

Supplementary Information

Ion migration inhibition and defect passivation via sulfonate salt coordination for high- performance perovskite solar cells with enhanced phase stability

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Experimental

Materials

The fluorine-doped tin oxide (FTO) glass substrates were purchased from Advanced Electronic Technology Co., Ltd. The SnO₂ colloid precursor was obtained from Alfa Aesar (15% in H₂O colloidal dispersion). Chlorobenzene (CB, 99.9%), N, N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.7%), isopropyl alcohol (IPA, 99.99%) and acetonitrile (99%) were obtained from Sigma-Aldrich. 6-Bromo-2-naphthyl triflate (BNT, 95%) was purchased from Picasso. lead iodide (PbI₂), cesium iodide (CsI), lead chloride (PbCl₂), Formamidinium iodide (FAI), methylamine bromide (MABr), methylamine hydrogen chloride (MACl), 2,2',7,7'-tetrakis (N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD, 99.5%), 4-tertbutylpyridine (tBP, analytically pure), and bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI) were purchased from Xi'an Yuri Solar Co., Ltd.

Device fabrication

The pre-patterned FTO glass substrates were cleaned sequentially by sonication washing with anhydrous ethanol, deionized water, acetone, and anhydrous ethanol for 15 min. After drying with pure N₂, the pre-cleaned FTO substrate was treated with Ultraviolet ozone for 20 min to remove residual organic matter on the surface, then the substrate was spin-coated with a thin layer of SnO₂ aqueous solution at 3,000 rpm for 30 s, and annealed on a hot plate at 150°C for 30 min. After cooling down to room temperature, the substrates were transferred into a glovebox filled with nitrogen for subsequent processing. To fabricate the CsFAMA-based perovskite film, PbI₂ (600

mg), CsI (16.9 mg), and PbCl₂ (9 mg) were dissolved in 1 mL of a mixed solvent of DMF-DMSO (v/v = 9:1) with different concentration of D-PFPAA solution, and then stirred on a hot plate at 70 °C. Besides, FAI (60 mg), MABr (6 mg), and MACl (6 mg) were dissolved in IPA. For first step, the PbI₂ solution was spin-coated on the SnO₂ substrate at 1500 rpm for 30 s and annealed at 70 °C for 10 s. And for second step, the organic cation precursor was spin-coated on the PbI₂ film at 1500 rpm for 30 s, followed by thermal annealing at 150°C for 15 min. Afterwards, the hole transport layer (HTL) was spin coated on the top of the perovskite layer at 4000rpm for 30 s. The HTL was prepared by dissolving 72.3 mg of Spiro-OMeTAD in CB (1 mL) doped with 17.5 μL Li-TFSI solution (520 mg of Li-TFSI in 1 mL of acetonitrile) and 28.8 μL tBP. Finally, the 90 nm thickness Ag electrode with active area of 0.08 cm² was deposited on the HTL and FTO glass substrates by magnetron sputtering deposited system (JGP-450A).

Devices Characterization

Perovskite film surface morphology was obtained by scanning electron microscopy (SEM, FEI Quanta 650 FEG). Perovskite crystal structure was analyzed by X-ray diffraction (XRD, X Pert PRO MPD) using Cu-Kα radiation as the X-ray source. Photoluminescence spectroscopy (PL) time-resolved photoluminescence spectroscopies (TRPL) were performed using a fluorescence spectrometer (FLS 1000, Edinburgh Instruments). X-ray photoelectron spectroscopy (XPS) was carried out by an X-ray photoelectron spectrometer (AXIS Ultra DLD) with a monochromatic Al Kα X-ray source. External Quantum Efficiency (EQE) was measured by an incident photo-to-electron conversion efficiency (IPCE) system (PVE300, Bentham, Inc.). The device

performance was tested by electrochemical workstation (CHI660D, CH Instruments)

under illumination of an AM 1.5G solar simulator (Zolix, 150ss).

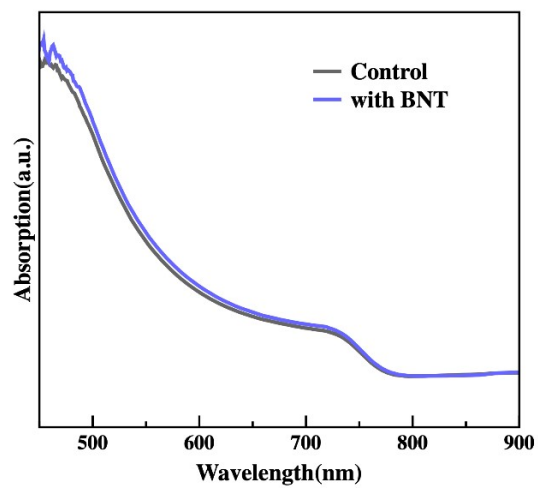


Figure S1. The UV-vis spectra of control film and film with BNT.

