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Perovskite-Structured Photovoltaic Materials

Ming-Chung Wu and Yin-Hsuan Chang

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Abstract

In this chapter, we provide the historical background and overview of perovskite-structured photovoltaic materials. The organolead halide perovskite-structured solar cell is considered as one of the most promising photovoltaic technologies due to its rapid progress in power conversion efficiency. However, the existence of lead in perovskite-structured photovoltaic materials raises toxicological and environmental issues. Therefore, many scientists focused on discovering new materials that can replace the lead and improve photovoltaic performance. There are still some issues to be overcome before commercialization of perovskite-structured photovoltaic materials. The fast degradation phenomenon under humidity or constant irradiation is one such issue. The hysteresis phenomena could cause inaccurate estimation of power conversion efficiency. The choice of selective contact also plays an important role in obtaining high performance device. Therefore, the interaction between each layer should be considered. Overall, we reported on state-of-the-art perovskite-structured photovoltaic materials and discussed the essential factor for fabricating high-performance perovskite-structured solar cells.

Keywords: perovskite, photovoltaic, active layer, lead-reduced, solar cells

1. Introduction

For several decades, there has been substantial development in solar cells. Solar cells can be roughly divided into three generations, including (1) single-crystalline and polycrystalline silicon solar cells, (2) thin film solar cells (CIGS, CdTe, and amorphous silicon), and (3) new generations of solar cells (organic solar cells, dye-sensitized solar cells, and perovskite solar cells). Among these solar cells, the third generation of solar cells, which adopt organic materials and nanotechnology, shows relatively low cost; the fabrication process is relatively uncomplicated. Therefore, the booming of research interest in third generation solar cells has taken placed. Particularly,
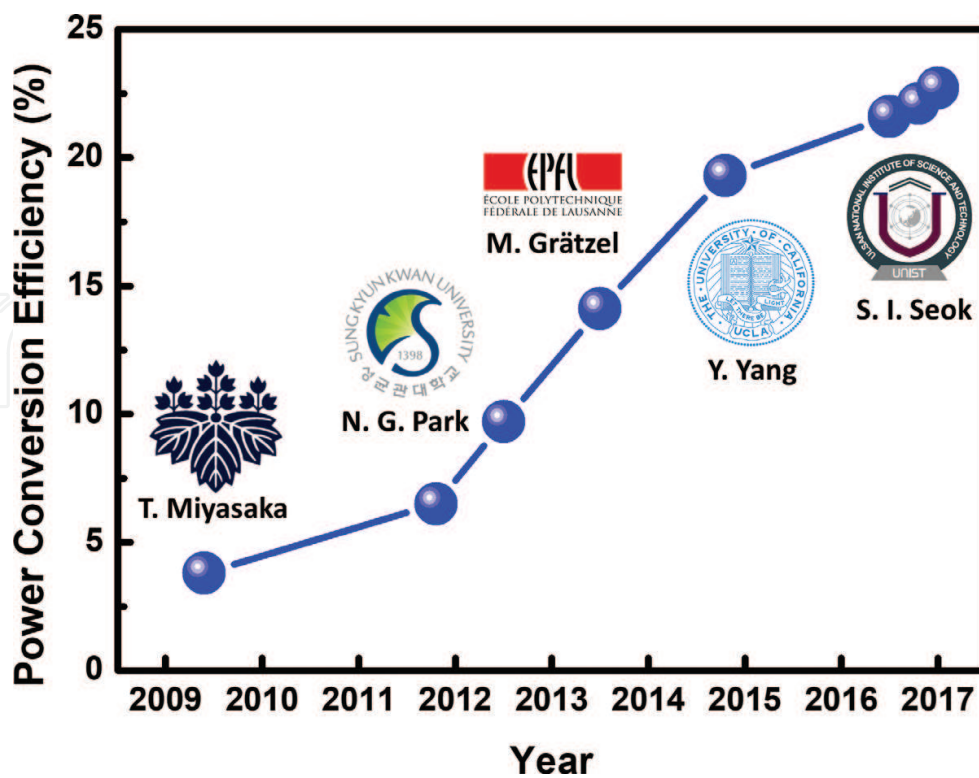
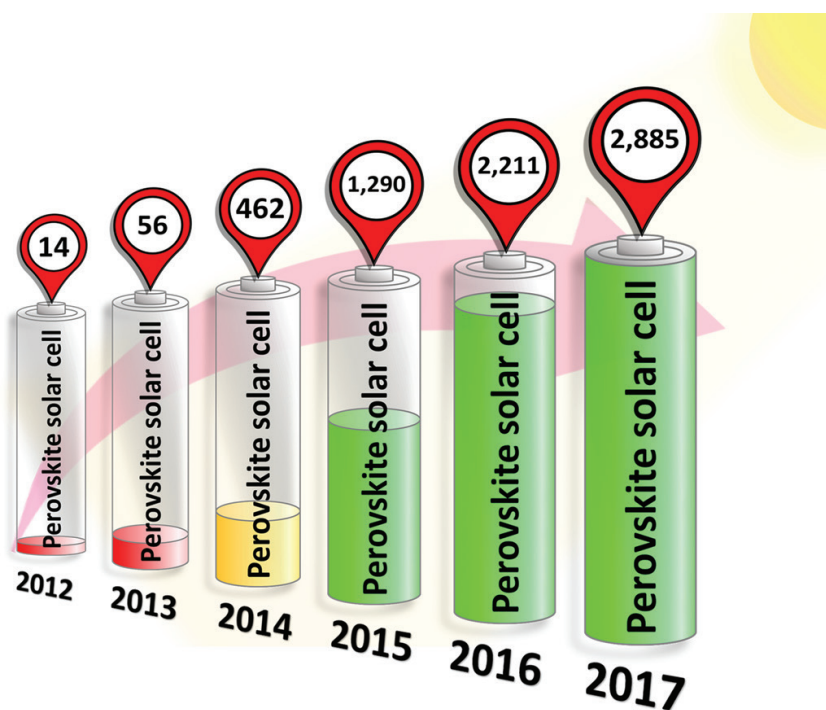**Figure 1.** Efficiency chart of perovskite-structured solar cells.

