Electronic Supplementary Material (ESI) for RSC Advances.

$NiCo_2O_4$ Thin Film Prepared by Electrochemically Deposition as Hole-Transport Layer for Efficient Inverted Perovskite Solar Cells

*Sen Wang,[a] Linqin Wang,[b] Chang Liu,[a] Yu Shan,[a] Fusheng Li,[*a] and Licheng Sun[ab]*

[a]State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, DUT-KTH Joint Education and Research Centre on Molecular Devices, Dalian University of Technology, Dalian 116024, P. R. China.

[b]Center of Artificial Photosynthesis for Solar Fuels, School of Science, Westlake University, 310024 Hangzhou, China.

*Corresponding author: fusheng@dlut.edu.cn

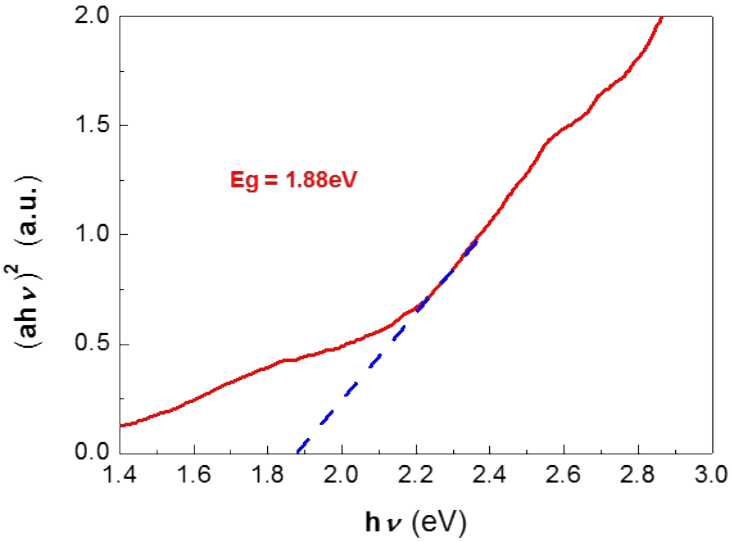

Figure S1. Tauc plot of $NiCo_2O_4$ film.

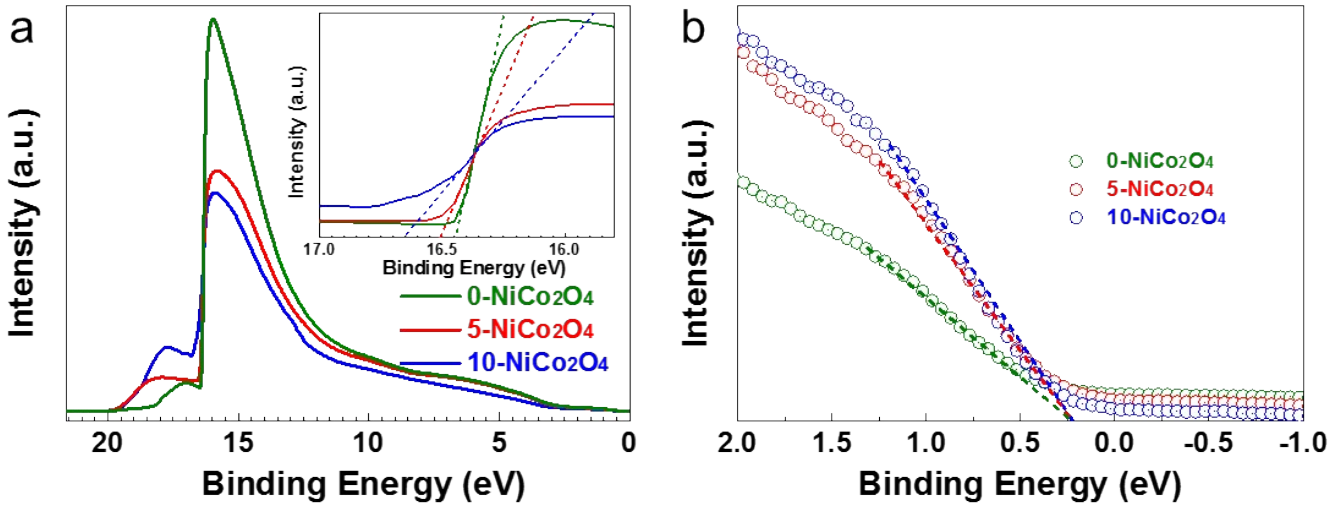

Figure S2. (a) UPS spectra of different $NiCo_2O_4$ films for work function and VB determination. The inset show the enlarged UPS spectra at the binding energy range of 15.5～17.0, respectively. (b) The enlarged valence band position of different $NiCo_2O_4$ films.

