

*Supplemental Information*

**Oxysalt Based Synergistic Dual Interfacial Engineering for  
High Performing P-I-N Structured Perovskite Solar Cells**

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## EXPERIMENTAL

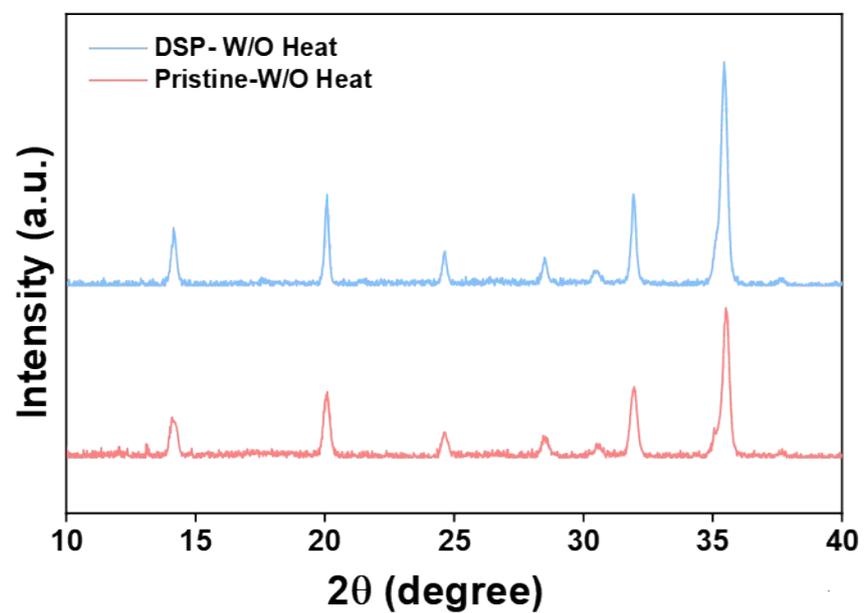
**Materials:** The materials used in this work were sourced from various suppliers. Indium-doped tin oxide (ITO) glass substrates were provided by AMG-Tech. The suspensions of NiO and ZnO nanoparticles (2.5 wt% in ethanol and isopropanol, respectively) and phenyl-C61-butyric acid methyl ester (PCBM) were all procured from 1-Material. Sodium nitrate salt ( $\text{NaNO}_3$ , purity  $\geq 99\%$ ) was obtained from Sigma-Aldrich. For the preparation of perovskite precursor, Lead (II) iodide ( $\text{PbI}_2$ ) and lead bromide ( $\text{PbBr}_2$ ) each with a purity of 99% were obtained from Tokyo Chemical Industry (TCI) and Great Cell Solar, respectively. Cesium iodide (CsI) with a purity of 99.99 % and methylammonium bromide (MABr) with a purity of  $\geq 99\%$  were obtained from Sigma-Aldrich. The solvents, including chlorobenzene (CB), isopropyl alcohol (IPA), dimethyl sulfoxide (DMSO), and toluene (TL), were obtained from Sigma-Aldrich and used as received without further purification.

**Device Fabrication:** The perovskite solar cells with structure ITO/NiO NPs/Perovskite/PCBM/ZnO NPs/Copper (Cu) were fabricated following the procedure described in our previous report<sup>1, 2</sup>. Briefly, ITO substrates were cleaned through ultrasonication in deionized water, acetone, and IPA for 10 minutes each, followed by drying in an oven at 80 °C for 10 minutes. Next, UV-ozone treatment was performed for 20 minutes. Then, the hole transport layer (HTL) was coated by spin-coating at 4000 rpm for 40 s using 40  $\mu\text{L}$  of NiO solution before being annealed in the air for 30 minutes. After cooling, the devices were coated with a 6 mM solution of  $\text{NaNO}_3$  in ethanol using a spin-coater at 3000 rpm for 30 s, and then annealed at 100 °C for 1 min. At this point, the devices were transferred to a nitrogen-filled glove box for further deposition. The perovskite solution of composition ( $\text{Cs}_{0.175}\text{FA}_{0.750}\text{MA}_{0.075}\text{Pb}(\text{I}_{0.880}\text{Br}_{0.120})_3$ ) was prepared by dissolving  $\text{PbBr}_2$  (0.080 g),  $\text{PbI}_2$  (0.568 g), CsI (0.066 g), FAI (0.187 g), and MABr (0.012 g) in DMSO (200  $\mu\text{L}$ ) and DMF

