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COMMUNICATION

Supporting Information

Highly efficient Zn_2SnO_4 perovskite solar cells through band alignment engineering

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Experimental

Preparation of electron transport layer

The solution for dipping the Zn_2SnO_4 solution was prepared by dissolving 1 mmol of $Zn(Ac)_2 \cdot 2H_2O$, 0.5 mmol of $Sn(Ac)_4$ and 2 mmol of ethanolamine in 2 mL 2-methoxy ethanol. The paste consisted of the sample powder, ethyl cellulose (10 wt%) and α-terpineol (5 wt%).

The FTO (14 Ω/sq^2) was prepatterned by Zn powder and 2 M HCl solution, cleared with DI water, ethanol, acetone, iso-propyl alcohol, respectively. The compact layer was formed by spin-coating of solution (dilute with 2-methoxy ethanol, v/v=1/3) at 1000 rpm for 6 s and 3000 rpm for 30 s, and then short baking at 100 ^{o}C for 10 min. The mesoporous Zn_2SnO_4 layer was prepared by spin-coating the Zn_2SnO_4 paste (dilute with ethanol, w/w=1/5) at 3000 rpm for 30 s, followed by annealed at 150 ^{o}C for 30 min and 550 ^{o}C for 30 min.

Preparation of perovskite precursor solution and perovskite film

$(MA_{0.17}FA_{0.83})Pb(I_{0.83}Br_{0.17})_3$ perovskite precursor solution was prepared from the mixture of FAPbI3 and MAPbBr3 solutions at the concentration of 1.08 M (PbI2 to FAI at the molar ratio of 1.09 to 1, same as the molar ratio of $PbBr_2$ to MABr). Differently, $(MA_{0.17}FA_{0.83})Pb(I_{0.89}Br_{0.11})_3$ perovskite precursor solution was prepared from the mixture of PbI2 (1.18 M), $PbBr_2$ (0.242 M), FAI (1.08 M) and MAI (0.220 M) $(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.89}Br_{0.11})_3$ perovskite precursor solution was composed of PbI_2 (1.18 M), FAI (1.08 M), $PbBr_2$ (0.242 M), MAI (0.220 M) and CsI (0.075 M). The solvent used for the above perovskites was the mixture of DMF and DMSO at the volume of 4 to 1. The perovskite layer was deposited by spin-coating in the steps program (10 s at 1000 rpm and 20 s at 6000 rpm), and 100 μL of chlorobenzene was dipped on the film at 15 s prior to the start of the program. Last, the substrates were annealed at 100 oC for 60 min.

Preparation of hole transport layer and Au electrode

Precursor solution of HTL was prepared by dissolving 28.8 μL of 4-tert-butylpyridine, 17.5 μL of Li-TFSI solution (520 mg Li-TFSI in 1.0 mL acetonitrile), 29.0 μL FK209-Co(III)-TFSI solution (300 mg FK209-Co(III)-TFSI in 1.0 mL acetonitrile) and 72.3 mg of Spiro-OMeTAD in 1.0 mL chlorobenzene. Precursor solution of HTL was deposited atop perovskite via spin-coating process at 4000 rpm for 30 s. Those 80-100 nm thick gold top electrodes were thermally evaporated. The active area of PSCs is 0.06 cm2 determined by the mask.

Characterizations of photovoltaic properties

The composition was characterized by X-ray diffraction (Rigaku, with Cu-Kα radiation of λ=0.15418 nm). The microscopic morphologies were measured via scanning electron microscope (FESEM, Hitachi S4800). The UV-vis absorption and transmittance spectra were performed by a UV-Vis spectrometer (PE Lambda 950). The energy band structure was analyzed by ultraviolet photoelectron spectroscopy (ESCALAB 250Xi, Thermo Fisher) using 21.2 eV He discharge lamp. The photovoltaic performance of the PSCs was collected with a source meter (Keithley 2400), the light source (PEC-L11 AM 1.5 solar simulator) and quantum efficiency measurement system (Crowntech-1000). Electrochemical impedance spectroscopy (EIS) was investigated by the electrochemical workstation (Zahner, IM6). The steady-state photoluminescence (PL) and time-resolved photoluminescence spectroscopy (TRPL) of different perovskite layers deposited on the ETLs were obtained by Edinburgh FLS 980 instrument with the excitation at 395 nm.

