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Cite this: *RSC Adv.*, 2017, 7, 17473

## Enhancement of thermal stability for perovskite solar cells through cesium doping†

Guangda Niu, Wenzhe Li, Jiangwei Li, Xingyao Liang and Liduo Wang\*

Organic–inorganic hybrid perovskite solar cells are found to be sensitive to moisture, oxygen, UV light, light soaking, heat, electric field, etc. Among all these factors, thermal stability is one of the most challenging concerns affecting PSCs stability, since it is hard to avoid a temperature increase for solar cells during operation. In this work, we systematically studied the thermal stability of  $\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$  film and solar cells. The introduction of Cs into the precursor solution would inevitably accelerate the film deposition rate, resulting in decreased grain size and more Cs atoms in the film than in the precursors. The study on thermal stability illustrated that perovskite degradation was highly related to the amount of oxygen in the air. A small amount of Cs doping ( $x = 0.09$ ) was beneficial for better thermal stability. In addition, Cs doping also enhanced the device performance. The improvement of short-circuit currents came from the increased film thickness, which was due to the faster deposition rate for Cs doped samples. Besides, Cs doping was vital to suppress the trap states in the film since the trap states were related to halide deficiency during thermal annealing. At last, the final performance of  $\text{Cs}_{0.09}\text{MA}_{0.91}\text{PbI}_3$  reached 18.1%, with a  $J_{\text{SC}}$  of  $22.57 \text{ mA cm}^{-2}$ ,  $V_{\text{OC}}$  of 1.06 V, FF of 0.76.

Received 21st December 2016  
 Accepted 10th March 2017

DOI: 10.1039/c6ra28501e

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## Introduction

The last several years have witnessed the rapid development of organic–inorganic perovskite materials with striking photonic and electronic properties, as well as successful demonstrations of their applications in solar cells, light emitting diodes, photodetectors, and lasers. The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has increased from 3.81% to 22.1% in seven years.<sup>1–4</sup> During this period, many reports have focused on the film fabrication process, composition control, and device structure.<sup>5–8</sup>

Almost at the same time, many researchers found the instability of perovskites despite their excellent electronic properties.<sup>9,10</sup> As far as we are concerned, perovskites are found to be sensitive to moisture, oxygen, UV light, light soaking, heat, electric field, and other potential factors.<sup>11–13</sup> Thereby, massive efforts have been made to study the degradation mechanism and stability enhancement strategies. Moisture and oxygen could cause the formation of hydrate intermediates and damage the perovskite accordingly. The moisture and oxygen instability could be well avoided by device encapsulation, including fluoropolymer encapsulation or metal oxide to protect the perovskite.<sup>14,15</sup> In addition, PSCs could be protected from UV light through adding UV filters onto devices. The

stability toward an electric field, which is also denoted as the typically observed hysteresis phenomenon, could be solved by suppressing the trap states of perovskites, by using  $\text{PC}_{61}\text{BM}$  or other fullerene derivatives.<sup>16,17</sup>

Currently, from our views, thermal stability and light soaking are the most challenging concerns affecting PSCs stability, since it is hard to avoid temperature increase and light illumination for solar cells during operation. Formamidinium ( $\text{HC}(\text{NH}_2)_2$ ), abbreviated as FA, has been demonstrated more stable than methylammonium ( $\text{CH}_3\text{NH}_3$ , shortened as MA) under high temperature.<sup>18,19</sup> However, as an organic molecules, degradation could still be observed for FA-based perovskite, especially when oxygen was present, which was caused by the oxidation of FA. Moreover, FA is also more sensitive to moisture than MA due to its high hygroscopicity, thus requiring more rigorous encapsulation and increasing the cost. In terms of the intrinsic property, Cs-based perovskite should exhibit higher thermal stability than FA- and MA-counterparts. Some recent papers indeed found that  $\text{CsPbBr}_3$ ,  $\text{CsPbI}_2\text{Br}$ ,  $\text{CsPbIBr}_2$  could endure harsh conditions with temperature as high as  $300^\circ\text{C}$ .<sup>20–22</sup> However, due to the non-ideal band gaps ( $>1.7 \text{ eV}$ ), the PCE for Cs-based perovskite is relatively lower than  $\text{MAPbI}_3$  and  $(\text{MAPbBr}_3)_x(\text{FAPbI}_3)_{1-x}$ . For single junction solar cells, researchers started to utilize mixture of Cs–MA, Cs–FA, Cs–MA–FA etc., to compose perovskite.<sup>23–25</sup> The role of Cs was found to be effective to stabilize the black phase of  $\text{FAPbI}_3$ , decrease trap states, and benefit device performance. However, there is still no detailed studies on thermal stability of Cs-based perovskite materials.

