reached $164 \pm 25 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ and $24.8 \pm 4.1 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$, respectively, and their diffusion lengths have exceeded 175 µm.[9]

Since light absorbing materials started to be utilized for solar cells in 2009, their PCE has increased from 3.8% to 25.2% (Figure 1). As indicated in Figure 2, in a typical PSC, there are five layers, the metal electrode, where current is derived, the HTM, usually made from 2,2',7,7'-tetrakis-(N,N-diphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD), Poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PASS), and so on, the light absorbing layer, made from perovskite, the ETM, usually made from oxides such as TiO$_2$ and ZnO$_2$, and a transparent conducting oxide (TCO) glass substrate, for which fluorine-doped tin oxide (FTO) glass is commonly used. When the light absorbing layer is excited by absorbing sunlight that goes through the FTO glass, electrons are collected by the ETM (cathode) while the holes are received by the HTM (anode), producing loop current at the metal electrode.

The fact that A is usually MA, FA, or Cs makes the structure of a 3D perovskite easily become metastable, and introducing 2D organic cations can further expand the band gap in the perovskite, satisfying the demand of a laminated solar cell. In addition, as the insulating layer, 2D cations can make electrons transport in a 2D space, forming a structure with multiple quantum wells, which is conducive to stabilizing excitons. Moreover, the 2D perovskite displays excellent resistance to moisture, which further enhances its stability.

2D perovskites are usually obtained by cutting 3D ones into slices along specific crystallography planes[10], represented by general formula, $(\text{RNH}_3)_{2}(\text{A})_{n-1}\text{MX}_{3n+1}$, where RNH$_3$ is a primary aromatic alkylammonium or aliphatic cation, which serves as an interlayer between perovskite layers, while the A and M cations and X anions together form the structure of the perovskite.[11] Because they have different sizes, polarity, and geometry, using different cations for A will cause the solar cell to have different properties, such as different bandgaps, which will consequently result in different efficiency. In this paper, the effects of different A ions in 2D perovskite solar cells is discussed.
2. MAIN TEXT

2.1 Classical Reduced-Dimensionality Lead Based Perovskites

Karunasada’s group first created the solar cells with 2D perovskites as absorbers.[10] They created the 2D perovskite (PEA)\(_2\)(MA)\(_2\)[Pb\(_3\)I\(_{10}\)] (PEA = C\(_6\)H\(_5\)(CH\(_2\))\(_2\)NH\(_3^+\), MA = CH\(_3\)NH\(_3^+\)). As its formula shows, the structure of the 2D perovskite is formed as PEA, the organic layer, pushes apart the inorganic layers. The 2D perovskite-based solar cell consists of a 425 nm FTO glass layer, a 50 nm compact TiO\(_2\) layer, a 425 nm perovskite layer, a 125 nm spiro-OMeTAD layer, and a 75 nm gold electrode, and it has a larger bandgap than the 3D perovskite-based solar cell, which results in a higher open-circuit voltage (V\(_{OC}\)) and a higher PCE. According to the powder X-ray diffraction (PXRD) patterns, films of the 2D perovskite stay unaffected to moisture even after a long period of time, while the patterns of films of the 3D perovskite start to show reflections after a few days, indicating that the 2D perovskite has strong resistance to moisture (Figure 3).

