

Nanocatalysts based on Ni nanoparticles in functionalized ionic liquids for chemoselective hydrogenation and transfer hydrogenation of α,β -unsaturated carbonyl compounds

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1. HRTEM and HAADF-STEM images

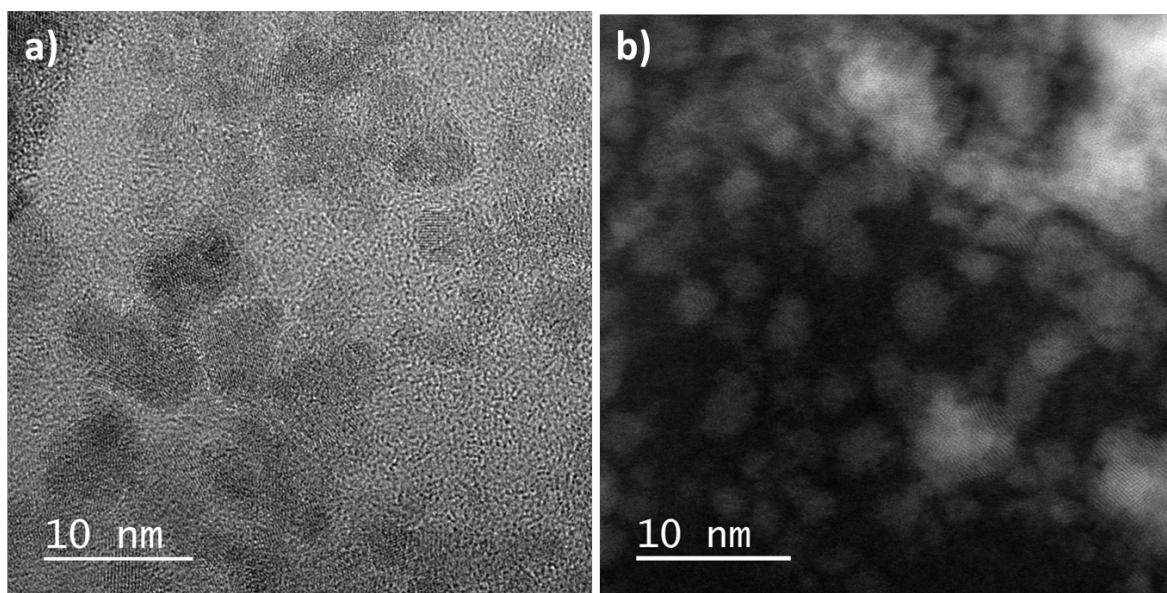


Figure S1 a) HRTEM and b) HAADF-STEM images of Ni/H.

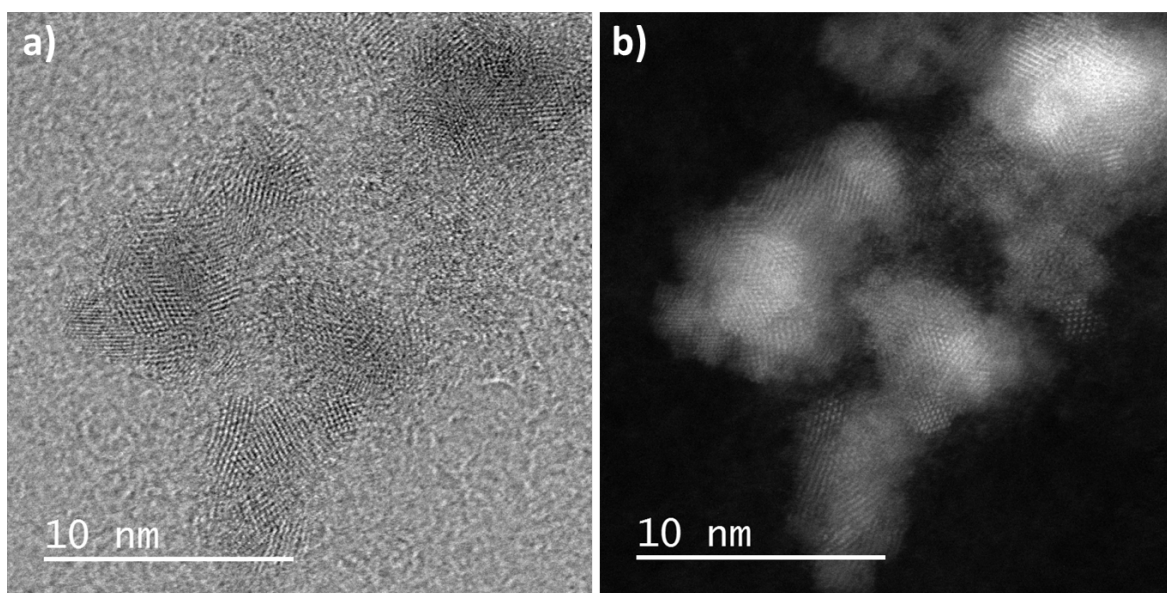


Figure S2 a) HRTEM and b) HAADF-STEM images of Ni/MEM.

