Supporting Information

In-situ Induced Core/Shell Stabilized Hybrid Perovskites via Gallium(III) Acetylacetonate Intermediate towards Highly Efficient and Stable Solar Cells

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Experimental Section

Materials and Methods

Unless stated otherwise, all materials were purchased from Sigma-Aldrich or Alfa. FAI was purchased from Xi'an polymer Light Technology Corp. All of the chemicals were used as received.

Preparation of single crystals

Gallium(III) acetylacetonate ($GaAA_3$) single crystal: it was prepared by simply dissolving 100 mg $GaAA_3$ in 1ml acetylacetonate solvent. Then the precursor solution was stirred at 100 ^oC overnight. The $GaAA_3$ single crystal can be obtained while the temperature of precursor solution was cooled down to room temperature. The growth process of $GaAA_3$ single crystal with suitable size usually takes 6-7 h.

Gallium(III) acetylacetonate ($[GaAA_3]_4$) single crystal: The growth procedure is basically same as the $GaAA_3$. Differently, 80 μL DMSO was added into the precursor to induce the growth of $[GaAA_3]_4$) single crystal. The color of precursor solution gradually changed to yellow while heating at 50 ^oC for 10 h without stirring. The clear solution after filtrating the cloudy species was cooled down to room temperature. The colorless $[GaAA_3]_4$ singe crystal can be obtained after ~4 h.

Gallium(III) acetylacetonate ($GaAA_3$-MAI) single crystal: 185 mg Gallium(III) acetylacetonate and 80 mg MAI were dissolved in a 1 mL mixed solvent of gamma-butyrolactone and acetylacetonate with a ratio of 7:3, then 66 μL HI solution (55%) was added. The solvable precursor was obtained after heating at 100 ^oC for 30 min. The colorless $GaAA_3$-MAI single crystal can be obtained after 6-8 days.

Solar cell fabrication

Fluorine tin oxide (FTO)-coated glass with sheet resistance of 8 Ω sq^{-1} was washed by sonication with deionized water, acetone, ethanol and isopropanol for 10 min, respectively, and then treated with oxygen plasma for 10 min. Then a hole-transport layer of NiO_x was deposited on the FTO substrate by spin coating 125 mg of nickel (II) acetate tetrahydrate dissolved in ethyl alcohol (5 mL) and ethanol amine (30μL) at 5000 rpm for 30 s, following by sintering at 400 ^oC for 30 min.

The perovskite layer was deposited by one-step spin-coating method in an oxygen filled glovebox. The perovskite precursor solution was comprised of CsI (0.18 M), FAI (1.02 M), and PbI_2 (1.2 M) in GBL:DMSO 7:3 (v:v). Then, the $GaAA_3$ (0-60mg/mL) was added into precursor. The perovskite solution was spin coated in a two-step program at 1000 rpm and 4000 rpm for 4 s and 30 s, respectively. During the second step, 400 μL of chlorobenzene was poured on the spinning substrate 10 s prior to the end of the program. The substrates were then annealed at 100 °C for 30 min.

A PCBM /chlorobenzene (15 mg/1 mL) solution was spin coated on the perovskite layer at 2000 rpm for 30 s. Finally, BCP (6 nm) and Ag electrode (120 nm) were deposited by thermal evaporation, the active area of this electrode was fixed at 0.09 cm^2. Note that all of the solutions were filtered with 0.22 μm PVDF filters before spin coating.

Characterizations

A series single crystals of perovskite with dimensions of ~0.2 × 0.2 × 0.2 mm^3 was mounted on an Gemini S Ultra CCD area-detector diffractometer, equipped with a

graphite monochromator situated in the incident beam, for data collection at a temperature of 293 (2) K (Agilent Co.). The determination of unit-cell parameters and data collections were performed using the scan technique with Mo Kα radiation (λ = 0.71073 Å). The single crystal structure was resolved and refined by SHELXT and OLEX2 [1-3]. All H atoms were placed in geometrically calculated positions and refined using a riding model with C—H = 0.97 (methylene) and 0.96 Å (methyl), with Uiso(H) = 1.2Ueq(C) or 1.5Ueq(methyl C). Due to unresolved probable disorder, similarity and rigid-bond restraints were necessary for the anisotropic displacement parameters of the single crystal.

