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Electronic Supplementary Information

Unraveling the Modification Effect at NiO_x/perovskite interfaces for Efficient and Stable Inverted Perovskite Solar Cells

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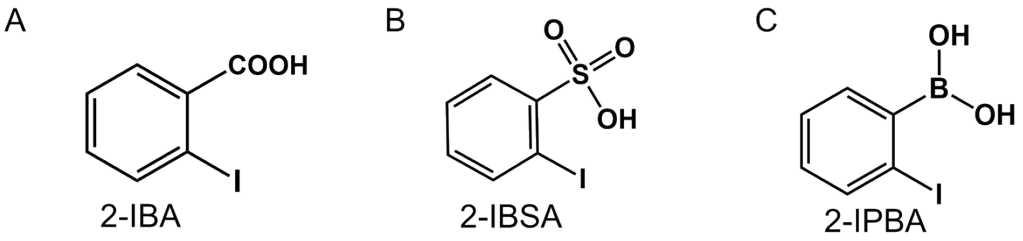

Figure S1. Chemical structures of (A) 2-IBA, (B) 2-IBSA and (C) 2-IPBA.

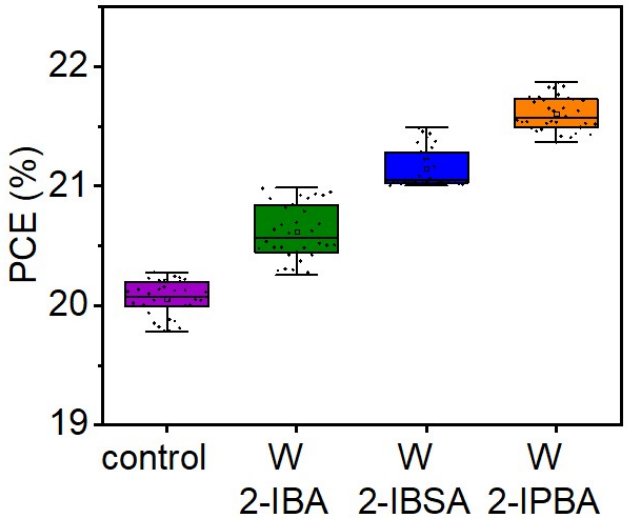

Figure S2. PCE statistics obtained from 35 individual control, 2-IBA, 2-IBSA and 2-IPBA modified PSCs.

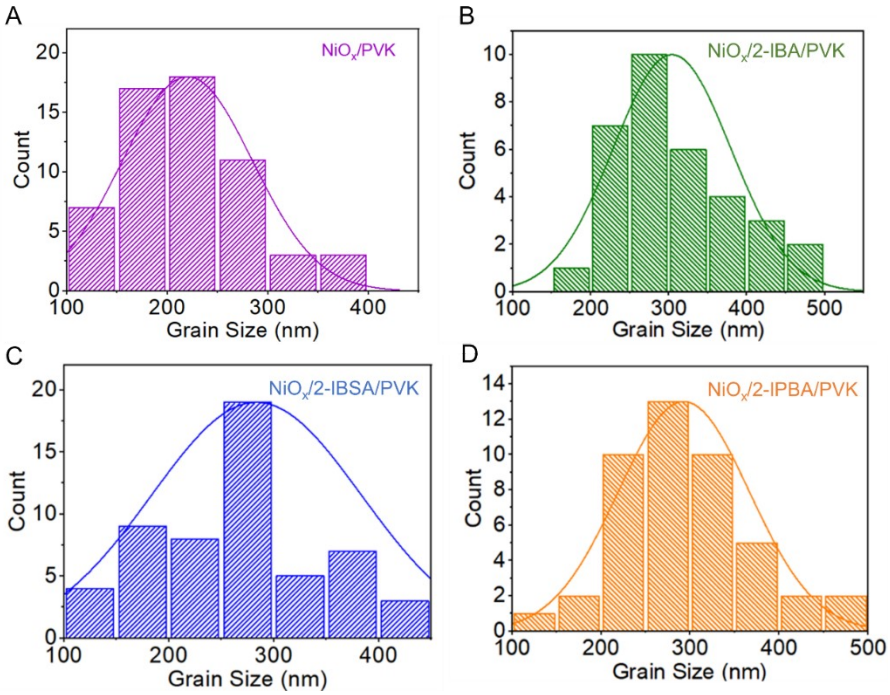

Figure S3. Size distributions of the perovskite grains deposited on (A) NiO_x, (B) NiO_x/2-IBA, (C) NiO_x/2-IBSA and (D) NiO_x/2-IPBA, respectively.