Figure 2. The number of articles related to the "perovskite solar cell" in the science citation index (SCI;Thomson Reuters) from 2012 to 2017.

the perovskite solar cells (PSCs), bearing the advantages including feasible solution process, low material cost, and rapid progress of efficiency, has drawn much attention. As one of the third generation photovoltaic material, the development of the perovskite solar cells (PSCs) efficiency chart, which was recorded by the National Renewable Energy Laboratory (NREL), is illustrated in **Figure 1** [1]. In 2009, Japanese scientist T. Miyasaka's group first reported methylammonium lead halide ($CH_3NH_3PbI_3$) as a light absorber in dye-sensitized solar cells with a power conversion efficiency (PCE) of 3.8% [2]. After that, many research groups dedicated to constructing various perovskite solar cells in the past eight years. By the apparent increase in the number of publications per year (**Figure 2**), PSCs have attracted the scientific community's attention for several years. Owing to the scientists' contribution, the PCE of PSCs has rapidly improved, and the latest record is up to 22.7% by the S. I. Seok group. However, the presence of lead ions in perovskite-structured materials is so toxic to both environment and human community that it will be an obstacle for possible commercialization. During the fabricating process of PSCs, the commonly used solvents, such as dimethylformamide (DMF, C_3H_7NO), acetonitrile (ACN, C_2H_3N), and chlorobenzene (CB, C_6H_5Cl), are also highly toxic, which may even result in cancer. Therefore, future development will focus on the reduction of lead content and the use of low-hazardous solvents.

2. What is perovskite?

In 1839, Gustav Rose, a German mineralogist, first discovered a kind of calcium titanium oxide mineral, composed of calcium titanate ($CaTiO_3$), in the Ural Mountains of Russia [3]. This mineral was then named after Russian mineralogist Lev Perovski. However, the material currently used in perovskite solar cells is not $CaTiO_3$ but a material that has a similar crystal structure to perovskite. The chemical formula of this material is commonly denoted as **ABX$_3$**, where **A** is a monovalent cation, **B** is a bivalent metal cation, and **X** is a halogen anion. Furthermore, the **A** cation with larger ionic radii occupying a cuboctahedral site is shared with 12 **X** anions. The 6 **X** anions surround the **B** cation with the smaller ionic radii occupying octahedral coordination and form a stable structure. The octahedron will connect with each other by corning sharing arrangement, and the center of each octahedron is the location of **A** cation [4]. The crystal structure of ABX$_3$ is shown in **Figure 3**.

The proposed perovskite structure and its stability can be determined by Goldschmidt's tolerance factor (TF) and octahedral factor (μ) [5]. For an ideal cubic perovskite, the unit cell axis, *a*, is geometrically related to the ionic radii and can be described with Eq. (1):

$$a = \sqrt{2}\left(R_A + R_X\right) = 2\left(R_B + R_X\right) \tag{1}$$

where R_A, R_B, and R_X are the ionic radii of **A** cation, **B** cation, and **X** anion, respectively. Goldschmidt's tolerance factor is the ratio of the two expressions of the unit cell axis. The equation of TF is as follows.

$$TF = \frac{\left(R_A + R_X\right)}{\sqrt{2}\left(R_B + R_X\right)} \tag{2}$$
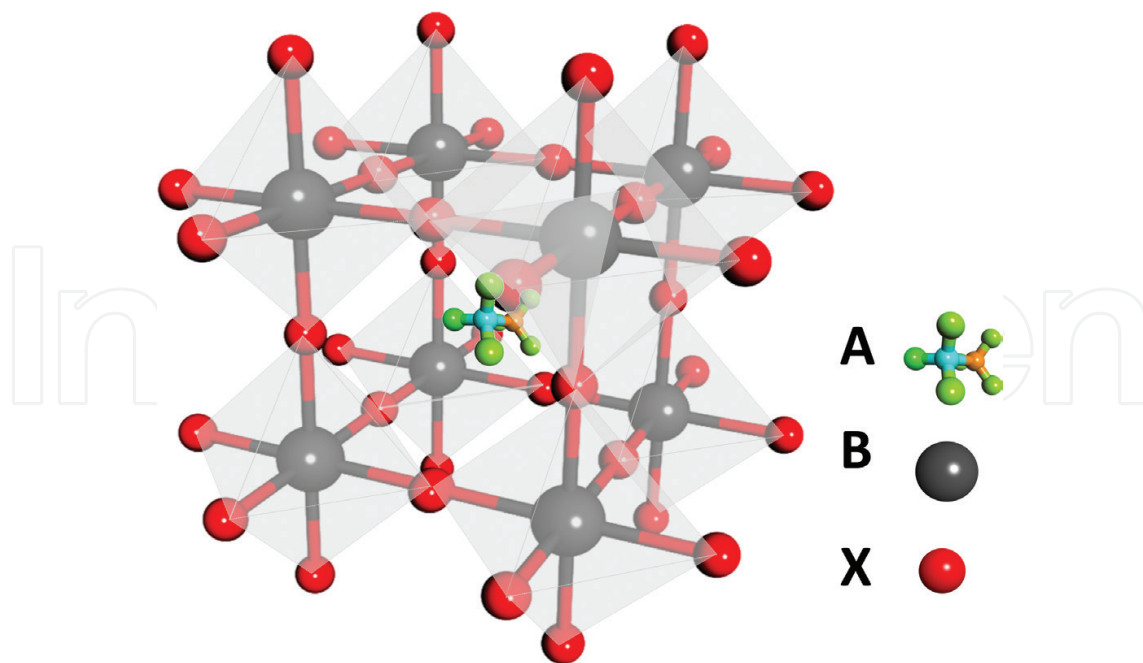
Figure 3. Crystal structure of an organic–inorganic metal halide perovskite.
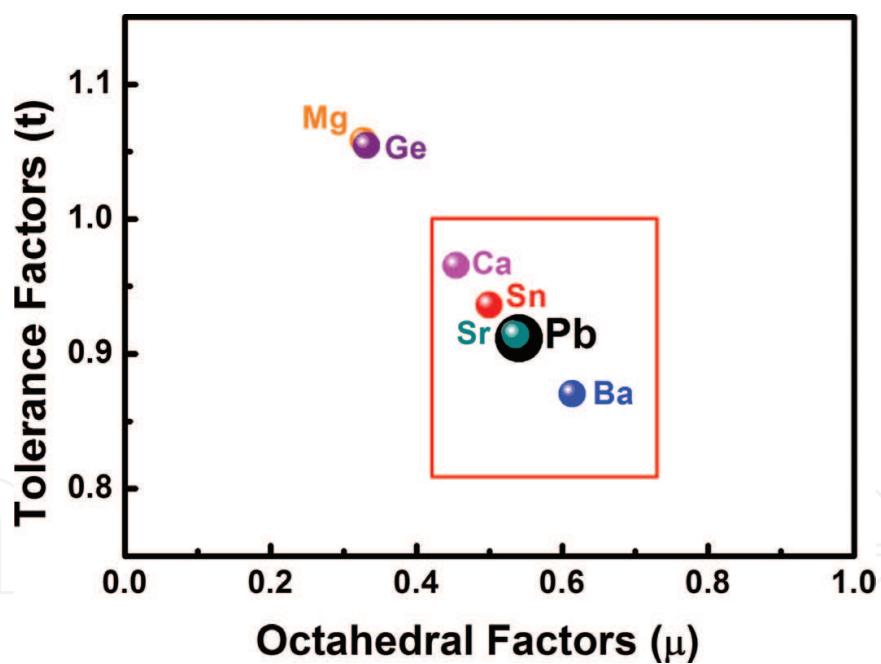

Figure 4. Comparison of calculated octahedral and tolerance factors for metal cations as a candidate for replacing toxic lead.

