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Supporting Information

Formamidinium planar heterojunction perovskite solar cells with alkali carbonate doped zinc oxide layer

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This supporting information presents the following contents.

Supporting Tables S1-S2
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Experimental Section

All chemicals were purchased from Sigma Aldrich and used as received.

Preparation of ZnO nanoparticle: ZnO nanoparticles were prepared by reaction between a zinc acetate solutions (23.6 mg ml^{-1} [$Zn(CH_3COO)_2.2H_2O$] in methanol) and a potassium hydroxide solution (31.6 mg ml^{-1} in metanol in a 250 mL round bottom flask at 60 ^oC for 21 h with string.[29] And then this particle was dissolved in CF, Methanol mixture.

Preparation of the perovskite precursor: MAI was prepared by reacting 30 ml of methylamine solution (40 % in water) with 30 ml of hydroiodic acid (57 wt% in water) in 250 ml round bottom flask at 0 ^oC for 2 h under string with the Argon condition. And the solvent was thermal evaporated under vacuum at 60 ^oC for 1 h to obtain a white raw product. The white raw product was washed with diethyl ether three times. After filtration, the product was dissolved in ethanol and recrystallized by ethanol for 20 h. Then the precipitate was washed with diethyl ether and filtered. The filtered solid was dried at 60 ^oC under vacuum for 24 h.

FAI was prepared by reacting 0.45 g ml^{-1} solution of formamidinium acetate in absolute methanol with 30 ml of HI. The reaction conditions and cleaning process were same to those of MAI preparation.

To prepare perovskite precursors, Firstly PbI_2 was dissolved in DMF for a concentration of 1.3 M with NMP 1 mM and secondly FAI(MAI) was dissolved in isopropanol of 80 mg ml$^-$1(65 mg ml^{-1}). This obtained solution was stirred at room temperature for 1 h in air and used subsequently for device fabrication.

Device fabrication and characterization: ITO-coated glass substrates were washed by ultrasonication with DI water, acetone, and isopropanol for 20 minutes each. ZnO nanoparticles were spin coated at 3000 rpm for 10 s. For the perovskite layer, PbI_2 was dissolved in DMF and spin coated at 5000 rpm for 30 s. Secondly 80 mg ml^{-1} FAI in isopropanol was dropped on the PbI_2 film and spin coated at 5000 rpm for 30 s and dried at 130 ^{o}C for 20 min. MAI are similar to FAI, apart from concentration and annealing condition, which was 65 mg ml^{-1}, and 100 ^{o}C for 2 min. During that process, perovskite film was formed. 20 mg ml^{-1} P3HT dissolved in CB were deposited on the perovskite layer by spin coating at 1000 rpm for 30 s. In that case, P3HT solution didn't contain any dopant like Li-TFSI or TBP. Finally, 70 nm gold was deposited by thermal evaporating under vacuum (<10^{-6} Torr).

The current density-voltage (J-V) characterization of the solar cell devices were obtained using a Kiethley 2635A Source Measure Unit under AM1.5G with irradiation intensity of 100 mW cm^{-1}. The active layer was 0.13 cm^{2}. External Quantum Efficiency (EQE) measurements were measured with a PV measurement QE system under ambient conditions. With monochromated light from a xenon arc lamp.

Film characterization: Scanning electron microscope measurements (SEM) were performed using an S-4800 Hitachi high-Technology microscope. SEM samples were prepared by deposited perovskite precursor solutions on ZnO or doped ZnO layer by spin-coating two step method, followed by annealing at 130 °C for 10 min on a hotplate. UV-vis absorption was measured using a Varian Cary 5000 spectrophotometer. AFM images were obtained using a Veeco Multimode AFM microscope in a tapping mode. Electrical characterization was performed using a Keithley semiconductor parametric analyzer (keithley 4200-SCS)

Photoluminesence (P.L.) characterization was measured using a spectrofluorometer (FP-8500SP)