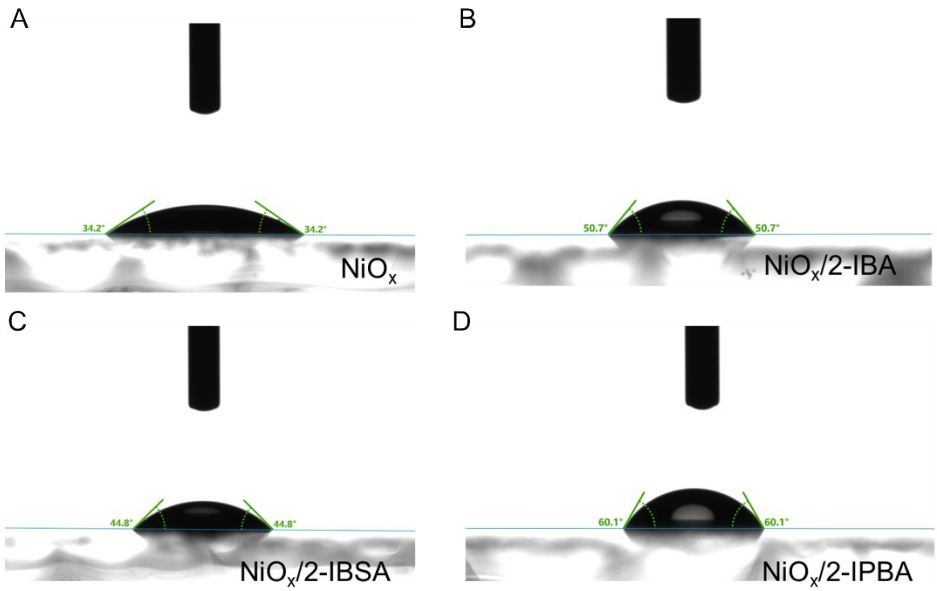

Figure S4. Contact angle testing for (A) the NiO_x, (B) NiO_x/2-IBA, (C) NiO_x/2-IBSA and (D) NiO_x/2-IPBA substrates.

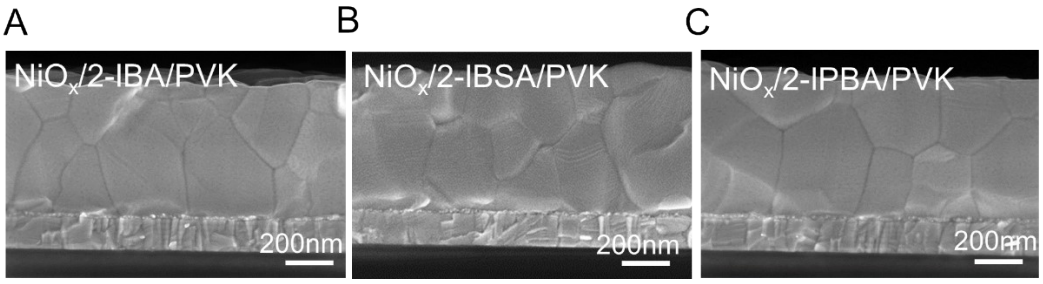

Figure S5. Cross-sectional SEM images of the perovskite films deposited on the (A) NiO_x/2-IBA, (B)NiO_x/2-IBSA and (C)NiO_x/2-IPBA substrate.