(800  $\mu\text{L}$ ) solvents. The perovskite layer was formed by spin-coating the precursor solution using a two-step spin-coating process on top of the HTL: The first step of spin-coating involved spinning at 500 rpm for 15 s followed by 5000 rpm for 45 s. The deposited perovskite layer was annealed at 100  $^{\circ}\text{C}$  for 30 min, which was followed by the deposition of  $\text{NaNO}_3$  in IPA.  $\text{NaNO}_3$  in IPA with a 4 mM concentration was deposited with a coating speed of 3000 rpm for 30 s and heated at 100  $^{\circ}\text{C}$  for 10 min. This was followed by the deposition of the electron transport layer (ETL). The PCBM solution ( $0.020 \text{ gmL}^{-1}$  in dichlorobenzene) was spin-coated on top of the perovskite layer with a speed of 6000 rpm for 50 s, followed by annealing at 100  $^{\circ}\text{C}$  for 10 min. Next, the ZnO solution was spin-coated onto the PCBM layer at 1000 rpm for 15 s and 8000 rpm for 40 s, respectively, followed by annealing at 100  $^{\circ}\text{C}$  for 10 min. Lastly, a Cu electrode with a 100 nm thickness (and an active area of  $0.0464 \text{ cm}^2$ ) was deposited on top in a thermal evaporation chamber under vacuum conditions of  $10^{-6}$  torr.

**Measurement and Characterizations:** The photocurrent density-voltage (J-V) measurement was conducted using a Keithley 2400 and an Oriel solar (Class AAA) simulator) under Air Mass 1.5 G, with light intensity calibrated using a standard Si reference cell certified by the International System of Units (SI) (SRC 1000 TC KG5N, VLSI Standards, Inc). The transient photocurrent (TPC) and transient photovoltage (TPV) were obtained using a Tektronix oscilloscope (DPO-2014B), a multi-functional organic semiconductor parameter test system with a 100 MHz bandwidth (T4000, McScience). The dependency of  $V_{\text{OC}}$  on the light intensity was analyzed by adjusting the optical filter (neutral-density (ND) filter, Newport). The surface potential analyses were performed under ambient conditions using atomic force microscopy with a scanning Kelvin probe (AFM, XE7 Park). Steady-state photoluminescence (PL) was determined using a Spectro-fluorophotometer (SHIMADZU Lab solutions, RF-6000) at room temperature. Time-resolved photoluminescence (TRPL) was analyzed using Fluorolog-QM, Horiba system with a laser source with 450 nm excitation whose instrument is installed Future

