Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Self-Doping Synthesis of Trivalent Ni_2O_3 as Hole Transport Layer for High Fill Factor and Efficient Inverted Perovskite Solar Cells

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Thermokinetic Parameters:

Nonisothermal methods determined the kinetic and thermodynamic parameters. The non-isothermal kinetic analysis for the thermal decomposition of Ni-Ac, Ni-Nt and Ni-Mix in this work was carried out by the application of Coats-Redfern method.[1] The kinetic parameters were evaluated only for clear-cut and non-overlapping stages. Kinetic studies were not attempted for decomposition stages, which occur within a very narrow temperature range, resulting in a TG curve too step for enough data to be collected. Furthermore, some decomposition steps are so small that within the accuracy of the measurements, a sufficient number of points from the TG curve could not be obtained to derive meaningful results for kinetic parameters. The kinetic parameters were calculated according to Coats-Redfern method methods.

Determination of reaction order of decomposition

The Horowitz and Metzger equation $Cs=n^{1/1-n}$, where n is the order of the reaction and Cs is the mass fraction of the substance present at the DTA peak temperature; Cs, is given by:

$$Cs=(W_s-W_f)(W_0-W_f) \qquad (1)$$

Where W_s stands for the mass remaining at a given temperature, Cs is the DTG peak temperature, W_0 and W_f are the initial and final masses of the substance, respectively.

Integral method used in this study:

The Coats-Redfern equation:-

$$\log\left[\frac{W_f/W_r}{T^2}\right]=\log\left[\frac{AR}{\theta E^*}\left(1-\frac{2RT}{E^*}\right)\right]-\left(\frac{E^*}{2.303RT}\right) \qquad (2)$$

Where W_f is the mass loss at completion of the reaction, W is the mass loss up to temperature T; (Wr $=W_f-W$), R is the gas constant, E^* is the activation energy in (KJ mol^{-1}), θ is the heating

rate. Since $1-2RT/E^* \cong 1$, a plot of the left-hand side of the above equation against 1/T was constructed and E^* was calculated from the slope and A (Arrhenius constant) were calculated from the slope and the intercept, respectively.

Degree of decomposition:

$$\alpha = \frac{W_0 - W_T}{W_0 - W_f} \qquad (4)$$

Where α is extent decomposition, W_T, W_0, W_f are the actual, initial, and final mass of the sample, respectively. The activation energy (E) can be calculated from a plot of $\log\left(g(\alpha)/T^2\right)$ vs. 1/T. The excellent correlation coefficients, which indicate a good fit of the linear function, were obtained for the Coats-Redfern method as shown in Figure S2. This figure gives the slope for calculation of E which used to calculate ΔH*, ΔS* and ΔG* using the following equations:

The following equations calculate the enthalpy, entropy and free energy:

Activation enthalpy:

$$\Delta H^* = E^* - RT \qquad (5)$$

The entropy of activation:

$$\Delta S^* = R\left[\ln\left(\frac{Ah}{KT}\right) - 1\right] \qquad (6)$$

Free energy:

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (7)$$

where K is the Boltzmann's constant and h is the Planck's constant.