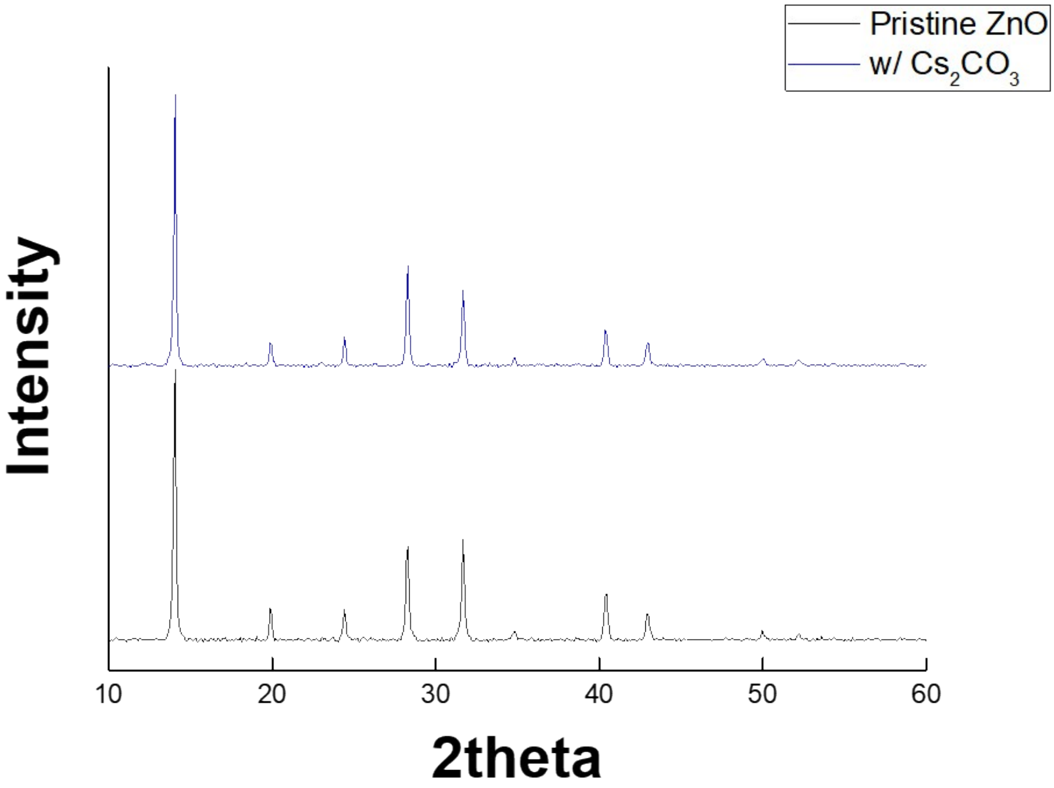

Figure S1. XRD patterns of perovskite film on the pristine ZnO and ZnO with Cs_2CO_3 layer

