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Electronic Supplementary Information (ESI)

Tuning A-site Cation Composition of FA Perovskite for Efficient and Stable NiO-based p-i-n Perovskite Solar Cells

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Experimental

Materials: Formamidinium iodide (FAI), methylammonium iodide (MAI), lead iodide(PbI_2) and lead bromide ($PbBr_2$)_are purchased from Dyesol. Cesium iodide (CsI) and other material are obtained from Sigma-Aldrich.

Device fabrication: The NiO films were deposited according to our previous work (reference). In brief, patterned FTO glass substrates were cleaned by successively sonicated in de-ionized water, acetone, iso-propanol and ethanol for 30 minutes. After dried at 120^{o}C, FTO glass were placed under UV-ozone treatment for 30 minutes. NiO precursor solution was the spin-coated onto the substrate at 2900 rpm for 25 s. Afterwards, the NiO films were sintered at 550 ^{o}C for 2 h in air followed by cooling down to room temperature. The perovskite solutions were prepared by dissolving PbI_2, MAI, FAI, CsI and $PbBr_2$ of desired compositions into dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) at a volume ratio of 2:3 and stirred at 60°C overnight. The perovskite dispersion consists of 1.2 M perovskite with 0.12 M PbI_2. Perovskite layer was deposited according to reported method with minor modifications (reference). Specifically, 35 microliter of perovskite dispersion was dropped onto the substrate and spin-coated at 2000 r.p.m. for 10s and 6000 r.p.m for 20s. At the 5th second of the second step, 0.7 mL of toluene was poured onto the spinning film. After the spin-coating, the perovskite films were annealed at 95°C for 1h. Thereafter, the cooled perovskite films were coated with PCBM (20 mg/mL in chlorobenzene) at 2500 rpm for 30 s. Finally, 100 nm of silver was thermally evaporated onto the substrate through a shadow mask at with active area confined by the cathode and anode at 0.10 cm^2.

Characterizations: Scanning Electron Microscopy images were obtained from JEOL 7100F operated at 5 kV. X-ray diffraction (XRD) patterns of the samples were done by Philips, PW 1830 with Cu Ka radiation. PCE output (J-V) were measured by a solar simulator (Oriel, 450 W Xe lamp, AM 1.5 global filter) equipped with an electrochemical workstation (Zanher, Zennium) with calibrated light source at 1 sun (100 mW/cm^2). Light source calibration was done by using an optical power meter (Newport, model 1916-C) equipped with a Newport818P thermopile detector. In addition, IPCE measurements were carried out with the tunable light source (TLS03) with a frequency of 100 Hz by the above electrochemical workstation. IMVS and IS were taken by the e Zahner Zennium C-IMPS system with a light-emitting diode (λ = 536 nm). UV–vis absorption spectra were recorded on a Perkin–Elmer UV–vis spectrophotometer (model Lambda 20). Ultra-violet photoelectron spectroscopy was measured by Axis Ultra DLD.

Table S1. Optimization of Br content.

Br content (%)	22	17	13	11	9	4	0
Efficiency (η/%)	12.3	13.9	14.5	14.7	14.3	12.6	10.0
Open circuit Voltage (Voc/V)	1.06	1.05	1.07	1.05	1.05	1.01	0.97
Short circuit current density (Jsc / mA/cm2)	18.0	19.7	18.9	19.5	20.0	18.5	17.2
Fill factor (FF)	0.643	0.671	0.718	0.719	0.686	0.679	0.596

Table S2. Photovoltaic performance of perovskites with various ratios of Cs^+ to MA^+.

Cationic composition	PCE (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)
$FA_{3/4}Cs_{3/40}MA_{7/40}$	15.5	1.07	20.7	69.5
$FA_{3/4}Cs_{5/40}MA_{5/40}$	16.4	1.07	21.3	72.6
$FA_{3/4}Cs_{7/40}MA_{3/40}$	18.6	1.09	22.8	74.6
$FA_{3/4}Cs_{8/40}MA_{2/40}$	17.3	1.11	22.5	69.1
$FA_{3/4}Cs_{9/40}MA_{1/40}$	15.8	1.10	22.0	65.4

