Supporting Information

The dual role of borohydride salts in enhancing perovskite solar cell performance and stability

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Materials

Formamidinium iodide (FAI, 99.99%) and methylammonium chloride (MACl, 98%) were purchased from GreatCell Solar. Lead iodide (PbI_2, >98%) from TCI. Cesium iodide (CsI, 99.99%), potassium borohydride (KBH_4, 99.9%), sodium borohydride ($NaBH_4$, 99%), dimethyl-sulfoxide (DMSO, anhydrous, >99.9%) and N,N-dimethylformamide (DMF, anhydrous, 99.9%) and chlorobenzene (CB, anhydrous, 99.8%) were purchased from Sigma-Aldrich.

Acetonitrile (ACN, Anhydrous, 99.8%), 4-tert-butylpiridine (tBP, 96%), Lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI, 99.95%), and cobalt from Sigma Aldrich. 2,20,7,70-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,90-spirobifluorene (Spiro-MeOTAD, 99%) from Feiming Chemical Limited. Tin oxide (SnO_2,15% in H_2O colloidal dispersion liquid) was supplied by Alfa Aesar.

Indium tin oxide (ITO) coated glass substrates (25 x 25 mm, Pilkington TEC-15, ~ 15 Ω/sq). For substrate cleaning, we used cleaner 2-propanol (IPA), ethanol and acetone were obtained from VWR International Ltd.

Device fabrication

Substrate cleaning

ITO-coated glass substrates were cleaned sequentially using soap, deionized water, acetone, and isopropanol under ultrasonication for 15 minutes each. The substrates were then dried using nitrogen (N_2) gas and further treated with ultraviolet ozone (UVO) for 15 minutes to remove organic impurities from their surface.

Electron transport layer (ETL) deposition

Before perovskite deposition, the SnO_2 was deposited by spin-coating a colloidal SnO_2 solution (1:1 M in deionized water) at 4000 rpm for 40 seconds. Subsequently, the substrates were annealed at 150°C for 30 minutes.

Perovskite Precursor Solution

$CsFAPbI_3$:

The $Cs_{0.1}FA_{0.9}PbI_3$ stock solution was prepared at a concentration of 1.5M in anhydrous DMF: DMSO (4:1 v/v). After ensuring complete dissolution, the solution was diluted to a final concentration of 1.4M. Additionally, 0.2 mmol of MACl was added and dissolved in the same solution.

$Cs_{0.1}FA_{0.9}PbI_3$ +KBH_4:

A KBH_4 stock solution (0.05 mg/ml, 0.93 mM) was prepared in anhydrous DMF: DMSO (4:1 v/v) and subsequently incorporated into the perovskite precursor solution.

$Cs_{0.1}FA_{0.9}PbI_3$ +$NaBH_4$:

Similarly, a $NaBH_4$ stock solution (0.05 mg/ml, 1.32 mM) was prepared in anhydrous DMF: DMSO (4:1 v/v) and incorporation into the perovskite precursor solution.

Perovskite Layer Deposition and Aging

The perovskite solution was deposited using a two-step spin-coated program: 10 seconds at 1000 rpm (ramp rate: 200 rpm/s), followed by 22 seconds at 4000 rpm (ramp rate: 4000 rpm/s). During the second step, 250 µL of chlorobenzene was dropped onto the spinning substrate 11 seconds before the end of the program. The substrates were then annealed at 150°C for 10 minutes. Some films were not used for fresh film characterization of solar cell fabrication and were aged for 3 months stored under dark in a dry box at 20% RH and 21ºC.

Hole Transport Layer (HTL) Deposition

The Spiro-MeOTAD solutions were prepared by dissolving (0.150 gr, 69.9 mM) in 1.75 mL chlorobenzene and followed by the addition of 4-tert-butylpyridine (t-BP, 59.17 µL, 228.3 mM), Lithium bis(trifluoromethylsulfonyl) imide (Li-TFSI; 0.458 gr,

1.8 M) Cobalto (Co; 0.147gr, 0.25 M). The Spiro-MeOTAD solution was deposited by spin coating at 4000 rpm for 35 s. Finally, thermal evaporation deposited an 80 nm gold electrode as a metal contact

Device characterization

X-ray diffraction (XRD)

The films' XRD patterns were obtained using a D8 Advance X-ray diffractometer (Bruker-AXS) in Bragg-Brentano geometry. Measurements were conducted using Cu Kα radiation with range of 10–55° with a step size of 0.02° and a dwell time of 5 seconds per step. The films were deposited on glass substrates.