The perovskite structure is stable when the TF is in the range of 0.82 < TF < 1.00. The octahedral factor calculated by Pauling's rule can determine the coordination numbers of the metal cation and the halogen anion. The equation of the octahedral factor is described in Eq. (3).

$$\mu = \frac{R_B}{R_X} \tag{3}$$

For the stable perovskite structure, the coordination number is 6, and the corresponding μ will be in the range of $0.414 < \mu < 0.732$. Calculating the tolerance factor and the octahedral factor could be an effective way to construct a new structural map leading to new principles of the formability of perovskite compounds.

To further complement the suitable metal cation candidates to replace toxic lead in perovskite while not to destroy its structure, **Figure 4** summarizes the comparison of tolerance and octahedral factors based on Goldschmidt's rule for non-toxic alkaline-earth metal cations. The homovalent substitution of Pb to alkaline-earth metal cations shows that it can meet the requirement of not only the charge balance but also the tolerance factor of Goldschmidt's rule in perovskite. As a result, alkaline-earth metal cations are widely considered as suitable candidates for replacing toxic lead.

3. Development of perovskite-structured photovoltaic materials

Perovskite-structured photovoltaic materials can be divided into four groups according to the demand of the research objectives. The first group, organolead halide perovskite, is used to improve the power conversion efficiency up to its theoretical limit ~31%. The second group is lead-free perovskite. The purpose of the lead-free perovskite-structured material is to find an alternative to replace the toxic lead. The third group is lead-reduced perovskite-structured material. Owing to the unstable performance of lead-free perovskite, partial substitution of lead can not only reduce the lead content but also retain the power conversion efficiency. The last group, two-dimensional (2D) perovskite-structured material, with the presence of hydrophobic alkyl ammonium, exhibits good moisture resistance. In this section, we provide a report of the four types of perovskite-structured photovoltaic materials and their relevant applications.

3.1. Organolead halide perovskite-structured materials

Up to now, the organolead halide perovskite is still the highest performance material for PSCs. The high performance perovskite-structured solar cells are commonly based on $MAPbI_3$, where MA is CH_3NH_3. To obtain high efficiency, one of the effective approach is to improve the grain boundaries of $MAPbI_3$ thin film. The grain boundary is a critical factor of charge carrier kinetics and recombination, and thus influences the photovoltaic performance. It is believed that less non-radiative pathways in grain boundaries can lead to higher photovoltaic performance. However, formation of grain boundaries is unavoidable while the $MAPbI_3$ is forming on the substrate during the solution process. Therefore, the N. G. Park group reported a grain boundary healing process and achieved a PCE of 20.4% [6]. The grain boundary healing process involves adding a slight excess of MAI to the precursor coating solution of $MAPbI_3$. After spin coating the non-stoichiometric precursor solution with slightly excess MAI, the excess MAI will not influence the crystal structure but form MAI on the surface of the $MAPbI_3$ grain. This MAI film prevents carrier recombination at the grain boundaries and also maximizes the extraction ability of the electron and hole.

Another notable organolead halide perovskite solar cell is based on $FA_{1-x}MA_xPbI_{3-y}Br_y$. The architecture of PSCs, deposition process, and compositional manipulation have been seen as

important factors for high-efficiency PSCs. The S. I. Seok group devoted themselves to overcoming these obstacles. They proposed a sandwich-type architecture consisting of $CH_3NH_3PbI_3$ perovskite as a light harvester on mesoporous TiO_2 and achieved a PCE of 12% [7]. Then, they demonstrated a solution-based process to deposit a uniform and dense perovskite layer. The adoption of γ-butyrolactone and dimethyl sulfoxide (DMSO) mixed solvent followed by toluene drop-casting will form an intermediate phase, CH_3NH_3I–PbI_2–DMSO, which leads to the formation of a uniform layer and significantly enhances the PCE to 16.2% with no hysteresis [8]. They also developed a two-step process based on an intramolecular exchange between organic cations and DMSO molecules to fabricate $FAPbI_3$-based PSCs with 20.2% of PCE [9]. To date, the S. I. Seok group have combined the contributions mentioned earlier and modified the content of iodide in $FAPbI_3$ for efficient PSCs as shown in **Figure 5**. The addition of iodide ion by a two-step process can decrease the deep-level defects that are seen at the nonradiative recombination centers and improve the PCE to 22.1% [10].

3.2. Lead-free perovskite-structured materials

The development of lead-free perovskite-structured absorbers for solar cells is an important step toward commercializing this technology. For the perovskite-structured solar cells, lead is a critical component in the archetypal $FA_{1-x}MA_xPbI_{1-\gamma}Br_\gamma$ material. However, the presence of lead has raised questions as to whether toxicology issues will become problematic in the future for widespread deployment of PSCs [11]. Among various metal, tin is seen as the most viable metal to replace lead in perovskite-structure materials. The H. J. Snaith group reported the first completely lead-free $CH_3NH_3SnI_3$ perovskite solar cell prepared on a mesoporous TiO_2 scaffold with a PCE of 6.4% [12]. Although Sn shows excellent carrier mobility, the instability state of Sn^{2+} also makes it prone to become metallic in ambient air. Furthermore, the significant difference between Sn-based perovskite and Pb-based perovskite is the crystallizing condition; Sn-based perovskite crystallizes without heating and can suppress the formation of the uniform film. All of the aforementioned factors have become obstacles for fabricating high-efficiency lead-free PSCs.

Sn-based lead-free perovskite-structured materials still have some problems that make it lag behind lead-contained PSCs. For instance, the Sn vacancies with low formation energy lead to high-doped holes, which will cause severe carrier recombination in PSCs. Zhao et al. reported
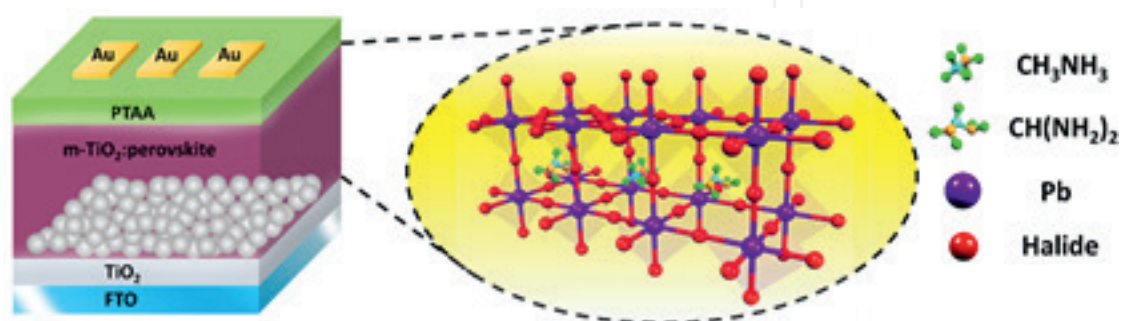

Figure 5. Schematic diagram of a perovskite device and crystal structure based on $FA_{1-x}MA_xPbX_3$ as an active layer.

