

Supporting Information

Suppression of Sn²⁺ Oxidation and Formation of Large-Size Crystal Grains with Multifunctional Chloride Salt for Perovskite Solar Cell Applications

Minghao Wang,^a Wei Wang,^a Yifan Shen,^a Kun Cao,^a Junwen Chen,^a Xiangqing Zhao,^a Meng Xie^a and Shufen Chen^{*a}

^aState Key Laboratory of Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China.

*Corresponding author (email: iamsfchen@njupt.edu.cn)

Experimental Section

1. Materials

Tin iodide (SnI₂, 99.99%), tin fluoride (SnF₂, 99%), 2,5-diaminohydroquinone dihydrochloride (C₆H₈N₂O₂ · 2HCl, 97%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.9%), chlorobenzene (CB, anhydrous, 99.8%), and bathocuproine (BCP, 99.9%). All above-mentioned chemicals were obtained from Sigma-Aldrich. Formamidinium iodide (FAI, 99.99%) and methylammonium iodide (MAI, 99.9%) were purchased from Xi'an Polymer Light Technology Corp. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, PVP AI 4083) was purchased from Heraeus Materials Technology Co. Ltd. Buckminsterfullerene (C₆₀, 99%) was purchased from Nano-C Tech. All chemicals were used as received without further purification.

2. Preparation of perovskite solutions

The perovskite solutions were prepared in a glove box with both H₂O and O₂ < 0.01 ppm, which were prepared by dissolving MAI (40 mg), FAI (129 mg), SnI₂ (373 mg) and SnF₂ (16 mg) in a mixed solvent of 800 μL DMF and 200 μL DMSO. Then the as-prepared solutions were stirred for three days. Before use, add *x* mol C₆H₈N₂O₂ · 2HCl (*x* = 0.005, 0.01, and 0.015) to the precursor solutions, and continue stirring until they are dissolved. Finally, the solutions were filtered before use.

3. Device Fabrication

Firstly, the ITO-coated glass substrates (17 mm × 17 mm) were ultrasonically rinsed with acetone, ethanol and deionized water in sequence. After blown with high purity N₂ and dried in a vacuum with an oven, the ITO substrates were treated with UV-ozone for 12 min. Then, The PEDOT:PSS aqueous solution was filtered with a 0.45 μm filter before use, and then it was spin-coated onto the patterned ITO glass substrates at 3000 rpm for 30 s, followed by a 120 °C thermal annealing for 30 min. Then perovskite precursor solution was spin-coated on the PEDOT:PSS-coated ITO substrates at 5000 rpm for 60 s, and 120 μL CB was used as the anti-solvent to treat the perovskite films at the 15th s. After the spin coating was completed, the perovskite film was placed on a 90 °C hot stage to treat for 15 minute. The above operations were all done in a glove box filled with N₂. Finally, 40 nm C₆₀, 9 nm of BCP and 100 nm of Ag were sequentially deposited by thermal evaporation under a high vacuum of >10⁻⁵ Pa, forming a series of PSCs. The active area for all devices is 0.1 cm².

4. Device characterization

The scanning electron microscope (SEM) images of FA_{0.75}MA_{0.25}SnI₃ perovskite films were obtained by using a Hitachi S-4800 field emission scanning electron microscopy. The X-ray diffraction (XRD) patterns were carried out using a Bruker D8 ADVANCE XRD equipment. The steady-state photoluminescence (PL) was measured with a Hamamatsu C12132 fluorescence lifetime spectrometer at an excitation wavelength of 479 nm. The X-ray photoelectron spectroscopy (XPS) spectra of FA_{0.75}MA_{0.25}SnI₃ perovskite films on ITO glass substrate were carried out by using PHI Quantera SXM (ULVAC-PHI) in an ultrahigh-vacuum environment of 5×10⁻¹¹ Pa. The current density-voltage characteristics were carried out using Keithley 2400 under AM 1.5G illuminations (100 mW cm⁻²) from a solar simulator (Oriel Sol3A Class Solar Simulator (94023A)) in a glove box with N₂ atmosphere (H₂O < 0.1 ppm and O₂ < 1 ppm). The incident photon to current efficiency (IPCE) spectra were carried out by QTest Station 500AD Solar Cell Quantum Efficiency System (CROWNTECH, INC). The ultraviolet photoelectron spectroscopy (UPS) was operated with a He discharged lamp (He I 21.22 eV, Kratos Axis Supra). The electrochemical impedance spectra (EIS) were studied with a CHI660 electrochemical workstation (CH Instrument Inc.), which were measured within a frequency range of 10⁵-1 Hz at 0.4 V under dark condition.