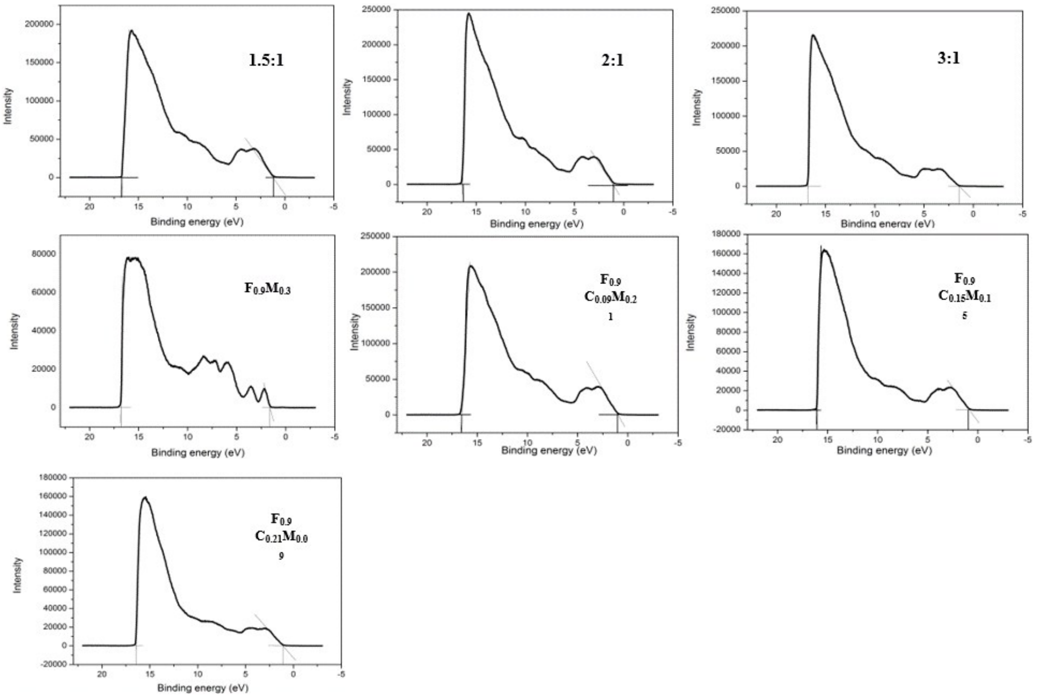

Figure S1. UPS spectra of the various perovskite compositions.

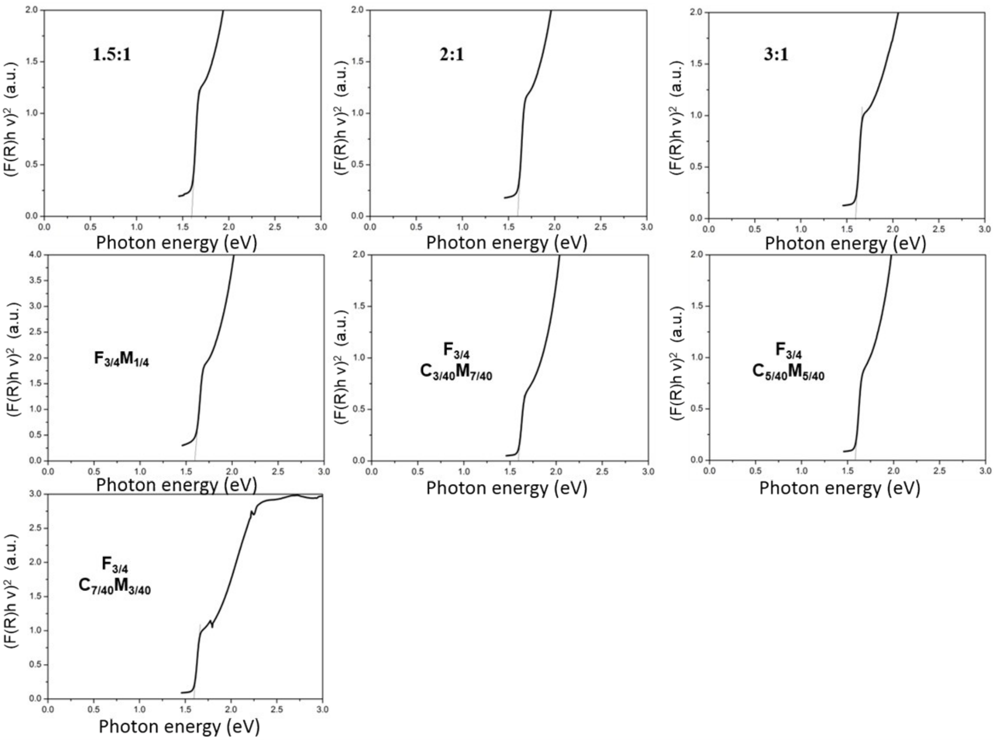

Figure S2. Absorption spectra of the various perovskite compositions.