The powder crystal structure was characterized by Bruker D8 Advance X-ray diffractometer (XRD) with Cu Kα radiation at 40 kV and 40 mA. The top-down morphologies of the film were tested with scanning electron microscopy (SEM; FEI Apreo LoVac). The SEM images were tested directly on the as-prepared films. High resolution transmission electron microscope (HRTEM) was performed on JEOL JEM-2100F with acceleration voltage of 200 KV. We scraped the as-prepared perovskite thin films from glass, and ultrasonically dispersed in anhydrous chlorobenzene solvent. Afterward, we dropped 10 μL of the as-prepared solution on copper mesh with microgrid for the test of HRTEM. X-ray photoelectron spectroscopy (XPS) was measured with a PHI 5300 ESCA PerkinElmer spectrometer. All spectra were shifted to account for sample charging using inorganic carbon at 284.80 eV as a reference. Transient photovoltage/photocurrent decay curves and dark J–V curve were measured by an electrochemical workstation (ZAHNER GIMPS, Germany). The fluorescence

lifetime imaging microscopy was measured using a FV1200 laser scanning confocal microscopy. A 514 nm pulsed diode laser was used for excitation, with repetition rate of 40 MHz. PL lifetime was measured by FLIM with a FV1200 laser scanning confocal microscopy. A 488 nm pulsed diode laser was used for excitation with repetition rates at 40 MHz. The emission was filtered through a 50/50 dichroic beam splitter and a 700–800 nm long pass filter. The photodiode was inversely triggered at the falling edge of input signals to eliminate the disturbance of induced overshoot noise between input and output. Current-voltage (J-V) curves were measured using a digital source meter (Keithley 2400) and a Newport solar simulator (ORIEL-SOI3A) with an AM 1.5 G spectrum. The light intensity on the sample was adjusted to 1000 W m^{-2} using a standard Si cell (91150V). A black mask with an aperture (9 mm^2) was placed on the top of the device to control the effective electrode area. The external quantum efficiency (EQE) of perovskite solar cell device was measured by using spectrum corresponding system (Enlitech QE-R), with a Si reference solar cell to determine the spectral response.

Table S1. The detailed crystallographic parameters of $[GaAA_3]_4$, $GaAA_3$ and $GaAA_3$-MAI single crystal.

Crystal type / Parameters	$GaAA_3$-MAI	$GaAA_3$	$[GaAA_3]_4$
CCDC No.	1582691	1582689	1582690
Empirical formula	C_{16} H_{28} Ga I N O_6	C_{15} H_{21} Ga O_6	$[C_{15}$ H_{21} Ga $O_6]_4$
Formula weight	527.01	367.04	367.04
Temperature	293 (2) K	293 (2) K	293 (2) K
Wavelength	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, 14	monoclinic, 14	orthorhombic, 14
Unit-cell dimensions	a=12.3537(6) Å b= 12.2717(5) Å c= 15.5166(7)Å α =γ=90 β =112.273(6)	a = 8.1962(6) Å, b = 12.9937(11) Å , c = 16.3299(12) Å , α =β=γ = 90º,	a = 15.7074(8) Å, b = 32.8408(16) Å , c = 13.4120(9) Å , α =β=γ = 90º,
Volume	2176.82(19) $Å^3$	1739.1(2) $Å^3$	6918.5(7)$Å^3$
Z, density (calculated)	4, 1.608 $g·cm^{-3}$	4, 1.402 $g·cm^{-3}$	16, 1.410 $g·cm^{-3}$
Absorption coefficient	2.710 mm-1	1.606 mm-1	1.614 mm-1
F(000)	1052	760	3040
Crystal size	1mm×1mm×0.6mm	2mm×2mm×0.8mm	2mm×2mm×1.5mm
θ *range for data collection*	3.9230-26.6370	3.8450 - 25.2930	3.6700- 27.0590
Index limits	-14 ≤ h ≤ 7, -164≤ k ≤ 9, -13 ≤ l ≤ 18	-6 ≤ h ≤ 9, -9 ≤ k ≤ 15, -19≤ l ≤ 17	-20 ≤ h ≤ 19, -30 ≤ k ≤ 41, -15 ≤ l ≤ 17
Absorption correction	Numerical	Numerical	Numerical
Maximum/minimum transmission coefficients	none	none	none
Refinement method	Least Squares	Least Squares	Least Squares
Data/restraints/parameters	3838 /0/234	2503/0/205	10773 / 1/ 817
Goodness-of-fit on F2	1.131	1.035	1.072
Final R indices [I>2σ> 2(I)]	R1= 0.0522，wR= 0.1266	R1= 0.0351，wR= 0.0774	R1= 0.0546，wR=0.1302
R indices (all data)	R1= 0.0700, wR= 0.1424	R1= 0.0867, wR= 0.0867	R1= 0.1453, wR= 0.1453
Extinction coefficient	none	none	none
Largest difference map peak/hole	0.63/-1.96 e Å-3	0.25 / -0.32 e Å-3	0.43 / -1.17 e Å-3