Further to this work, Sargent’s group has created the series PEA\(_2\)(CH\(_3\)NH\(_3\))\(_{n-1}\)Pb\(_n\)I\(_{3n+1}\), where n = \(\infty\) corresponds to the cubic 3D perovskite, and n = 1 means the 2D perovskite structure, and n > 1 corresponds to quasi-2D perovskite structures, by mixing lead iodide (PbI\(_2\)), methylammonium iodide (MAI, CH\(_3\)NH\(_3\)I), and phenylethylammonium iodide (PEAI). They have reported excellent stability of reduced-dimensionality (quasi-2D) perovskite films over 3D ones combining experimental and density functional theory (DFT).[12] Figure 4a shows that layered perovskites with lower n values exhibit better stability than the ones with higher n values. In addition, the XRD spectra (Figure 4b) show that films of the 3D perovskite (n = \(\infty\)) display a strong reflection of PbI\(_2\) that intensifies over time, while for films of the quasi-2D perovskites (n = 40 and n = 60), the reflections are relatively weak and remain almost unchanged even after a long period of time. Moreover, the results of the measurements of solar cell performance and its stability over time show that in terms of PCE, the perovskite devices with lower n values have better stability. After being exposed to a low-humidity atmosphere for 60 days, the decline in PCE gets larger as the n value in the perovskite device increases, and PCE of the 3D perovskite drops to a very low value, indicating great instability. For a more in-depth study of the improved stability of the 2D perovskite, Kanatzidis’s group has fabricated films of the 2D perovskite with the formula (CH\(_3\)(CH\(_2\))\(_3\)NH\(_3\))\(_2\)(CH\(_3\)NH\(_3\))\(_n\)Pb\(_n\)I\(_{3n+1}\) (n = 1, 2, 3, and 4) and reported their properties.[13] They obtained a PCE of 4.02%, a V\(_{OC}\) of 929 mV, and a short-circuit current density (J\(_{SC}\)) of 9.42 mA/cm\(^2\) for the n = 3 compound. Moreover, they discovered that films of the 2D compounds self-assemble with preferential growth perpendicular to the substrate, which favors charge transport and provides essential access to ultrasmooth and high-surface coverage thin films. In addition, the 2D perovskite display higher stability and resistance to moisture than films of the 3D perovskite, which is supported by the fact that the (BA)\(_2\)(MA)\(_2\)Pb\(_3\)I\(_{10}\) film remains unchanged after being placed in an environment of 40% relative humidity for 2 months. These findings provide guidance for the development of stable PbX absorbing agents based on the structure of 2D/3D mixed perovskites.

![Fig.3. PXRD patterns of films: (PEA)\(_2\)(MA)\(_2\)[Pb\(_3\)I\(_{10}\)] (1), (MA)[PbI\(_2\)] formed from PbI\(_2\) (2a), and (MA)[PbCl\(_2\)] formed from PbCl\(_2\) (2b). All the films were exposed to 52% relative humidity. Films of 2a](image-url)
(15 minutes) and 2b (80 minutes) were annealed at 100℃ prior to humidity exposure. Asterisks denote the major reflections from PbI₂.

Fig. 4. Relative absorption intensity near the absorption onset for different n values (a), and film XRD spectra for different n values at 90% humidity level with various aging time (b).

2.2 Substitution of Halides in Reduced-Dimensionality Perovskites
Iodides are the most commonly used halides in 2D perovskites. They provide suitable optoelectronic properties for perovskite solar cells, but pure iodine compounds have limited tunability, so they cannot satisfy the demands of all the types of perovskite-based solar cells. Substitution of iodides with bromides increases the band gaps, and experimental results further demonstrate that bromide-based 2D and quasi-2D perovskites do have larger band gaps than their iodide counterparts, which can lead to high Voc.[14]

Etgar’s group has produced quasi 2D bromide perovskites with three different long organic barriers, benzyl ammonium (BA), phenylethyl ammonium (PEA), and propyl phenyl ammonium (PPA). The optimized cell has a PCE of 22.1%, and of the four barriers, BA has the highest efficiency. Low mobility of charge carriers in quasi-2D perovskites results in low short-circuit current density, especially when bromide is introduced. Contact angle measurements show that longer hydrophobic organic barriers provide higher resistance to moisture than shorter ones (PPA > PEA > BA > 3D).[15] Also, it is shown that the absorbing layer with a wide band gap of 2.25 eV can reach a high Voc of 1.46 V. Besides, results of stability measurements show that quasi 2D perovskite-based solar cells have better stability than the 3D perovskite-based solar cell. In addition, according to the results of density functional theory (DFT) with spin-orbit coupling, holes on the surface of the BA-based device are delocalized over the whole molecule, while for PEA- and PPA-based ones, holes are delocalized more at the phenyl ring. This factor makes the holes conductivity of the BA-based cell the highest compared with the other ones.

