Control of organic–inorganic halide perovskites in solid-state solar cells: a perspective

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Abstract Since the year of 2009 when the first application of organohalide lead perovskite as the light harvester in solar cells was reported, tremendous attention has been devoted to these new types of perovskite-based solid-state solar cells and remarkable power conversion efficiency of over 20 % has been achieved to date. In this review, we first introduce the properties of organic–inorganic halide perovskites and then focus on the notable achievements made on the perovskite layer to improve the power conversion efficiency of solid-state perovskite solar cells, which is featured by process engineering of the state-of-the-art lead methylammonium triiodide perovskite and material control of lead triiodide perovskites and other newly emerged perovskites. In the end, we wish to provide an outlook of the future development in solid-state perovskite solar cells. Provided that the instability and toxicity of solid-state perovskite solar cells can be solved, we will witness a new era for cost-effective and efficient solar cells.

Keywords Perovskite solar cells · Fabrication procedures · High performance

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1 Introduction

Perovskites can generally be expressed as AMX_3, where A stands for an organic or inorganic cation, M is a metal ion and X is an anion [1]. The crystallographic stability is influenced by a tolerance factor t and an octahedral factor u [2]. For the organohalide metal perovskite of present interest, A is an organic cation, and X is halide anion. The most commonly used perovskite in the state-of-art solid-state solar cells is $CH_3NH_3PbI_3$ ($MAPbI_3$), where A is $CH_3NH_3^+$, M is Pb^{2+} and X is I^- (Fig. 1). The crystal structures of perovskites can be transited between cubic, tetragonal and orthorhombic depending on the temperature [3, 4]. Many well-known perovskites are fully inorganic, e.g., $BaTiO_3$ [5], $BiFeO_3$ [6] or $SrTiO_3$ [7], and they are featured by piezoelectric or ferroelectric properties and abnormal photovoltaic effect [8–10]. At present, the ferroelectric property of organohalide lead perovskites and observed hysteresis in photovoltaic performance in perovskite solar cells are still under debate [11–16].

Organic–inorganic lead perovskites recalled attentions from photovoltaic area began with the application of them as light absorbers in dye-sensitized solar cells (DSCs) in 2009. Miyasaka's group [17] pioneered the first perovskite solar cells where $MAPbX_3$ (X = I, Br) were loaded on top mesoporous TiO_2 photoanodes by dropping $MAPbX_3$ (X = I, Br) solutions on TiO_2 photoanodes and spin cast. However, compared with DSCs based on ruthenium sensitizer [18–21] or porphyrin sensitizer [22–24], the resulting power conversion efficiencies (PCEs) were quite poor (3.81 % for $MAPbI_3$ and 3.13 % for $MAPbBr_3$). One of the reasons for its poor performance may be determined by its configuration. In a sandwich-type open cell, liquid electrolyte was dropped between two electrodes, and the contact
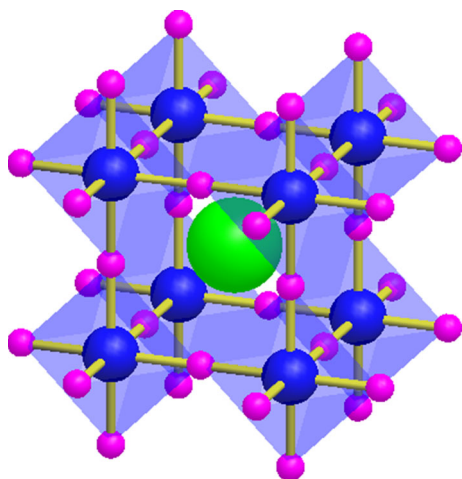
Fig. 1 Cubic crystal structures of MAPbI$_3$ perovskite where the organic group MA$^+$, inorganic metal Pb^{2+} and halide I$^-$ occupy positions A (green), B (blue) and X (pink), respectively

between electrons and liquid electrolyte is not as good as that in a sealed solar cells. Later, Park's group [25] chose MAPbI$_3$ as light absorber in sealed DSCs with thinner TiO$_2$ photoanodes and investigated the performance of DSCs with different concentrations of MAPbI$_3$ in solutions. In their case, self-made liquid electrolyte was introduced into the system via vacuum back-filling method, following the procedures used for the assembly of conventional DSCs [26]. Although their work boosted the performance of MAPbI$_3$-based DSCs, the liquid electrolyte was demonstrated to be corrosive for MAPbX$_3$ (X = I, Br).