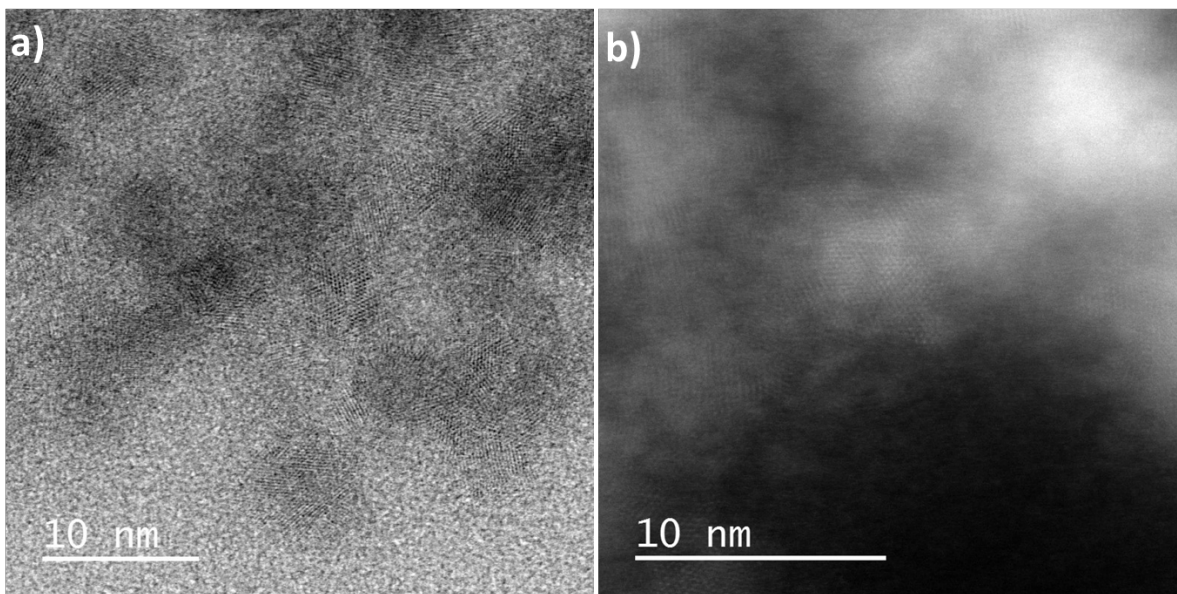


Figure S3 a) HRTEM and b) HAADF-STEM images of Ni/MME

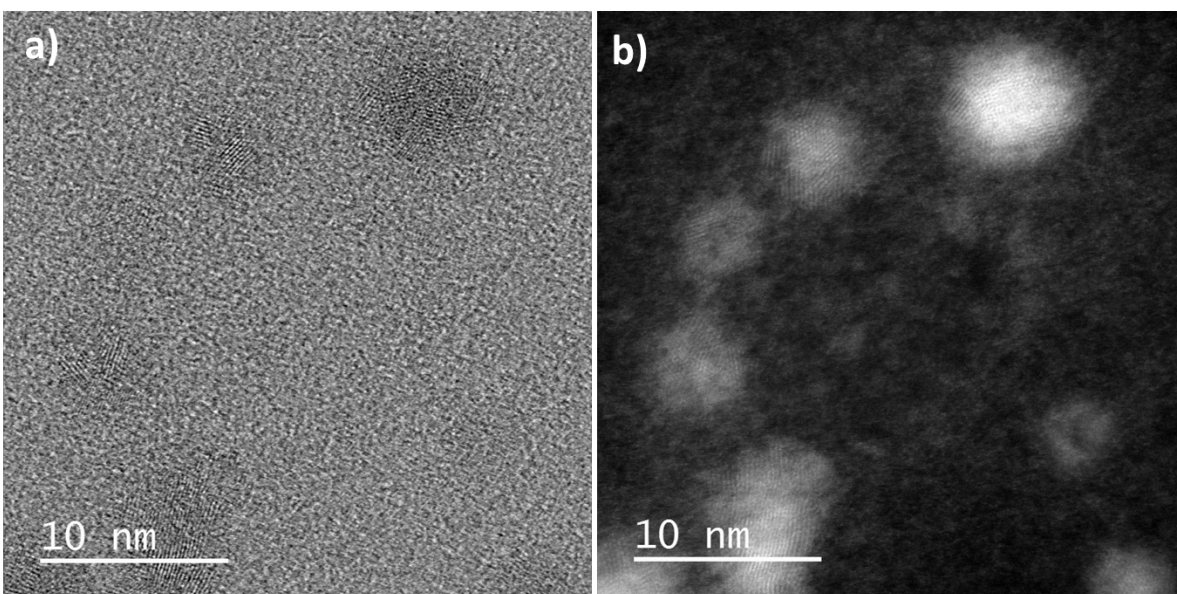


Figure S4 a) HRTEM and b) HAADF-STEM images of Ni/CN.

