Electronic Supplementary Information (ESI)

Guanidinium Induced Phase Separated Perovskite Layer for Efficient and Highly Stable Solar Cells

Weihai Zhang,[a] Juan Xiong,[b] Jinhua Li[c] and Walid A. Daoud*[a]

[a]*School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Hong Kong*

[b]*Faculty of Physics & Electronic Sciences, Hubei University, Wuhan, 430062, China*

[c]*School of Materials Science and Engineering, Hubei University, Wuhan 430062, China*

*Corresponding Author: *E-mail: wdaoud@cityu.edu.hk*

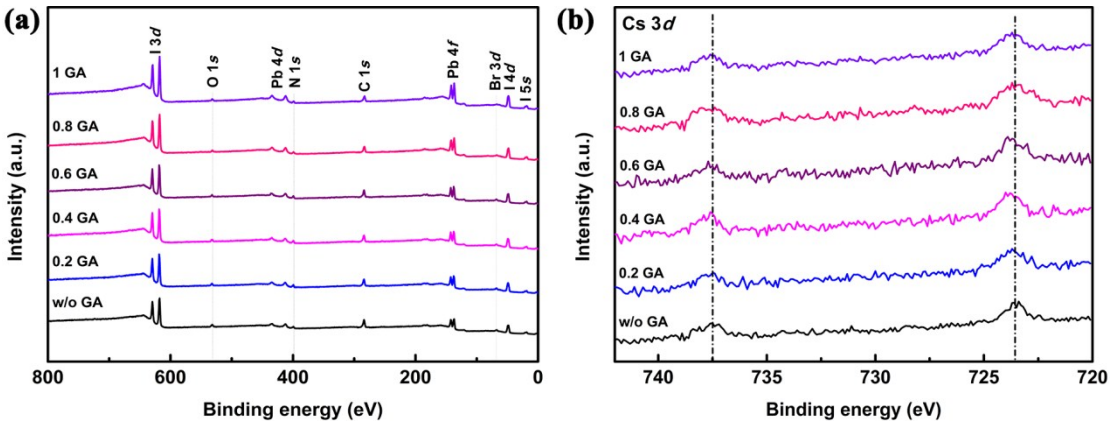

Fig. S1 (a) XPS survey spectra and (b) Cs 3*d* XPS core spectra of perovskite films with different *x* value (*x*=0, 0.2, 0.4, 0.6, 0.8, 1).

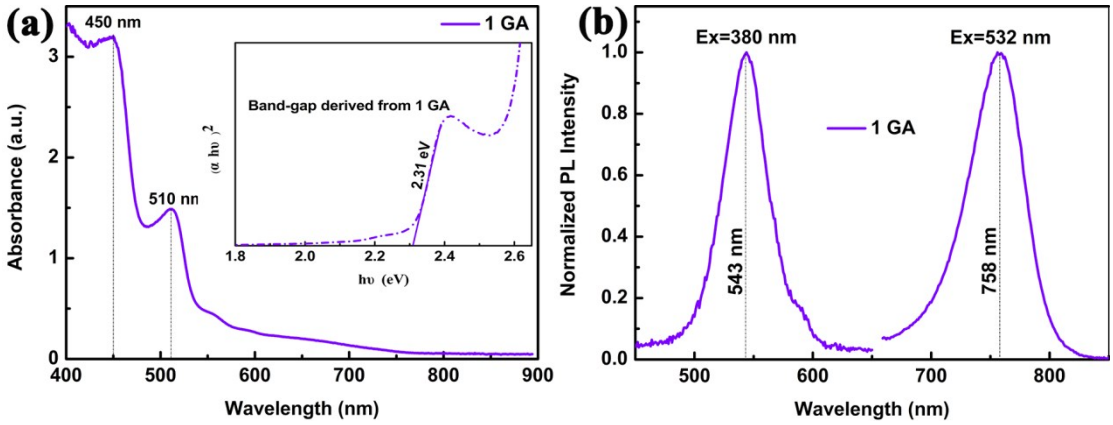

Fig. S2 (a) UV-vis absorption and $(\alpha h\upsilon)^2$ versus energy (in the inset) of 1 GA film. (b) Photoluminescence (PL) spectra for 1 GA film, excited at 380 nm (related to 2D phase $FAGAPbI_4$) and 532 nm (related to 3D phase $CsFAMA_{1-x}GA_x$).