Scanning Electron Microscope (SEM)

SEM characterization was performed using a field-emission gun scanning electron microscope (FEG-SEM) JEOL 3100F operated at 15 kV to obtain top-view images and analyze the morphology of the perovskite layers.

UV-Vis Spectra

Absorbance measurements of the perovskite films deposited on glass substrates were conducted using a UV-Vis spectrophotometer (Varian Cary 300).

Photoluminescence Spectra (Visible and infrared)

PL spectra (visible and infrared regions) were obtained to evaluate the photophysical properties of the perovskite films were conducted using Horiba Fluorolog exciting the samples at 532 nm. The PL were recorded from films deposited on top of the glass substrate.

Incident-photon-to current conversion efficiency (IPCE)

IPCE measurements were performed using a QEPVSI-b Oriel system in DC mode.

Electrochemical Impedance Spectroscopy (EIS)

EIS was carried out using a Potentiostat Autolab PGSTAT-30. Light intensity varied up to 1 sun using filters, and measurements were conducted with a 20 mV AC voltage perturbation over a frequency range of 1 Hz to 100 kHz. Measurements were recorded under different applied potentials (0 to 1.2 V) and 1 sun illumination. Data acquisition was performed using Nova software, and spectra fitting was conducted with Z-View software using an equivalent circuit model previously reported.

Solar Cell Characterization

Solar Cell Characterization was carried out using a Keithley 2612 source meter under AM 1.5 G (1000 W/m^2) provided by an Abet Solar Simulator equipped with a 150-watt Xenon short-arc lamp (Ushio). Measurements were performed in ambient air at ~ 25°C and without encapsulation.

J–V (current density–voltage) curve measurements were performed using a voltage sweep starting from 1.2 V to a final potential of -0.05 V for reverse scan and vice versa for forward scan. The scan rate was maintained at 10 mV/s. The active area of solar cell was 0.086 cm^2.