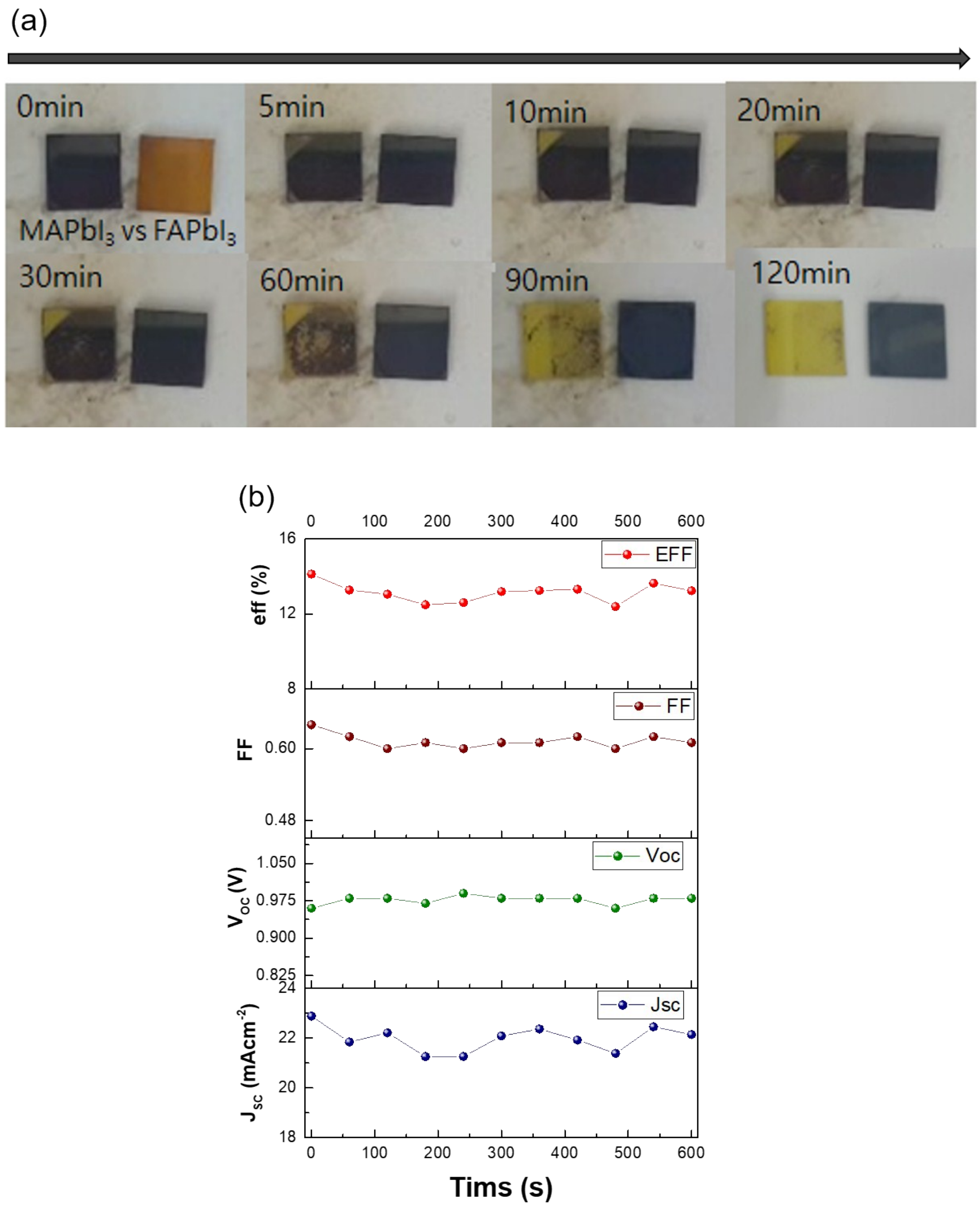

Figure S2. (a) Thermal stability of $MAPbI_3$ and $FAPbI_3$ deposited on ZnO layer, when the substrates are annealed in N_2 at 100°C for the times indicated. (b) Steady-state measurements of J_{SC}, V_{OC}, FF and PCE for $FAPbI_3$.