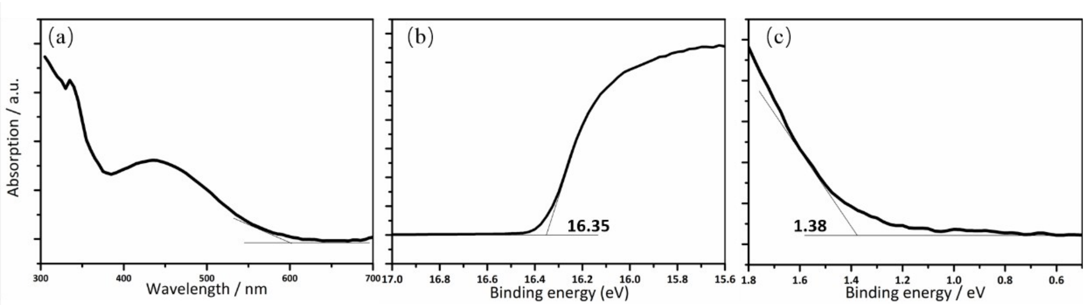

Figure S3. Absorption and UPS spectra and of PCBM thin film.

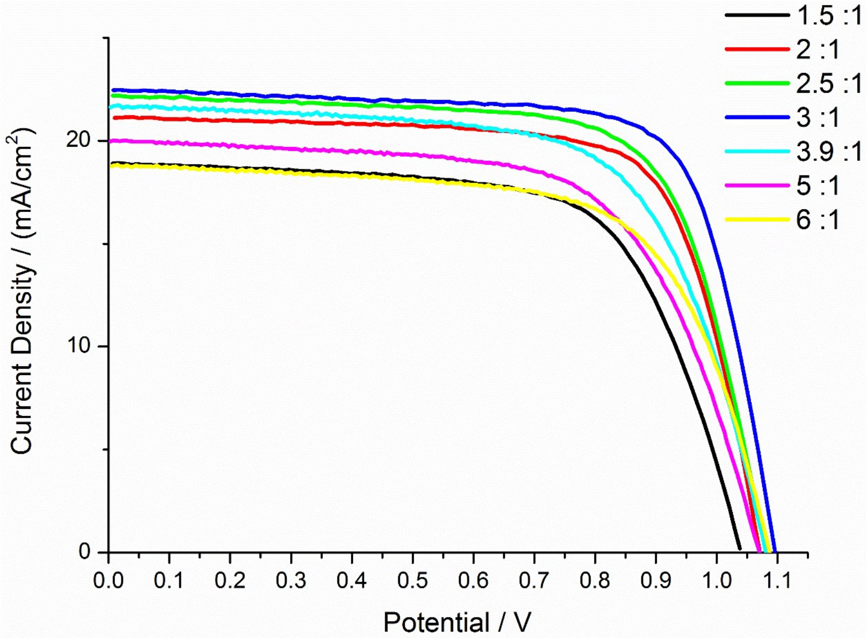

Figure S4. Effect of the FA：(Cs+MA) ratio on performance of the NiO p-i-n perovskite solar cells.