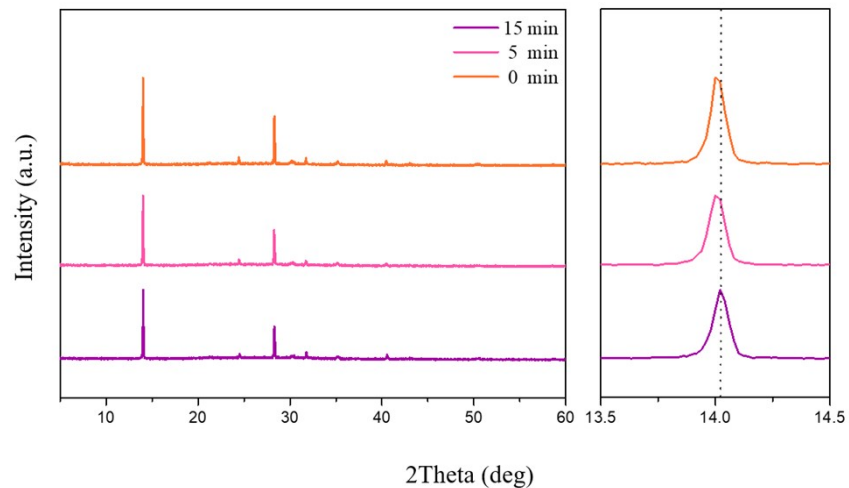


Fig. S1. XRD patterns for the precursor films annealed for 0 min, 5 mins and 15 mins.

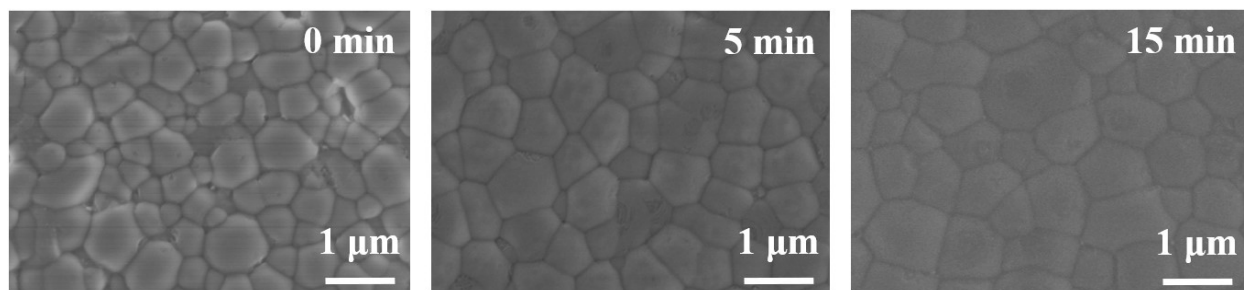


Fig. S2. SEM patterns for the $\text{FA}_{0.75}\text{MA}_{0.25}\text{SnI}_3$ films annealed for 0 min, 5 mins and 15 mins.