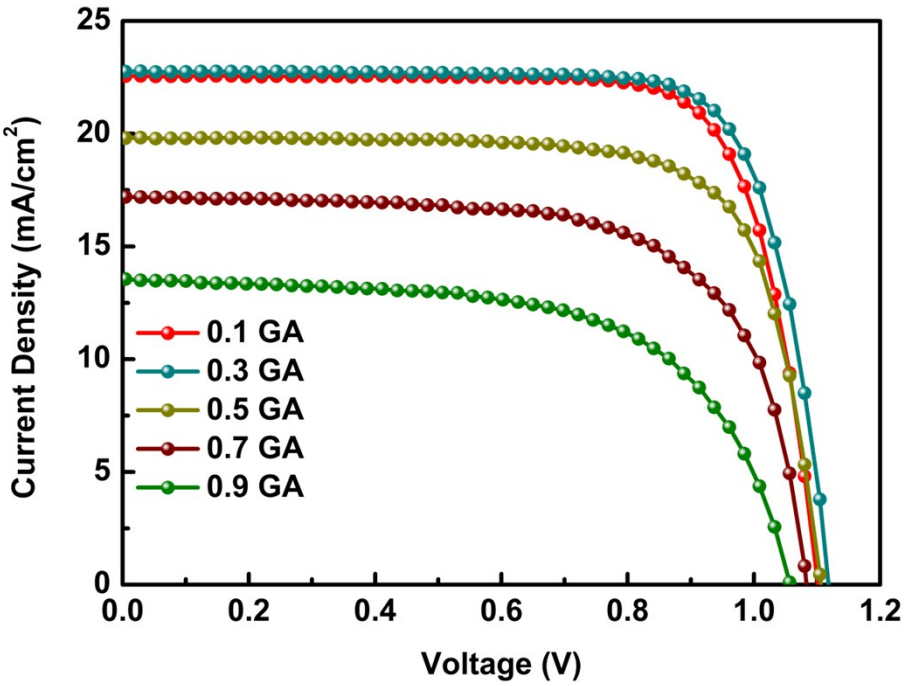

Fig. S3 J-V curves of the devices based on $CsFAMA_{1-x}GA_x$ perovskite films (x=0.1, 0.3, 0.5, 0.7, 0.9).