$FA_xMA_{1-x}SnI_3$ served as the light harvesting layer with SnF_2 employed as an additive in DMSO [13]. Mixing cations such as MA and FA is a conventional method in the composition engineering to improve the PSCs performance. The addition of additives to perovskite precursor solution can reduce the doped-hole density and enhance the stability of Sn-base PSCs. Due to the fast crystallization of $MASnI_3$, which makes it difficult to control the film morphology, DMSO is further introduced to the perovskite precursor solution. Adding DMSO is seen as a critical step because it will react with SnI_2 and form an intermediate phase, $SnI_2 \cdot 3DMSO$, that suppresses the fast crystallization and thus obtains a homogeneous film. Up to date, the lead-free perovskite-structured material, $FA_{0.75}MA_{0.25}SnI_3$, with SnF_2 as an additive can achieve a PCE of 8.12% as shown in **Figure 6**.

3.3. Lead-reduced perovskite-structured materials

Although lead-free perovskite-structured photovoltaic materials solve the toxicity issues, efficiency is sacrificed for the replacement of lead. Partial substitution of lead in perovskite-structured materials is the alternative solution which can not only reduce the toxicity but also maintain the power conversion efficiency. Many literature indicates that owing to the facile oxidation of Sn^{2+} to Sn^{4+}, lead-free $CH_3NH_3SnI_3$ perovskite-structured material usually exhibits reduced efficiency and lack of reproducibility [14]. Therefore, many scientists attempted to prepare perovskite film with partial replacement of lead. The M. G. Kanatzidis group fabricated a perovskite material with 50% of Sn doping concentration ($CH_3NH_3Sn_{0.5}Pb_{0.5}I_3$), and found that doping Sn into the perovskite active layer can efficiently regulate the band gap of the perovskite material from 1.55 to 1.17 eV [15]. With the tunable band gap, it is also observed that light absorption extends to the near-infrared region. In addition, $CH_3NH_3Sn_{0.5}Pb_{0.5}I_3$ shows superior film coverage and better film morphology, which ensures connectivity between grains and overcomes short-circuiting and charge leaking issues.
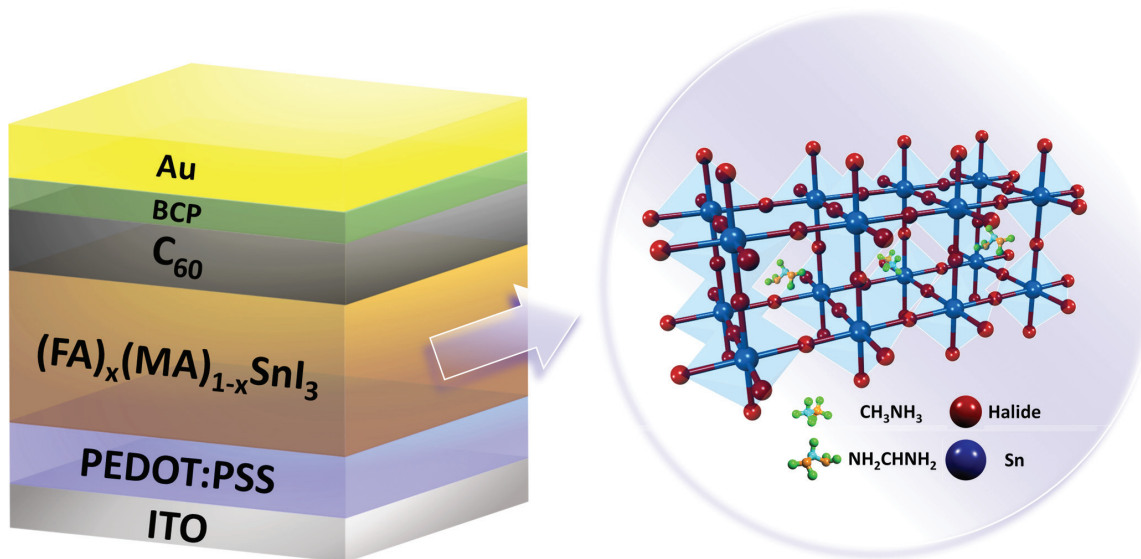

Figure 6. Schematic diagram of a perovskite device and crystal structure based on $FA_xMA_{1-x}SnX_3$ as an active layer.

The J. Navas group reported a theoretical study on partially replaced Pb^{2+} in $CH_3NH_3PbI_3$ with Sn^{2+}, Sr^{2+}, Cd^{2+}, and Ca^{2+} [16]. By doping the dopant into the perovskite-structured material, the different crystal structure and band gap will further affect the optical properties. In addition, the change in band gap mainly depends on the crystal structure of the perovskite-structured material. Undoped perovskite-structured material in company with the dopant of Sn^{2+}, Sr^{2+}, and Cd^{2+} is present in the tetragonal crystalline structure. In the case of Ca^{2+} doped perovskite, the predominant crystalline phase is a cubic phase. The values of the band gap with different dopants is in the trend of Sr^{2+} (1.50 eV) < Cd^{2+} (1.54 eV) < $CH_3NH_3PbI_3$ (1.57 eV) ≈ Sn^{2+} (1.57 eV) for the tetragonal structure and Ca^{2+} (1.52 eV) < $CH_3NH_3PbI_3$ (1.57 eV) for the cubic structure. With the greater ionic nature of the dopant–iodine interaction, a lower band gap can be obtained. By understanding the characteristic of the dopant, the growth of highly lead-substituted PSCs and high-efficiency PSCs will become a breakthrough for the commercialization in the near future.

The M.-C. Wu group adopted four kinds of alkaline–earth metal cations, including Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, to replace lead cations partially [17]. Among the four alkaline-earth metals, Ba^{2+} is most suitable for Pb^{2+} replacement in perovskite films; it also exhibits high power conversion efficiency. The Ba^{2+}-doped perovskite films that can be processed in the environment containing moisture (1.0% relative humidity) are stable. At the optimal 3.0 mol% Ba^{2+} replacement, the PCE of the fabricated solar cell is increased from 11.8 to 14.0%, and the PCE of champion devices is as high as 14.9% with increased storage stability (**Figure 7**).

