Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for:

Stabilizing $FASnI_3$-based perovskite light-emitting diodes with crystallization control

Guoling Zhang[a#], Shiyu Xing[a#], Xuhui Cao[a], Baodan Zhao[a*], and Dawei Di[a*]

[a]State Key Laboratory of Extreme Photonics and Instrumentation, College of Optical Science and Engineering; International Research Center for Advanced Photonics, Zhejiang University, Hangzhou, 310027, China

[#]These authors contributed equally to this work.

*Corresponding author, E-mail: daweidi@zju.edu.cn (D.D.); baodanzhao@zju.edu.cn (B.Z.).

Methods

Materials

Formamidinium iodide (FAI, TCI, 99.99%), phenethylamine iodide (PEAI, TCI, > 98.0%), tin (Ⅱ) iodide (SnI_2, Alfa Aesar, 99.999%), tin (Ⅱ) fluoride (SnF_2, Sigma-Aldrich, 99%), Tin (powder, Sigma-Aldrich, 99.8%), Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios PVP Al4083, Heraeus), 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi, Xi'an Polymer Light, > 99.9%), lithium fluoride (LiF, Sigma-Aldrich, 99.995%). All the materials were used as received without any purification.

Preparation of perovskite precursors

The perovskite precursor solution was prepared by dissolving FAI, PEAI and SnI_2 in a mixed solution of DMSO and DMF (v/v = 1:4) at a molar ratio of (1-x%):x%:1 with a concentration of 0.4 M, and 5 mg mL^{-1}. Sn powder and 10% molar ratio SnF_2 (10 mol% relative to SnI_2) were added into the precursor to suppress the oxidation of Sn^{2+}. All precursor solutions were stirred at room temperature 2 hours in the glovebox and filtered through a 0.22 μm PTFE filter before use.

PeLED fabrication

The ITO glasses substrates were ultrasonically cleaned in detergent solution, deionized water, acetone, isopropyl alcohol, and ethanol for 30 min, respectively, and then dried by nitrogen flow. The substrates were further exposed to UV-Ozone for 20 min before use. A hole-transport layer (HTL) was prepared by spin-coating PEDOT:PSS at 5000 r.p.m. for 50 s, and annealing at 150 °C for 15 min in ambient air. After cooling to room temperature, the substrates were transferred into the N_2-filled glovebox. The perovskite films were deposited with two-step spin-coating procedures: (1) 1,000 r.p.m. for 10 s with an acceleration of 200 r.p.m. s^{-1} and (2) 5,000 r.p.m. for 40 s with a ramp-up of 800 r.p.m. s^{-1}. Antisolvent (200 μL of Toluene) was dropped on the spinning substrate during the second spin-coating step at 7 s before the end of the procedure. The substrates were then transferred onto a hotplate and heated at 70 °C for 10 min. After cooling to room temperature, the substrates were transferred to the evaporation system. Finally, TPBi (40 nm), LiF (1 nm) and Al (100 nm) were sequentially deposited on top of the perovskite by thermal evaporation.

Characterization of PeLED performance

The current density–voltage–radiance (*J–V–R*) and EQE data of the PeLEDs were acquired by scanning the voltage from zero bias to forward bias at a rate of 0.2 V s^{-1} in a glovebox by using a Keithley 2400, and an integration sphere fiber coupled with a QE Pro spectrometer. The stability measurements were performed in a N_2 glovebox at ambient temperature (20 ± 5 °C). The concentrations of water and oxygen in the glovebox were maintained to be <0.1 ppm.

XRD measurements

The XRD patterns were taken by an X-ray diffraction system with a Bruker APEXII diffractometer (Cu Kα irradiation, λ = 1.5406 Å). The scan speed is 5.0 deg/min. We performed XRD measurements of glass/ITO/PEDOT:PSS/perovskite samples.

Steady-state PL measurements

The steady-state PL spectra of the films were collected using an Ocean Optics QE-Pro spectrometer; a 405 nm continuous-wave laser was used to excite the perovskite films.

SEM measurements

SEM images were collected by using a Hitachi SU-8010 instrument.

UV–Visible absorption measurements

The UV-vis absorption spectra were measured using an Agilent Cary 5000 UV–Vis–NIR spectrophotometer. We performed the UV-vis absorption spectra of glass/ perovskite samples.