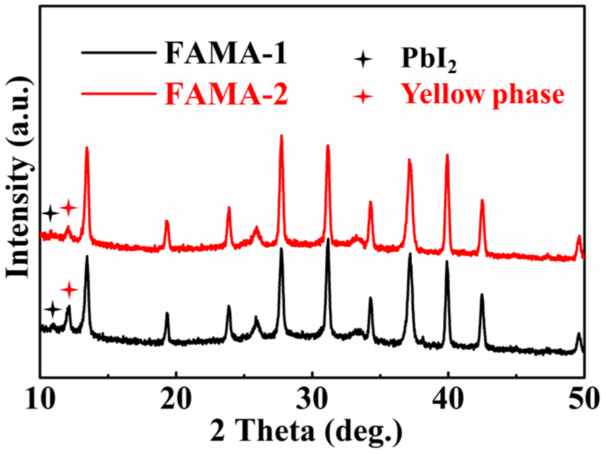

Figure S1. XRD patterns of FAMA-1 (black) and FAMA-2 (red) perovskite films deposited on the Zn_2SnO_4 ETLs.

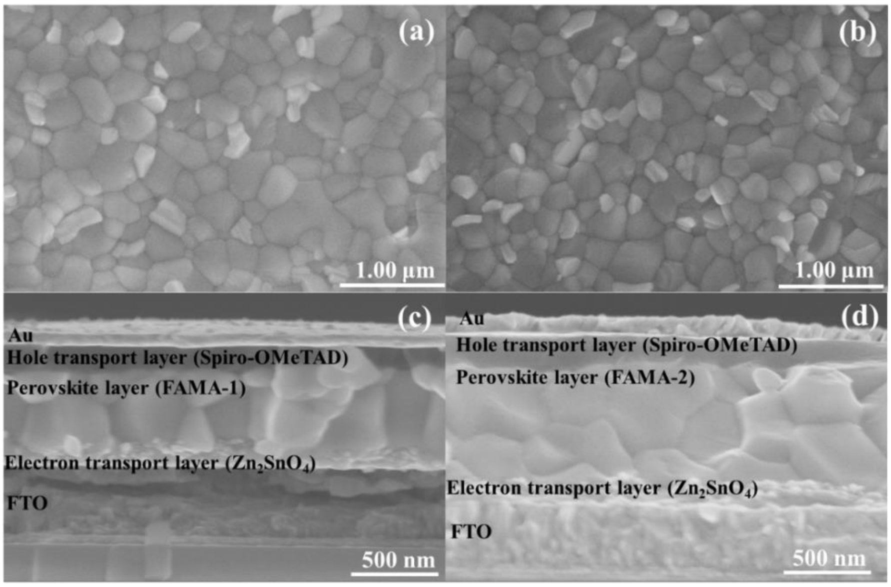

Figure S2 Surface morphology of a) FAMA-1 perovskite and b) FAMA-2 perovskite films, and cross-sectional SEM images of c) FAMA-1 perovskite and d) FAMA-2 perovskite films, respectively.

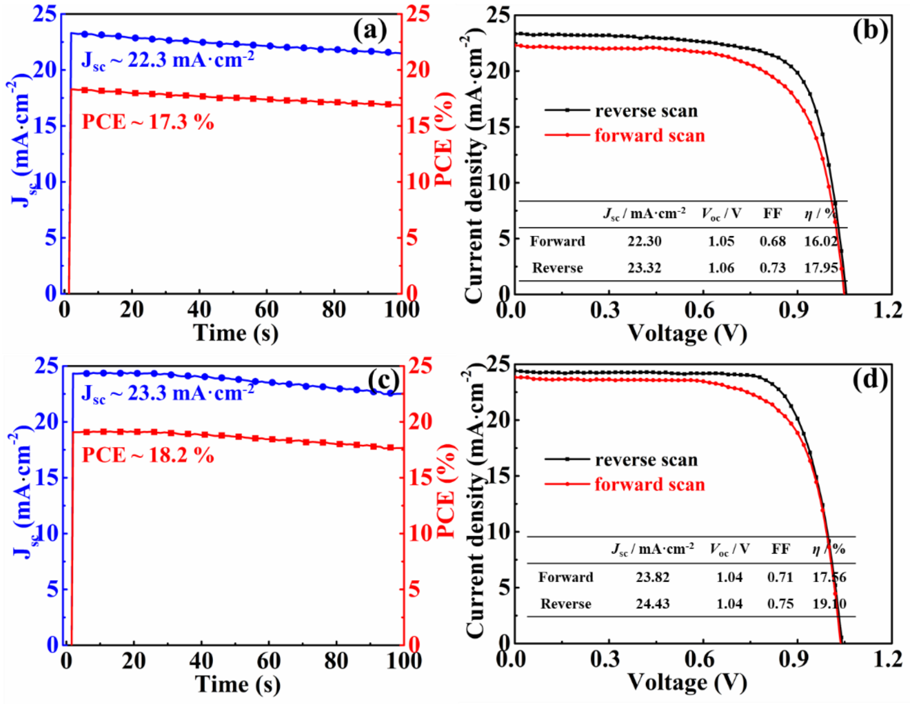

Figure S3. The stabilized PCE of devices based on (a) FAMA-1 and (c) FAMA-2 perovskite layers obtained from MPP tracking for 100 s; J-V curves of the PSCs based on (b) FAMA-1 and (d) FAMA-2 perovskite layers at reverse and forward scans.