3. LOW-DIMENSIONAL NON-LEAD BASED PEROVSKITES
Pb²⁺ is a common B cation in classical perovskite-based solar cells. However, Toxicity of lead causes irreversible damage to the environment and biology. Therefore, researchers hope to partially or fully replace lead with other metals. Because Sn and Pb are in the same main group, they have the same electronic configuration, which makes tin-based perovskites inherit the unique photoelectric properties of lead-based perovskites. As a metal that is in the same group as lead, tin and lead have similar outer shell configuration, and thus Pb-based perovskites have advantageous photoelectric properties of Pb-based perovskites. The bandgap of the perovskite FASnI₃ is about 1.34 eV,[16] but that of MAPbI₃ has reached 1.58 eV, which is somewhat different from Shockley-Queisser limit. Therefore, Sn-based perovskites can reach higher efficiencies in theory. Besides, Sn-based perovskites have higher mobility of charge carrier than Pb-based ones and relatively low excitation-binding energy. Hence Sn-based
perovskites are the most suitable light-absorbing materials to substitute for Pb-based ones. Unfortunately, the PCE of tin-based perovskite solar cells has not yet exceeded 14% because of its easy oxidation of Sn$^{2+}$, which makes high defect concentration and background charge carrier concentration. On the contrary, preparing 2D Sn-based perovskites can effectively prevent the oxidation of Sn$^{2+}$ and they have become a promising candidate for 2D materials.

Kanatzidis’s group first created the Sn-based perovskite.[17] They have successfully fabricated mixed Pb-/Sn- based perovskites with various Pb to Sn ratios, (HA)Pb$_{1-x}$Sn$_x$I$_4$ and (BZA)$_2$Pb$_{1-x}$Sn$_x$I$_4$ (x = 1, 0.75, 0.50, 0.25, 0), and obtained their crystalline structures by using single-crystal XRD. As expected, introduction of 2D perovskites has greatly improved their stability. They have also found that the bandgap of the device increases as the concentration of Sn increases, which is consistent with theoretical calculations. However, due to rapid nucleation of Sn-based perovskites, they have not been able to successfully fabricate the Sn-based 2D perovskite device, but they have successfully created the powder. Nazeeruddin’s group has fabricated Sn-based 2D perovskites by using benzimidazolium (Bn) and benzodimidazolium (Bdi), and found that the perovskites with those symmetrical imidazolium-based cations have narrower bandgaps than the ones with traditional -NH$_3^+$ amino groups.[16] Also, they found that those 2D devices had higher resistance to oxidation than 3D analogues. Ning’s group fabricated Sn-based 2D perovskite thin films with PEA as an organic separating interlayer, and they found that when ammonium thiocyanate (NH$_4$SCN) is added, the films grow perpendicular to the substrate, which improves both the charge carrier transport and the stability of the perovskite.[18]

By adding ethylammonium iodide (EAI) to a 2D/3D Sn-based perovskite film, Portale’s group has successfully improved the crystallinity of the 3D formamidium tin iodide (FASnI$_3$) grains, increased their size, and perfected their orientation, which results in a decrease traps and background charge carrier density, and thus a decrease of charge recombination in EA$_x$ 2D/3D based devices[19]. Figure 5 is the SEM image and we can see that EA$_{0.08}$2D/3D Sn-based perovskite films have fewer pinholes than films without EA. In addition, EA$_{0.08}$2D/3D films overall have higher PCE than 2D/3D films (Figure 6), and they maintain a stable PCE of 7.87% for over 700 s (Figure 6d). The fact that the J-V curves under forward and reverse scan overlap well also indicate that the EA$_{0.08}$2D/3D-based device has negligible hysteresis (Figure 6b).

Huang’s group has created [(BA$_{0.4}$PEA$_{0.6}$)$_2$FA$_3$Sn$_4$I$_{13}$] 2D perovskites and found that the devices based on mixed BA/PEA cations can effectively suppress the intermediate phase that usually appears in pure BA- and PEA- based devices.[20] Those devices have a PCE of 8.82%. XRD patterns show that the intermediate phase is formed during annealing in BA and PEA perovskites, and that the perovskites made from the mixture of BA and PEA do not display any intermediate phase during annealing. As shown in scanning electron microscope (SEM) and atomic force microscope (AFM) images, the surface of BA and PEA films contains a significant number of pinholes and protrusions (Figure 7a, b), which causes direct contact between electrons and holes and thus inadequate contact between the perovskite layer and the transport layer, while the surface of mixed BA/PEA films contains very few pinholes and protrusions (Figure 7c). Moreover, XRD patterns (Figure 7g, h, i) show that of the three systems, the BA+PEA one has the least amount of Sn$^{2+}$ being oxidized. In addition, not only does the mixed BA+PEA device have the highest power, but it is able to maintain a stable output of higher than 8% PCE at $V_{bias} = 0.46$ V for 120 s and higher than 60% of initial efficiency for 24 h.
Fig. 5. SEM images. (a) Pure perovskite 3D film, (b) EA_{0.08}3D, (c) Mixed 2D/3D, and (d) EA_{0.08}2D/3D samples.