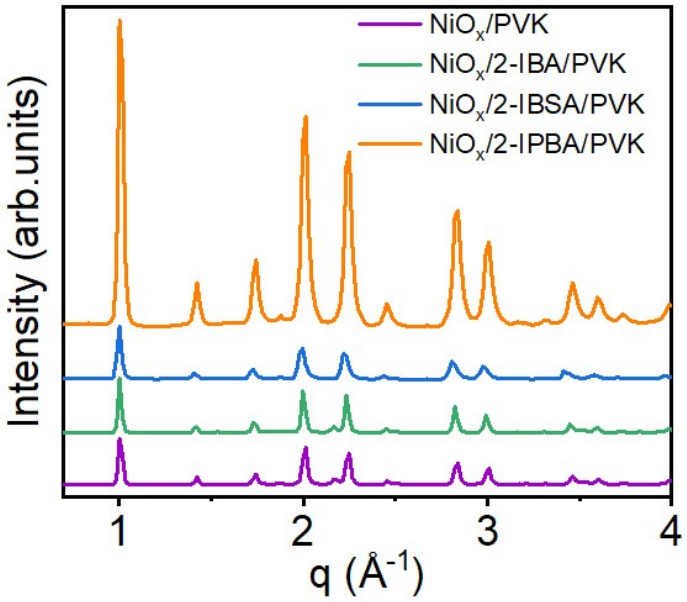

Figure S6. The sector-averaged integrals obtained from the 2D GIWAXS data for the perovskite films deposited on the NiO_x, NiO_x/2-IBA, NiO_x/2-IBSA and NiO_x/2-IPBA substrates.

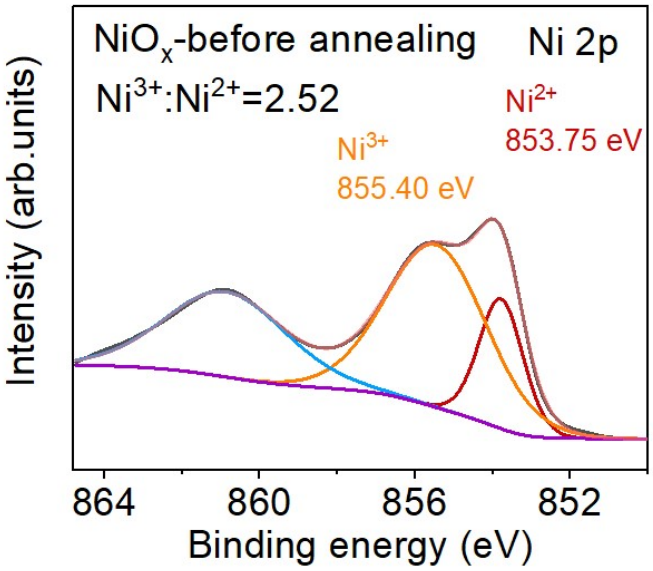

Figure S7. XPS spectra of Ni 2p for the NiO_x film before thermal annealing.

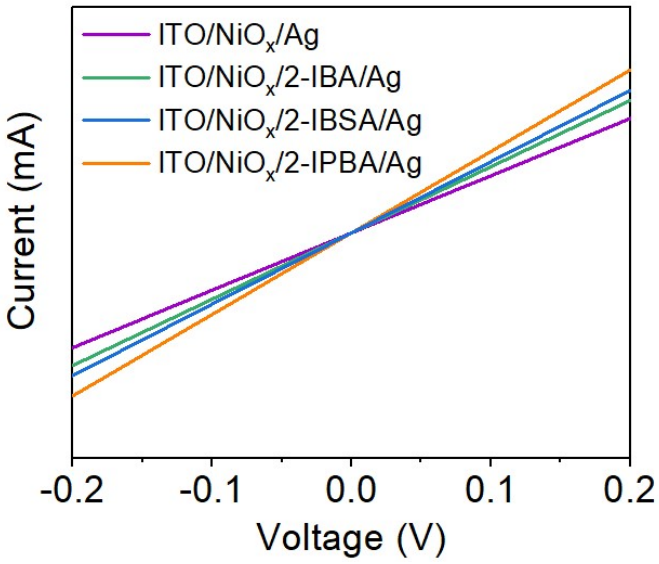

Figure S8. I–V curves of the NiO_x, NiO_x/2-IBA, NiO_x/2-IBSA and NiO_x/2-IPBA films, respectively.