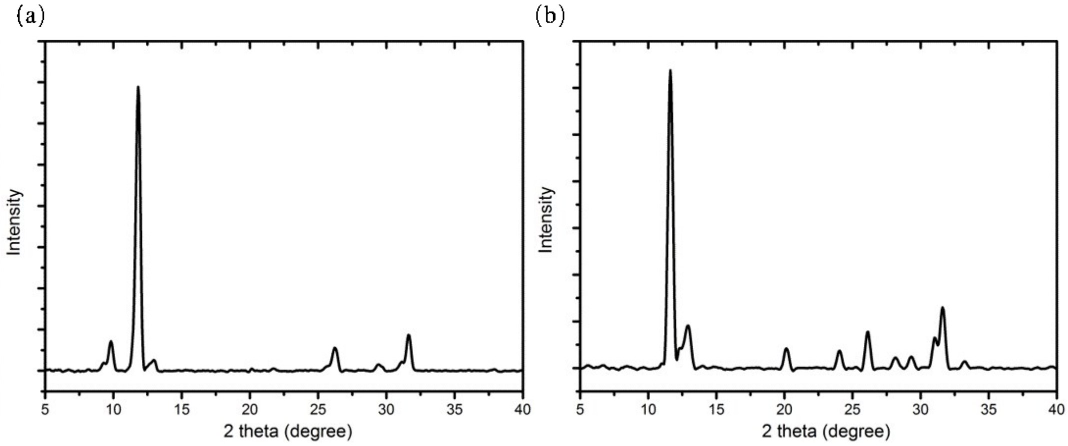

Figure S5. XRD spectra of mono-cation FA-perovskite films. (a) As prepared. (b) After thermal annealing at 95^{o}C for one hour.

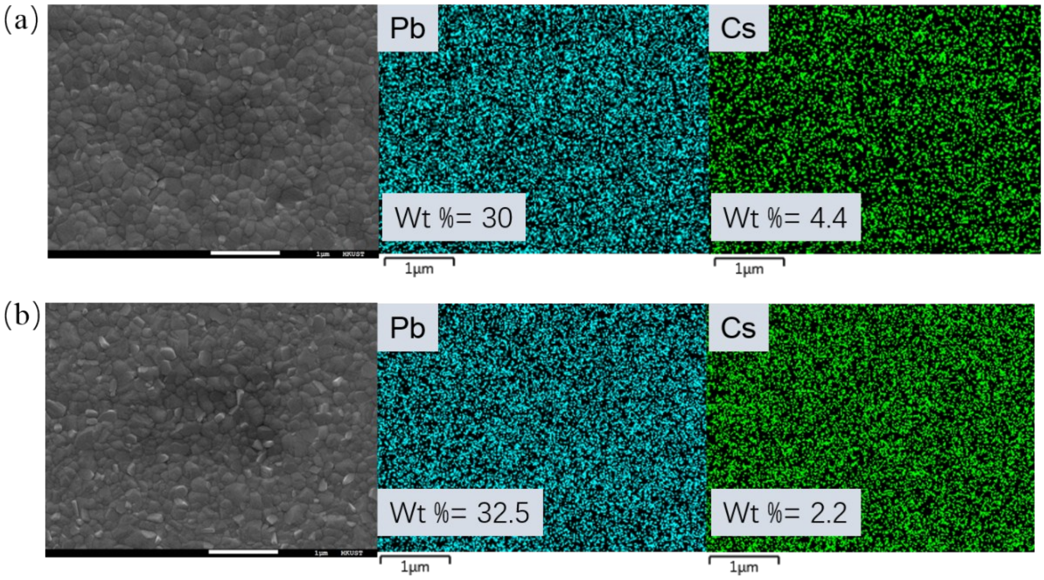

Figure S6. SEM images and EDS mapping of (a) $FA_{3/4}MA_{3/40}Cs_{7/40}$ (b) $FA_{3/4}MA_{7/40}Cs_{3/40}$.