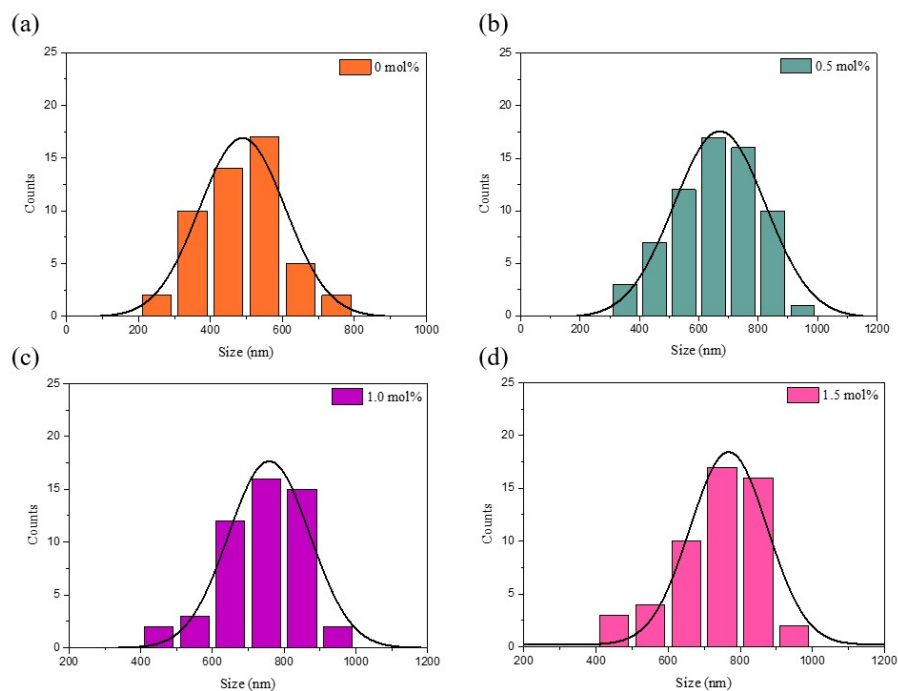


Fig. S3. Grain size statistics of the pristine perovskite and $C_6H_8N_2O_2 \cdot 2HCl$ -incorporated perovskites with different doping concentration from top-view SEM images: (a) 0 mol%, 497 nm, (b) 0.5 mol%, 678 nm, (c) 1.0 mol%, 764 nm, (d) 1.5 mol%, 781 nm.

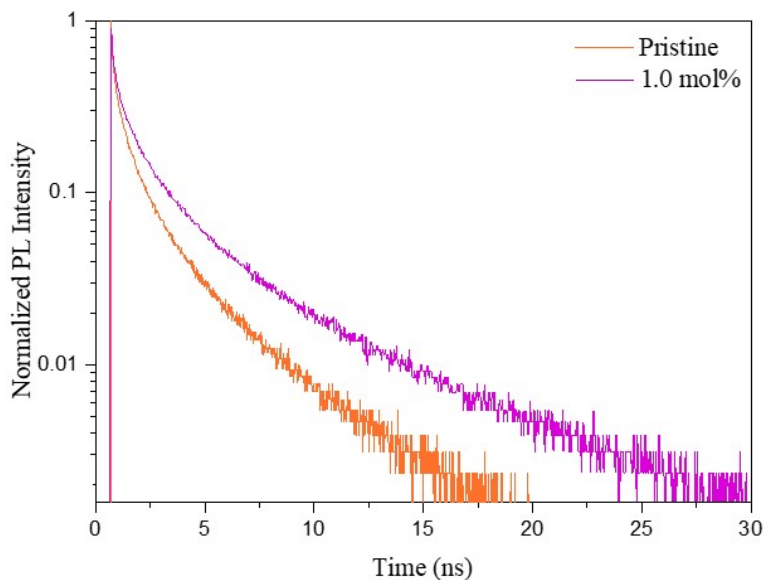


Fig. S4. Time-resolved PL spectra of pristine and 1.0 mol% $C_6H_8N_2O_2 \cdot 2HCl$ -doped perovskites.