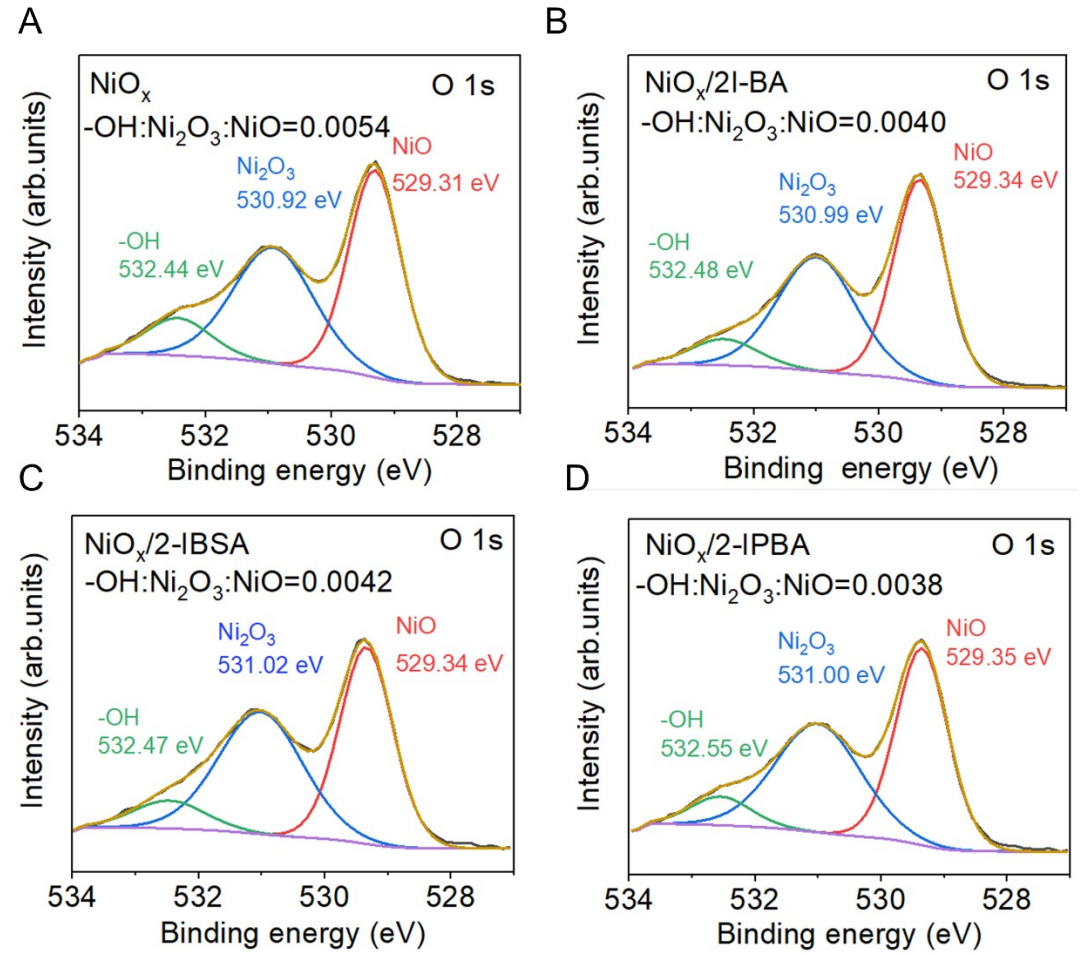

Figure S9. XPS spectra of O 1s for (A) the NiO_x, (B) NiO_x/2-IBA, (C) NiO_x/2-IBSA and (D) NiO_x/2-IPBA films.