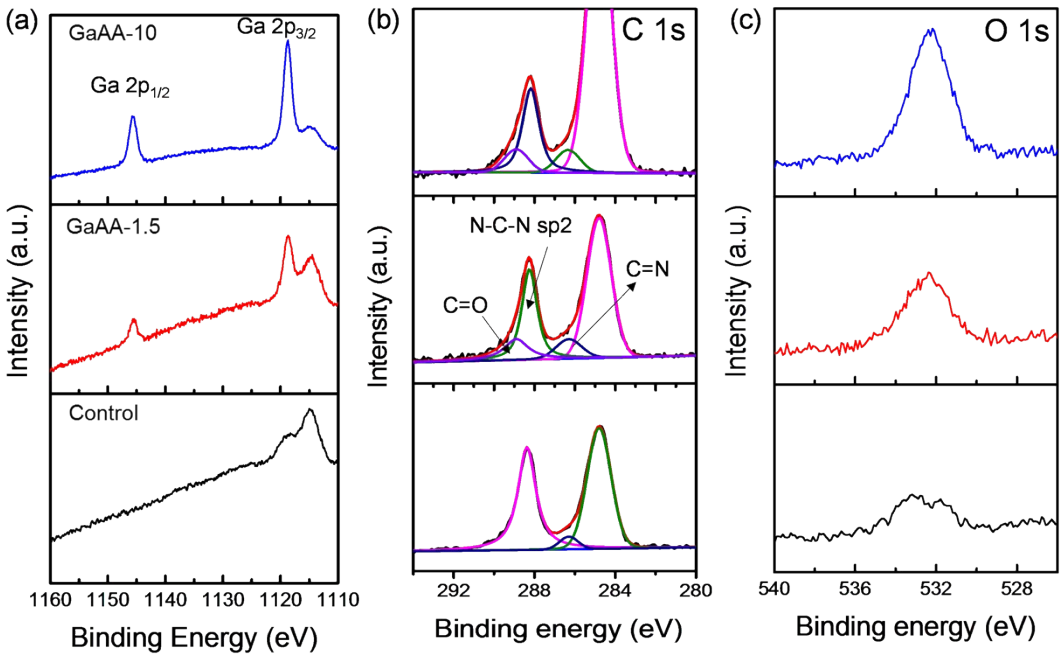

Fig. S1 High resolution XPS of $Cs_xFA_{1-x}PbI_3$-$[GaAA_3]_4$ thin films with different $GaAA_3$ concentration (Ga-0, Ga-1.5 and Ga-10). (a) $Ga2p_{1/2}$ and $Ga2P_{3/2}$. (b) C1s. (c) O1s.