TCSPC measurements

Time-correlated single photon counting (TCSPC) measurements was used to determine the PL lifetimes of the samples. A 400 nm laser excitation beam was focused onto the perovskite samples, and the PL was collected by an object and detected after a long-pass filter (FELH450, Thorlabs) by a fiber-coupled avalanche photodiode (APD; ID100, IDQ). A PicoHarp 300 counter (PicoQuant) was used to obtain the time-resolved decay curves. The excitation energy density was attenuated to 160 nJ cm^{-2} using a tunable neutral-density filter. For the TCSPC measurements, the perovskite films were sealed in a N_2-filled chamber with a pair of quartz windows.

XPS measurements

XPS measurement was performed in a Thermo Scientific ESCALAB 250Xi surface analysis system equipped with a monochromatic Al KαX-ray gun (hv = 1486.6 eV).

Femtosecond transient absorption measurements

Femtosecond transient absorption (TA) experiments were carried using a Yb:KGW femtosecond laser (Pharos, Light Conversion Ltd; 1030 nm, ~270 fs, 200 μJ/pulse and 50 kHz) and a Femto-TA100 spectrometer (Time-Tech Spectra LLC). The 1030 nm output pulse from the laser was split in two parts with a 90/10 beam splitter. The reflected part was used to pump an Orpheus-F optical parametric amplifier to generate a laser pulse of 400 nm as the pump beam. The transmitted beam was split again into two beams. One of the beams (~30%) was attenuated with a neutral density filter and focused into a 3-mm thick YAG crystal to generate a white light continuum used for probe beam. The probe beam was focused with an Al parabolic reflector onto the sample. After the sample, the probe beam was collimated and then focused into a fiber-coupled spectrometer with CMOS sensors and detected at a frequency of 10 kHz. The intensity of the pump pulse was controlled by a tunable neutral-density filter

wheel. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump pulses were chopped by a synchronized chopper at 5 kHz. For TA measurements, the perovskite films were sealed in a N_2-filled chamber with a pair of quartz windows for light propagation.

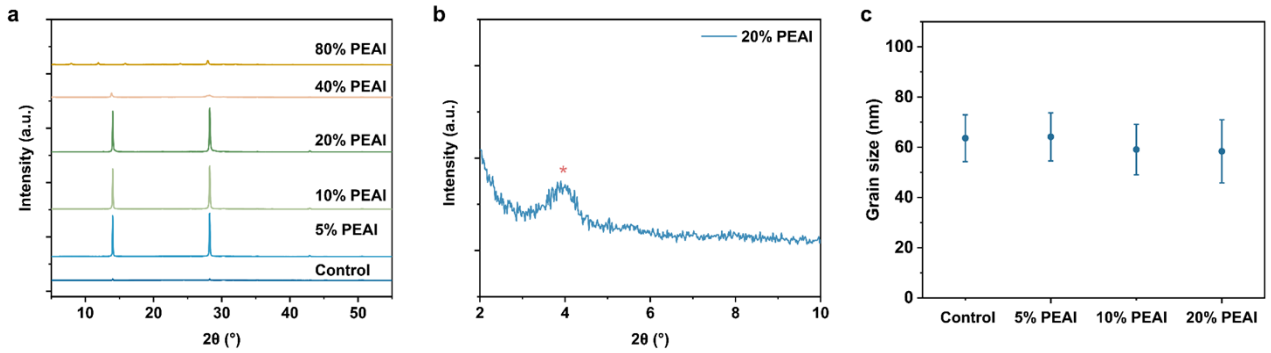

Figure S1. Additional structural characterization of the perovskite samples. a) XRD patterns of the perovskite samples (control, 5% PEAI, 10% PEAI, 20% PEAI, 40% PEAI, 80% PEAI) with a MgF_2 capping layer. b) XRD patterns of the 20% PEAI samples for a 2θ range of 2-10 degrees. c) The average grain sizes of the samples estimated using Scherrer's equation (control, 5% PEAI, 10% PEAI, 20% PEAI).

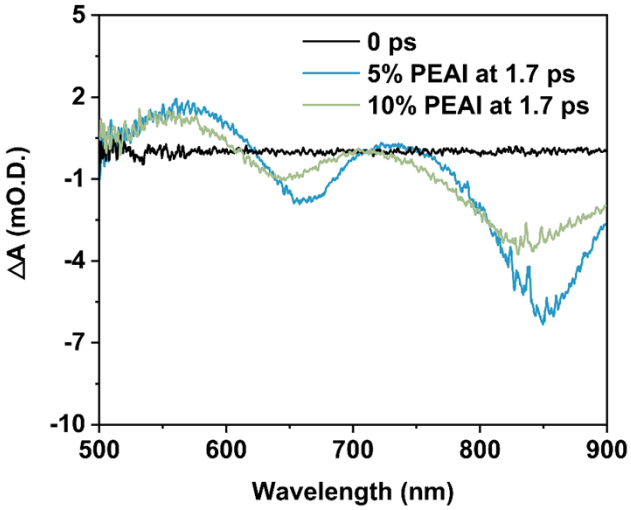

Figure S2. Transient absorption spectra of the 5% and 10% PEAI samples.