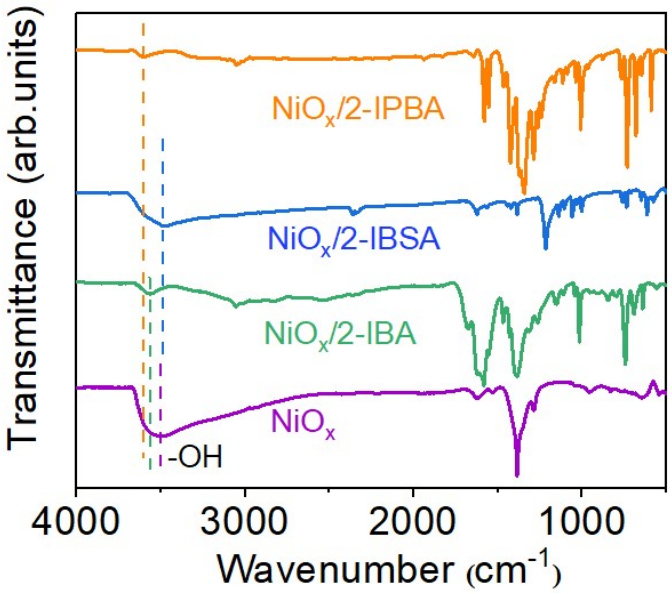

Figure S10. FT-IR spectra of the NiO_x, NiO_x/2-IBA, NiO_x/2-IBSA and NiO_x/2-IPBA films.

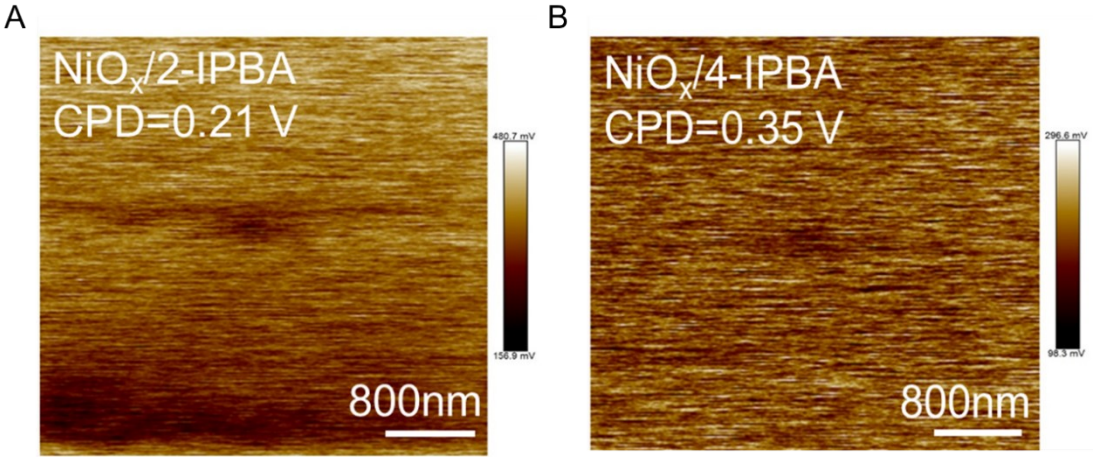

Figure S11. KPFM images of (A) the NiO_x/2-IPBA and (B) NiO_x/4-IPBA films.