The work function (E_{work} corresponding to the Fermi level), valence band (VB), and conduction band (CB) of $NiCo_2O_4$.

$$E_{\text{work}} = \text{h}\nu - \left(E_{\text{cutoff}} - E_F\right) \qquad equation\ S1$$

$$E_{VB} = E_{\text{work}} + E_{VBM} \qquad equation\ S2$$

$$E_{CB} = E_{VB} - E_{\text{g}} \qquad equation\ S3$$

Where, the E_{cutoff} is cut-off energy edge, the E_F is initial edge energy, the E_{VBM} is the energy from valence band maximum to Fermi level, the E_g is band gap energy (obtained by UV-vis spectra), the E_{VB} is valance band energy and the E_{CB} is conduction band energy.

For 0-$NiCo_2O_4$ film,

$E_{\text{work}} = 21.22 - (16.45 - 0) = 4.77$ eV ; $E_{VB} = 4.77 + 0.22 = 4.99$ eV ; and $E_{CB} = 4.99 - 1.88 = 3.11$ eV .

For 5-$NiCo_2O_4$ film,

$E_{\text{work}} = 21.22 - (16.50 - 0) = 4.72$ eV ; $E_{VB} = 4.72 + 0.22 = 4.94$ eV ; and $E_{CB} = 4.94 - 1.88 = 3.06$ eV .

For 10-$NiCo_2O_4$ film,

$E_{\text{work}} = 21.22 - (16.65 - 0) = 4.57$ eV ; $E_{VB} = 4.57 + 0.22 = 4.79$ eV ; and $E_{CB} = 4.79 - 1.88 = 2.91$ eV .

$E_{\text{work}} = 21.2 - (17.15 - 0) = 4.05$ eV ; $E_{VB} = 4.05 + 1.76 = 5.81$ eV ; and $E_{CB} = 5.81 - 2.09 = 3.72$ eV .

