Auto-passivation of crystal defects in hybrid imidazolium/methylammonium lead iodide films by fumigation with methylamine affords high efficiency perovskite solar cells

Yi Zhang\textsuperscript{a,b}, Giulia Grancini\textsuperscript{a}, Zhaofu Fei\textsuperscript{a,⁎}, Erfan Shirzadi\textsuperscript{a}, Xuehui Liu\textsuperscript{b}, Emad Oveis\textsuperscript{c}, Farzaneh Fadaei Tirani\textsuperscript{a}, Rosario Scopelliti\textsuperscript{a}, Yaqing Feng\textsuperscript{b}, Mohammad Khaja Nazeeruddin\textsuperscript{a,⁎}, Paul J. Dyson\textsuperscript{a,⁎}

\textsuperscript{a} Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
\textsuperscript{b} School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
\textsuperscript{c} Interdisciplinary Centre for Electron Microscopy, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

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\textbf{ABSTRACT}

Hybrid perovskite solar cells have attracted tremendous interest in the photovoltaic community. Despite their high defect tolerance, reducing the trap density by material engineering and surface modification is still critical to further boost performance. Here, methylammonium lead(II) iodide perovskite has been doped with imidazolium iodide in high concentrations (10–30 mol%) to boost solar cell performance, by passivating defects. Fumigation with methylamine results in the deprotonation of the embedded imidazolium cations, generating imidazole and methylammonium cations. The resulting (neutral) imidazole is extruded from the 3-D perovskite crystal and distributes around the crystal leading to auto-passivation of crystal defects. The structure of the imidazolium-PbI\textsubscript{3} salt intermediate (i.e. formed in the absence of the methylammonium cation) has been determined and the resulting perovskite film characterized. Employed in solar cells, a power conversion efficiency (PCE) up to 20.14% is demonstrated.

1. Introduction

In recent years the performance of perovskite-based solar cells (PSCs) has improved considerably [1–4], with the most widely used light absorber comprising methylammonium lead triiodide (MAPbI\textsubscript{3}) combined with other cations [5–8]. To boost device efficiency compositional engineering by incorporating mixed cations such as Cs\textsuperscript{+} or Rb\textsuperscript{+} has been the most explored route [9]. However, increasing the control on the quality of the perovskite layer [10,11] and the interfaces between the perovskite layer and the electron transport layer (ETL) [12,13], and hole transport layer (HTL) [14,15], are of crucial importance. In recent years, to improve the quality of the perovskite layers, several techniques have been applied, including healing the defects of the perovskite layers through chemical passivation. As an example, an excess of PbI\textsubscript{2} in nonstoichiometric precursor solution has been shown to increase the device PCE resulting in a reduced defect density compared to that of stoichiometric reference cell [16,17]. Extending this approach, different compounds (including salts) have been used to adjust the defects and interfaces of perovskite layer. Examples include passivation with Lewis bases that stabilize under-coordinated Pb(II) ions [18], and iodopentafluorobenzene, which coats the perovskite forming halogen bonding donor-acceptor interactions [19]. An amine-based polymer has been also used as a surfactant to promote uniform crystallization, while passivating the MAPbI\textsubscript{3} and assisting the growth of a more uniform distribution of crystals, leading to improved open circuit voltages [20]. Most recently, quaternary ammonium halides have been used for the passivation of perovskite films resulting in enhanced PSC [17]. However, almost all these compounds have been directly mixed within the perovskite precursor solution, affecting the growth of perovskite crystals. The use of additives not only plays an important role in passivating defects, but also in improving the interfacial interactions with the ETLs and/or HTLs, which ultimately results in improved PCEs [21,22,23], as well as modulating the crystal growth and overall film surfaces [24,25]. In order to improve interface interactions, fumigation of pre-formed perovskite films with gaseous methylamine, as a post-treatment, has been also proposed as a way to improve the quality of perovskite surfaces enhancing the interactions between the perovskite layers and the HTL [26].
Here, we describe the use of high concentrations of imidazolium iodide (IMI) as a doped co-reactant for the fabrication of perovskite films, followed by fumigation with gaseous methylamine. This second step further fine-tunes the quality of the perovskite film and, due to the stronger basicity of methylamine compared to imidazole [27,28], resulting in the deprotonation of the imidazolium cation in the perovskite film which releases imidazole (IMD). The released IMD distributes around the crystal edges, leading to auto-passivation of crystal defects. Using this approach, a PSC with a PCE of 20.14% was obtained as measured at standard AM 1.5.