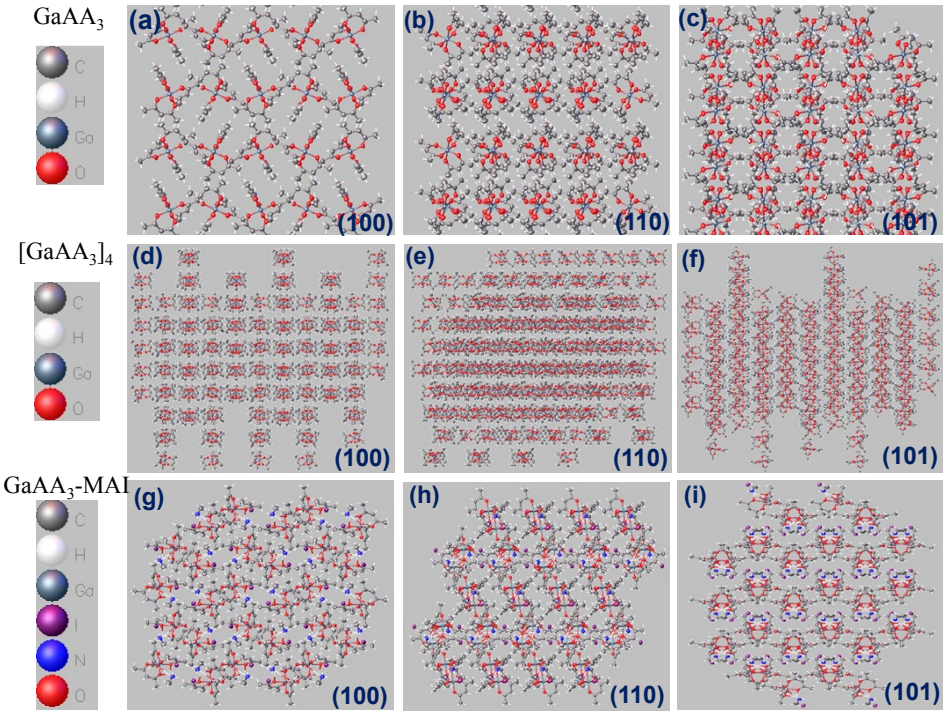

Fig. S2 Thermal ellipsoid representation of these single crystals along different directions. (a), (b), and (c) $GaAA_3$; (d), (e) and (f) $[GaAA_3]_4$; (g), (h) and (i) $GaAA_3$-MAI.

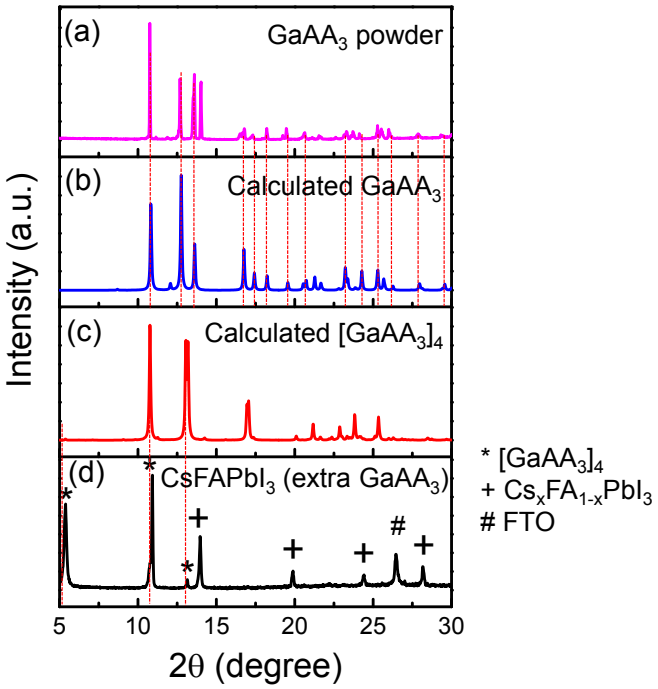

Fig. S3 XRD patterns of (a) $GaAA_3$ powder. (b) Calculated $GaAA_3$ from single crystal data. (c) Calculated $[GaAA_3]_4$ from single crystal. (d) $Cs_xFA_{1-x}PbI_3$-$[GaAA_3]_4$ with extra $GaAA_3$ additive.

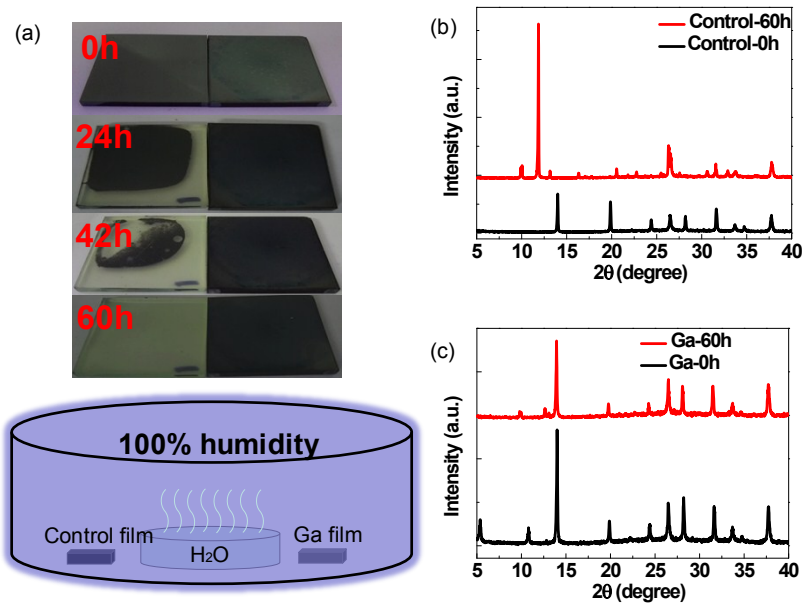

Fig. S4 Stability test on the as-prepared $Cs_xFA_{1-x}PbI_3$-$[GaAA_3]_4$ and control thin films with time. (a) Photo displays how the color of the films changed with time. (b) The corresponding XRD patterns.