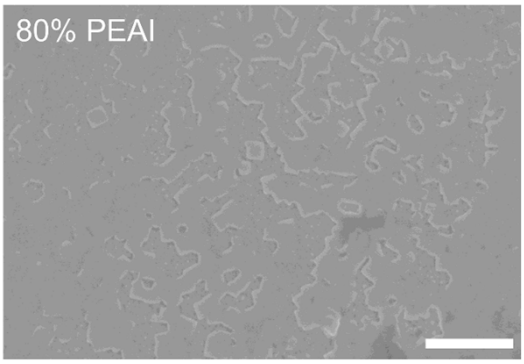

Figure S3. The SEM images of the 80% PEAI sample. Scale bar: 2 μm.

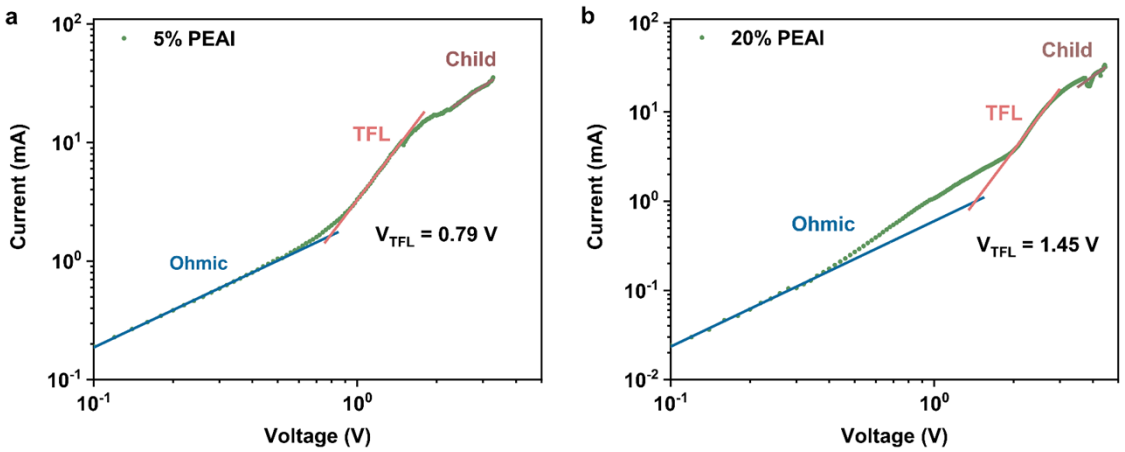

Figure S4. Additional SCLC measurements. a, b) Current-voltage characteristics of the 5% and 20% PEAI samples.

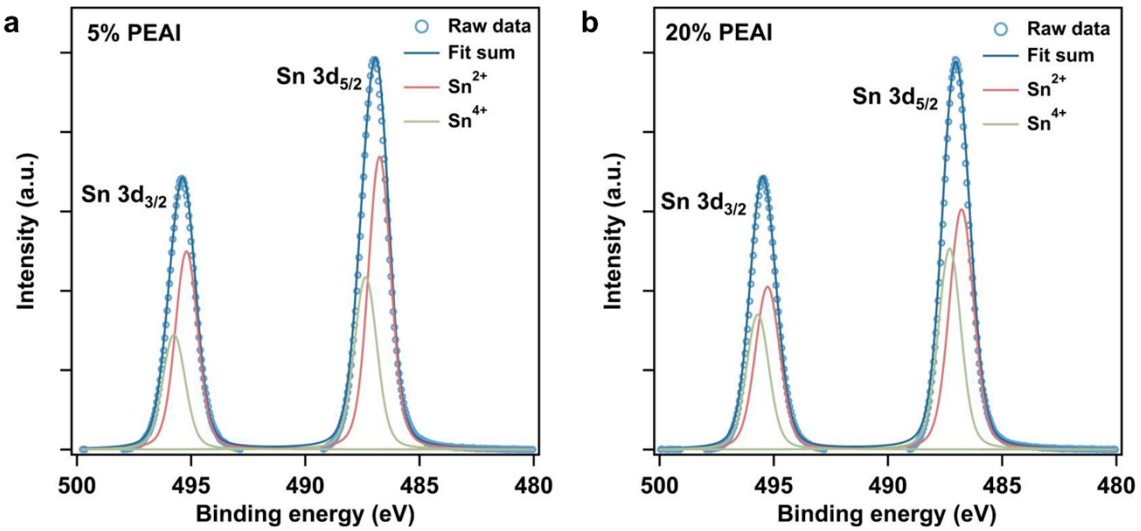

Figure S5. Additional XPS data of the perovskite samples. a, b) Sn 3d spectra of the 5% and 20% PEAI samples.