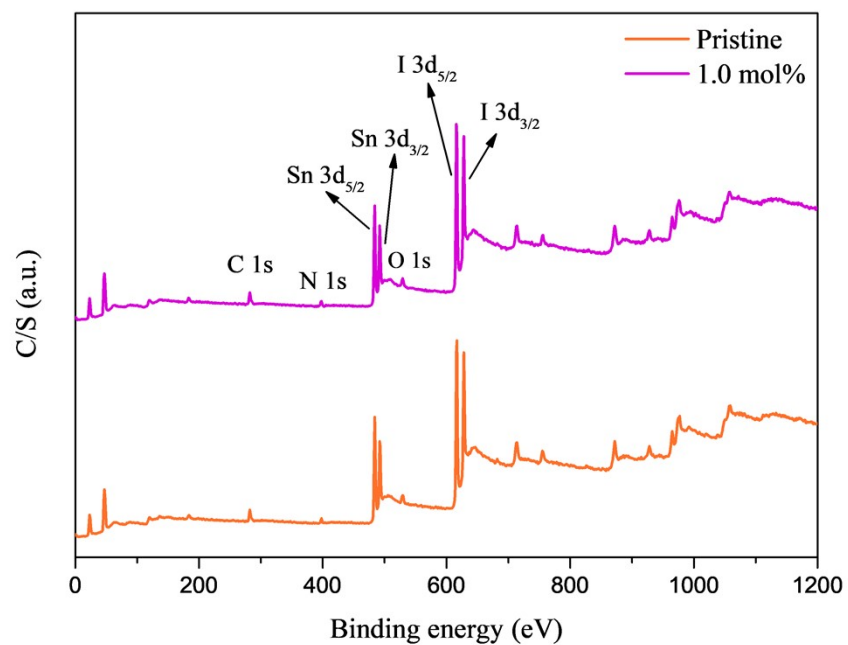


Fig. S5. XPS survey spectra obtained from control and $C_6H_8N_2O_2 \cdot 2HCl$ -doped perovskite films.

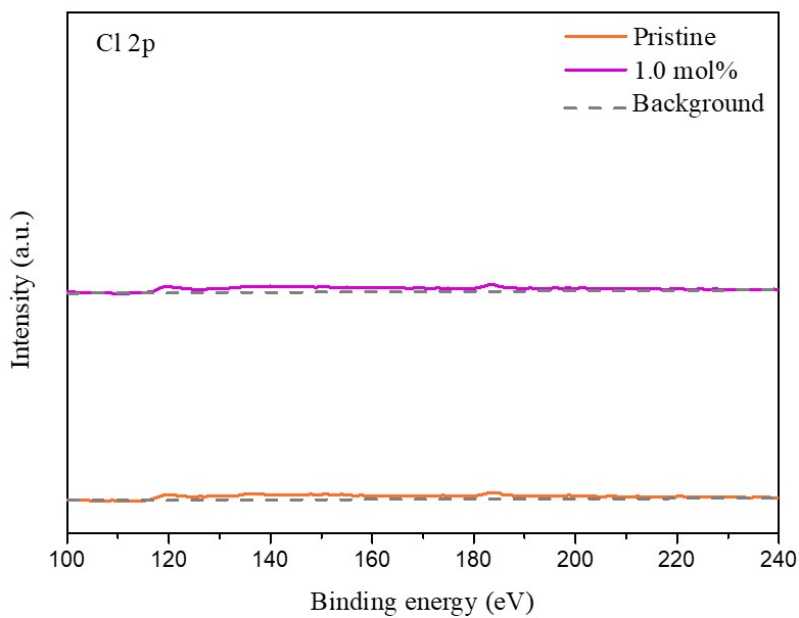


Fig. S6. The Cl 2p XPS spectra of $C_6H_8N_2O_2 \cdot 2HCl$ -doped and control $FA_{0.75}MA_{0.25}SnI_3$ films.

Table S1. Fitted photoluminescence lifetimes for pristine and 1.0 mol% C₆H₈N₂O₂ · 2HCl -doped FA_{0.75}MA_{0.25}SnI₃ perovskite films with a bi-exponential decay model. Here, A₁ and A₂ are fractional intensities, and τ₁ and τ₂ are lifetimes. The average carrier lifetime was calculated with $\tau_{\text{avr}} = A_1\tau_1 + A_2\tau_2$.

Sample	τ ₁ (ns)/A ₁ (%)	τ ₂ (ns)/A ₂ (%)	χ ²	τ _{avr} (ns)
Pristine	0.75/36.32	5.59/63.68	0.934	3.83
1.0 mol% C ₆ H ₈ N ₂ O ₂ · 2HCl	0.92/32.46	8.12/67.54	1.027	5.77