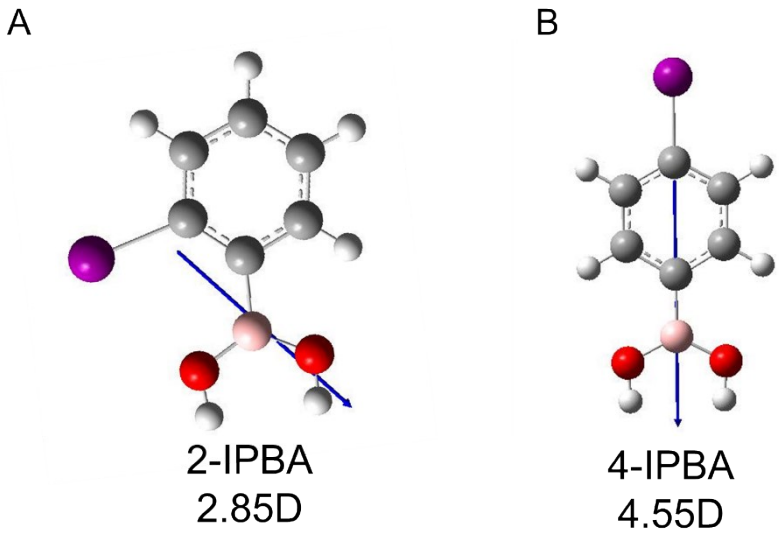

Figure S12. Molecular structures and dipole moments of (A) 2-IPBA and (B) 4-IPBA molecules.

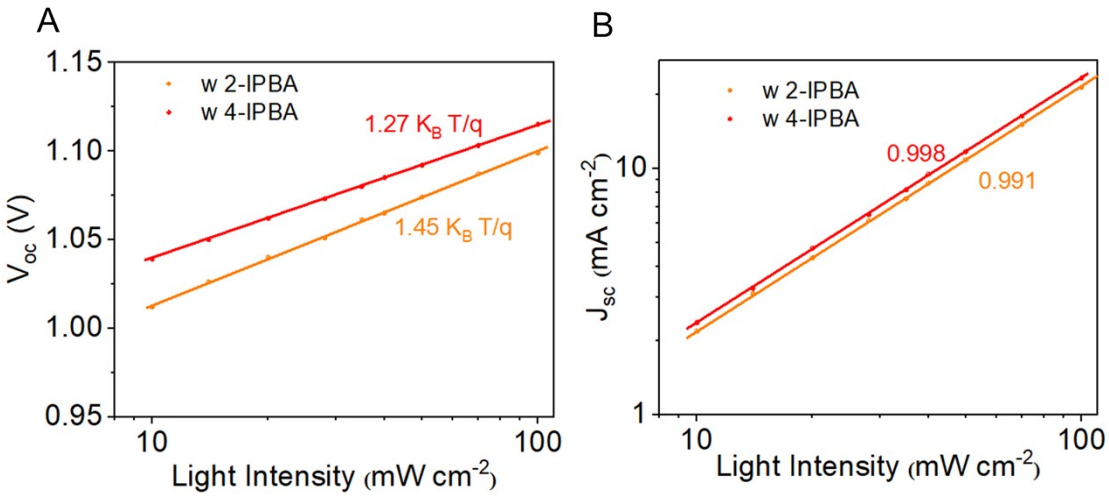

Figure S13. (A) V_{oc} and (B) J_{sc} versus light intensity of PSCs with the 2-IPBA and 4-IPBA modification.

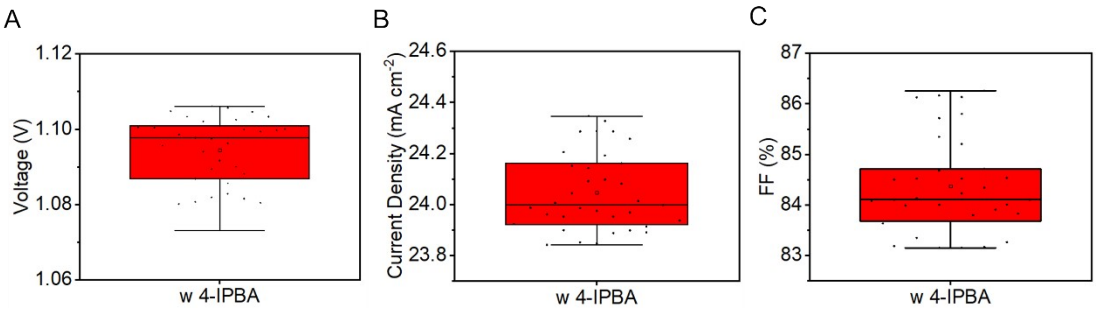

Figure S14. (A) V_{oc}, (B) J_{sc} and (C) FF statistics obtained from 35 PSCs with the 4-IPBA modification.