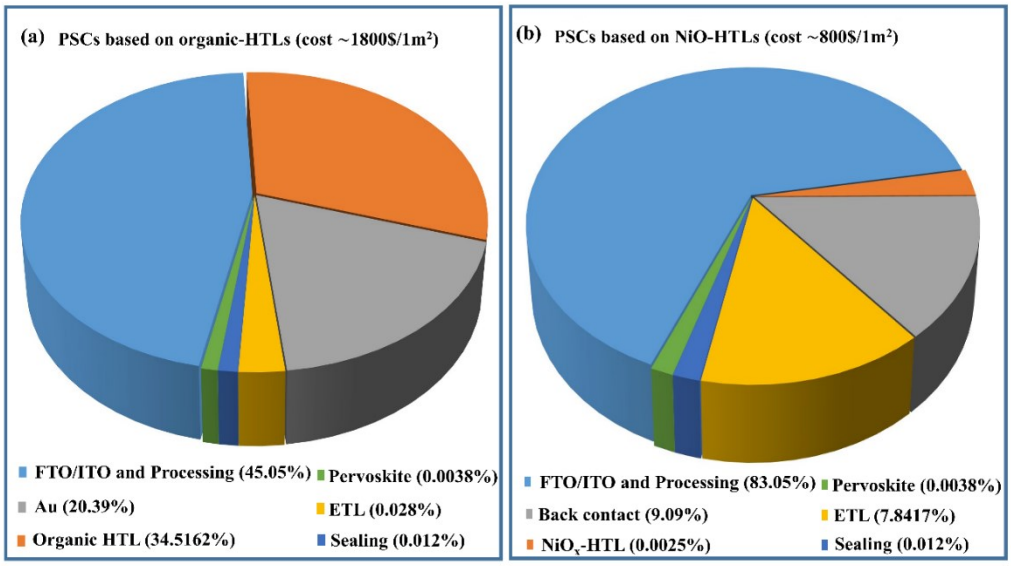

Figure S1. Pie charts illustrate the cost-breakdown for PSCs incorporated with (a) Organic-HTMs (b) NiO_x-HTMs.[2]

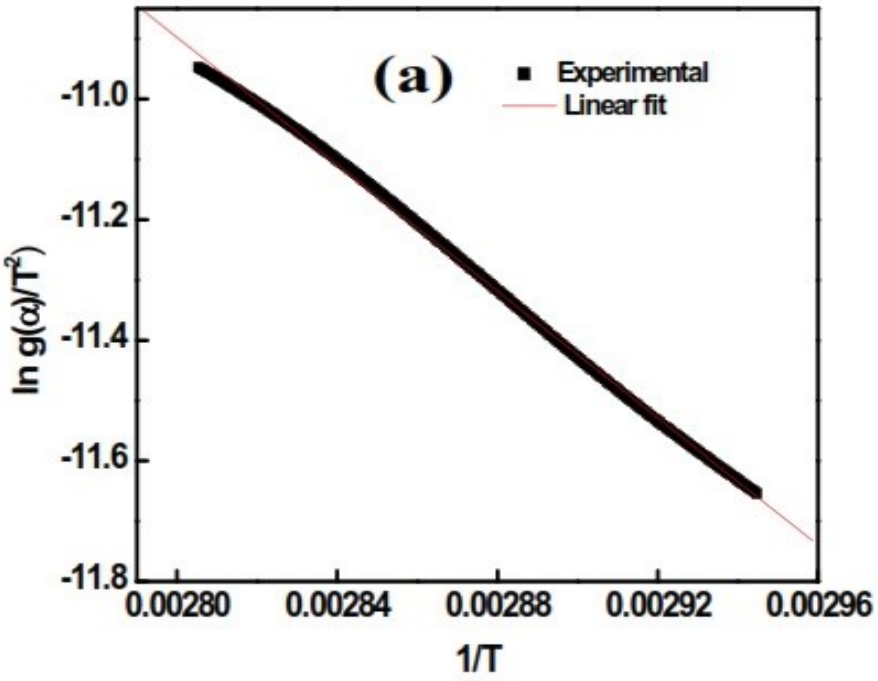

Figure S2. Linearization curves obtained by Coats–Redfern method for Ni-Mix sample.