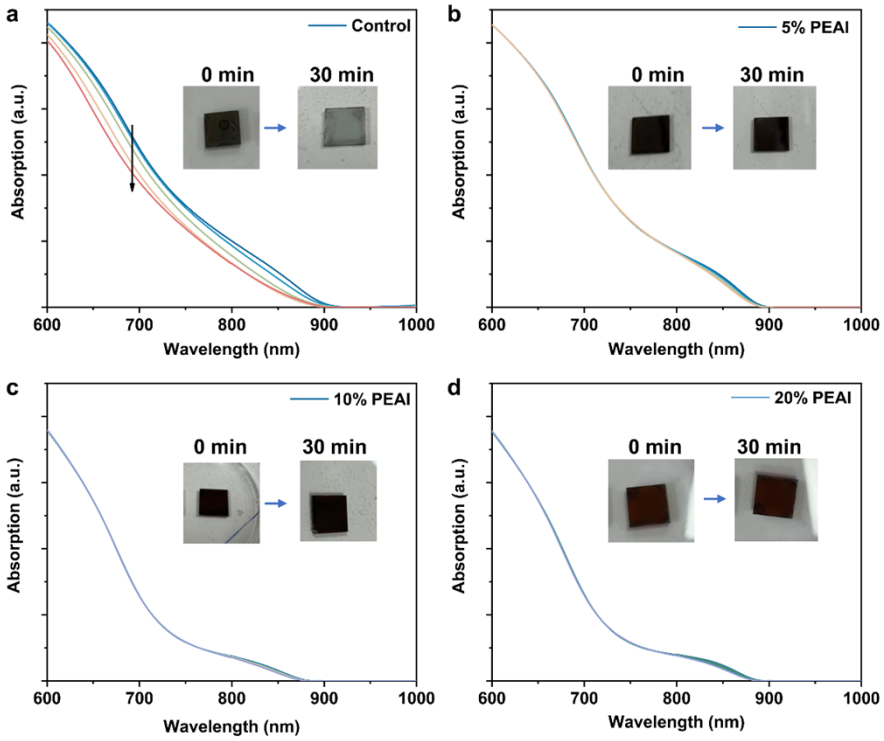

Figure S6. Absorption spectra of perovskite samples exposed in air. a-d) Evolution of the absorption spectra of $FASnI_3$ films with different ratio of PEAI (0%, 5%, 10%, 20%) exposed in air over 30 min. The inserts show the photos of perovskite film under ambient light.

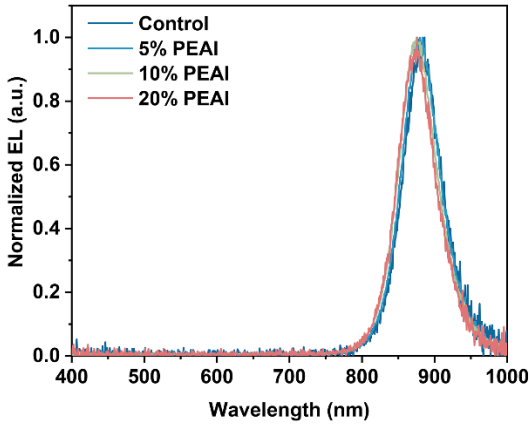

Figure S7. Normalized EL spectra of the PeLEDs.