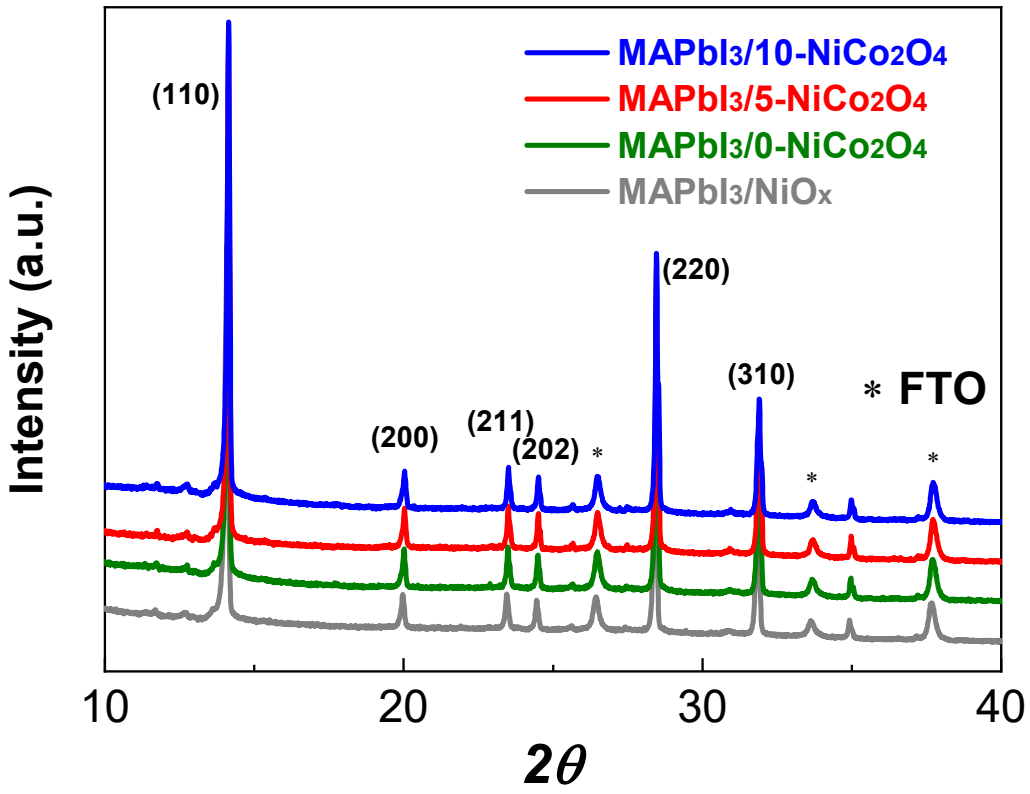

Figure S3. XRD patterns of $MAPbI_3$ films deposited on NiOx and $NiCo_2O_4$ HTLs.