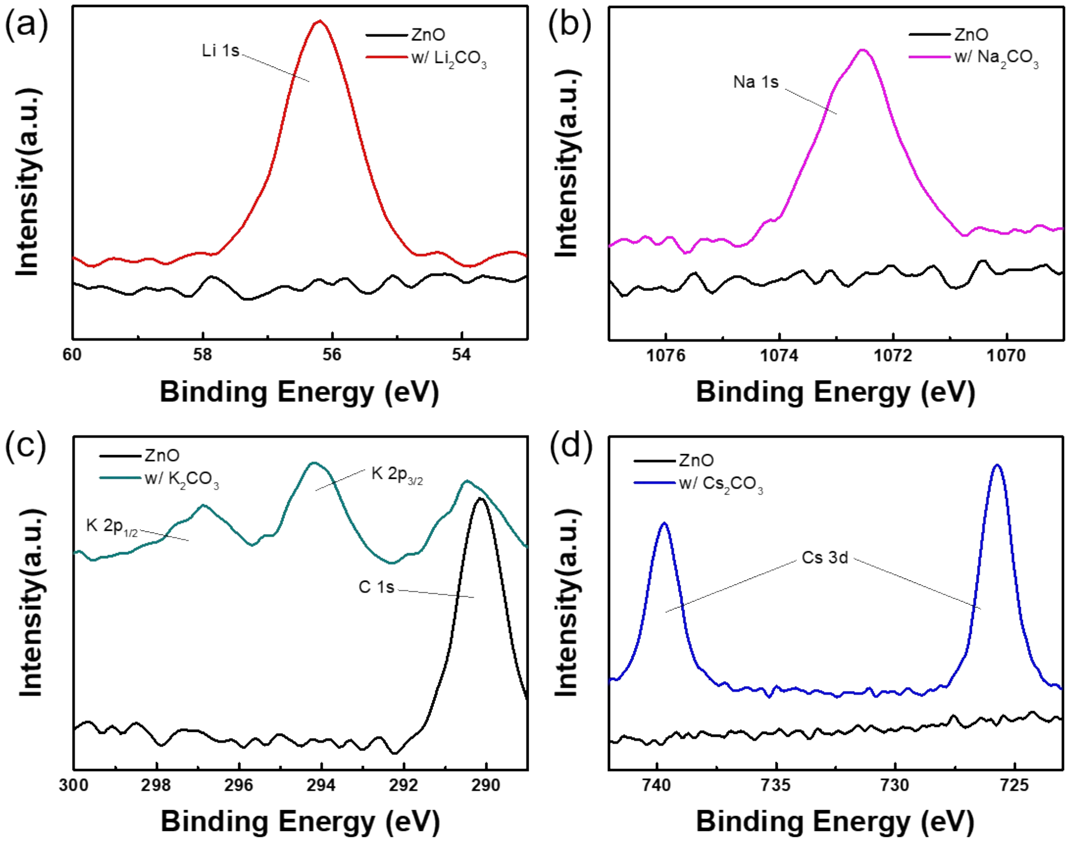

Figure S3. X-ray photoelectron spectra (XPS) data (a) of the Li peak compared between pristine ZnO layer and ZnO doped with Li_2CO_3 layer. (b) of the Na peak compared between pristine ZnO layer and ZnO doped with Na_2CO_3 layer. (c) of the K peak compared between pristine ZnO layer and ZnO doped with Na_2CO_3 layer. (d) of the Cs peak compared between pristine ZnO layer and ZnO doped with K_2CO_3 layer. (d) of the Cs peak compared between pristine ZnO layer and ZnO doped with Cs_2CO_3 layer.

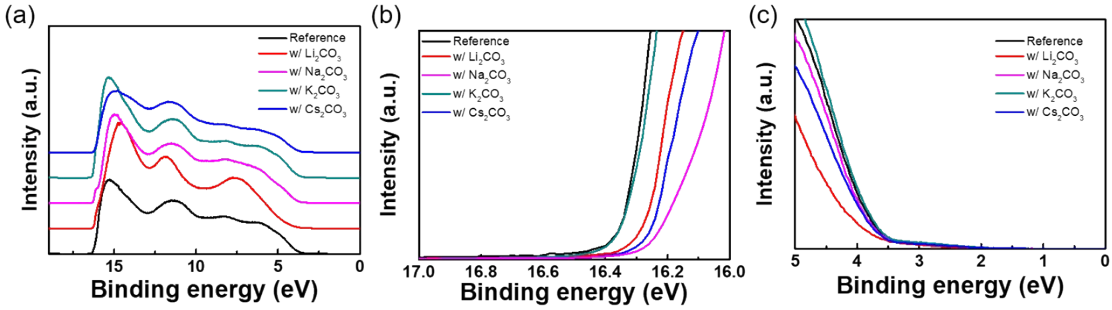

Figure S4. (a), (b), (c) Ultra-violet photoelectron spectra (UPS) data of the Pristine ZnO layer and each ZnO doped with metal carbonate layer.

Table S1. Valence Band (E_v) work function of Pristine ZnO and each ZnO doped with metal carbonate layer from UPS measurement.

	Valence band (eV)	Work function (eV)
Pristine ZnO	6.82	4.86
w/ Li_2CO_3	7.51	4.95
w/ Na_2CO_3	7.00	5.14
w/ K_2CO_3	6.84	4.88
w/ Cs_2CO_3	7.18	5.04

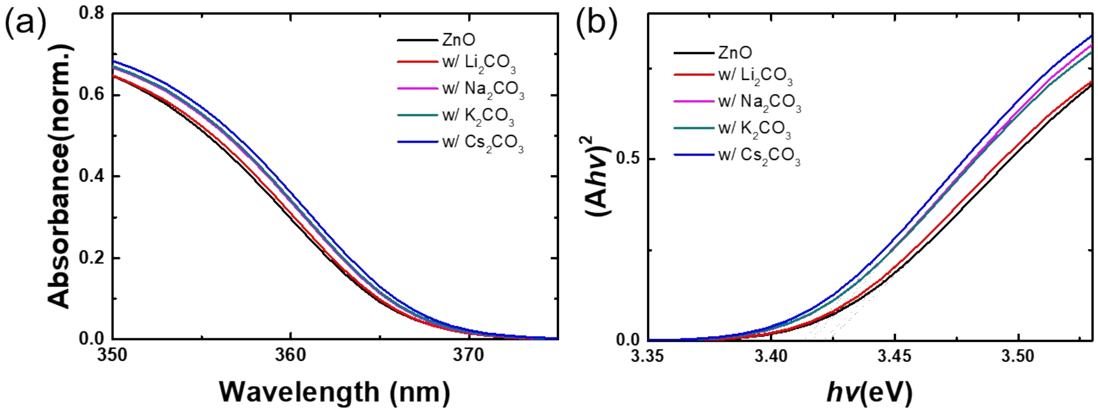

Figure S5. (a) UV-Vis absorption sepecturm and (b) tauc plot spectra of pristine ZnO and each ZnO doped with metal carbonate layer.