Department of Chemistry, Tsinghua University, 100084, China. E-mail: [chldwang@mail.tsinghua.edu.cn](mailto:chldwang@mail.tsinghua.edu.cn)

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra28501e







Fig. 1 Thermal stability study of perovskite films with different Cs content. (a) Perovskite films with compositions of  $Cs_xMA_{1-x}PbI_3$  before thermal treatment, where  $x$  represents Cs content. (b) Perovskite films after thermal treatment at 120 °C for 3 hours exposing to air. (c) Retained absorption at 700 nm for perovskite films with  $x$  ranging from 0 to 0.86. (d) Photographs of perovskite films exposing to different atmosphere.

$PbI_2$  was much higher than perovskite, demonstrating most of  $MAPbI_3$  has degraded to  $PbI_2$ . For  $x = 0.09$ , the formation of  $PbI_2$  was effectively suppressed, due to the better thermal stability. For  $x = 0.23$ , in contrast, the peak for perovskite was even lower than that of  $x = 0$ .

Fig. 2c and d shows the morphology of the films. Before thermal treatment, all the films were flat with no pinholes, while Cs content could lead to smaller grain size, probably due to the increased nucleation sites in the early stage of film formation. In contrast, after thermal treatment, the films became rugged, especially for  $x = 0$ . The pits and pinholes were caused by the loss of MAI or  $CH_3NH_2$ , leaving the film recrystallized as  $PbI_2$ . When Cs was introduced into the film, the pinholes was effectively suppressed. In addition, as Cs content increased, the pinholes became smaller due to the much more stable A site (Cs) in the films and decreased crystal volume.

We assembled perovskite solar cells with  $x = 0$  and  $x = 0.09$ , since if  $x > 0.09$ , the thermal stability was not good enough. As shown in Fig. 3a and b, the cross-sectional SEM images exhibited that the thickness of perovskite ( $x = 0.09$ ) was  $\sim 500$  nm, including the mesoporous  $TiO_2$  layer and top perovskite layer, higher than that of  $x = 0$  (405 nm). During the experiment, all the parameters were kept the same except the composition of precursor solution. The higher thickness of  $x = 0.09$  was probably due to the increased film formation rate when

Cs was introduced into the film. If the film formation rate was fast, more perovskite would precipitate out when chlorobenzene was added onto the film to quench the precursor solution. Due to the increased film thickness, the short-circuit current ( $J_{SC}$ ) of  $x = 0.09$  was higher than that for  $x = 0$ . As shown in Table 2 and Fig. 3c, the champion device of  $x = 0.09$  showed a  $J_{SC}$  of  $22.57\text{ mA cm}^{-2}$ , a  $V_{OC}$  of 1.06 V, FF of 0.76, leading to a final power conversion efficiency of 18.1%. In contrast, the champion device of control sample exhibited a  $J_{SC}$  of  $20.59\text{ mA cm}^{-2}$ , a  $V_{OC}$  of 1.04 V, FF of 0.74, and a PCE of 15.8%. Fig. 3d shows the IPCE spectra of the champion devices. Although Cs atoms could inevitably increase the band gap of perovskite, the absorption region was almost the same for  $x = 0$  and 0.09 due to the small doping ratio. The integrated photocurrent for  $x = 0$  and 0.09 was  $18.6$  and  $19.9\text{ mA cm}^{-2}$ , respectively, slightly lower than the value derived from  $J-V$  curves. The reason is that our devices exhibited hysteresis effect, while IPCE recorded the steady state current. We have also averaged data from 12 devices to obtain statistic information. The average  $J_{SC}$  was increased from  $20.34 \pm 1.20\text{ mA cm}^{-2}$  for  $x = 0$  to  $22.42 \pm 0.33\text{ mA cm}^{-2}$  for  $x = 0.09$ . Additionally, besides the increase of  $J_{SC}$  after Cs introduction, the fill factors have also been increased from  $0.70 \pm 0.02$  to  $0.74 \pm 0.01$ . During this work, we employed mesoporous  $TiO_2$  as anode and found hysteresis effect for the fabricated devices (Fig. S3†). Further improvement on







Fig. 3 (a, b) Cross-sectional SEM images of perovskite films with  $x = 0$  and  $0.09$ . (c)  $J$ - $V$  characteristics of champion devices with different Cs content. (d) IPCE and integrated photocurrent for the champion devices. (e) Recombination resistance derived from electrochemical impedance spectra (EIS). (f) Electron recombination time from EIS spectra.