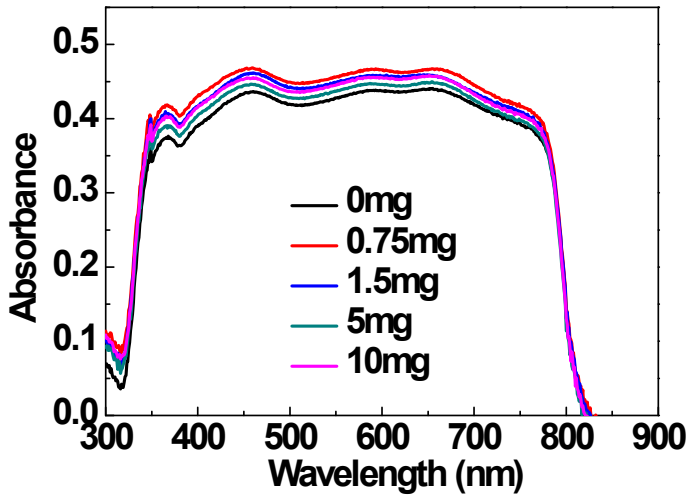

Fig. S5 Absorbance spectra of $Cs_xFA_{1-x}PbI_3$-$[GaAA_3]_4$ thin films with different $GaAA_3$ concentration.

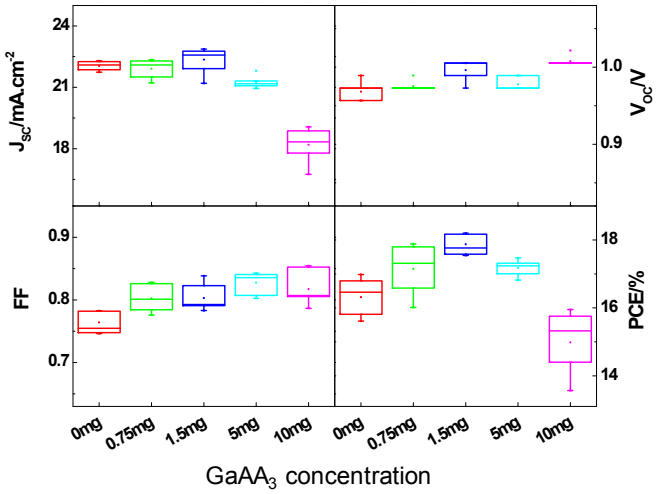

Fig. S6 Photovoltaic performances of core-shell $Cs_xFA_{1-x}PbI_3$-$[GaAA_3]_4$ solar cells as the function of $GaAA_3$ additive concentration.

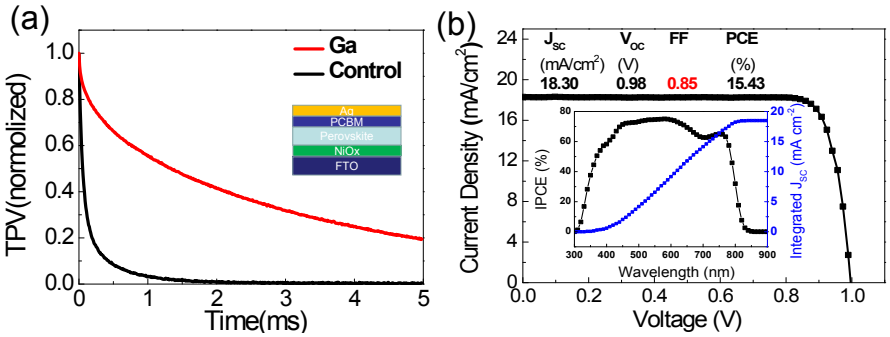

Fig. S7 (a) V_{OC} decay as the function of time. (b) J–V curve of the perovskite solar cell with the best FF as high as 0.85, inset shows the corresponding EQE and the integrated photocurrent.

References:

1 Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.

2 Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 6.14. Bruker AXS, Madison, Wisconsin, USA 2000.

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