Table S2. Energy gap (E_g) of Pristine ZnO and each ZnO doped with metal carbonate layer derived from Tauc plots.

	Energy Gap (eV)
Pristine ZnO	3.42
w/ Li_2CO_3	3.41
w/ Na_2CO_3	3.40
w/ K_2CO_3	3.41
w/ Cs_2CO_3	3.40

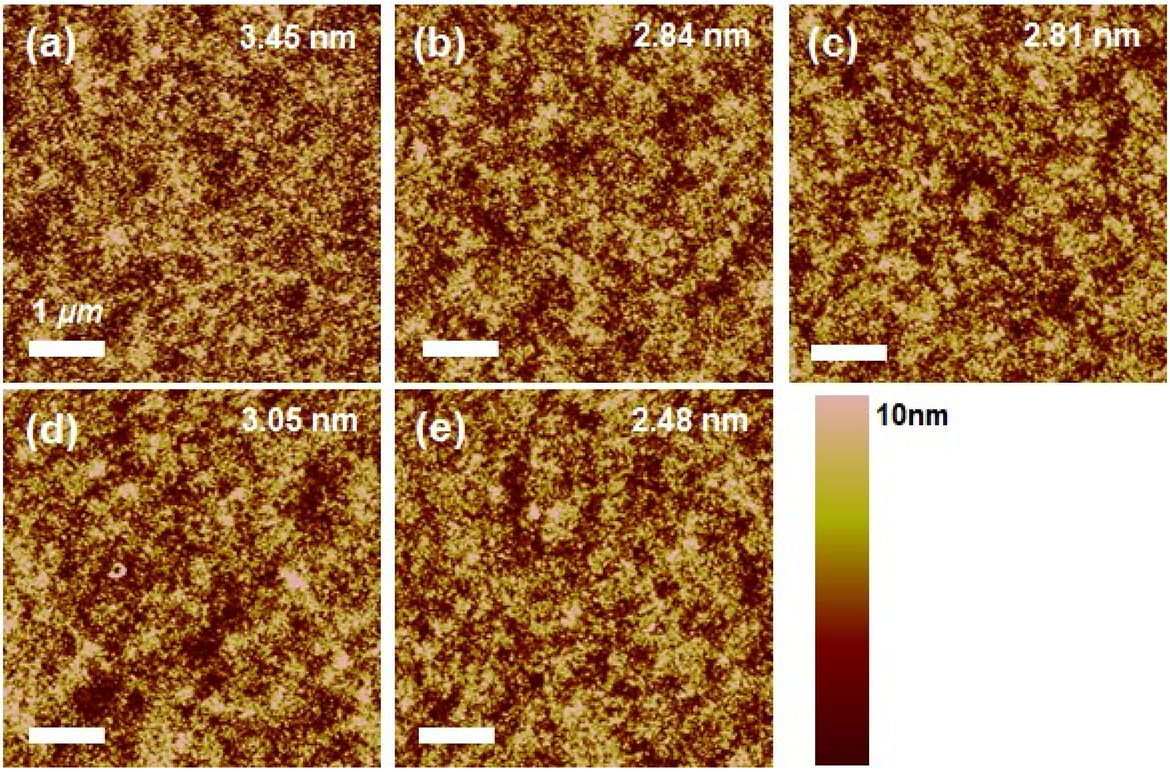

Figure S6. AFM height images (10 μm * 10 μm) of (a) pristine ZnO nanoparticle layer (b) Li_2CO_3 deposited on the ZnO layer (c) Na_2CO_3 deposited on the ZnO layer (d) K_2CO_3 deposited on the ZnO layer (e) Cs_2CO_3 deposited on the ZnO layer.