Table 2 Performance summary for perovskite solar cells with different Cs content

	$J_{SC}$ ( $\text{mA cm}^{-2}$ )	$V_{OC}$ (V)	FF	$\eta$ (%)
$x = 0$	$20.34 \pm 1.2$	$1.05 \pm 0.01$	$0.70 \pm 0.02$	$14.9 \pm 1.3$
Champion	20.59	1.04	0.74	15.8
$x = 0.09$	$22.42 \pm 0.33$	$1.05 \pm 0.01$	$0.74 \pm 0.01$	$17.5 \pm 0.5$
Champion	22.57	1.06	0.76	18.1

small peaks at 136.9 eV and 141.3 eV could be assigned to metallic Pb ( $\text{Pb}^0$ ), which was due to unsaturated Pb, according to recent studies. Henry Snaith and co-workers demonstrated that the presence of unsaturated Pb atoms was related to the iodide deficiencies, and metallic lead species could act as

recombination sites, leading to poor performance.<sup>26</sup> In our assumption, during thermal annealing process, the loss of iodide was accompanied with the loss of methyl ammonium. When we replaced some MA with Cs atoms, due to the better thermal stability and thus less loss of molecular groups from A site and iodide atoms, unsaturated Pb was effectively suppressed. For XPS spectra of  $x = 0.09$ , there are no additional peaks from  $\text{Pb}^0$ . Furthermore, we also measured transient photoluminescence spectra to study the defect density in the film (Fig. 4b). The decay curves could be well fitted by a biexponential decay function. The fast component is attributed to the surface recombination, while the slow component is caused by the recombination in the bulk of perovskite. We average the two components according to their amplitude to obtain the





7 : 3 vol%). The total concentration of Pb was set as 0.96 M for all the solutions. The solutions were then coated onto the substrate by two consecutive spin-coating steps, at 1500 rpm for 10 s, and 5000 rpm for 30 s. During the second step, 0.3 mL chlorobenzene was poured onto the substrate. Then the film was heated at 90 °C for 10 min. Spiro-MeOTAD solution was prepared by dissolving 102.7 mg spiro-MeOTAD in 1 mL chlorobenzene, to which 9.85  $\mu\text{L}$  4-*tert*-butyl pyridine and 42.22  $\mu\text{L}$  lithium bis(trifluoromethanesulfonyl)imide solution (170 mg LITFSI in 1 mL acetonitrile) were added. Spiro-MeOTAD was deposited on the substrate at 2000 rpm for 45 s. Then the films were left in air overnight. Finally, 50 nm gold electrode were thermally evaporated under vacuum of  $\sim 10^{-6}$  Torr, at a rate of  $\sim 0.2 \text{ \AA s}^{-1}$ .

### Characterization

X-ray diffraction (XRD) spectra was measured with smart LAB instruments Cu K $\alpha$  beam ( $\lambda = 1.54 \text{ \AA}$ ). UV-Vis absorption spectra were obtained with a Hitachi U-3010 spectroscope. SEM images were measured by JEOL JSM-7401F and TEM images by Hitachi HT7700 with an acceleration voltage of 100 kV. The composition of the film was measured by ICP-AES (Thermo IRIS intrepid II). *J*-*V* curves were measured by a Keithley 2400 source meter under one sun illumination (AM 1.5G, 100 mW cm $^{-2}$ ), simulated by a solar simulator (ORIEL 81193) calibrated with an NREL-calibrated silicon solar cell. External quantum efficiency (EQE) spectra were recorded by a setup, consist of a xenon light source, a monochromator, and a potentiostat. EIS were measured by an electrochemical workstation (Zahner, CIMPS) with frequency from 10 to 10 $^6$  Hz under applied voltage with an amplitude of 10 mV under light condition. The active area of each cell was 0.16 cm $^2$  with a mask of 0.09 cm $^2$ . Time-resolved PL decay was measured by a FV1200, excited at 488 nm.

### Acknowledgements

The research was funded by the National Natural Science Foundation of China under Grant no. 51273104 and 91433205.

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