Fig. 6. (a) J-V curves of devices under one sun AM 1.5 G condition. 2D/3D devices in black and EA_{0.08}2D/3D-based devices in red. (b) J-V curves of the EA_{0.08}2D/3D-based champion solar cell measured at different rates under forward and reverse scans. (c) Steady-state PCE measured at the highest power point of the EA_{0.08}2D/3D-based device. (d) Distribution of PCE for the samples. 2D/3D in black and EA_{0.08}2D/3D-based devices in red.
Fig. 7. SEM images. 2DRP Sn perovskite films with BA (a), PEA (b), and BA+PEA (c). AFM images of 2DRP Sn perovskite films with BA (d), PEA (e), and BA+PEA (f). XPS spectra of 2DRP Sn perovskite films with BA (g), PEA (h), and BA+PEA (i).

Ning’s group has also fabricated the perovskite solar cells based on PEA15-SCN films with indeneC60 bisadduct (ICBA) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as electron transport layers (ETL).[21] SEM images of PEA15 and PEA15-SCN films show that both films are morphologically smooth, despite the fact that the pinholes on the surface of the PEA15-SCN film are a little smaller (Figure 8). Therefore, From the results of their experiments, they found that the ICBA-based device had a much higher efficiency (12.4%) than the PCBM-based device (7.7%). Also, the ICBA-based device has a low hysteresis as the curves under reverse and forward scan overlap well.

Fig. 8. SEM images of perovskite films. (scale bar = 1 µm)

4. CONCLUSION
Preparing 2D perovskites is a relatively effective method to get solar cells with high stability and efficiency. This paper mainly talks about the latest developments of Pb- and Sn- based perovskite solar cells. 2D perovskites, while they have lower PCE than 3D ones, do have wider bandgaps and higher...
stability and resistance to moisture. Replacing iodides with bromides can provide devices with wider bandgaps. Moreover, considering the damage Pb brings to the environment, researchers have successfully fabricated perovskites with Sn, and they also found that fabricating devices with the mixture of BA and PEA can effectively suppress the intermediate phase. Another important finding is that adding EA to the 2D/3D perovskite films can also enhance the device’s function.

As is known, using large organic cations leads to wide bandgaps and thus high $V_{OC}$. Introduction of large organic cations enhances the hydrophobicity of the perovskite, but makes it less conductive at the same time, which reduces its electron transport properties. Therefore, one of the future research directions is to find an optimal size for the organic cation that offers both good stability and electrical conductivity. Besides size, another thing to consider is to use conjugated organic cations since they have relatively high conductivity.

In addition, adjusting the crystal plane orientation of two-dimensional perovskite is also one of the feasible methods to improve conductivity. If films are made to grow vertical base, the conductivity and PCE of their perovskites will be greatly enhanced. Over and above, monocrystalline devices are generally more advantageous than polycrystalline ones as monocrystalline devices do not have as many grain boundaries, where electrons are quenched. Hence, another promising research direction is to fabricate monocrystalline perovskites, especially thin film ones. Furthermore, there are difficulties to overcome during industrial scale-up of the fabrication process. For example, when the fabrication process is magnified, there will likely be more direct contact between electron and hole transport layers at the coating step, which, as discussed earlier, causes recombination.

Finally, while replacing Pb with Sn can effectively avoid the environmental pollution caused by Pb metal, one great challenge, as mentioned earlier in this paper, is that Sn is easily oxidized, which worsens the performance of the device. A potential solution to this issue is to use a mixture of germanium (Ge) and Sn cations rather than pure Sn cation to fabricate the device. The logic behind it is that when Ge is oxidized, it forms a protective oxide film on the surface of Sn cation, which can theoretically protect Sn$^{2+}$ from being oxidized.

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