The real breakthrough came when Kim et al. [27] used MAPbI$_3$ as a light absorber in combination with the solid-state hole conductor, 2,2′,7,7′-tetrakis-(*N,N*-dimethoxyphenyl-amine)-9,9′-spirobifluorene (spiro-OMeTAD). A PCE of 9.7 % was achieved with much better stability compared with its liquid counterparts. Soon after that, Lee et al. [28] introduced meso-superstructure solar cells where mesoporous layer was composed of insulator Al$_2$O$_3$, instead of TiO$_2$. It was studied that Al$_2$O$_3$ mesoporous layer worked as a scaffold for more loading of MAPbI$_3$ perovskite. Since then, there have been exponentially increased research effort devoted to this field, and there were also a number of excellent review articles published in the relevant fields [29–32]. However, to date no review article has put particularly focus on control of the perovskite layer in terms of morphology and materials engineering. In this review, we firstly introduced the general properties of MAPbX$_3$ (X = Cl, Br, I) perovskites, the structure and components of perovskite solid-state solar cells, and then elaborated various fabrication procedures for the preparation of perovskite films and their influences on the morphology of perovskite film and performance of solar cells. Recent works on lead-free perovskites were also discussed. In the end, we summarized some most useful and facile methods

for deposition of organic–inorganic halide perovskites based on our experiment and experience, and we prospected that development of lead-free perovskites with high stability would be the next breakthrough in this area.

1.1 Optical properties of MAPbX$_3$ (X = Cl, Br, I) perovskites

Different from all inorganic perovskites that generally have a large indirect energy band gap of around 3 eV [33, 34], three-dimensional (3D) organic–inorganic halide perovskites exhibit strong absorbance in the visible wavelength range with a direct energy band gap of around ~1.5 eV for MAPbI$_3$ and huge absorbance coefficient of one order of magnitude higher than that of traditional dye sensitizers [27]. By adjusting the ratio of halide in a hybrid perovskite (MAPbX$_3$, X = Br or I), the energy band gap and absorbance spectra of perovskites can be easily tuned [35]. Initially, researchers have investigated the luminescent properties of two-dimensional (2D) layer structures [36–38]. It was soon discovered that the 3D perovskites can also exhibit broad and strong photoluminescence (PL) [39]. PL quantum efficiencies of up to 70 % have been observed for solution-processed MAPbI$_{3-x}$Cl$_x$ perovskite films [40]. It was also reported that the PL emission wavelengths and electron lifetimes can be affected by the halide in MAPbX$_3$ perovskites [41–44].

1.2 Electronic properties of MAPbX$_3$ (X = Cl, Br, I) perovskites

In addition to special optical properties, their unique electronic properties also contribute to their success in perovskite solar cells. It was reported that the electron-hole diffusion length of mixed halide (MAPbI$_{3-x}$Cl$_x$) and triiodide (MAPbI$_3$) perovskite absorbers was in orders of micrometer and few hundred nanometers [43, 44]. Moreover, by reducing non-radiative electron-hole recombination within MAPbI$_{3-x}$Cl$_x$ perovskite using Lewis bases thiophene and pyridine, Noel et al. [45] can improve its PL lifetimes by nearly an order of magnitude. Besides, these 3D organohalide lead perovskites exhibit high hole mobility of around 60 cm^2/(V s) [46]. Thus, efficient perovskite solar cells can be made without any hole transporter materials due to the ambipolar semiconducting nature of perovskite [47, 48]. By mapping the variation in efficiency of charge separation and collection across the perovskite solar cells, Edri et al. [49] revealed two important interfaces, one at/near the absorber/hole transport material (HTM) and the other at/near the absorber/ electron transport material (ETM). Their work implies that the perovskite solid-state solar cells operate as a p-i-n device similar to amorphous silicon-based solar cells. In