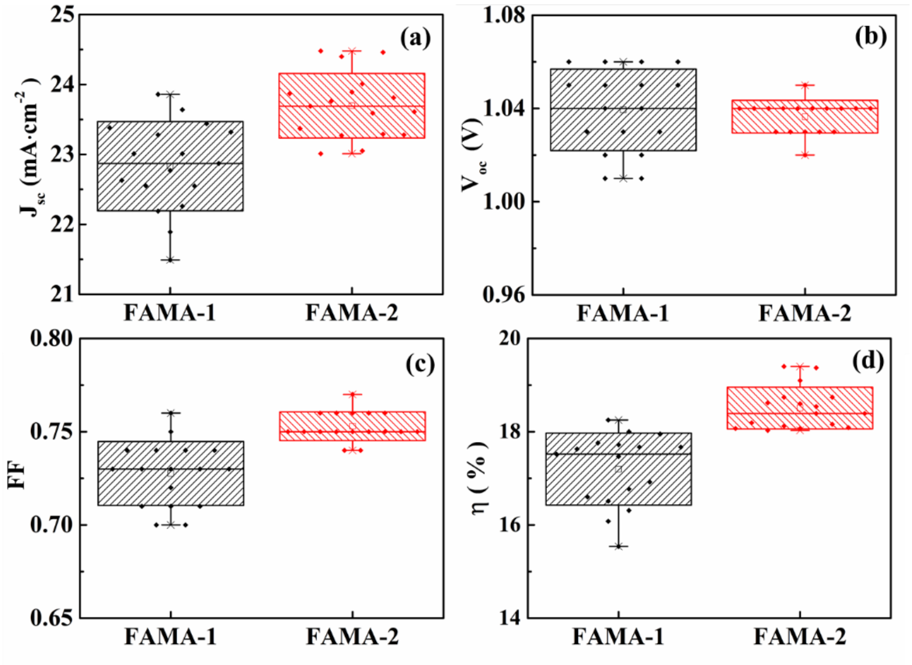

Figure S4. Box charts of photovoltaic parameters of (a) J_{sc}, (b) V_{oc}, (c) FF and, (d) η extracted from J-V measurements for the PSCs based on FAMA-1 (black) and FAMA-2 (red) perovskites respectively.

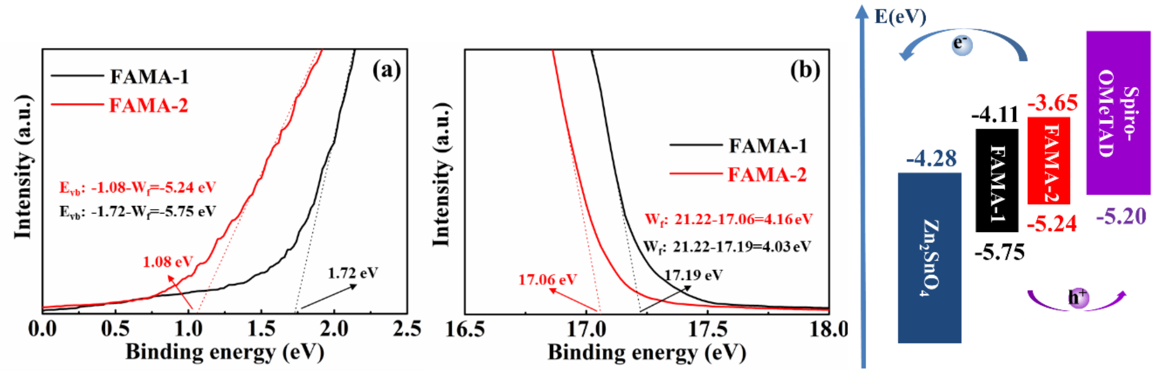

Figure S5. Ultraviolet photoelectron spectrometer (UPS) absorption spectra of (a) the Fermi edge, (b) cut-off energy, and (c) schematic band alignment of between FAMA-1 (black) and FAMA-2 (red) perovskite films. The horizontal value of the intercept of the left part, corresponds to $E_f - E_{vb}$ in Figure S5a; W_f equals to 21.22 eV minus the horizontal value of the intercept of the right part in Figure S5b.