Supplementary Figures Section

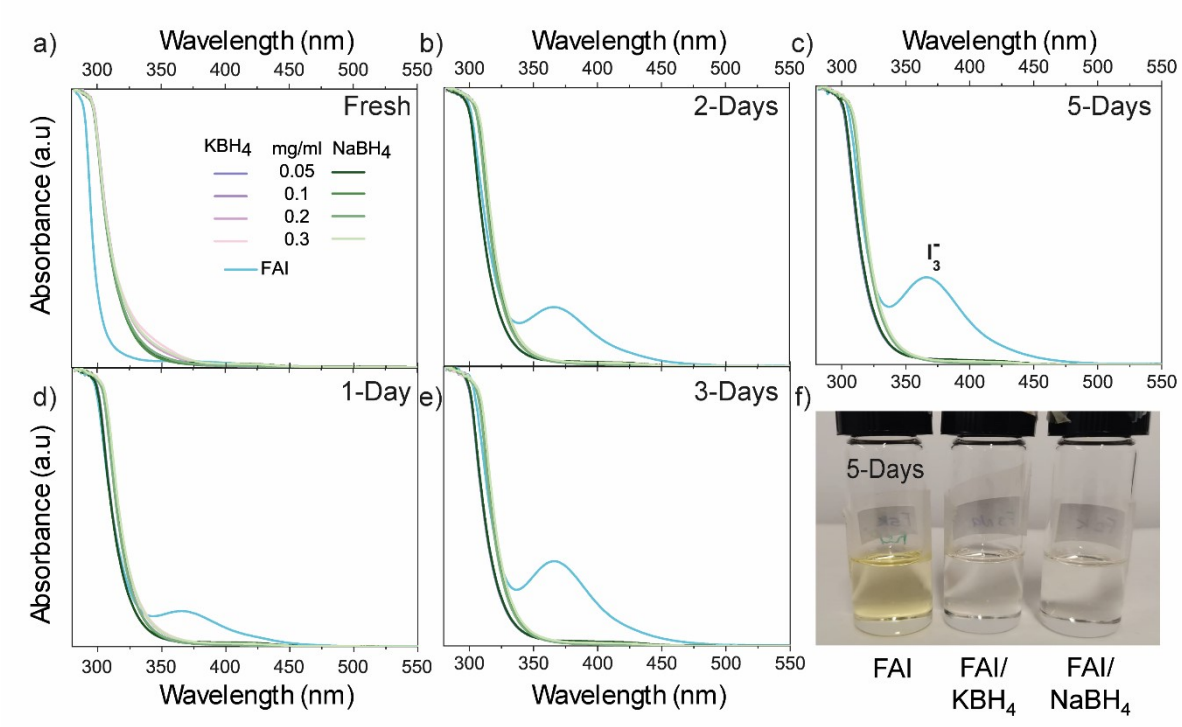

Figure S1 UV-Vis absorption spectra of FAI, FAI +KBH_4 and FAI +$NaBH_4$ at different concentrations of 0.05, 0.1, 0.2, and 0.3 mg/mL, in DMF: DMSO (4:1 v/v) (a-e) and the f) FAI solutions from freshly prepared to five days of aging in air from fresh to 5 days.

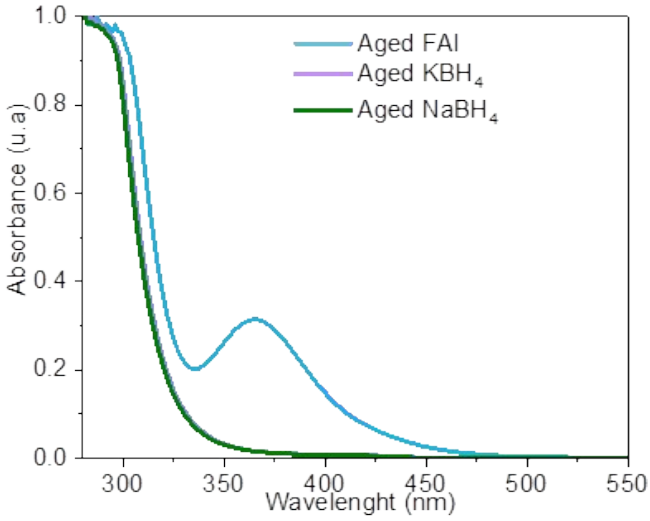

Figure S2 UV-Vis absorption spectra of aged FAI, aged KBH_4 and aged $NaBH_4$ were prepared to five days of aging in air. FAI solution in DMF was exposed in air and clearly exhibited the formation of I_2. As evidenced by the appearance of a yellowish color and showing a characteristic absorption peak at 365 nm corresponding to the I_3^- species. When the borohydride additive was added to aged FAI solution, the yellow color disappeared immediately and the solution regained its transparent appearance confirming that I_2 was reduced to I^-.

Table S1 Statistical parameters of the domain size distribution to fresh and 3-months aged perovskite films sample with/without +KBH_4 and +$NaBH_4$.

Sample	Mean size (nm)	Standard deviation (nm)	Minimum size (nm)	Maximum size (nm)
Fresh Reference	630	110	363	945
3-months	730	120	512	983
Fresh +KBH_4	720	130	506	1138
3-months	780	90	596	1020
Fresh +$NaBH_4$	960	170	742	1467
3-months	960	130	718	1229