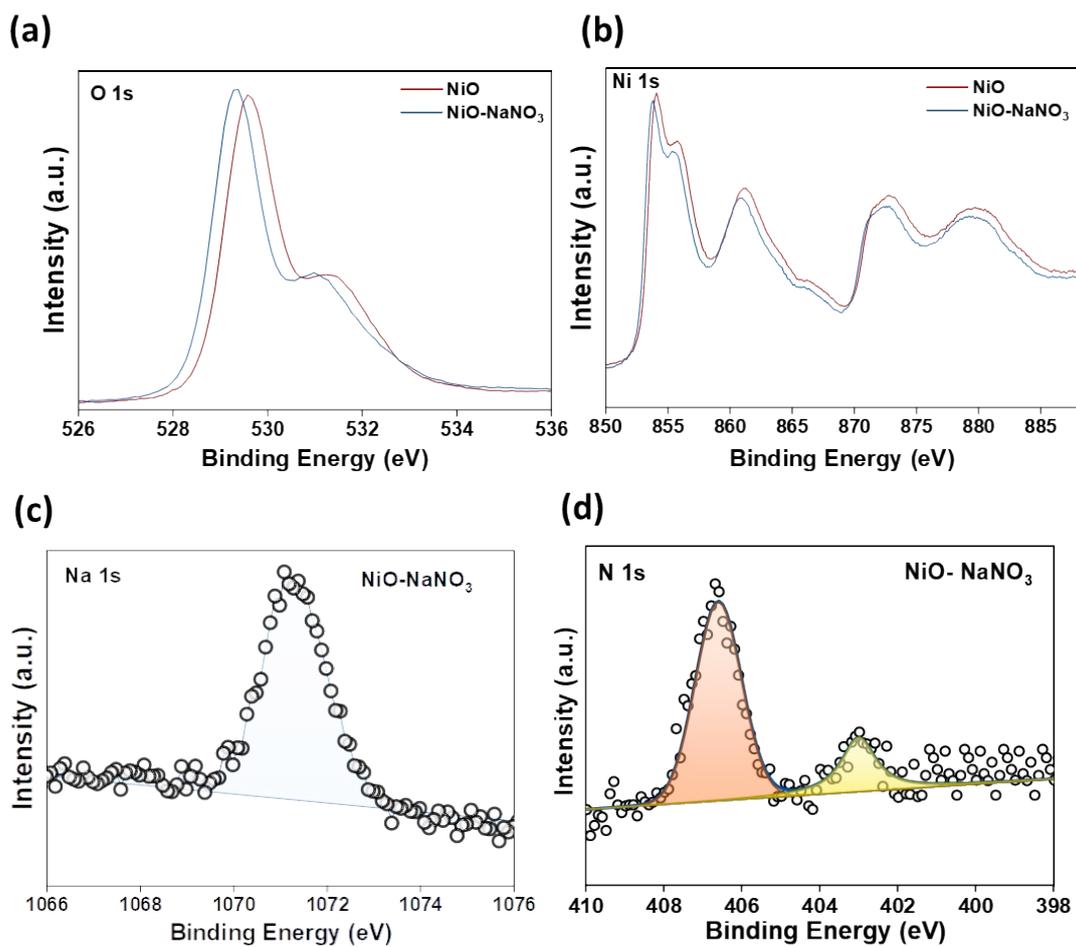
Energy Convergence Core Center (FECC) at Jeonbuk National University. X-ray photoelectron spectroscopy (XPS) was conducted using the Nexsa XPS system, Monochromatic Al K $\alpha$ , Thermo Fisher Scientific, UK, to analyze the energy levels, chemical composition, and interactions in the films whose instrument is installed at the Jeonju Center of the Korea Basic Science Institute (KBSI). Lastly, Fourier-transform infrared spectrometry (FTIR) was performed in the range from 4000 – 500 cm<sup>-1</sup> (FTIR-4100, Jasco, JP), whose instrument is installed at Future Energy Convergence Core Center (FECC) at Jeonbuk National University.