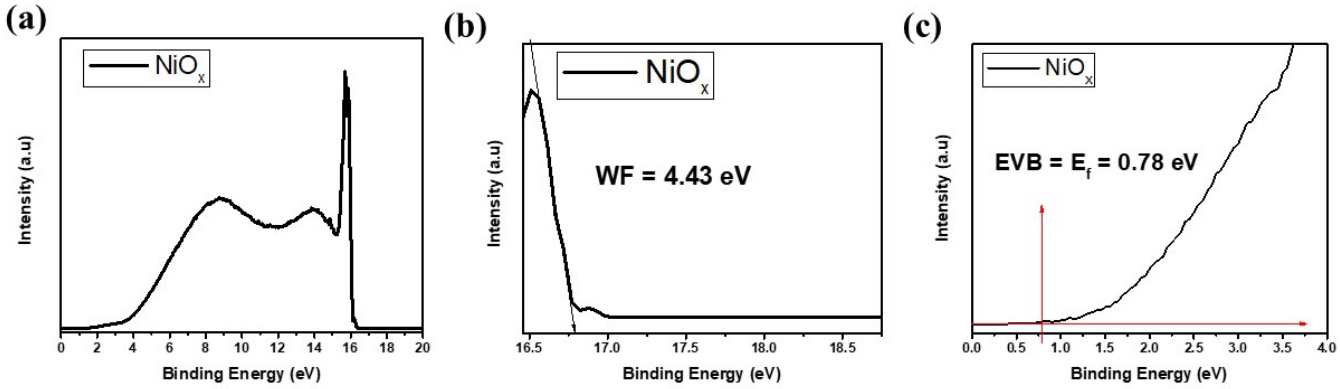

Figure S3. (a) UPS spectra of NiO_x. (b) and (c) The valence band maximum (VBM) and work function (WF) of NiO_x thin film.

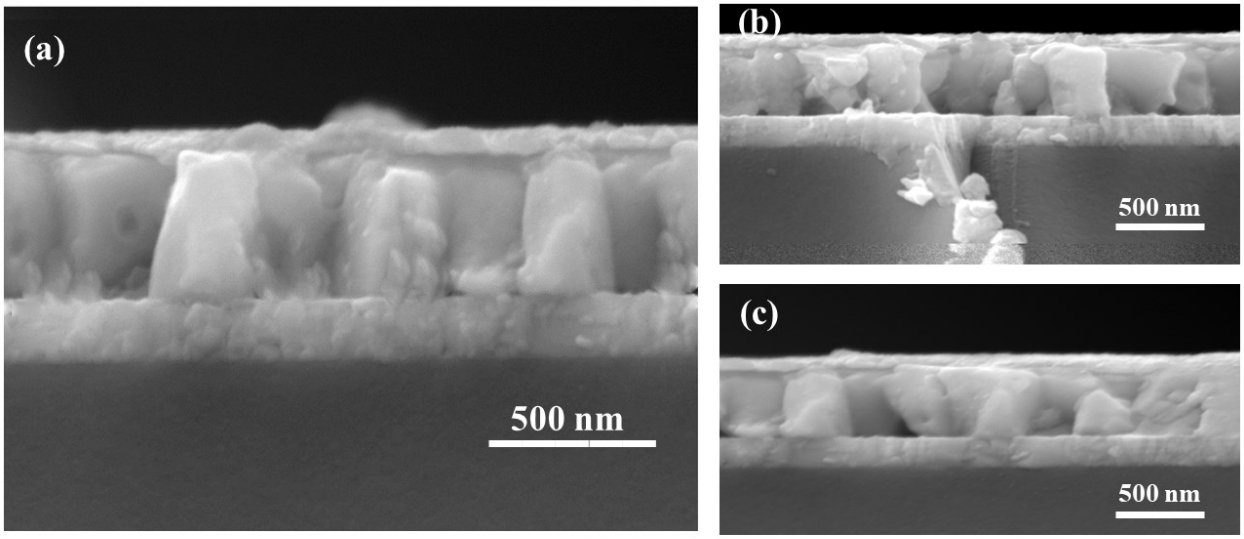

Figure S4. Cross-sectional image by scanning electron microscope for the optimized device based on (a) Ni_2O_3, (b) NiO_x, and (c) PEDOT:PSS as HTL with configuration FTO/HTL/$MA_{0.85}FA_{0.15}PbI_{0.9}Cl_{0.1}$/PCBM/BCP/Ag.