2. XPS analyses

Ni/ILs

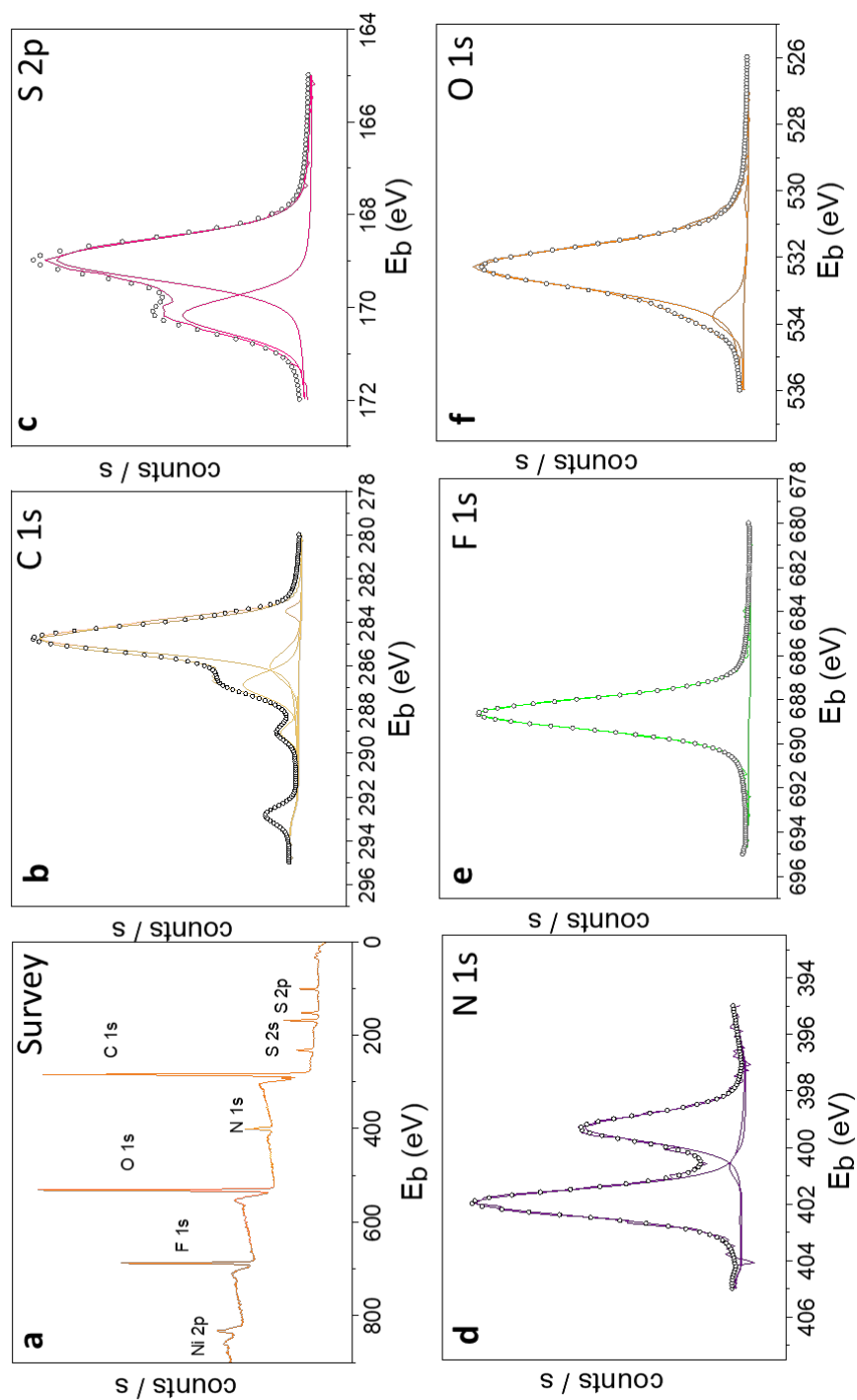


Figure S5 a) XPS survey spectrum of Ni/H and high-resolution scan spectra of b) C 1s, c) S 2p d) N 1s, e) F 1s, and f) O 1s.