**Figure S1:** XRD patterns for perovskite films for pristine and DSP perovskite layers without heating.

**Table S1:** FWHM calculated from XRD spectra.

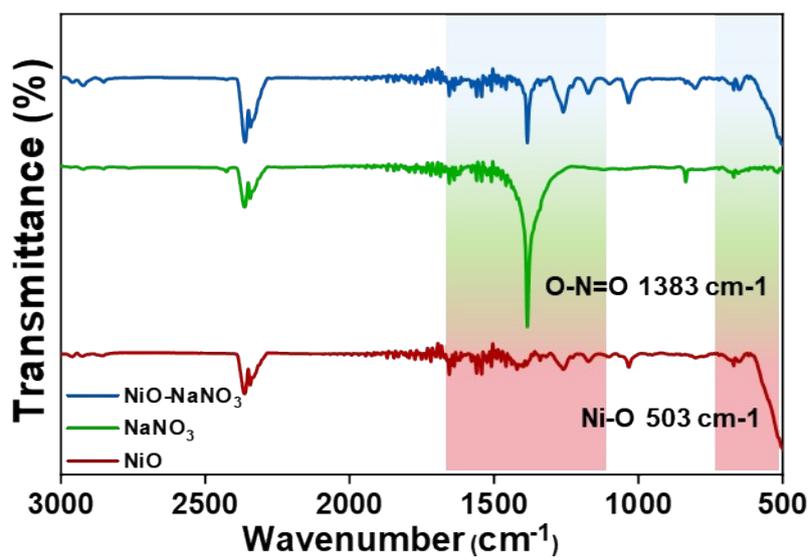
<b>ANGLE (DEGREE)</b>	<b>FWHM</b>			
	<b>PRISTINE WITHOUT HEAT</b>	<b>DSP WITHOUT HEAT</b>	<b>PRISTINE WITH HEAT</b>	<b>DSP WITH HEAT</b>
<b>14</b>	0.333	0.227	0.272	0.129
<b>20</b>	0.281	0.184	0.221	0.114
<b>24</b>	0.268	0.198	0.217	0.121
<b>28</b>	0.320	0.206	0.224	0.167
<b>32</b>	0.303	0.203	0.236	0.160



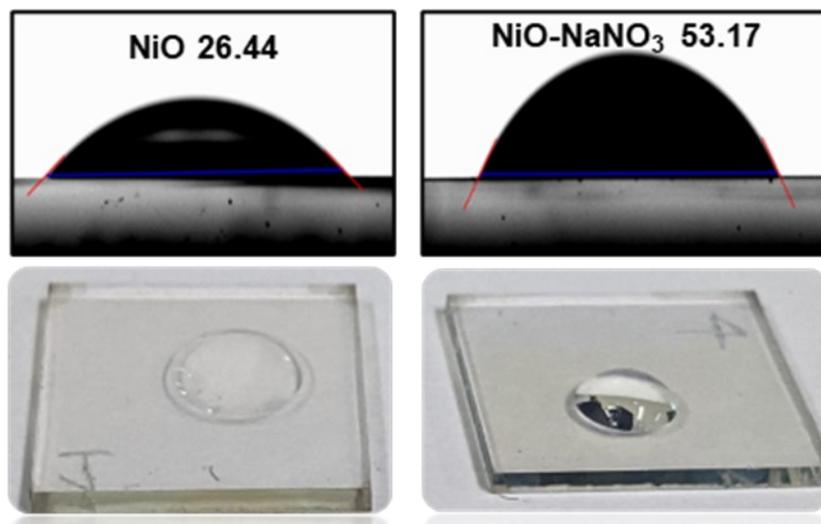
**Figure S2:** XPS Spectra for NiO and NiO-NaNO<sub>3</sub> coated layers and corresponding O, Ni, Na and N.

**Table S2:** Relative composition and relative ratio of nickel oxidation species determined from peak fitting of Ni 2p<sub>3/2</sub> and O 1s core level spectra.

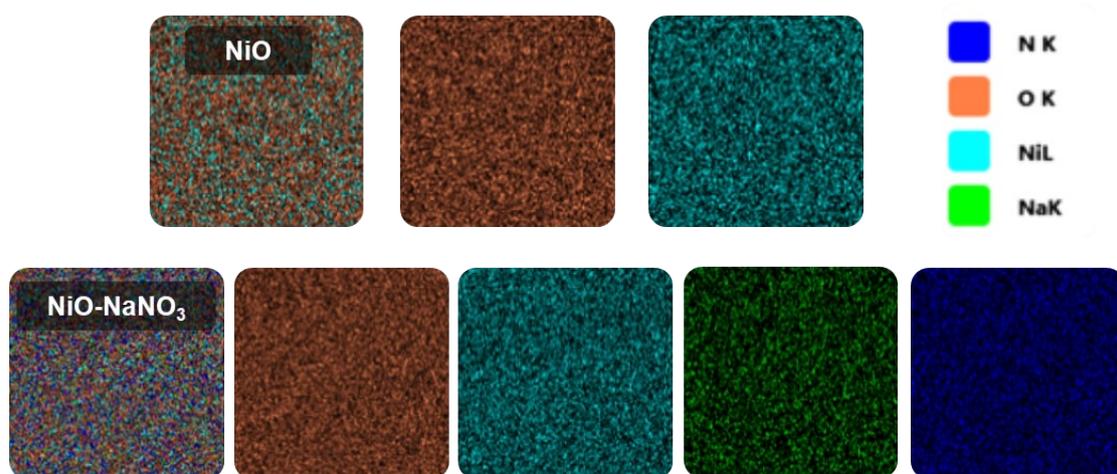
Category		Composition			Ratio of nickel oxidation species	
		NiO	Ni <sub>2</sub> O <sub>3</sub>	NiOOH	Ni <sub>2</sub> O <sub>3</sub> /NiO	NiOOH/NiO
Ni 2p <sub>3/2</sub>	Pristine	52.3	24.7	22.9	0.47	0.43
	with NaNO <sub>3</sub>	41.4	44.5	13.9	0.59	0.39
O 1s	Pristine	61.98	30.62	7.38	0.49	0.12
	with NaNO <sub>3</sub>	58.86	35.24	5.88	0.59	0.10