3.4. Two-dimensional perovskite-structured materials

The three-dimensional (3D) perovskite-structured material shows outstanding power conversion efficiency owing to its tremendous advantage, including long carrier diffusion lengths for electrons and holes, small exciton binding energy, appropriate band gap, and high extinction coefficient. However, moisture instability results from the hygroscopic nature of MA and suppresses the commercialization of 3D PSCs. The two-dimensional (2D) perovskite-structured
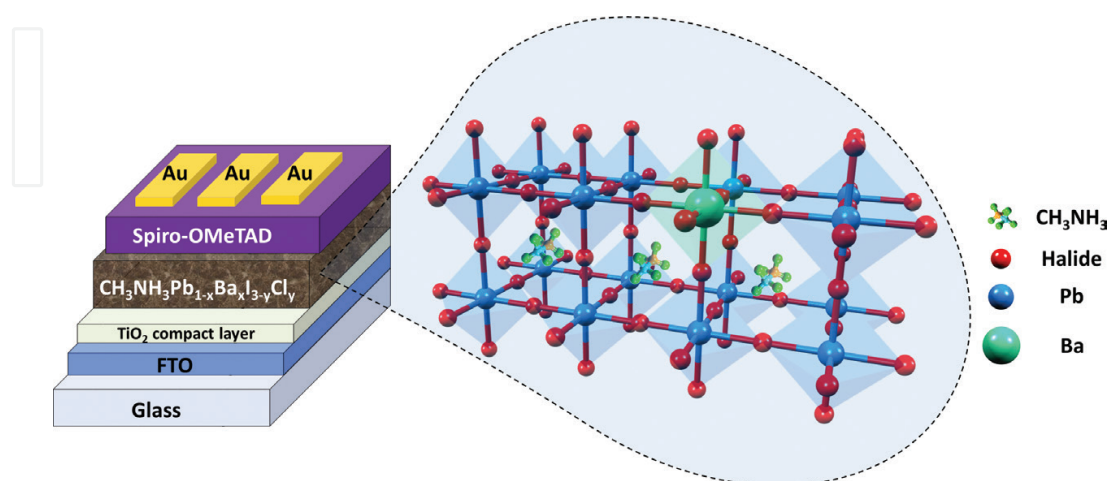

Figure 7. Schematic diagram of a perovskite device and crystal structure based on $CH_3NH_3Pb_{1-x}Ba_xX_3$ an active layer.

material based on $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$, where BA is a long-chain aromatic alkylammonium cation, opens a new trend for optoelectronic devices. Its long organic side group with hydrophobic property seems to be beneficial for improving moisture stability. The inorganic layer of the 2D structure stack with each other by intercalated bulky alkylammonium cations and maintain structural integrity by weak van der Waals forces [18]. The band gap and the thickness of the 2D layer can be tuned by increasing the n values. For $n = 1$ structure, the 2D perovskite is a simple structure with the thinnest layer. At $n = \infty$, the structure becomes the typical 3D perovskite structure. An attempt to introduce 2D perovskite into the solid-state solar cell as a light-absorbing material showed poor efficiency (~4.0%) [19]. The poor device efficiency can be explained by the difficult charge transport in the out-of-plane direction. The long-chain organic cation between the conducting inorganic layers is similar to the insulating spacing layers. The H. Tsai group overcame this obstacle by fabricating near-single-crystalline thin films with the hot-casting process; they reported a PCE of 12.52% with no hysteresis [20]. It also shows outstanding light-soaking stability and moisture resistance that retains over 60% of its initial PCE after 2250 h irradiation without encapsulation. Furthermore, when the 2D PSCs is encapsulated, it shows no degradation after irradiation or under humidity. The significant breakthrough of power conversion efficiency for 2D PSCs is attributed to the enhanced charge mobility, which is facilitated by the near-perfect vertical orientation of the $\{(MA)_{n-1}Pb_nI3_{n+1}\}^{2-}$ layer. The 2D perovskite layer fabricated using the hot-casting technique can form a high-quality film, which is ideal for a photovoltaic device. Compared with conventional spin-coating film, the hot-casting technique provides a uniform and substantially large grain size film that is much more reflective. The film also presents a low density of pinhole, which is profitable for improving efficiency. Based on these results, the S. Liu group further doped Cs^+ into a 2D perovskite to replace MA^{2+} (**Figure 8**) [21]. The Cs doping enhances the optoelectronic properties attributed to the improvement of charge transfer kinetics, charge carrier mobility, and decreased of trap density. With this modification, the PCE can be successfully improved from 12.52% to 13.7%.
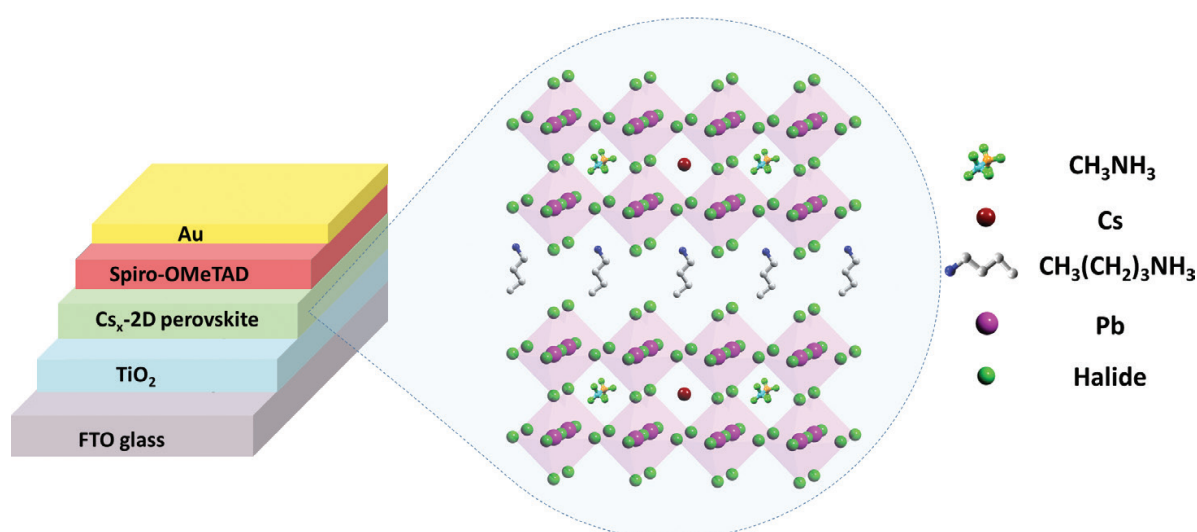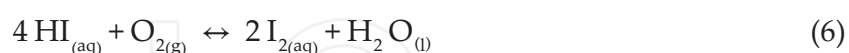

Figure 8. Schematic diagram of a perovskite device and crystal structure based on Cs^+ doped 2D perovskite as an active layer.