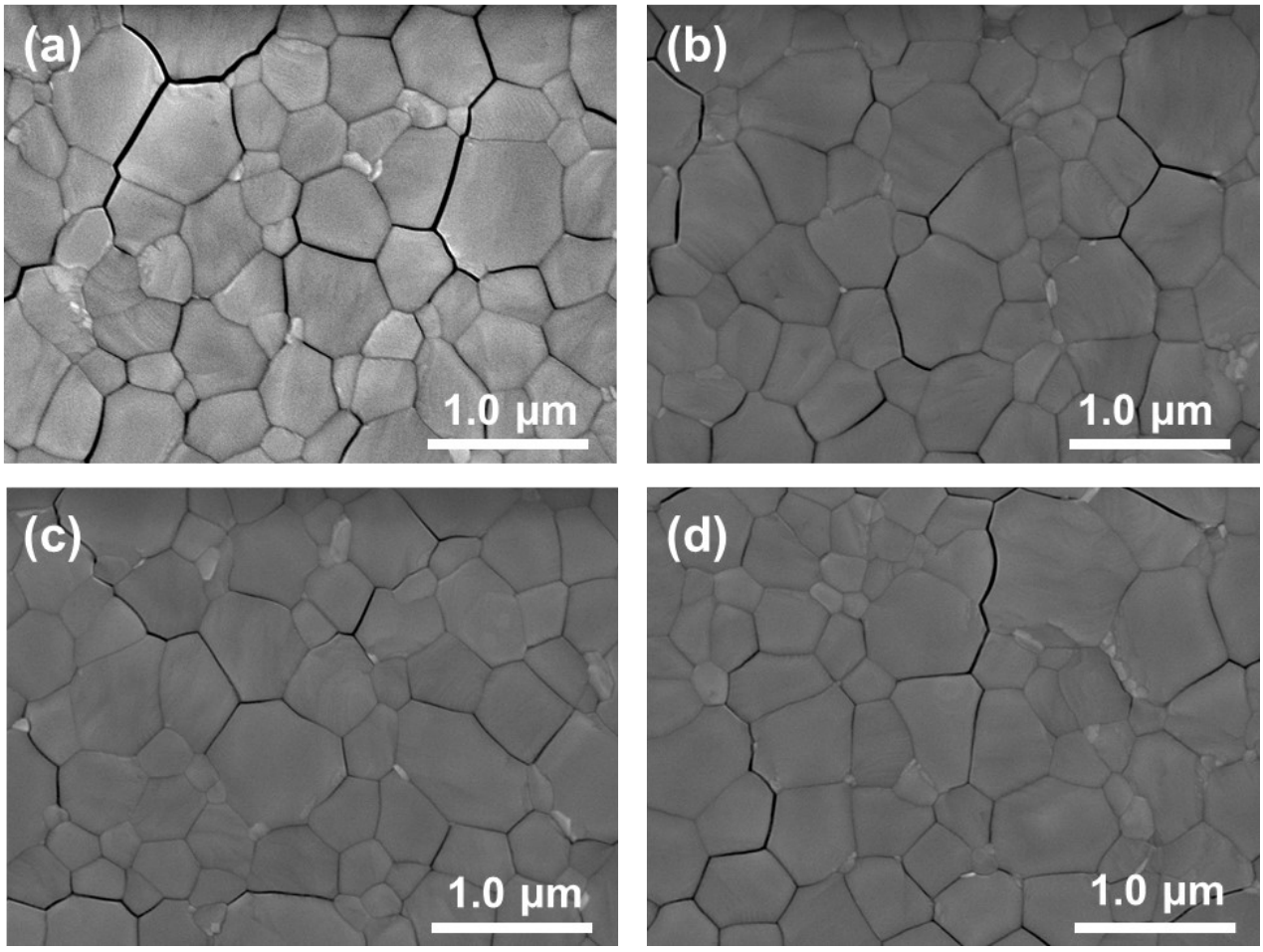

Figure S4. Top-view SEM images of the perovskite film deposited on a) NiO_x, b) 0-$NiCo_2O_4$, c) 5-$NiCo_2O_4$, and d) 10-$NiCo_2O_4$ HTL films prepared by the charge density of 10 $mC \cdot cm^{-2}$.

Table S1 Parameters of the TRPL spectroscopy based on different samples.

Samples	τ_{ave} (ns)	τ_1(ns)	A1	τ_2 (ns)	A2
NiO_x/PSK	42.63	32.72	0.953	105.51	0.047
0-$NiCo_2O_4$/PSK	34.34	22.25	0.943	86.25	0.057
5-$NiCo_2O_4$/PSK	31.74	15.41	0.944	82.98	0.056
10-$NiCo_2O_4$/PSK	64.68	45.55	0.699	87.74	0.301

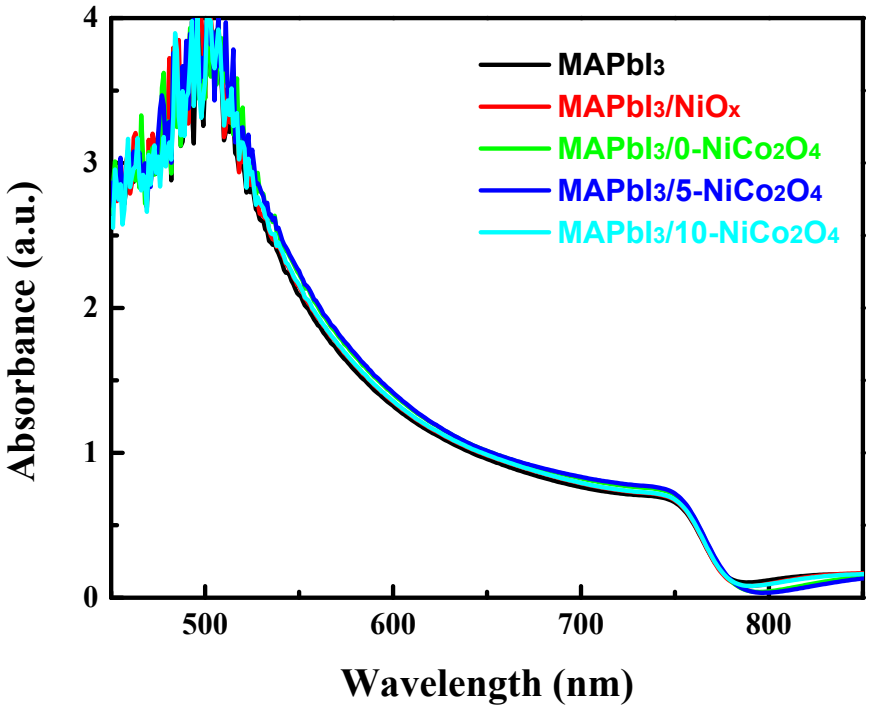

Figure S5. UV-vis absorption spectra of perovskite films on NiO_x and different $NiCo_2O_4$ films.