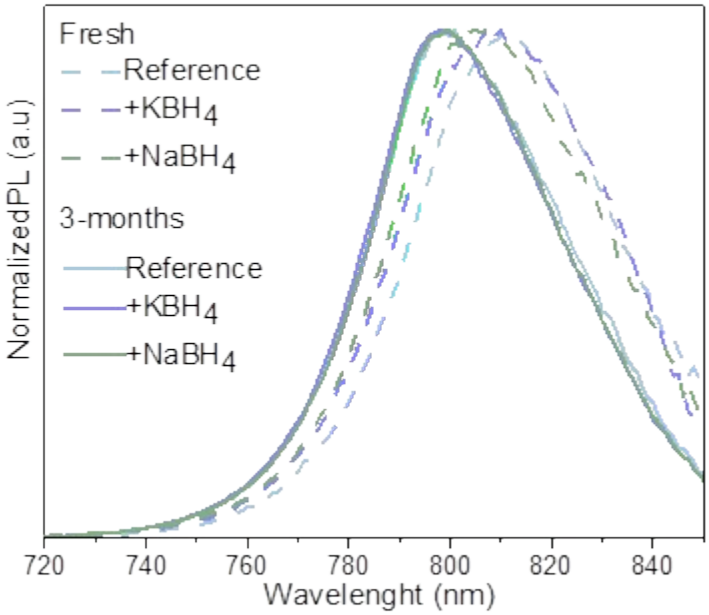

Figure S3. Steady-state PL spectra of fresh and 3-months aged “reference”, “reference +KBH_4”, and “reference +$NaBH_4$” perovskite films. After that, show a blueshift of peak wavelength of 810 to 798nm.

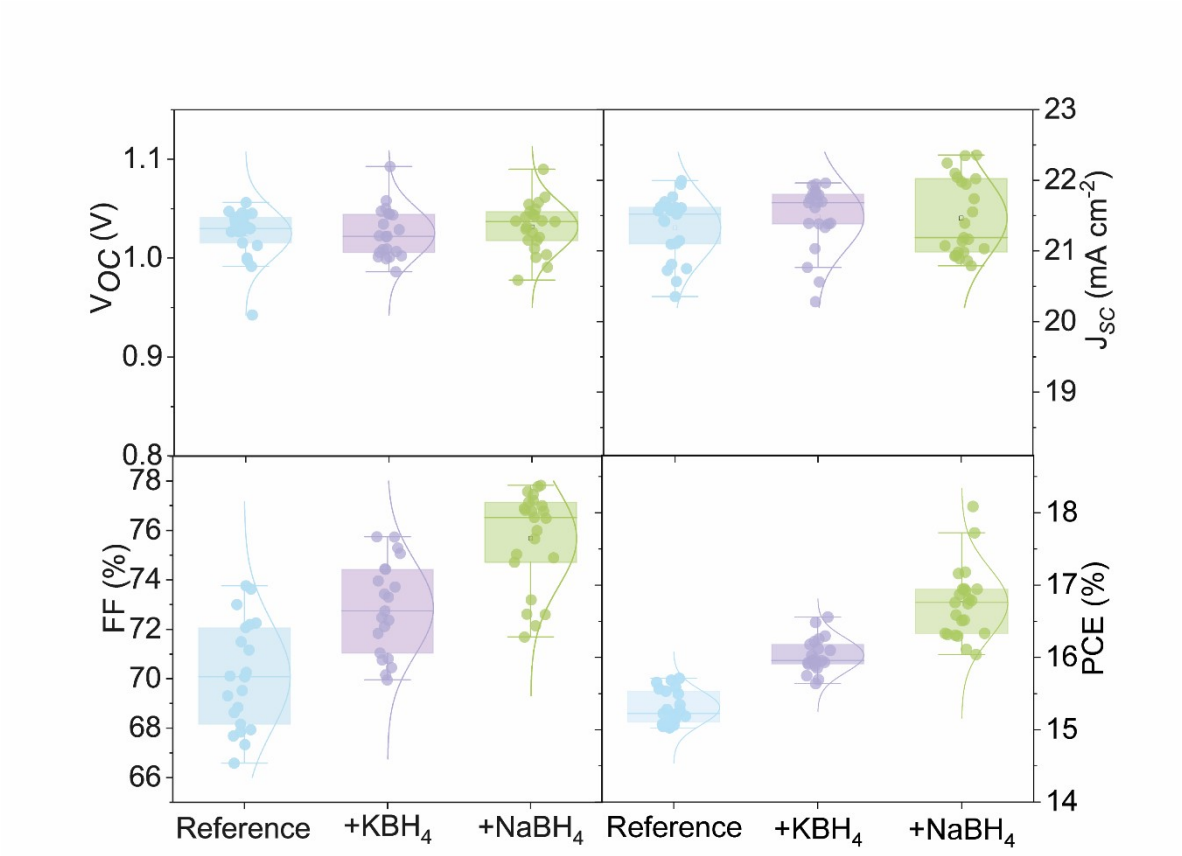

Figure S4. Photovoltaic performance showing J_{sc}, V_{oc}, *FF* and PCE of fresh perovskite solar cells with the statistical analysis. The statistical photovoltaic parameters of perovskite type $Cs_{0.1}FA_{0.9}PbI_3$ were three types of reference devices, KBH_4 and $NaBH_4$ were collected from ~20 devices.