**Figure S3:** FTIR Spectra for NiO, NaNO<sub>3</sub> and NiO-NaNO<sub>3</sub> coated layers.



**Figure S4:** Contact angle analysis for NiO, and NiO-NaNO<sub>3</sub> layers.



**Figure S5:** Energy-dispersive X-ray spectroscopy (EDS) element mapping of corresponding elements (Ni, O, Na and N) for NiO and NiO-NaNO<sub>3</sub> thin films.

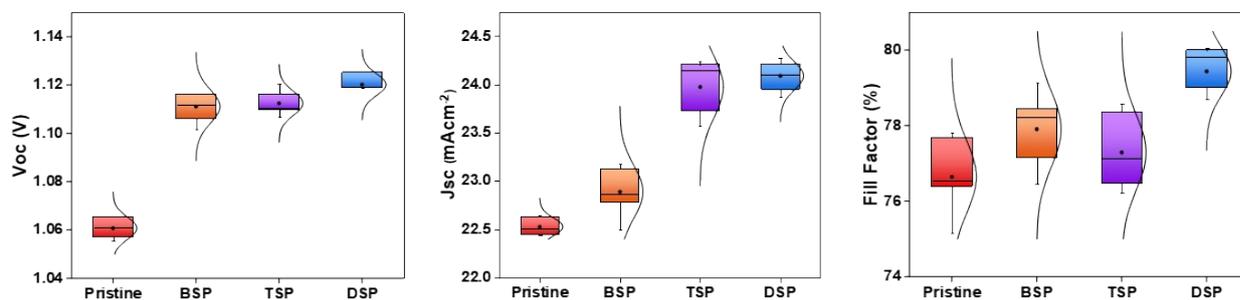
**Table S3:** Atomic percentage of perovskite films for Pristine and TSP; Br 3d, C 1s, Cs 3d, I 3d, N 1s, O 1s, and Pb 4f.

<b>Sample</b>	<b>Br 3d</b>	<b>C 1s</b>	<b>Cs 3d</b>	<b>N 1s</b>	<b>O 1s</b>	<b>I 3d</b>	<b>Pb 4f</b>	<b>Na 1s</b>
Pristine	4.32	25.29	2.3	18.73	2.64	36.93	10.29	0
TSP	3.68	28.28	1.81	16.51	4.11	34.45	9.86	1.88

**Table S4:** Fitting parameters for TRPL analysis.

Average decay time is calculated according to the equation:  $\tau_w = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$