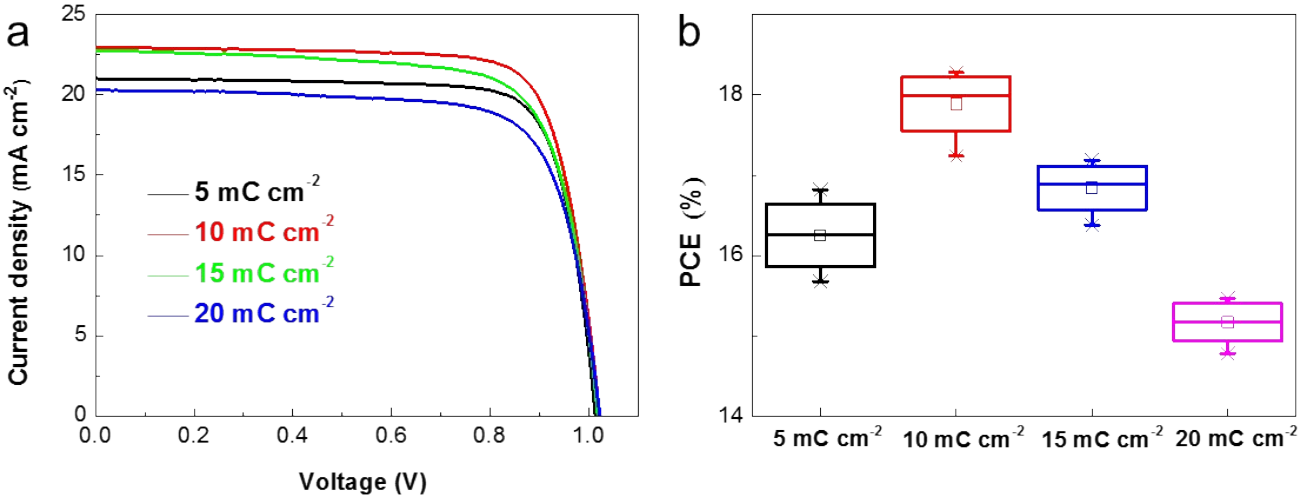

Figure S6. a). *J–V* characteristics of the best PSCs based on **0-$NiCo_2O_4$** HTLs prepared by different charge densities. b). The statistics of 10 pieces of PSCs based on **0-$NiCo_2O_4$** HTLs prepared by different charge densities.

Table S2. Device parameters of the PSCs based on 0-$NiCo_2O_4$ HTLs prepared by different charge densities.

Depositon charge density ($mC \cdot cm^{-2}$)	*Voc* (mV)	*Jsc* ($mA \cdot cm^{-2}$)	*FF* (%)	PCE (%)
5	1.01 ± 0.01 (1.01)	20.84 ± 0.37 (21.00)	77.69 ± 1.42 (79.07)	16.35 ± 0.51 (16.82)
10	1.02 ± 0.01 (1.02)	22.67 ± 0.25 (22.93)	77.85 ± 1.24 (78.05)	17.93 ± 0.29 (18.28)
15	1.02 ± 0.01 (1.02)	22.59 ± 0.30 (22.71)	72.62 ± 2.00 (74.37)	16.68 ± 0.37 (17.19)
20	1.02 ± 0.01 (1.03)	20.28 ± 0.36 (20.36)	73.78 ± 1.49 (73.80)	15.24 ± 0.16 (15.47)

Table S3. Photovoltaic parameters of PSCs based on NiOx and $NiCo_2O_4$ HTLs under the illumination.

HTL	V_{oc} (V)	J_{sc} (mA·cm^{-2})	*FF* (%)	PCE (%)
NiO_x	1.02 ± 0.01	20.63 ± 0.28	78.34 ± 1.38	18.17 ± 0.32
0-$NiCo_2O_4$	1.03 ± 0.01	22.73 ± 0.36	77.29 ± 1.55	18.26 ± 0.37
5-$NiCo_2O_4$	1.02 ± 0.01	23.88 ± 0.37	77.99 ± 1.17	18.94 ± 0.29
10-$NiCo_2O_4$	1.01 ± 0.01	22.90 ± 0.44	72.66 ± 1.33	16.76 ± 0.23