Table S2. The photovoltaic parameters of perovskite solar cells based three types of devices fresh and 3-months aged of reference, +KBH_4, and +$NaBH_4$. The average photovoltaic characteristics of solar cells include the standard deviations of the J_{sc}, V_{oc}, *FF* and PCE. The champion cell efficiency is marked in black. The statistical distribution is based on ~20 devices.

Sample	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
Fresh Reference	1.02 ± 0.02	21.3 ± 0.5	70 ± 2	15.3 ± 0.2
Champion	1.0	22	74	15.7
3-months	0.99 ±41	20.7 ± 0.8	69.3 ±3	14.3 ± 0.9
Champion	1.0	21.5	71	15.5
Fresh +KBH_4	1.02 ± 0.02	21.4 ± 0.5	73 ± 2	16 ± 0.2
Champion	1.0	22	76	16.5
3-months	1.05 ±24	21.2 ± 0.4	73.7 ± 2	16.4 ± 0.4
Champion	1.1	21.8	75	17.7
Fresh +$NaBH_4$	1.03 ± 0.02	21.4 ± 0.5	75 ± 2	16.7 ± 0.4
Champion	1.1	22.3	78	17.7
3-months	1.07 ± 17	21.8 ± 0.4	75.9 ± 2	17.8 ± 0.5
Champion	1.1	21.7	80	18.9

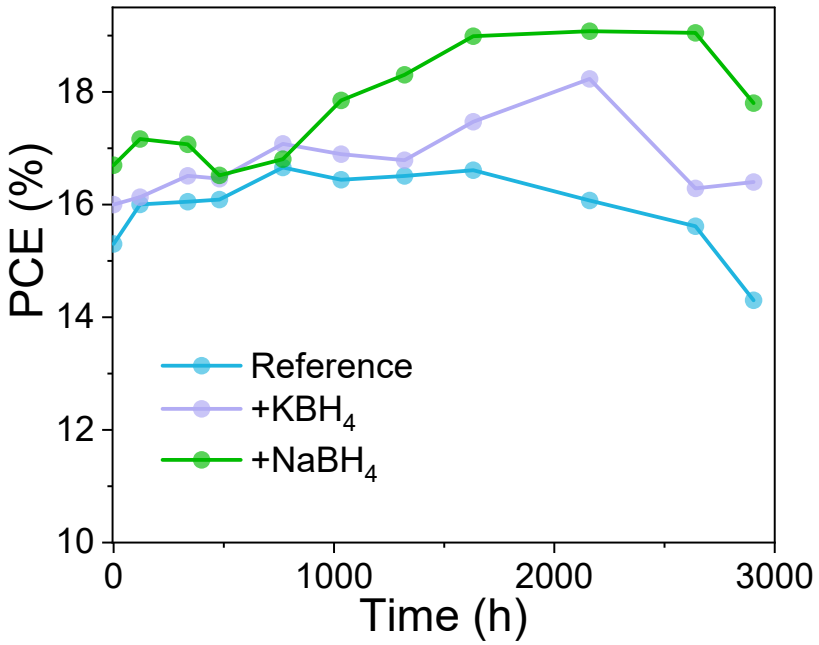

Figure S5. The long-term stability comparison of the unencapsulated with/without KBH_4 and $NaBH_4$ (0.05 mg/mL) shows the normalized power conversion efficiency (PCE). The devices were stored in ambient air (25 °C, RH 20% in dark conditions).