4. Current issues and future challenges

To date, perovskite-structured photovoltaic devices have presented considerable progress to achieve high efficiency. However, many issues have to be overcome before the commercialization. The fast degradation phenomenon under humidity or constant irradiation bears the brunt. The other crucial factor is the presence of $J - V$ hysteresis. With the existence of the hysteresis phenomena, the accuracy of power conversion efficiency will fall under suspicion. The fundamental mechanisms of the efficient carrier transport in perovskite should also be considered. The complication of the synthesis methods and the construction of PSCs make it much more difficult to overcome these obstacles. Recently, many researchers have devoted lots of effort to address these issues and adapt the properties of corresponding materials.

4.1. Instability under humidity

The stability of PSCs is dominated by lots of factors, such as high humidity, intense illumination, and increased temperature [22]. Exposure to such a severe condition leads to the rapid degradation of efficiency and restricts PSCs from outdoor application. Many studies have revealed that when the MAPbI$_3$ is exposed to moisture, it will immediately degrade into methylammonium (MA), hydrogen iodide (HI), and lead iodide (PbI$_2$) owing to its solubility in water [23]. Hence, how to effectively prevent the invasion of moisture in the environment should be considered thoroughly. Prior to developing the encapsulations material, it is important to understand what happens during the degradation. CH$_3$NH$_3$PbI$_3$ taken as an example of the degradation mechanism of perovskite is shown as follows:

$$CH_3NH_3PbI_{3(s)} \leftrightarrow PbI_{2(s)} + CH_3NH_3I_{(aq)} \tag{4}$$

$$CH_3NH_3I_{(aq)} \leftrightarrow CH_3NH_{2(aq)} + HI_{(aq)} \tag{5}$$

$$4\,HI_{(aq)} + O_{2(g)} \leftrightarrow 2\,I_{2(aq)} + H_2O_{(l)} \tag{6}$$

$$HI_{(aq)} \overset{h\nu}{\leftrightarrow} H_{2(g)} + I_{2(s)} \tag{7}$$

First, the CH$_3$NH$_3$PbI$_3$ will degrade into PbI$_2$ and CH$_3$NH$_3$I owing to the sensitivity to water. The formation of CH$_3$NH$_3$I results in the co-existence of CH$_3$NH$_3$I, CH$_3$NH$_2$, and HI toward the progress of equilibrium reaction. After that, the HI tends to decompose in two ways, redox reaction and photochemical reaction. Based on the aforementioned equilibrium reactions, it is easy to understand that not only the moisture in the environment but also the oxygen and UV radiation affect the stability severely [24]. The design of the encapsulant should consider the permeation mechanisms of the organic and inorganic materials. For an organic polymer encapsulant, gas or vapor permeates into the PSCs by the typical solution—the diffusion model. Although an organic polymer encapsulant possesses lots of advantages including flexibility, conformability, and processability, the permeability of gas is too high, which is not

conducive to PSCs. In the case of inorganic material, it provides a barrier toward permeant penetration. Defect-free inorganic thin films as encapsulant material show the characteristic of brittleness, which will not be break resistant to moisture conditions [25]. Therefore, constructing a material consisting of both organic and inorganic materials can combine both advantages and meet the flexibility and gas barrier conditions.

4.2. J-V hysteresis phenomena

In the characterization of photovoltaic performance, a hysteretic response appears with different scanning conditions; thus the accuracy of the cell efficiency is doubted. The photocurrent density-voltage (J-V) hysteresis behavior will be affected by scanning direction, scanning rate, and applied voltage [26]. The hysteresis J-V behavior remains a challenge for the advancement of PSCs. Here are some situations that result in erroneous device efficiencies. For operating in different scanning directions, the forward scan that holds at short-circuit conditions to open circuit voltage conditions tends to have a lower efficiency than holding at the reverse scan. Hence, the forward scan is inclined to underestimate the power conversion efficiency of PSCs. In contrast, the reverse scan tends to overestimate the power conversion efficiency. If the scan rate of measuring the device is faster than its response time, hysteretic behavior will also be deteriorated. While holding at the reverse scan, the efficiency increases with the increasing scan rate. On the other hand, the efficiency measured at the forward scan decreases with the increasing scan rate. Moreover, the J-V hysteresis phenomenon becomes more intense under the faster scan rate in both scanning directions. Another important factor that can also affect the J-V hysteresis is the starting biases. The tendency is similar to the previous condition. The more positive the starting voltage holding at the reverse scan, the higher the efficiency can be measured; whereas, while holding at the forward scan, the more negative the starting voltage, the lower the efficiency of PSCs can be recorded. The existence of J - V hysteresis plays a crucial role in the accuracy of power conversion efficiency; hence, many scientists have dedicated research to searching for the solution. One of the possible methods of J - V hysteresis elimination is to measure the device with a slow scan rate. That hysteresis influenced by applied voltage can be solved by light-soaking at different biases was reported by the M. D. McGehee group [27]. Prior to the characterization, the precondition for perovskite-absorber devices with different biases presents a significant effect on the photovoltaic performance. The short-circuit current density, fill factor, and power conversion efficiency under reverse scan can be suppressed by light-soaking with a more negative bias. In contrast, the photovoltaic performance under the forward scan will be enhanced by light-soaking with a more positive bias. Hence, the declined performance under the reverse scan and the increased performance under the forward scan prevent PSCs from the J-V hysteresis phenomenon.

4.3. Carrier transport behavior

Although a perovskite-structured active layer presents high efficiency of light-harvesting behavior, finding the suitable electron transport layer (ETL) and hole transport layer (HTL) is a critical issue for improving the performance of the photovoltaic device. After solar irradiation, an electron-hole pair will be generated at the perovskite-structured active layer. How to
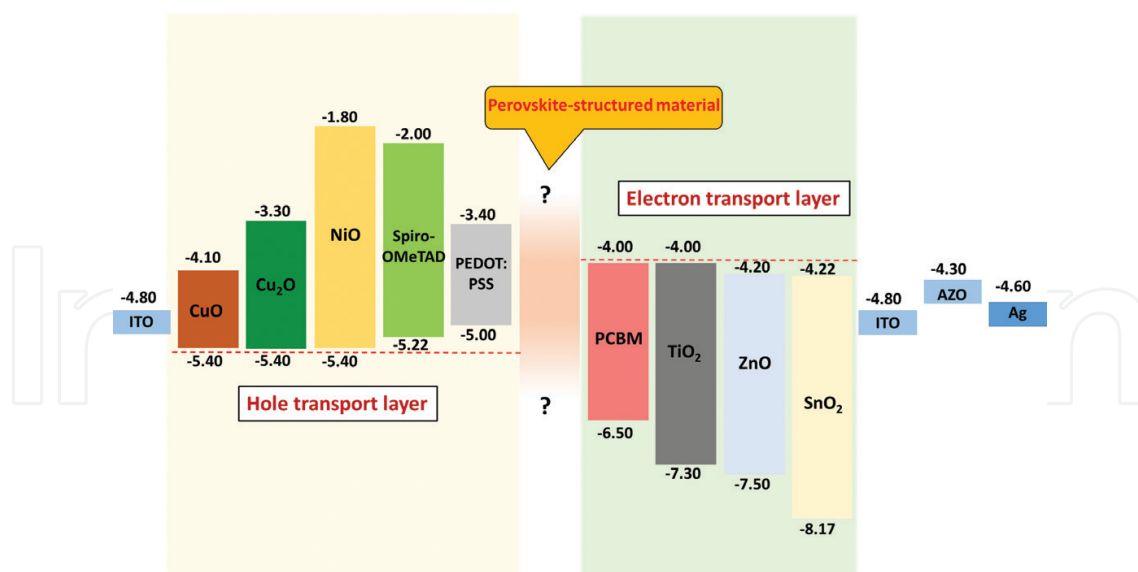
Figure 9. Energy band diagram of different electron and hole transport layers with respect to perovskite-structured photovoltaic devices.