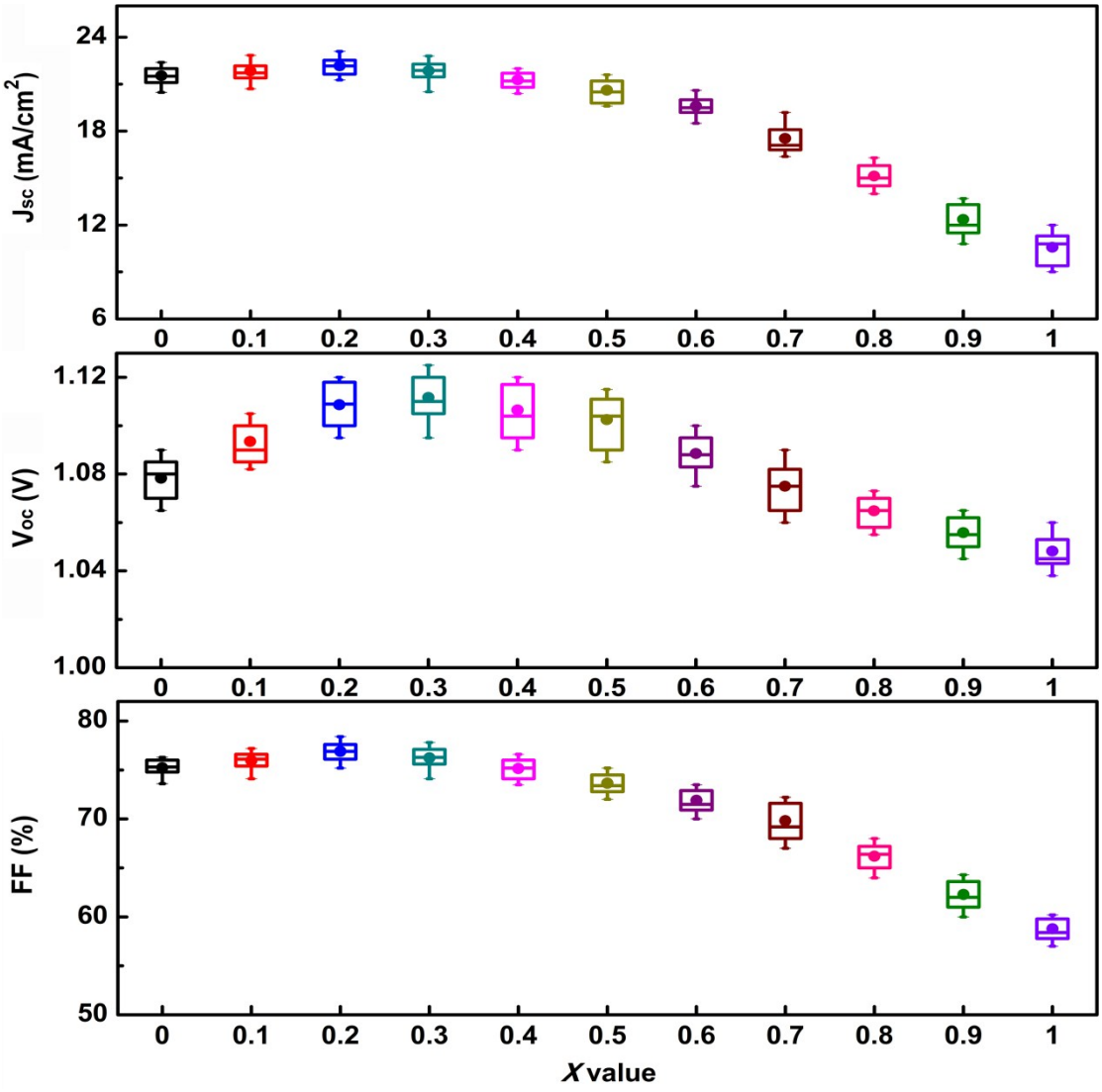

Fig. S4 Statistical distribution of the J_{sc}, V_{oc}, and FF derived from the devices with different *x* value (collected from 15 devices for each *x* value).

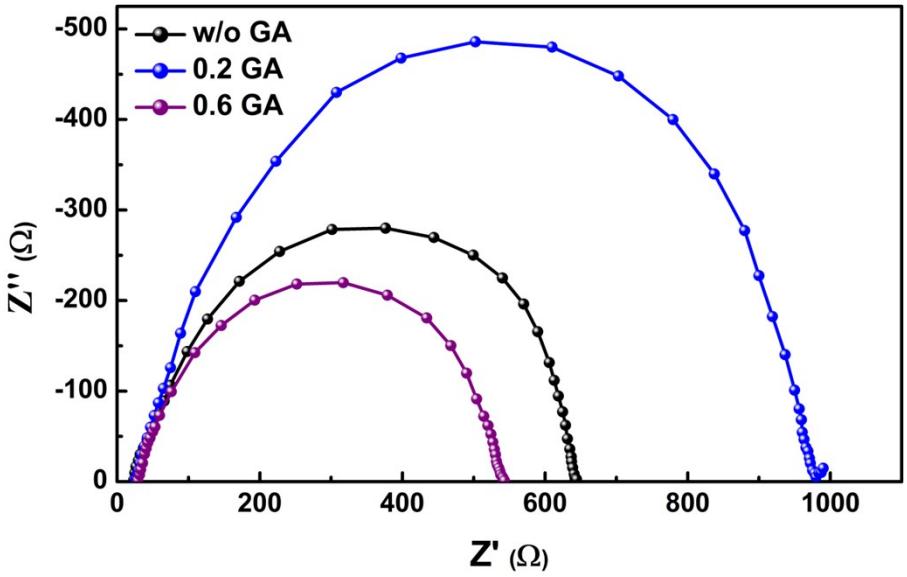

Fig. S5 EIS plots of the devices with different *x* value (*x*=0, 0.2, 0.6). A bias of the open-circuit voltage was applied during measurement.