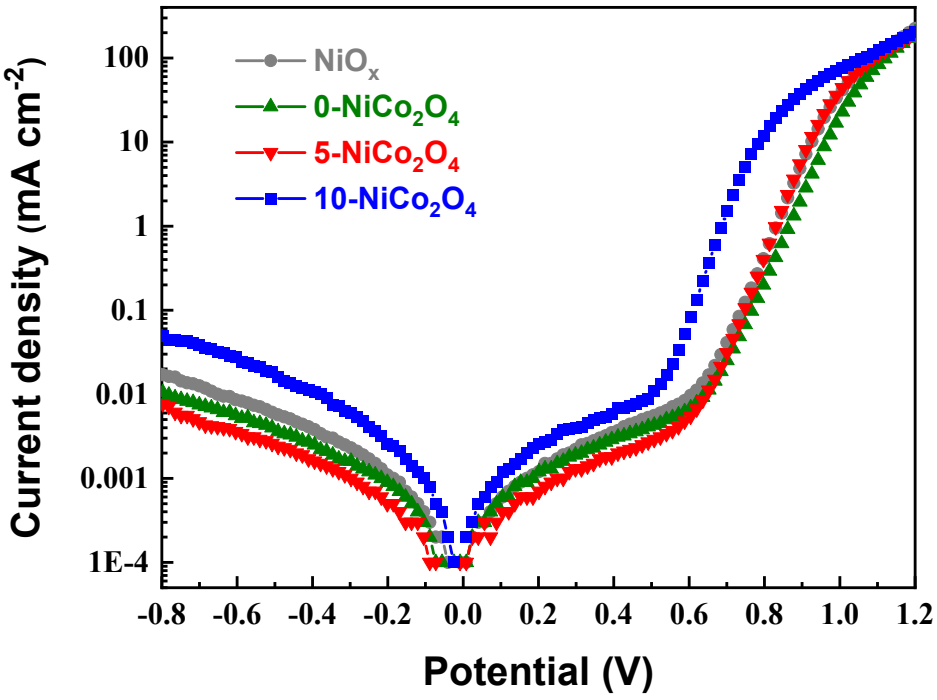

Figure S7. Dark *J-V* characteristics of the devices based on NiO_x and $NiCo_2O_4$ HTLs.

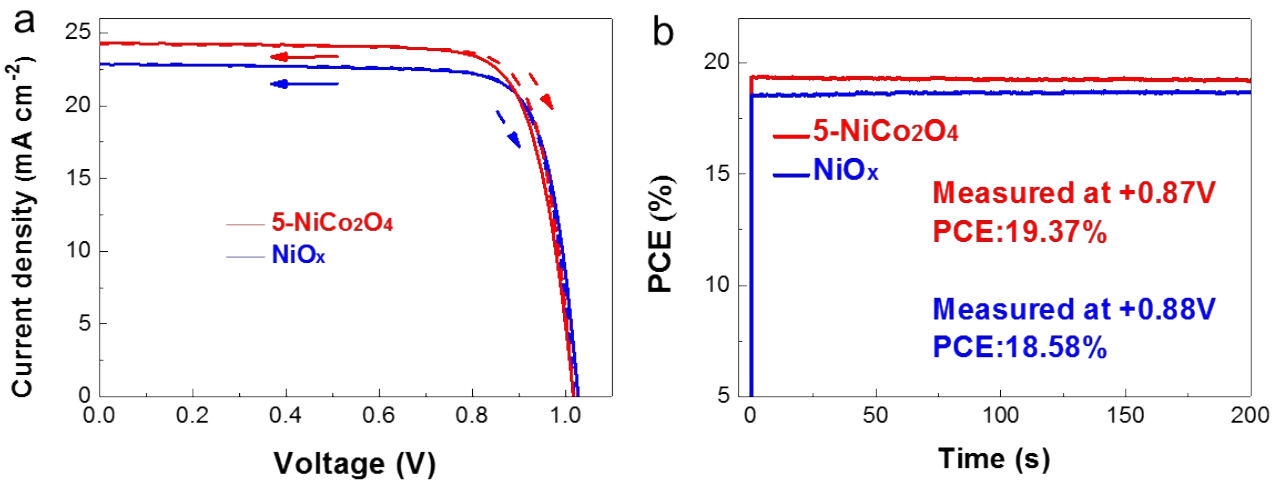

Figure S8. a) Current–voltage curves with reverse scan mode for the best-performing devices based on 5-$NiCo_2O_4$ and NiO_x HTLs. b) The steady-state power output at the maximum power point for the optimized devices.

Table S4. Device parameters of the PSCs based on 5-$NiCo_2O_4$ and NiO_x HTLs with reverse scan mode.

HTLs	Scan direction	V_{oc} (V)	J_{sc} (mA·cm^{-2})	*FF*	PCE (%)
NiO_x	Re	1.03	22.86	0.79	18.68
	Fw	1.02	22.89	0.80	18.75
5-$NiCo_2O_4$	Re	1.02	24.31	0.78	19.24
	Fw	1.02	24.25	0.80	19.73