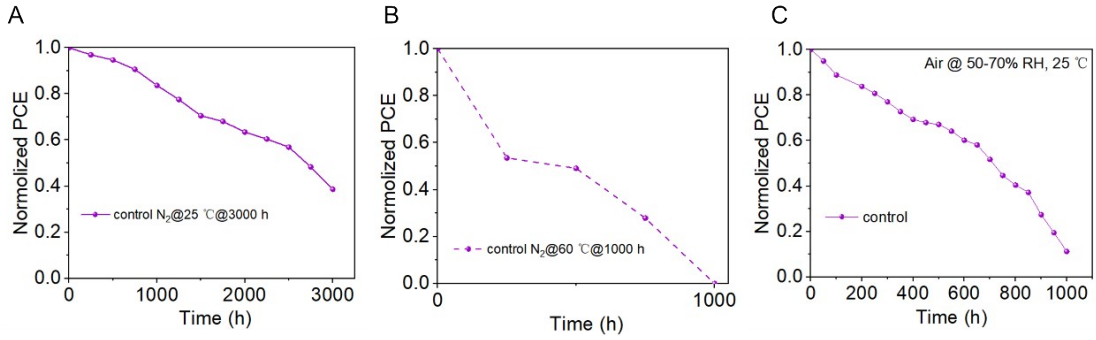

Figure S15. Normalized PCEs of the control device stored in (A) N_2 atmosphere at 25 °C for 3000 h, (B) 60 °C for 1000 h and (C) air (RH of 50-70%, 25 °C) for 1000 h.

Table S1. The average data collected out of 35 cells

	Voc (V)	Jsc (mA cm^{-2})	FF (%)	PCE (%)
control	1.03±0.008	24.23±0.277	79.89±1.324	20.06±0.148
W 2-IBA	1.06±0.010	24.19±0.160	80.93±0.144	20.61±0.236
W 2-IBSA	1.10±0.002	23.95±0.196	80.32±0.206	21.20±0.166
W 2-IPBA	1.10±0.001	23.57±0.336	82.08±0.709	21.70±0.140

Table S2. FWHM and DoO parameters from Figure 2E-H

Samples		$\chi \approx 0$	$\chi \approx 40$	$\chi \approx 65$
NiO_x/PVK	FWHM	52.18	48.24	17.68
	DoO	2.34%	28.06%	11.20%
NiO_x/2I-BA/PVK	FWHM	34.41	31.81	41.76
	DoO	5.58%	30.38%	15.62%
NiO_x/2I-BSA/PVK	FWHM	20.57	41.14	36.91
	DoO	6.21%	22.48%	10.64%
NiO_x/2I-PBA/PVK	FWHM	8.37	43.66	42.76
	DoO	8.02%	18.58%	8.28%

Table S3. Fitted TRPL parameters from Figure 3C

Samples	τ_1 (ns)	τ_2 (ns)	A_1	A_2	ave. (ns)
NiO_x/PVK	20.75	149.46	39.84%	60.16%	98.18
NiO_x/2I-BA/PVK	20.14	144.81	40.43%	59.57%	94.41
NiO_x/2I-BSA/PVK	19.76	143.88	38.34%	61.66%	96.29
NiO_x/2I-PBA/PVK	19.38	136.86	37.41%	62.59%	92.91

Table S4. Binding energy and atomic ratios of pristine NiO_x, NiO_x with 2-IBA treatment, NiO_x with 2-IBSA treatment, and NiO_x with 2-IPBA from Figure 3D-G and Figure S6

Samples	Ni^{3+} (eV) Ratio (%)	Ni^{2+} (eV) Ratio (%)	Ni^{3+}/ Ni^{2+} (%)
NiO_x	855.42 51.32	853.75 16.82	3.05
NiO_x/2I-BA	855.46 49.09	853.76 18.95	2.59
NiO_x/2I-BSA	855.48 49.42	853.76 19.31	2.56
NiO_x/2I-PBA	855.52 49.26	853.76 18.68	2.63
NiO_x/before annealing	855.40 53.53	853.75 21.27	2.52