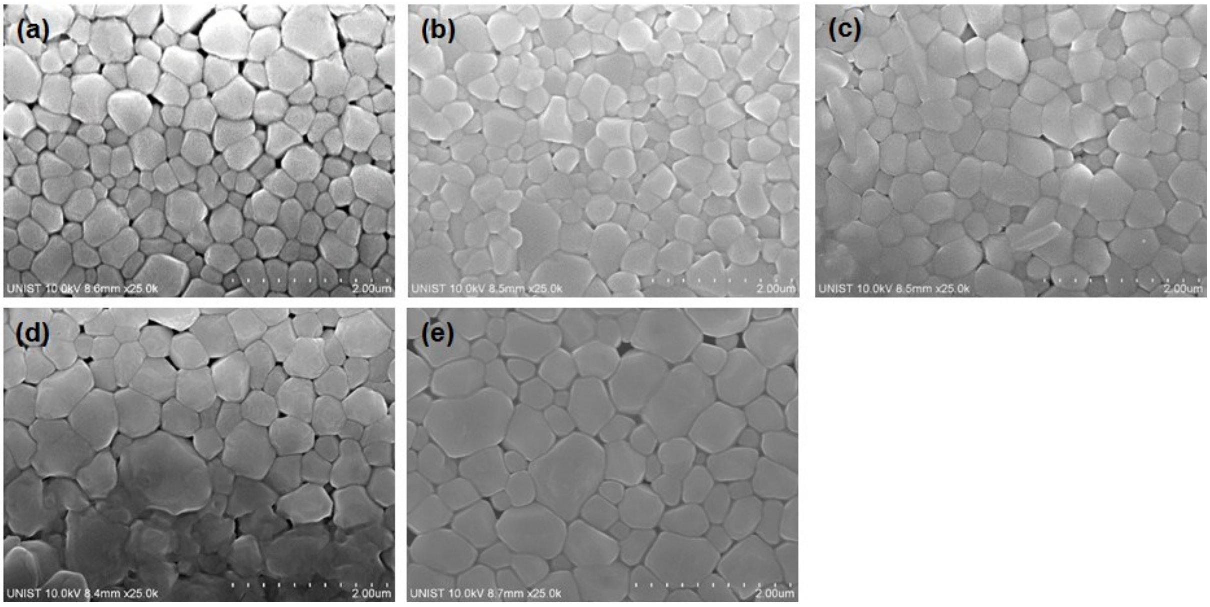

Figure S7. SEM top-view images of FAPbI3 deposited on (a) pristine ZnO nanoparticle layer, (b) ZnO doped with Li_2CO_3 layer, (c) ZnO doped with Na_2CO_3 layer, (d) ZnO doped with K_2CO_3 layer and (e) ZnO doped with Cs_2CO_3 layer.