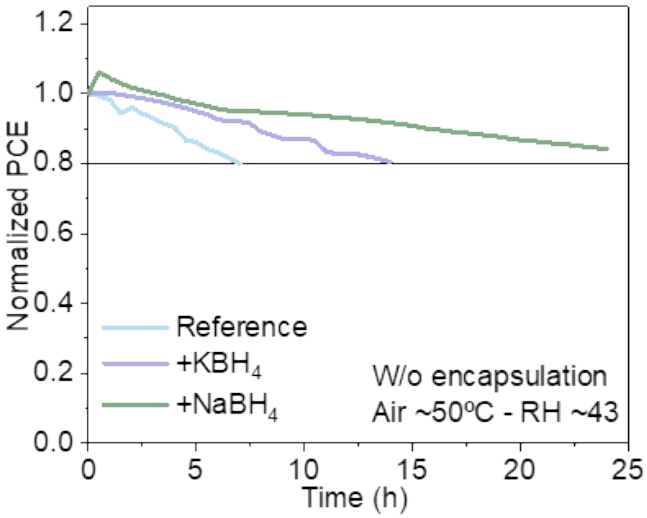

Figure S6. MPP measurements for the control, KBH_4 and $NaBH_4$ devices without any encapsulation.

Table S3. Photovoltaic parameters of the perovskite cells were exposed to high relative humidity (RH~60 ± 10%) and measured every week for a period of 5-weeks under illumination 1 sun in air.

Sample	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
Fresh Reference				
Fresh	23.2	1.0	68	16.1
1-week	19.9	1.0	62	12.7
2-weeks	21.5	1.1	45	10.7
5-weeks	17.8	0.9	25	4.0
Fresh +KBH_4				
Fresh	21.2	1.1	68	15.3
1-week	22.7	1.0	79	18.5
2-weeks	23.4	1.0	77	18.7
3-weeks	24.9	1.0	63	16.5
4-weeks	24.5	1.0	70	17.8
5-weeks	18.3	1.0	52	9.5
Fresh +$NaBH_4$				
Fresh	21.8	1.1	70	16.2
1-week	24.8	1.0	78	20.1
2-weeks	23.5	1.1	76	18.9
3-weeks	23.5	1.0	74	17.9
4-weeks	26.5	1.0	72	20.1
5-weeks	20.8	1.0	70	15.1

Table S4. The ideality factor (n) of the cells obtained by linear adjustment of **Figure 7**.

Weeks aged	Reference	+KBH4	+NaBH4
Fresh	1.85	1.76	2.26
1-week	5.0	1.8	1.6
2-weeks	4.78	1.56	1.78
3-weeks		2.2	1.6
4-weeks		2.3	1.8
5-weeks		4.23	1.82

Table S5. Parameters between the open-circuit voltage and the illumination level. These data indicate that n_{id} = 1.85 for the fresh device, 1.76 and 2.26 for the KBH_4 and $NaBH_4$ device. The measurements were carried out at room temperature (25 °C, RH~60 ± 10%).

Filters	Illumination (W m^{-2})	Reference V_{OC} (V)	KBH_4 V_{OC} (V)	$NaBH_4$ V_{OC} (V)
0	1000	1.05	0.99	1.04
0.3	501	0.90	0.92	0.91
0.5	310	0.93	0.93	0.92
1	100	0.23	0.92	0.88
2	10	0.83	0.84	0.81
3	1	0.66	0.65	0.58

Table S6. Parameters between the open-circuit voltage and the illumination level. These data indicate that n_{id} = 4.78 for the reference, 1.56 and 1.78 for the KBH_4 and $NaBH_4$ device after 2-weeks of aging. The measurements were carried out at room temperature (25 °C, RH~60 ± 10%).

Filters	Illumination (W m^{-2})	Reference V_{OC} (V)	KBH_4 V_{OC} (V)	$NaBH_4$ V_{OC} (V)
0	1000	1.03	1.08	1.05
0.3	501	0.89	0.84	0.90
0.5	310	0.90	0.89	0.91
1	100	0.89	0.85	0.90
2	10	0.83	0.50	0.84
3	1	0.69	0.19	0.66

Table S7. Parameters between the open-circuit voltage and the illumination level. These data indicate that n_{id} = 4.23 and 1.86 for the KBH_4 and $NaBH_4$ device after 5-weeks of aging. The measurements were carried out at room temperature (25 °C, RH~60 ± 10%).

Filters	Illumination (W m^{-2})	KBH_4 V_{OC} (V)	$NaBH_4$ V_{OC} (V)
0	1000	0.94	1.04
0.3	501	0.47	0.87
0.5	310	0.47	0.89
1	100	0.19	0.87
2	10	0.19	0.80
3	1	0.00	0.64