transport the electron and hole efficiently to ETL and HTL, respectively, has been discussed thoroughly. Therefore, selecting the appropriate materials for the carrier transport layer is considered as a primary issue to prevent charge recombination and diminish energy loss at the interface between the perovskite active layer and ETL or HTL. In recent studies, the electron transport materials and the hole transport materials have been explored to construct an optimal band alignment for achieving high efficiency [28–30].

A good electron-transporting material should exhibit (1) good electron mobility to facilitate electron collection, (2) wide band gap for not hindering the absorption behavior of the perovskite active layer, and (3) both the valence band/conduction band should be lower than that of perovskite-structured material to promote electron migrate to ETL and block the hole to transport. Metal oxides, such as TiO_2, ZnO, and SnO_2, are widely applied as ETLs, especially TiO_2, owing to their electrical and optical properties [31]. A good hole-transporting material should exhibit (1) efficient hole mobility to promote hole collection, (2) the valence band/conduction band both should be higher than the perovskite-structured active layer to promote hole migration to HTL and further transport to the electrode, and (3) there should be photochemical stability. The most widely-explored materials for HTL has been divided into 3 groups: (1) small molecules (e.g., spiro-OMeTAD), (2) inorganic materials (e.g., CuI, CuSCN, NiO, etc.), and (3) conducting polymers (e.g., P3HT, PEDOT, PTAA, etc.) [32, 33]. **Figure 9** examines the proposed band alignment for the commonly used materials for ETL and HTL which is helpful for understanding interface properties and constructing high-efficiency perovskite-structured photovoltaic devices.

5. Conclusion

Perovskite-structured photovoltaic materials attract a lot of interest due to its facile fabrication process and rapid progress in device performance. A series of perovskite-structured

photovoltaic materials with high power conversion efficiency, including (1) organolead halide perovskite-structured materials, (2) lead-free perovskite-structured materials, (3) lead-reduced perovskite-structured materials, and (4) two-dimensional perovskite-structured materials, are reported herein in detail. Many problems that occur with these materials must be overcome before commercialization. It has been proved that the element in perovskite-structured material plays an important role in enhancing stability under humidity or constant irradiation and achieving high power conversion efficiency. Numerous alternative materials for ETL and HTL have been discovered to facilitate carrier transport at perovskite-structured material interface/ ETL and perovskite-structured material/HTL interface. If there is a breakthrough development in fabrication methods, enhancement of stability, and optimized device structure can be realized, the commercialization of environmental-friendly high-efficiency PSC will be in the near future.

Acknowledgements

Conflict of interest

There are no conflicts of interest to declare.

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References

[1] Research Cell Record Efficiency Chart [Internet]. 2017. Available from: https://www.nrel. gov/pv/assets/images/efficiency-chart.png [Accessed: January 27, 2018]

[2] Kojima A, Teshima K, Shirai Y, Miyasaka T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. Journal of the American Chemical Society. 2009;**131**: 6050-6051. DOI: 10.1021/ja809598r

[3]   Giorgi G, Yamashita K. Organic-inorganic halide perovskites: An ambipolar class of materials with enhanced photovoltaic performances. Journal of Materials Chemistry A. 2015;**3**:8981-8991. DOI: 10.1039/C4TA05046K

[4]   Johnsson M, Lemmens P. Crystallography and chemistry of perovskites. In: Kronmueller H, Parkin S, editors. Handbook of Magnetism and Advanced Magnetic Materials. Hoboken, New Jersey: John Wiley & Sons, Ltd; 2007. DOI:10.1002/9780470022184.hmm411

[5]   Mehmood U, Al-Ahmed A, Afzaal M, Al-Sulaiman FA, Daud M. Recent progress and remaining challenges in organometallic halides based perovskite solar cells. Renewable and Sustainable Energy Reviews. 2017;**78**:1-14. DOI: 10.1016/j.rser.2017.04.105

[6]   Son D-Y, Lee J-W, Choi YJ, Jang I-H, Lee S, Yoo PJ, Shin H, Ahn N, Choi M, Kim D, Park N-G. Self-formed grain boundary healing layer for highly efficient $CH_3NH_3PbI_3$ perovskite solar cells. Nature Energy. 2016;**1**:16081. DOI: 10.1038/nenergy.2016.81

[7]   Heo JH, Im SH, Noh JH, Mandal TN, Lim C-S, Chang JA, Lee YH, Kim H-J, Sarkar A, Nazeeruddin MK, Grätzel M, Seok SI. Efficient inorganic–organic hybrid heterojunction solar cells containing perovskite compound and polymeric hole conductors. Nature Photonics. 2013;**7**:486-491. DOI: 10.1038/nphoton.2013.80

[8]   Jeon NJ, Noh JH, Kim YC, Yang WS, Ryu S, Seok SI. Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells. Nature Materials. 2014;**13**:897-903. DOI: 10.1038/nmat4014

[9]   Yang WS, Noh JH, Jeon NJ, Kim YC, Ryu S, Seo J, Seok SI. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. Science. 2015;**348**:1234-1237. DOI: 10.1126/science.aaa9272

[10] Yang WS, Park B-W, Jung EH, Jeon NJ, Kim YC, Lee DU, Shin SS, Seo J, Kim EK, Noh JH, Seok SI. Iodide management in formamidinium-lead-halide–based perovskite layers for efficient solar cells. Science. 2017;**356**:1376-1379. DOI: 10.1126/science.aan2301

[11] Liang L, Gao P. Lead-free hybrid perovskite absorbers for viable application: Can we eat the cake and have it too? Advanced Science. 2017;**5**:1700331. DOI: 10.1002/advs.201700331

[12] Noel NK, Stranks SD, Abate A, Wehrenfennig C, Guarnera S, Haghighirad A-A, Sadhanala A, Eperon GE, Pathak SK, Johnston MB, Petrozza A, Herz LM, Snaith HJ. Lead-free organic-inorganic tin halide perovskites for photovoltaic applications. Energy & Environmental Science. 2014;**7**:3061-3068. DOI: 10.1039/C4EE01076K