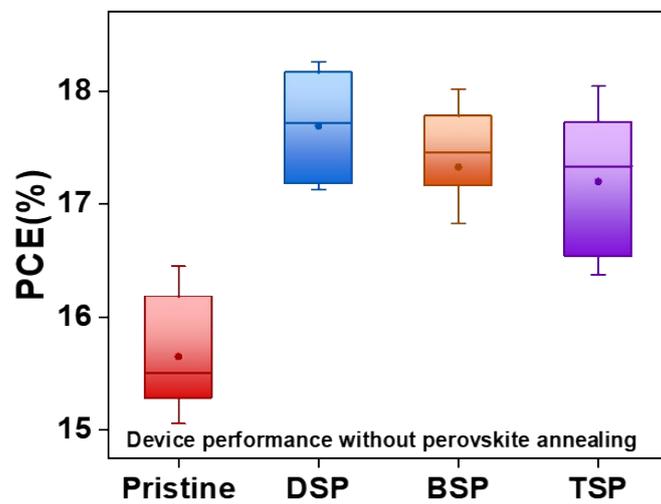
<b>Sample</b>	<b>A<sub>1</sub></b>	<b><math>\tau_1</math></b>	<b>A<sub>2</sub></b>	<b><math>\tau_2</math></b>	<b><math>\tau_{PL}</math> (ns)<sup>a)</sup></b>
Pristine	0.393	7.54	0.358	76.43	40.37
TSP	0.318	7.66	0.409	86.63	52.12



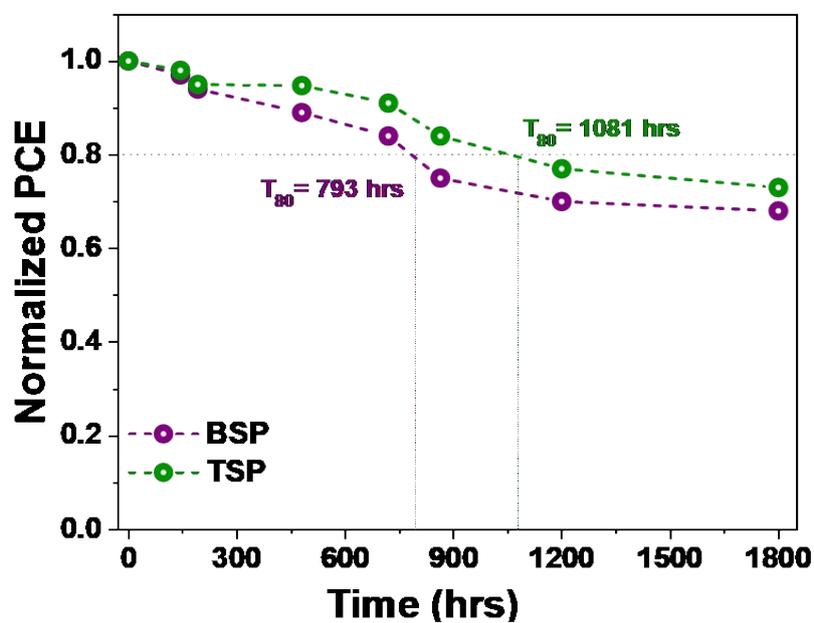
**Figure S6:** Corresponding statistical photovoltaic parameters of pristine and modified devices under optimal conditions

**Table S5:** Representative photovoltaic parameters of PSCs for all modified and control samples under AM 1.5G illumination at 100 mW cm<sup>-2</sup>.

<b>Average</b>	<b>V<sub>oc</sub> (V)</b>	<b>J<sub>sc</sub> (mA cm<sup>-2</sup>)</b>	<b>FF (%)</b>	<b>PCE (%)</b>
Pristine	1.06	22.63	75.18	19.08
BSP	1.11	22.80	78.35	20.16
TSP	1.11	24.25	77.40	20.83
DSP	1.12	24.20	79.49	21.53



**Figure S7:** Statistical photovoltaic parameters of pristine and modified devices without heat.



**Figure S8:** Normalized PCE as a function of time for the unencapsulated devices stored in the nitrogen environment for the PSC with BSP and TSP samples.

## REFERENCES

1. P. Patil, D. S. Mann, U. T. Nakate, Y.-B. Hahn, S.-N. Kwon and S.-I. Na, *Chemical Engineering Journal*, 2020, 397, 125504.
2. S.-N. Kwon, J.-H. Yu and S.-I. Na, *Journal of Alloys and Compounds*, 2019, 801, 277-284.