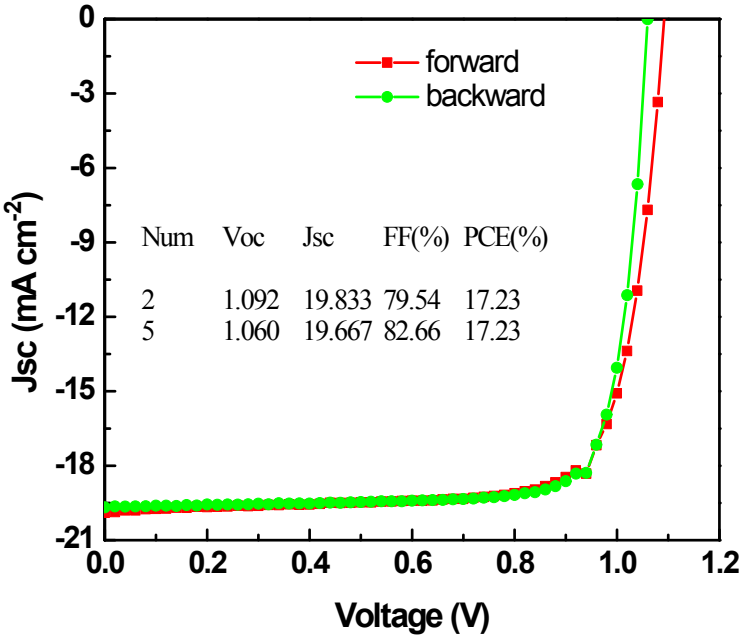

Figure S5. J–V curves of perovskite solar cells based on Ni_2O_3 measured under different scan directions.

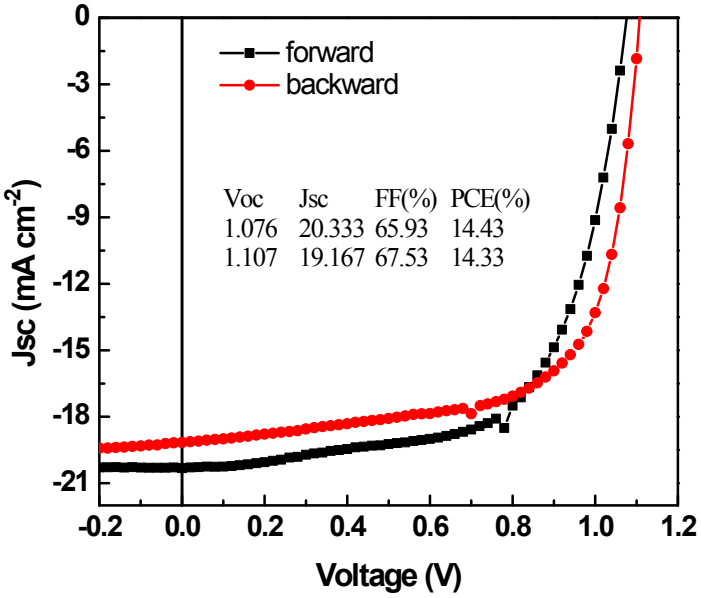

Figure S6. J–V curves of perovskite solar cells based on NiO_x measured under different scan directions.

Table S1. Kinetic data of the thermal decomposition of Ni-Ac, Ni-Nt, and Ni-Mix compounds by Coats-Redfern method.

Compounds	Steps	Cs	∝	Coats - Redfern					
				R^2	E_a KJ mol^{-1}	A S^{-1}	ΔS* KJ $mol^{-1}K^{-1}$	ΔH* KJ mol^{-1}	ΔG* KJ mol^{-1}
Ni-Ac	1st	0.04	0.02	0.868	23.99	$1.08x10^3$	180.4	-26.85	47.1
	2nd	0.91	0.09	0.970	57.77	$7.8x10^4$	149.2	-55.85	98.1
Ni-Nt	1st	0.26	0.017	0.992	64.9	$2.5x10^8$	79	-62.95	74.02
	2nd	0.28	0.024	0.996	46.4	$2.5x10^2$	203.6	-42.8	146.75
Ni-Mix	1st	0.4	0.001	0.970	72.46	$3.1x10^3$	182	-68.9	162.01

References

1. R. Ebrahimi-Kahrizsangi and M. H. Abbasi, *T. Nonferr. Metal. Soc.*, 2008, **18**, 217-221.
2. S. Sajid, A. M. Elseman, H. Huang, J. Ji, S. Dou, H. Jiang, X. Liu, D. Wei, P. Cui and M. Li, *Nano Energy*, 2018, **51**, 408-424.