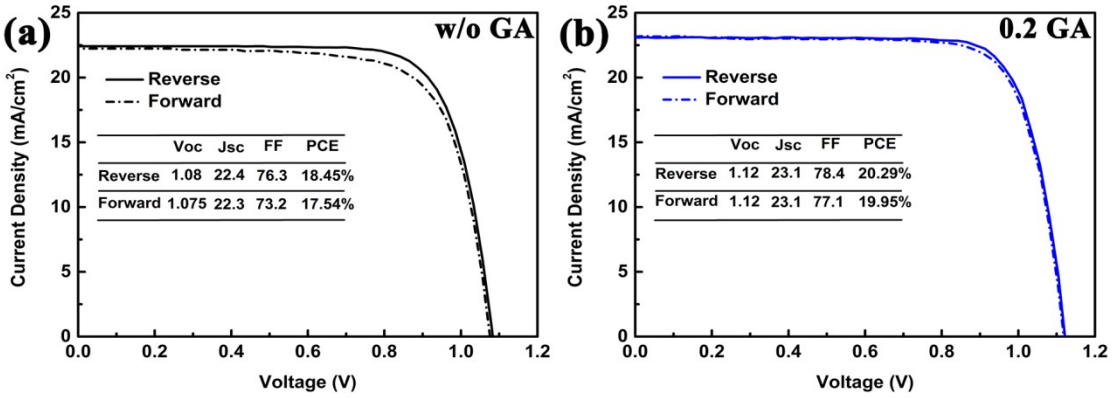

Fig. S6 J-V curves from reverse and forward scan of the devices based on (a) w/o GA and (b) 0.2 GA perovskite films.

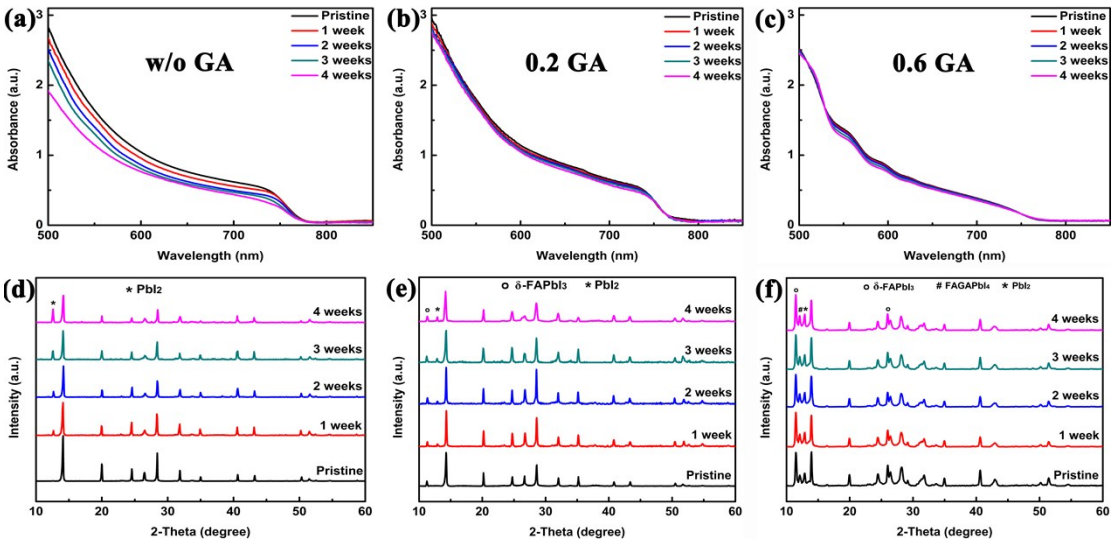

Fig. S7 UV-vis absorption spectra of (a) w/o GA, (b) 0.2 GA and (c) 0.6 GA films. Corresponding XRD patterns of (d) w/o GA, (e) 0.2 GA and (f) 0.6 GA films. The samples were stored in ambient environment of 25 ℃ and 25 % humidity in dark condition.