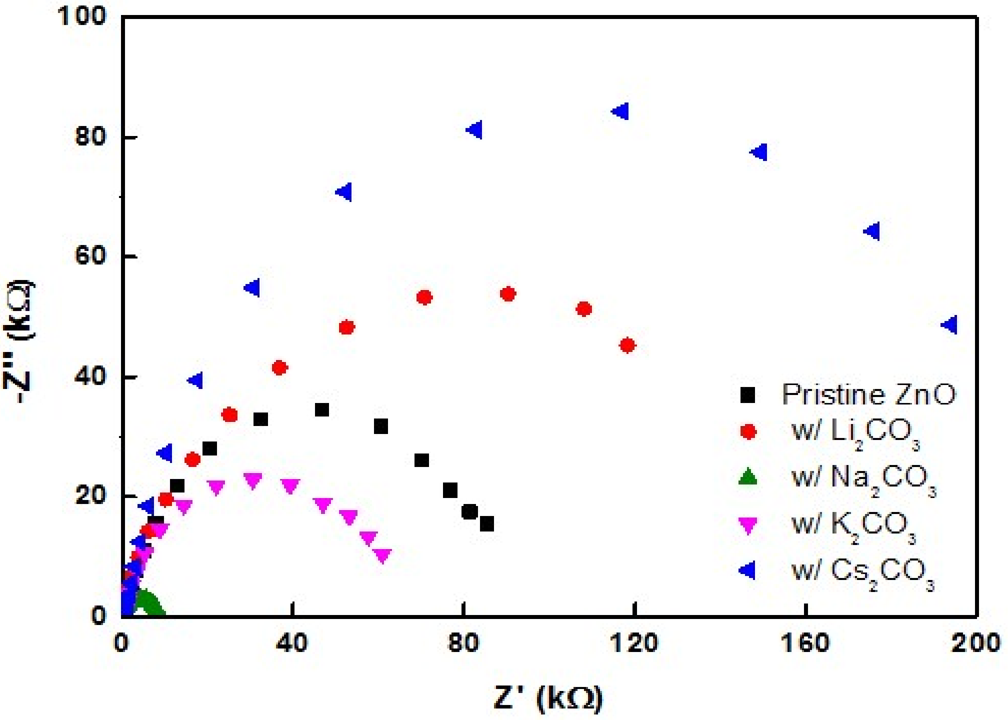

Figure S8. Nyquist plots of pristine ZnO nanoparticle layer(black), ZnO doped with Li_2CO_3 layer(red), ZnO doped with Na_2CO_3 layer(green), ZnO doped with K_2CO_3 layer(magenta) and ZnO doped with Cs_2CO_3 layer(blue).

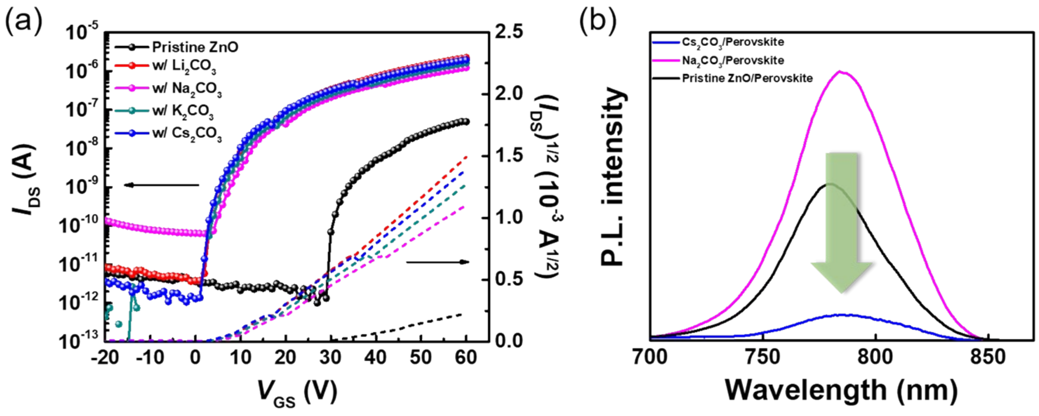

Figure S9. (a) field-effect transistors (FETs) characteristics of ZnO and ZnO with various alkali metal carbonate series. (b) photoluminescence (PL) for pristine ZnO, ZnO doped with Na_2CO_3 and ZnO doped with Cs_2CO_3.

Table S3. Summary of FET results of ZnO and ZnO with various alkali metal carbonate series.

Transport Layer	Mobility [cm^2 V^{-1} s^{-1}]	I_{on} [A]	I_{off} [A]	I_{on}/I_{off}	V_{th} [V]
Pristine ZnO	1.80×10^{-4}	4.89×10^{-8}	1.32×10^{-12}	3.71×10^{4}	29.3
w/ Li_2CO_3	3.10×10^{-3}	2.22×10^{-6}	3.65×10^{-12}	6.08×10^{5}	13.1
w/ Na_2CO_3	1.49×10^{-3}	1.22×10^{-6}	6.19×10^{-11}	1.97×10^{4}	13.9
w/ K_2CO_3	2.22×10^{-3}	1.62×10^{-6}	1.69×10^{-12}	9.59×10^{5}	13.9
w/ Cs_2CO_3	2.60×10^{-3}	1.94×10^{-6}	1.06×10^{-12}	1.83×10^{6}	13.7