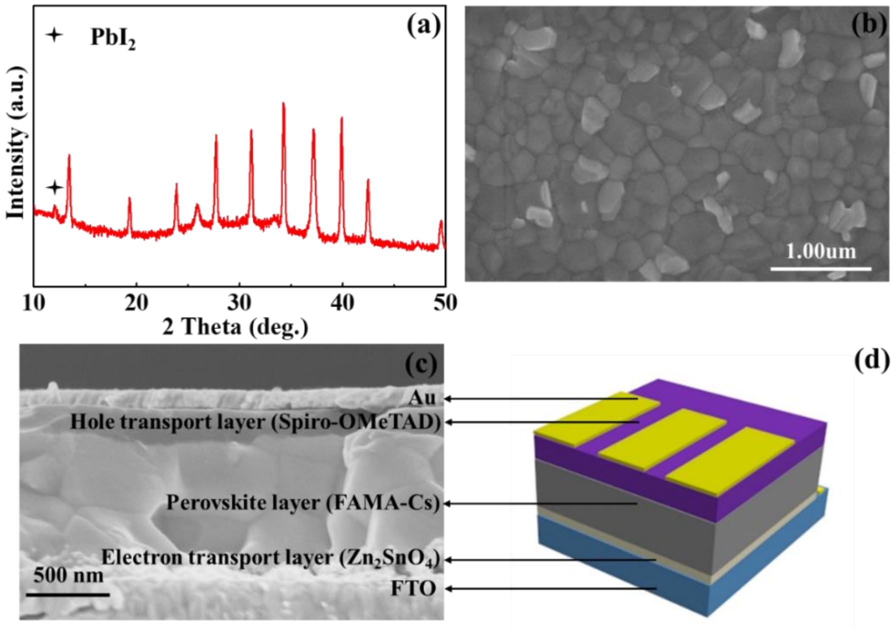

Figure S6 (a) XRD pattern, (b) top-view SEM image of the FAMA-Cs perovskite layer, (c) the cross-section SEM image, and (d) schematic illustration of the perovskite solar cell.

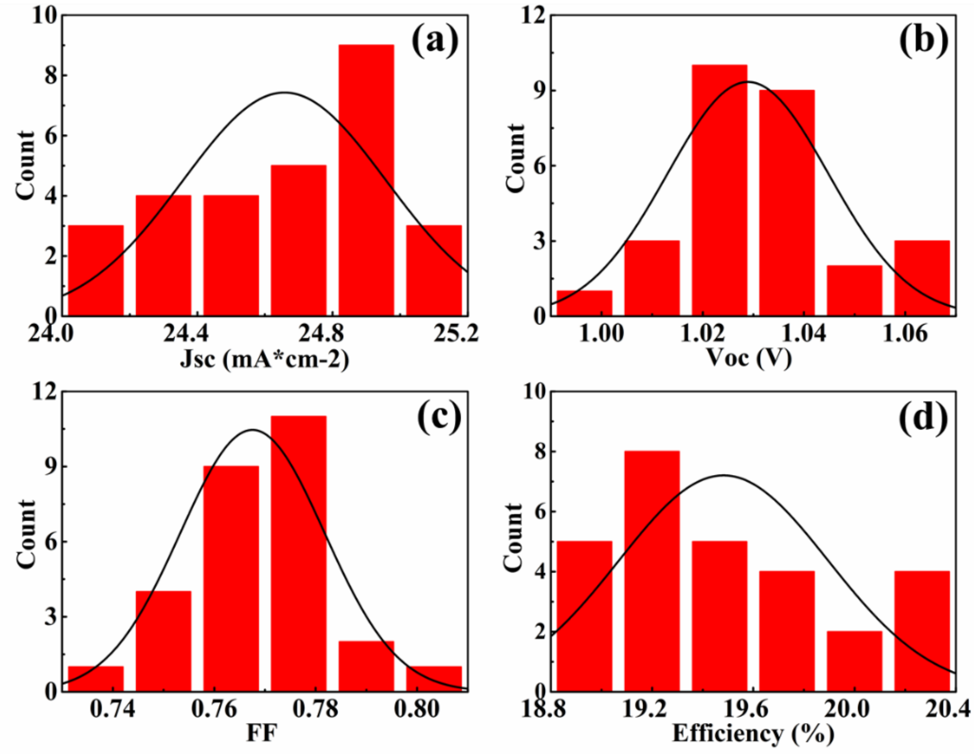

Figure S7 Histograms of (a)J_{sc}, (b) V_{oc}, (c) FF and (d) efficiency for PCEs

Table S1 Energy band parameters of the PSCs deposited on different perovskite layers

Samples	**E_{vb}/eV**	**E_g/eV**	**E_{cb}/eV**
FAMA-1	-5.75	1.64	-4.11
FAMA-2	-5.24	1.59	-3.65

Table S2. The summary of carrier lifetime from TRPL analysis.

Film	**Ratio/%**	**τ_1/ns**	**Ratio/%**	**τ_2/ns**	**τ_{ave}/ns**
FAMA-1	83.3	8.4	16.7	57.6	36.9
FAMA-2	85.8	6.4	14.2	47.3	28.9