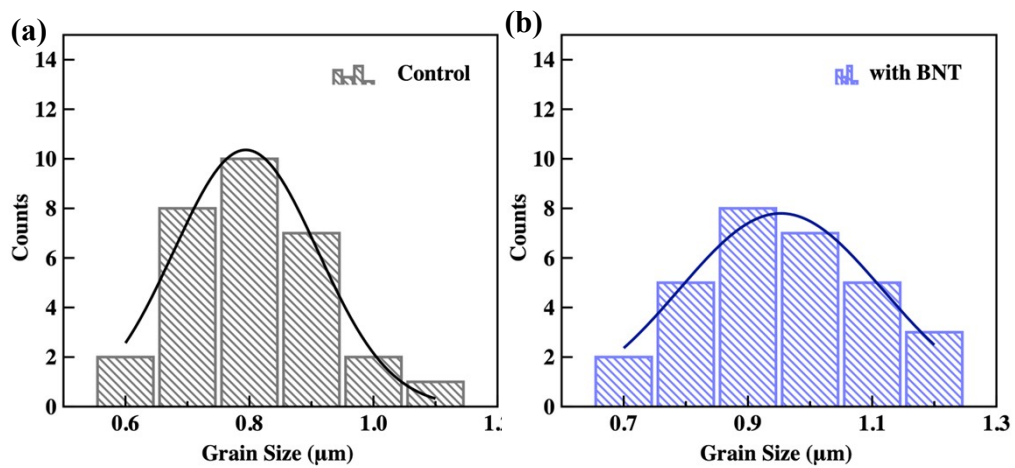


Figure S2. The histogram of the grain size distribution obtained from the SEM for the control and BNT modified perovskite films.

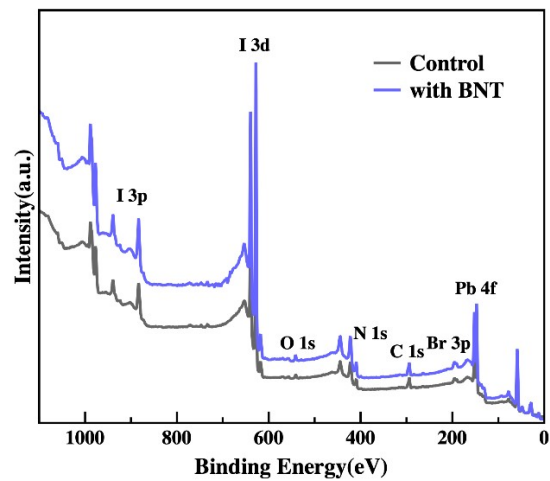


Figure S3. XPS measurement result of pure perovskite film and perovskite/BNT film.

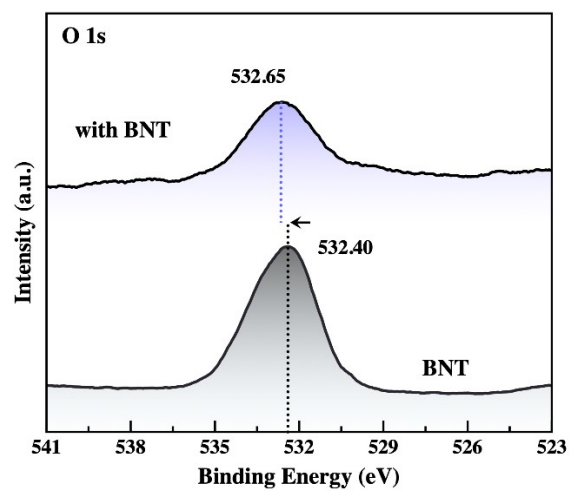


Figure S4. O 1s XPS spectra of control film and film with BNT.

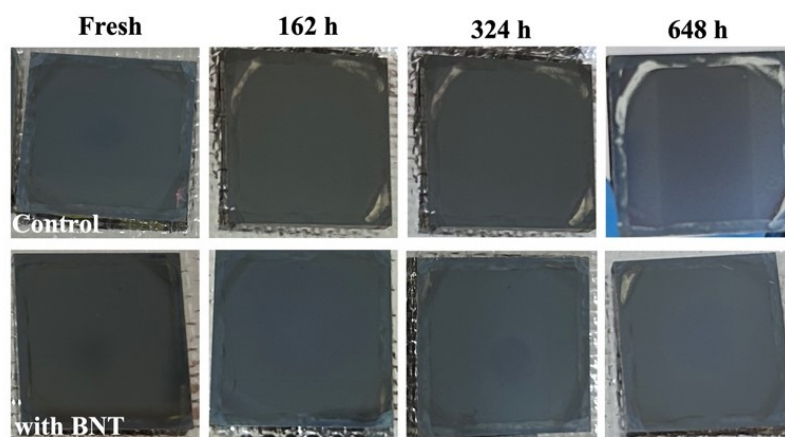


Figure S5. Camera pictures of control film and film with BNT after humidity environment aging.

Table S1. the fit results of Carrier lifetime parameters for perovskite film

Sample	τ_{ave} (ns)	τ_1 (ns)	A ₁ (%)	τ_2 (ns)	A ₂ (%)
Control	106.9	142.1	36.4	53.0	63.7
with BNT	266.3	320.5	44.0	68.9	56.1