Table S5. Fitted TRPL parameters from Figure 4E

Samples	τ_1 (ns)	τ_2 (ns)	A_1	A_2	ave. (ns)
NiO_x/4I-PBA/PVK	16.41	137.80	42.58%	57.42%	86.11

Table S6. Comparing the performance of PSCs based on halogenated phenyl acids-modified NiO_x HTLs

Modifiers	Architecture	Performance	Ref
4-iodo-2,3,5,6-tetrafluorobenzoic acid (I-TFBA)	ITO/NiO_x/I-TFBA/ $Cs_{0.05}(FA_{0.92}MA_{0.08})_{0.95}Pb(I_{0.92}Br_{0.08})_3$/PEAI/PCBM /BCP/Ag	V_{oc}=1.17 V J_{sc}=22.3 mA cm^{-2} FF=82.2% PCE=22.02%	1
p-chlorobenzenesulfonic acid (CBSA)	ITO/NiO_x/CBSA/ $MAPbI_3$/ PCBM/BCP/Ag	V_{oc}=1.11 V J_{sc}=23.23 mA cm^{-2} FF=80.17% PCE=20.7%	2
Br-benzoic acid (Br-BA)	ITO/NiO_x/Br-BA/$MAPbI_3$/ PCBM/C_{60}/Ag	V_{oc}=1.11 V J_{sc}=21.7 mA cm^{-2} FF=76.3% PCE=18.4%	3
4-bromobenzoic acid	ITO/NiO_x/4Br-BA/ $FAMAPbI_3$/ PCBM/C_{60}/Ag	V_{oc}=1.01 V J_{sc}=19.8 mA cm^{-2} FF=64% PCE=12.6%	4
4-bromobenzylphosphonic acid	ITO/NiO_x/4-Br-BPPA/ $CsFAMAPbBr_3I_3$/ PCBM/Ag	V_{oc}=1.09 V J_{sc}=18.58 mA cm^{-2} FF=67.18% PCE=12.73%	5
[2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic Acid+4-Bromobenzoic acid	ITO/NiO_x /MeO-2PACz+Br-BA/PVK/ PEAI/C_{60}/SnO_2/Ag	V_{oc}=1.05 V J_{sc}=23.40 mA cm^{-2} FF=83% PCE=20.38%	6
2-iodobenzoic acid (2-IBA)	**ITO/NiO_x/2-IBA/ $Cs_{0.05}(FA_{0.98}MA_{0.02})_{0.95}Pb(I_{0.98}Br_{0.02})_3$/PCBM /BCP/Ag**	**V_{oc}=1.06 V J_{sc}=24.20 mA cm^{-2} FF=80.81% PCE=20.77%**	**This Work**
2-iodobenzenesulfonic acid (2-IBSA)	**ITO/NiO_x/2-IBSA/ $Cs_{0.05}(FA_{0.98}MA_{0.02})_{0.95}Pb(I_{0.98}Br_{0.02})_3$/PCBM /BCP/Ag**	**V_{oc}=1.10 V J_{sc}=23.95 mA cm^{-2} FF=80.97% PCE=21.37%**	**This Work**
2-iodophenylboronic acid (2-IPBA)	**ITO/NiO_x/2-IPBA/ $Cs_{0.05}(FA_{0.98}MA_{0.02})_{0.95}Pb(I_{0.98}Br_{0.02})_3$/PCBM /BCP/Ag**	**V_{oc}=1.10 V J_{sc}=23.76 mA cm^{-2} FF=82.9% PCE=21.81%**	**This Work**
4-iodophenylboronic acid (4-IPBA)	**ITO/NiO_x/4-IPBA/ $Cs_{0.05}(FA_{0.98}MA_{0.02})_{0.95}Pb(I_{0.98}Br_{0.02})_3$/PCBM /BCP/Ag**	**V_{oc}=1.08 V J_{sc}=24.42 mA cm^{-2} FF=86.18% PCE=22.91%**	**This Work**

Notes and references

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