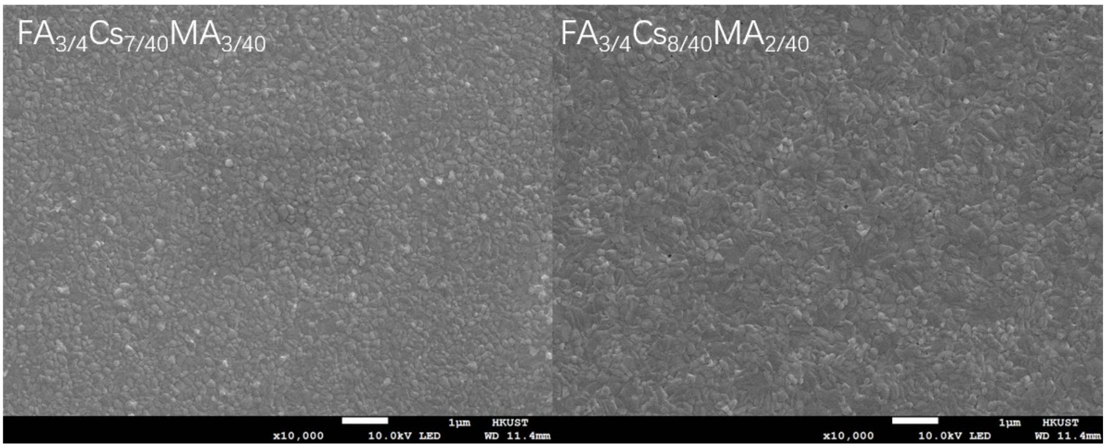

Figure S7. Top-view SEM image of $FA_{3/4}MA_{3/40}Cs_{7/40}$ and $FA_{3/4}MA_{2/40}Cs_{8/40}$ film.

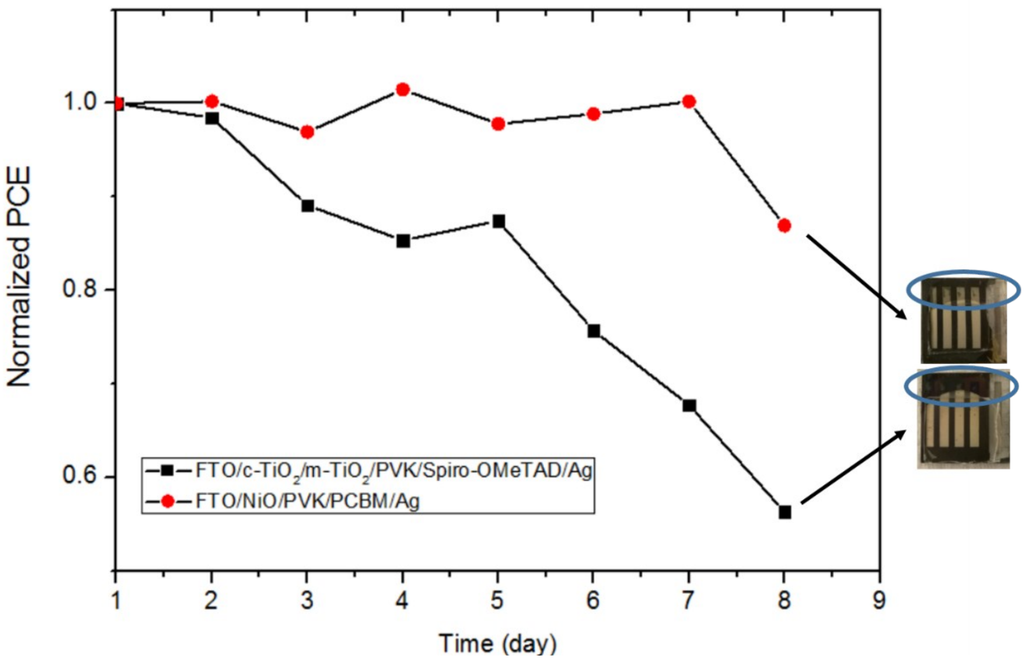

Figure S8. Stability record of normal (black) and inverted (red) devices with encapsulations by UV glue under ambient environment (humidity 20%-30%).

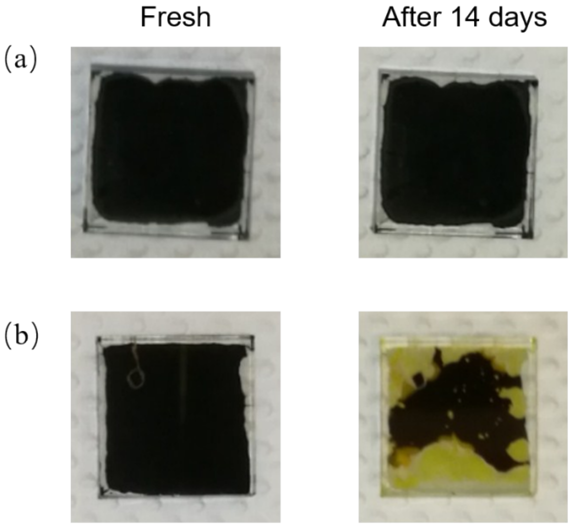

Figure S9. Film appearances of (a) $FA_{3/4}MA_{7/40}Cs_{3/40}$and (b) $MAPbI_3$ perovskite at different storage time under ambient environment (humidity 20%-30%).