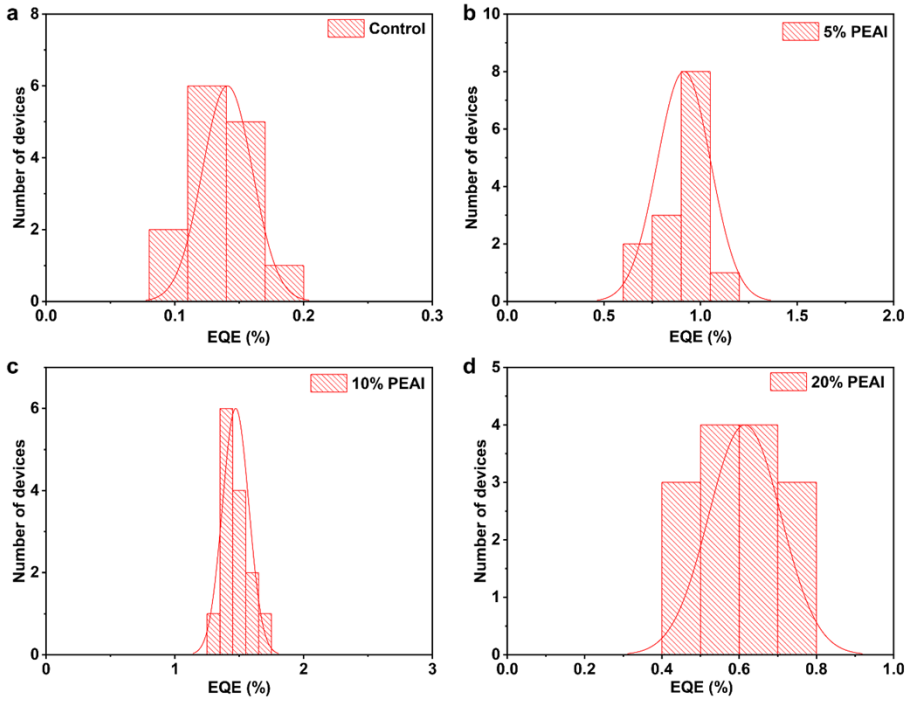

Figure S8. Peak EQE histograms for the PeLEDs. a-d) Peak EQE histograms of the control (14 devices), 5% PEAI (14 devices), 10% PEAI (14 devices) and 20% PEAI (14 devices)-based PeLEDs.

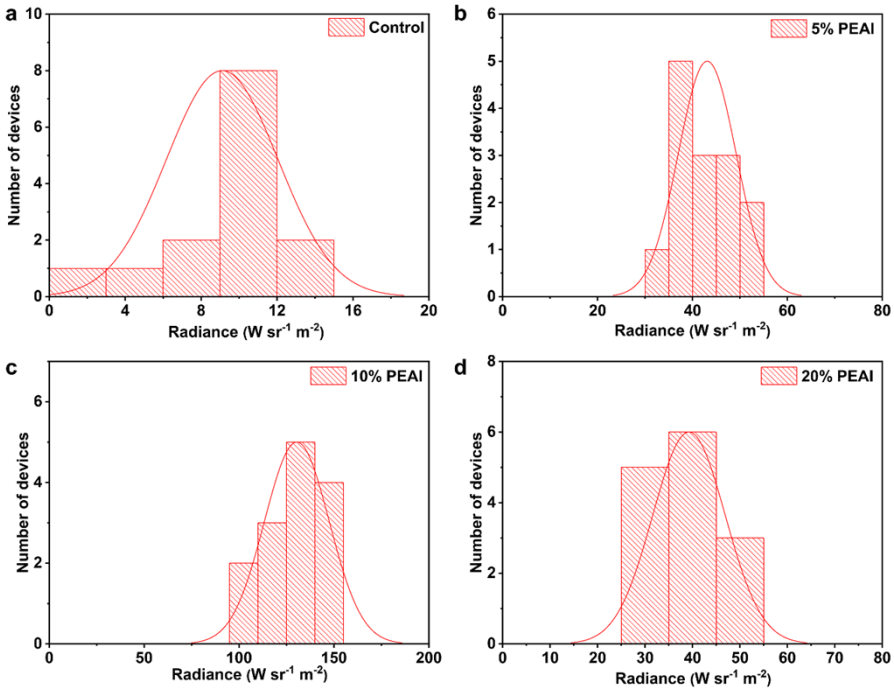

Figure S9. Histograms of maximum radiance for the PeLEDs. a-d) Maximum radiance histograms of the control (14 devices), 5% PEAI (14 devices), 10% PEAI (14 devices) and 20% PEAI (14 devices)-based PeLEDs.

Table S1. Perovskite film thickness information.

PEAI molar fraction (%)	Control (0)	5	10	20	40	80
Film thickness (nm)	149	101	100	102	97	79

Table S2. Summary of PeLED performance.

PEAI molar fraction (%)	Peak EQE (%)	Max radiance (W sr^{-1} m^{-2})	T_{50} at 100 mA cm^{-2} (h)
Control (0)	0.13	11.2	0.1
5	0.98	63.1	1.8
10	1.5	145.5	10.3
20	0.74	32.5	1.1