2. Results and discussion

High concentrations of IMI were included in the preparation of MAPbI₃ perovskite films, i.e. 10, 20 or 30 mol% IMI relative to MAI and PbI₂ (0.9:1, 0.8:1 or 0.7:1 ratio) in DMSO, to afford films of formula IM₀.₁MA₀.₉PbI₃, IM₀.₂MA₀.₈PbI₃ and IM₀.₃MA₀.₇PbI₃. As controls, films of pure MAPbI₃ and IMPbI₃ were also prepared from dimethyl sulfoxide (DMSO). The resulting films were obtained by spin-coating onto FTO glass and fumigation with methylamine gas (see Experimental for full details). Both the untreated and fumigated films were characterized by X-ray diffraction (XRD, Fig. 1).

Fig. 1a shows the XRD patterns of the spin-coated (non-fumigated) perovskite films IMPbI₃, IM₀.₃MA₀.₇PbI₃, IM₀.₂MA₀.₈PbI₃ and IM₀.₁MA₀.₉PbI₃ and pure IMPbI₃, in the region between 10° and 15° (expanded in Fig. 1b). The pure IMPbI₃ film shows a peak at 11.34°, i.e. in a similar position to that observed for the δ-FAPbI₃ phase [29–31], which can be assigned to the (110) peak of a 1-dimensional phase (note that the single crystal X-ray structure of IMPbI₃ has been determined and confirms this structure – see below). Indeed, it is important to mention that due to the limit set by the Goldschmidt tolerance factor rule, only the cations with an active radius < 2.56 Å can be incorporated and centred inside the three-dimensional perovskite structures within the octahedral PbI₆ cages, thus limiting the choice according to the dimensions of the cation. Other cations, such as guanidinium (GA), alkylammonium or alkyl imidazolium, being larger in size than the empirical limit, are indeed unable to fit inside the PbI₆ cages of the perovskite structures, leading to the collapse of the three-dimensional network, or forming lower dimensional perovskites [32]. However, despite the slightly larger dimensions, it has been predicted and recently demonstrated that even larger cations such as GA and imidazolium (IM) can be incorporated into the octahedral PbI₆ cages when mixed in small amount with MA, keeping a stable three-dimensional perovskite structures [33,34]. This is valid only if a certain percentage of GA is added together with MA (up to 15%) [35]. Beyond that, phase segregation occurs and pure GA-based perovskite forms two or one-dimensional perovskite phase [35]. Although the effective radii of the imidazolium cation (2.58 Å) is only marginally larger than that of the formamidinium (2.53 Å) which forms three-dimensional structures [36], the reaction of pure imidazolium iodide (IMI) [37] with PbI₂ leads to the formation of imidazolium lead triiodide (IMPbI₃) arranging into a one-dimensional structure [38]. The XRD pattern of the film containing 10% IMI, i.e. IM₀.₁MA₀.₉PbI₃, does not contain the peak at 11.34°, instead a peak at 14.06° is observed similar to that of the pure untreated MAPbI₃ film (14.15°), but slightly shifted when compared to pure MAPbI₃, suggesting that the structure of IM₀.₁MA₀.₉PbI₃ comprises of a
typical 3-dimensional orthorhombic perovskite phase. The calculated d-spacing of the perovskite crystal unit changes from 6.28 Å in MAPbI₃ to 6.32 Å in IMₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐ¢
The SEM image of the f-IM0.1MA0.9PbI3 film reveals a larger grain size compared to that of the reference material (Fig. 4b), and as the dopant concentration increases, the grain size increases correspondingly. However, it is worth mentioning that there appears to be an amorphous substance attached to the film, which increases as the IMI content is increased. In the f-IM0.2MA0.8PbI3 and f-IM0.3MA0.7PbI3 films, where the IMI content is the highest, this amorphous substance appears to be separated between crystals, which is not conducive to electronic...
transmission (Fig. 4c and d).

PSCs were fabricated from the fumigated films and the J-V characteristics of the devices under simulated air mass 1.5 global standard sunlight (AM 1.5 G) are summarized in Fig. 5a with the device parameters listed in Table 1.