[13] Zhao Z, Gu F, Li Y, Sun W, Ye S, Rao H, Liu Z, Bian Z, Huang C. Mixed-organic-cation tin iodide for lead-free perovskite solar cells with an efficiency of 8.12%. Advanced Science. 2017;**4**:1700204. DOI: 10.1002/advs.201700204

[14] Liu C, Li W, Fan J, Mai Y. A brief review on the lead element substitution in perovskite solar cells. Journal of Energy Chemistry. 2017;**000**:1-13. DOI: 10.1016/j.jechem.2017.10.028

[15] Hao F, Stoumpos CC, Chang RPH, Kanatzidis MG. Anomalous band gap behavior in mixed sn and pb perovskites enables broadening of absorption spectrum in solar cells. Journal of the American Chemical Society. 2014;**136**:8094-8099. DOI: 10.1021/ja5033259

[16] Navas J, Sanchez-Coronilla A, Gallardo JJ, Hernandez NC, Pinero JC, Alcantara R, Fernandez-Lorenzo C, De los Santos DM, Aguilar T, Martin-Calleja J. New insights into organic-inorganic hybrid perovskite $CH_3NH_3PbI_3$ nanoparticles. An experimental and theoretical study of doping in Pb^{2+} sites with Sn^{2+}, Sr^{2+}, Cd^{2+} and Ca^{2+}. Nanoscale. 2015;**7**:6216-6229. DOI: 10.1039/C5NR00041F

[17] Chan S-H, Wu M-C, Lee K-M, Chen W-C, Lin T-H, Su W-F. Enhancing perovskite solar cell performance and stability by doping barium in methylammonium lead halide. Journal of Materials Chemistry A. 2017;**5**:18044-18052. DOI: 10.1039/C7TA05720B

[18] Chen S, Shi G. Two-dimensional materials for halide perovskite-based optoelectronic devices. Advanced Materials. 2017;**29**:1605448. DOI: 10.1002/adma.201605448

[19] Cao DH, Stoumpos CC, Farha OK, Hupp JT, Kanatzidis MG. 2D homologous perovskites as light-absorbing materials for solar cell applications. Journal of the American Chemical Society. 2015;**137**:7843-7850. DOI: 10.1021/jacs.5b03796

[20] Tsai H, Nie W, Blancon J-C, Stoumpos CC, Asadpour R, Harutyunyan B, Neukirch AJ, Verduzco R, Crochet JJ, Tretiak S, Pedesseau L, Even J, Alam MA, Gupta G, Lou J, Ajayan PM, Bedzyk MJ, Kanatzidis MG, Mohite AD. High-efficiency two-dimensional Ruddlesden–popper perovskite solar cells. Nature. 2016;**536**:312. DOI: 10.1038/nature18306

[21] Zhang X, Ren X, Liu B, Munir R, Zhu X, Yang D, Li J, Liu Y, Smilgies D-M, Li R, Yang Z, Niu T, Wang X, Amassian A, Zhao K, Liu S. Stable high efficiency two-dimensional perovskite solar cells via cesium doping. Energy & Environmental Science. 2017;**10**:2095-2102. DOI: 10.1039/C7EE01145H

[22] Cheacharoen R, Rolston N, Harwood D, Bush KA, Dauskardt RH, McGehee MD. Design and understanding of encapsulated perovskite solar cells to withstand temperature cycling. Energy & Environmental Science. 2018;**11**:144-150. DOI: 10.1039/C7EE02564E

[23] Matteocci F, Cinà L, Lamanna E, Cacovich S, Divitini G, Midgley PA, Ducati C, Di Carlo A. Encapsulation for long-term stability enhancement of perovskite solar cells. Nano Energy. 2016;**30**:162-172. DOI: 10.1016/j.nanoen.2016.09.041

[24] Niu G, Guo X, Wang L. Review of recent progress in chemical stability of perovskite solar cells. Journal of Materials Chemistry A. 2015;**3**:8970-8980. DOI: 10.1039/C4TA04994B

[25] Seethamraju S, Ramamurthy PC, Madras G. Encapsulation for improving the efficiencies of solar cells. In: Viswanathan B, Subramanian V, Lee JS, editors. Materials and Processes for Solar Fuel Production. New York: Springer-Verlag; 2014. pp. 23-40. DOI: 10.1007/978-1-4939-1628-3_2

[26] Chen B, Yang M, Priya S, Zhu K. Origin of J–V hysteresis in perovskite solar cells. The journal of physical chemistry letters. 2016;**7**:905-917. DOI: 10.1021/acs.jpclett.6b00215

[27] Unger EL, Hoke ET, Bailie CD, Nguyen WH, Bowring AR, Heumuller T, Christoforo MG, McGehee MD. Hysteresis and transient behavior in current-voltage measurements of hybrid-perovskite absorber solar cells. Energy & Environmental Science. 2014;**7**:3690-3698. DOI: 10.1039/C4EE02465F

[28] Correa Baena JP, Steier L, Tress W, Saliba M, Neutzner S, Matsui T, Giordano F, Jacobsson TJ, Srimath Kandada AR, Zakeeruddin SM, Petrozza A, Abate A, Nazeeruddin MK, Gratzel M, Hagfeldt A. Highly efficient planar perovskite solar cells through band alignment engineering. Energy & Environmental Science. 2015;**8**:2928-2934. DOI: 10.1039/C5EE02608C

[29] Wang J-F, Zhu L, Zhao B-G, Zhao Y-L, Song J, Gu X-Q, Qiang Y-H. Surface engineering of perovskite films for efficient solar cells. Scientific Reports. 2017;**7**:14478. DOI: 10.1038/s41598-017-14920-w

[30] Zhou H, Chen Q, Li G, Luo S, Song T-B, Duan H-S, Hong Z, You J, Liu Y, Yang Y. Interface engineering of highly efficient perovskite solar cells. Science. 2014;**345**:542-546. DOI: 10.1126/science.1254050

[31] Mohamad Noh MF, Teh CH, Daik R, Lim EL, Yap CC, Ibrahim MA, Ahmad Ludin N, ARb MY, Jang J, Mat Teridi MA. The architecture of the electron transport layer for a perovskite solar cell. Journal of Materials Chemistry C. 2018;**6**:682-712. DOI: 10.1039/C7TC04649A

[32] Yu Z, Sun L. Recent progress on hole-transporting materials for emerging Organometal halide perovskite solar cells. Advanced Energy Materials. 2015;**5**:1500213. DOI: 10.1002/aenm.201500213

[33] Vivo P, Salunke J, Priimagi A. Hole-transporting materials for printable perovskite solar cells. Materials. 2017;**10**:1087. DOI: 10.3390/ma10091087