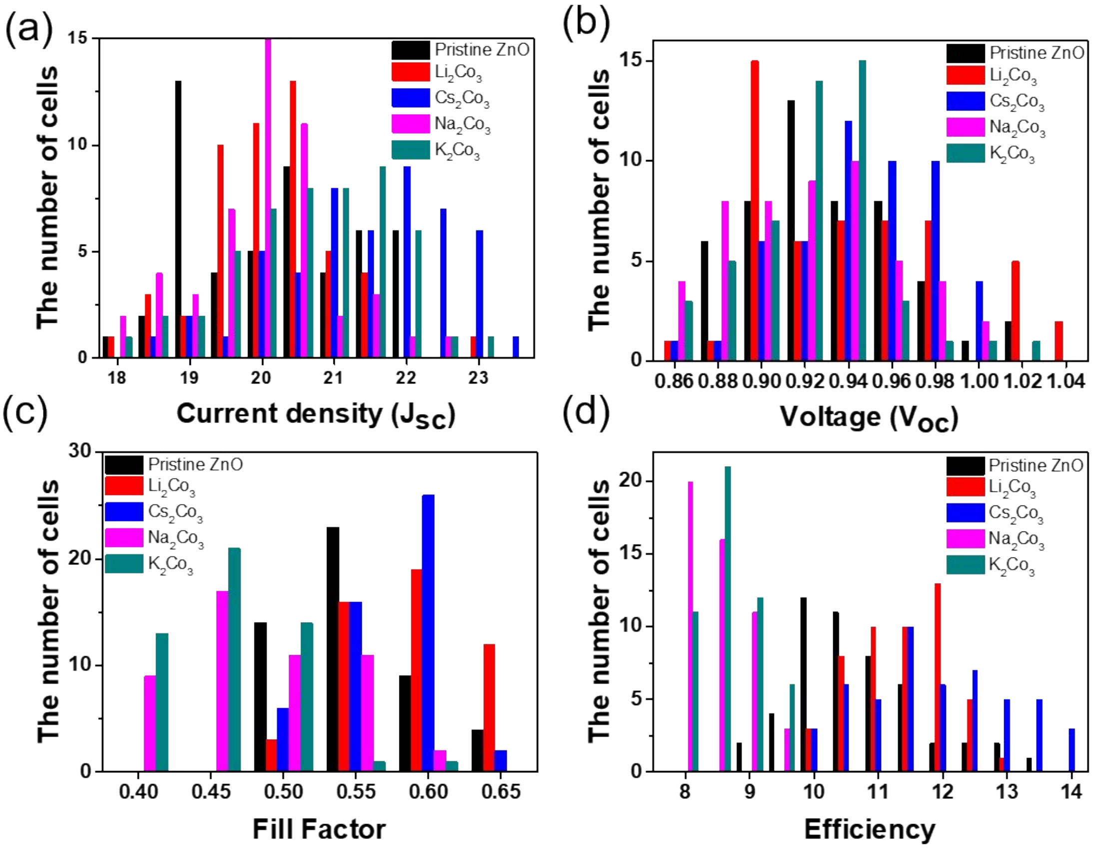

Figure S10. (a) Histogram of the device short circuit current density about FAPbI$_3$ perovskite solar cell deposited on the pristine ZnO, ZnO doped with Li$_2$CO$_3$, Cs$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$. (b) of the device open circuit voltage. (c) of the device fill factor, (d) of the device efficiency.

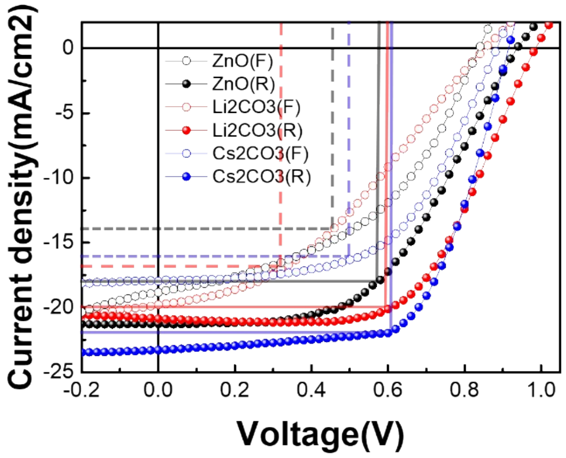

Figure S11. Hysteresis characteristic and maximum power point (MPP) of the pristine ZnO and ZnO doped with Li_2Co_3 and Cs_2Co_3.

Table S4. Summary of Hysteresis characteristic and maximum power point (MPP) of the pristine ZnO and ZnO doped with Li_2CO_3 and Cs_2CO_3.

		J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	PCE (%)	Maximum Power Point (MPP) Efficiency (%)
Pristine ZnO	reverse	21.27	0.94	0.52	10.37	10.36
	forward	18.83	0.84	0.46	7.24	6.95
Li_2CO_3	reverse	20.86	0.99	0.61	12.53	12.06
	forward	19.79	0.85	0.38	6.38	5.47
Cs_2CO_3	reverse	23.54	0.91	0.63	13.64	13.42
	forward	17.97	0.88	0.56	8.89	8.16