Champion devices of the f-MAPbI3 shows a PCE of 18.22%, obtained from the reverse scanned data of $J_{SC} = 22.18$ mA cm$^{-2}$, $V_{OC} = 1.06$ V and FF = 0.775. The most efficient f-IM$_{0.1}$MA$_{0.9}$PbI$_3$-based device provides a PCE of 20.13%, due to the auto-passivation of crystal defects by IMD, significantly outperforming that based on the f-MAPbI3 reference material. However, in the devices prepared with fumigated films prepared using higher amounts of IMI, i.e. f-IM$_{0.2}$MA$_{0.8}$PbI$_3$ and f-IM$_{0.3}$MA$_{0.7}$PbI$_3$, the PCE is 18.21% and 17.72%, respectively. The PCE of the champion device made with the IMD doped film, f-IMD$_{0.1}$MA$_{0.9}$PbI$_3$, is 18.74%, significantly lower than the PCE of 20.13% obtained from the champion device containing f-IM$_{0.1}$MA$_{0.9}$PbI$_3$. The performance of the corresponding devices prepared under the anti-solvent method is provided in Fig. S4 and Table S6, and are all lower than the devices containing the fumigated perovskite films. This provides statistical relevance to the results, confirming that the improvement of device performance is not due to IMI doping alone. An evaluation of the J-V hysteresis based on the scan direction was conducted (Fig. 5b and Table S5) and, compared to the reference f-MAPbI$_3$ device, a similar hysteresis is observed for the f-IM$_{0.1}$MA$_{0.9}$PbI$_3$ device. This may be reflected in the hysteresis index [30], which is calculated from the ratio between $\eta_{rev}/\eta_{for}$. The hysteresis index of the f-MAPbI$_3$-based cells and f-IM$_{0.1}$MA$_{0.9}$PbI$_3$ devices are calculated as 1.03 and 1.05. Moreover, the high $J_{SC}$ of 22.88 mA cm$^{-2}$ obtained using the f-IM$_{0.1}$MA$_{0.9}$PbI$_3$ device is markedley better than that of the reference cell. In addition, the f-IM$_{0.1}$MA$_{0.9}$PbI$_3$ device exhibits a higher incident photon-to-current efficiency (IPCE) as a function of wavelength with a very broad plateau of over 80% between 400 and 725 nm, yielding an integrated $J_{SC}$ value of 22.32 mA cm$^{-2}$, which is in good agreement with that determined from the J-V curves (Fig. 5c).

A total of 60 solar cells were fabricated with the f-IM$_{0.1}$MA$_{0.9}$PbI$_3$ and f-MAPbI$_3$ films. Fig. 5d shows the statistical distribution of all four photovoltaic parameters of the two groups of solar cells illustrating the reproducibility of each condition. In the case of the PSCs containing the f-IM$_{0.1}$MA$_{0.9}$PbI$_3$ films, the average values (with standard deviation, s.d.) of the short-circuit current density ($J_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF) and PCE are $22.75 \pm 0.36$ mA cm$^{-2}$, $1.1 \pm 0.01$ V, $0.78 \pm 0.02$ and $19.44 \pm 0.51\%$, respectively (Table S3, SI). Compared to the f-IM$_{0.1}$MA$_{0.9}$PbI$_3$-containing cells, a smaller PCE of $17.88 \pm 0.45\%$ was obtained for the f-MAPbI$_3$-based devices (as well as a $J_{SC}$ of $22.1 \pm 0.38$ mA cm$^{-2}$, $V_{OC}$ of $1.05 \pm 0.01$ V and FF of $0.77 \pm 0.01$). As can be seen in Fig. 5d, all the photovoltaic parameters of the f-IM$_{0.1}$MA$_{0.9}$PbI$_3$-based solar cells showed higher average values and smaller standard deviation (except FF) over those of devices containing the f-MAPbI$_3$ films (Table S4, SI). The stability of devices containing the f-IM$_{0.1}$MA$_{0.9}$PbI$_3$ solar cell was evaluated at the maximum power output (MPO) decay of the devices. The unsealed devices were maintained in an argon atmosphere under a constant illumination of 100 mW cm$^{-2}$. The current-voltage curves were recorded every 2 h and the f-IM$_{0.1}$MA$_{0.9}$PbI$_3$ was found to be very stable (Fig. 5e), as shown in the fitted decay lifetime. The performance of device decreased slowly during the aging study and after 1000 h of continuous light soaking the MPO values of the devices kept more than 70% of the initial values, which is significantly better than the pure f-MAPbI$_3$.

3. Concluding remarks

Several routes to engineering the hybrid perovskites have been reported, such as cation alloying and halide alloying. However, most of the alloying approaches are limited to the well-studied, 3-dimensional perovskites such as MAPbI$_3$ and FAPbI$_3$. In this study, using IMI at a high doping level, combined with passivation using methylvamine gas, affords a high-quality perovskite film delivering in a champion PSC a PCE of 20.14% and remarkable stability. The mechanism by which the structure of the film is improved involves protonation of the imidazolium to affording MA and IMD. The imidazolium cations are then replaced by the newly generated MA cations resulting in a type of melting/freezing process that improves the quality of the film. Overall, this work shows that classical perovskite materials can potentially be doped with many different organic cations. In addition to the size of the cation being important, the $pK_a$ should be below that of methylvamine to ensure that in the fumigation step the organic cation can be deproto-
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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2019.01.027.