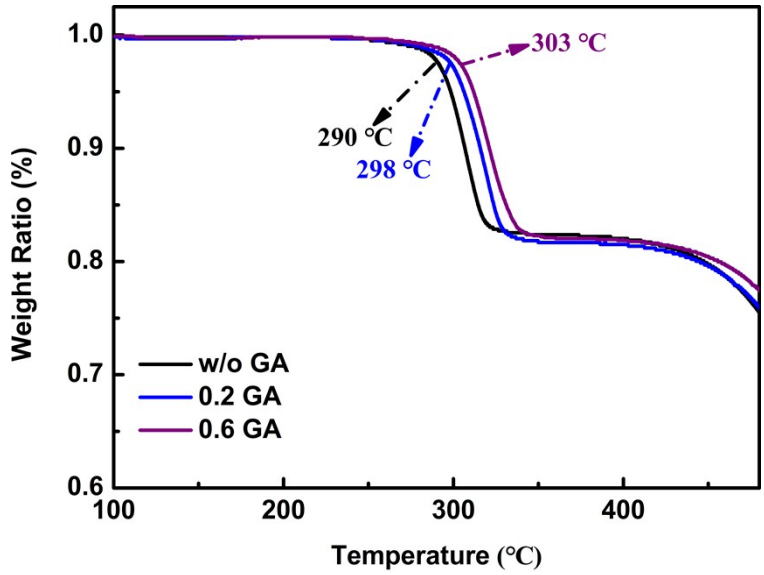

Fig. S8 Thermogravimetric analysis of w/o GA, 0.2 GA and 0.6 GA films. Heated from room temperature (25 ℃) to 500 ℃ in nitrogen atmosphere.

Table S1 Calculated Goldschmidt tolerance factors (in bold) for $CsFAMA_{1-x}GA_x$ perovskite films with different *x* value.

x value	Composition	R_A(pm)	R_B(pm)	R_X(pm)	*t*
0	$Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	242.89	119	215.92	**0.969**
0.1	$Cs_{0.05}(FA_{0.83}(MA_{0.9}GA_{0.1})_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	243.87	119	215.92	**0.971**
0.2	$Cs_{0.05}(FA_{0.83}(MA_{0.8}GA_{0.2})_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	244.86	119	215.92	**0.973**
0.3	$Cs_{0.05}(FA_{0.83}(MA_{0.7}GA_{0.3})_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	245.84	119	215.92	**0.975**
0.4	$Cs_{0.05}(FA_{0.83}(MA_{0.6}GA_{0.4})_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	246.83	119	215.92	**0.977**
0.5	$Cs_{0.05}(FA_{0.83}(MA_{0.5}GA_{0.5})_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	247.81	119	215.92	**0.979**
0.6	$Cs_{0.05}(FA_{0.83}(MA_{0.4}GA_{0.6})_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	248.8	119	215.92	**0.981**
0.7	$Cs_{0.05}(FA_{0.83}(MA_{0.3}GA_{0.7})_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	249.78	119	215.92	**0.983**
0.8	$Cs_{0.05}(FA_{0.83}(MA_{0.2}GA_{0.8})_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	250.77	119	215.92	**0.985**
0.9	$Cs_{0.05}(FA_{0.83}(MA_{0.1}GA_{0.9})_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	251.75	119	215.92	**0.987**
1	$Cs_{0.05}(FA_{0.83}GA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	252.74	119	215.92	**0.99**

Table S2 The atom ratios of N between NH_3 and NH_2 groups in different films estimated from XPS spectra and perovskite precursor.

	0 GA	0.2 GA	0.4 GA	0.6 GA	0.8 GA	1 GA
N atom ratio estimated from XPS spectra	0.21	0.159	0.12	0.076	0.038	0
N atom ratio calculated from Precursor	0.205	0.157	0.114	0.073	0.035	0

Table S3 Photovoltaic parameters of devices based on perovskites with different *x* value (*x*= 0.1, 0.3, 0.5, 0.7, 0.9).

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0.1 GA	1.1	22.6	76.8	19.1
0.3 GA	1.12	22.8	77.1	19.7
0.5 GA	1.11	19.8	74.2	16.3
0.7 GA	1.085	17.2	67.5	12.6
0.9 GA	1.066	13.5	61.8	8.9

Table S4 The fitted TRPL parameters of the films with different *x* value (*x*= 0, 0.1, 0.2, 0.3, 0.6, 1).

Perovskites	A_1	τ_1 (ns)	A_2	τ_2 (ns)
w/o GA	38.2%	3.14	61.8%	16.02
0.1 GA	34.8%	3.98	65.2%	19.57
0.2 GA	22.7%	4.76	77.3%	27.96
0.3 GA	30.1%	4.46	69.9%	27.56
0.6 GA	37.4%	2.99	62.6%	14.5
1 GA	40.9%	1.95	59.1%	8.13