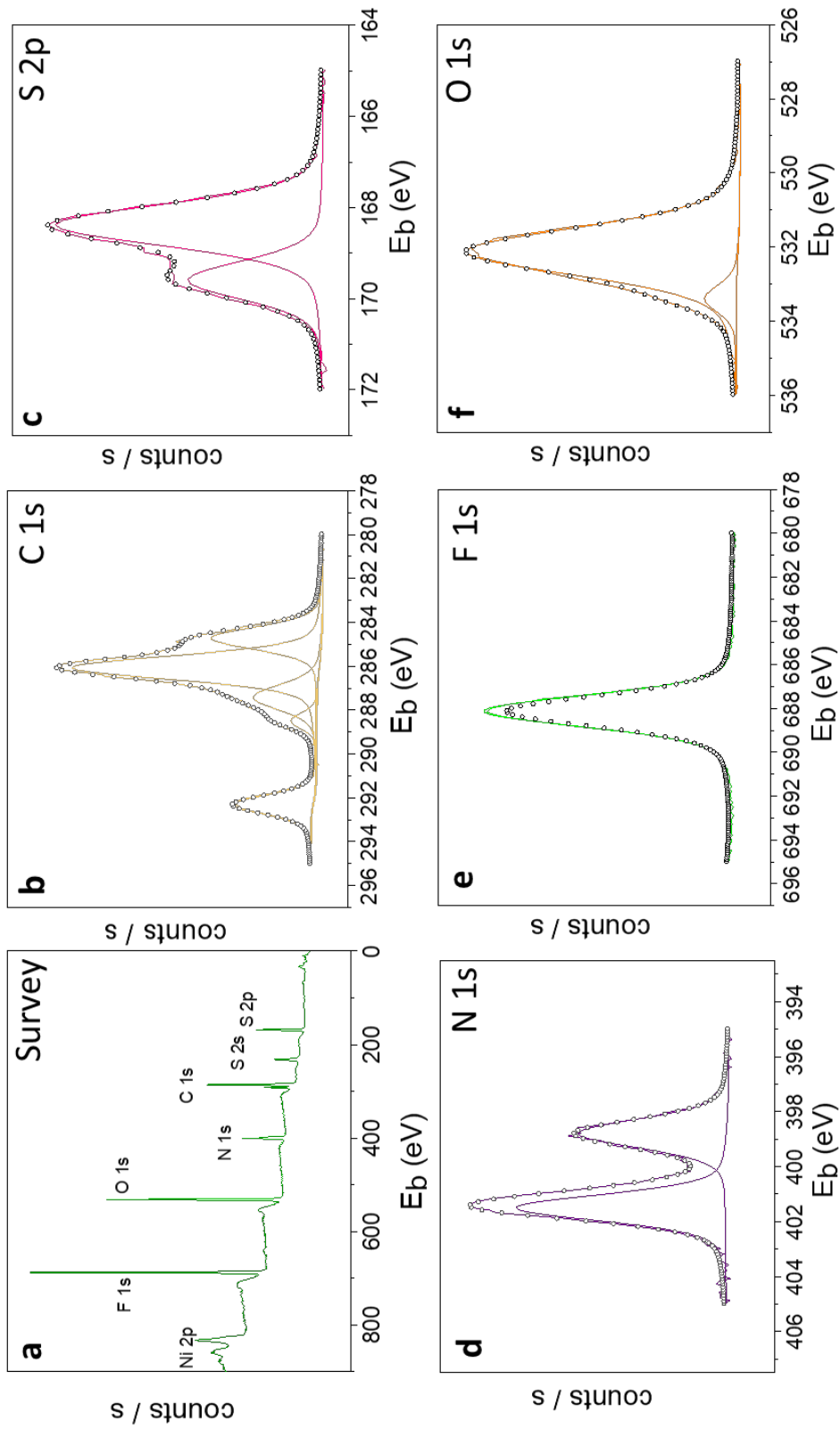


Figure S6 a) XPS survey spectrum of Ni/MEM and high-resolution scan spectra of b) C 1s, c) S 2p d) N 1s, e) F 1s, and f) O 1s.

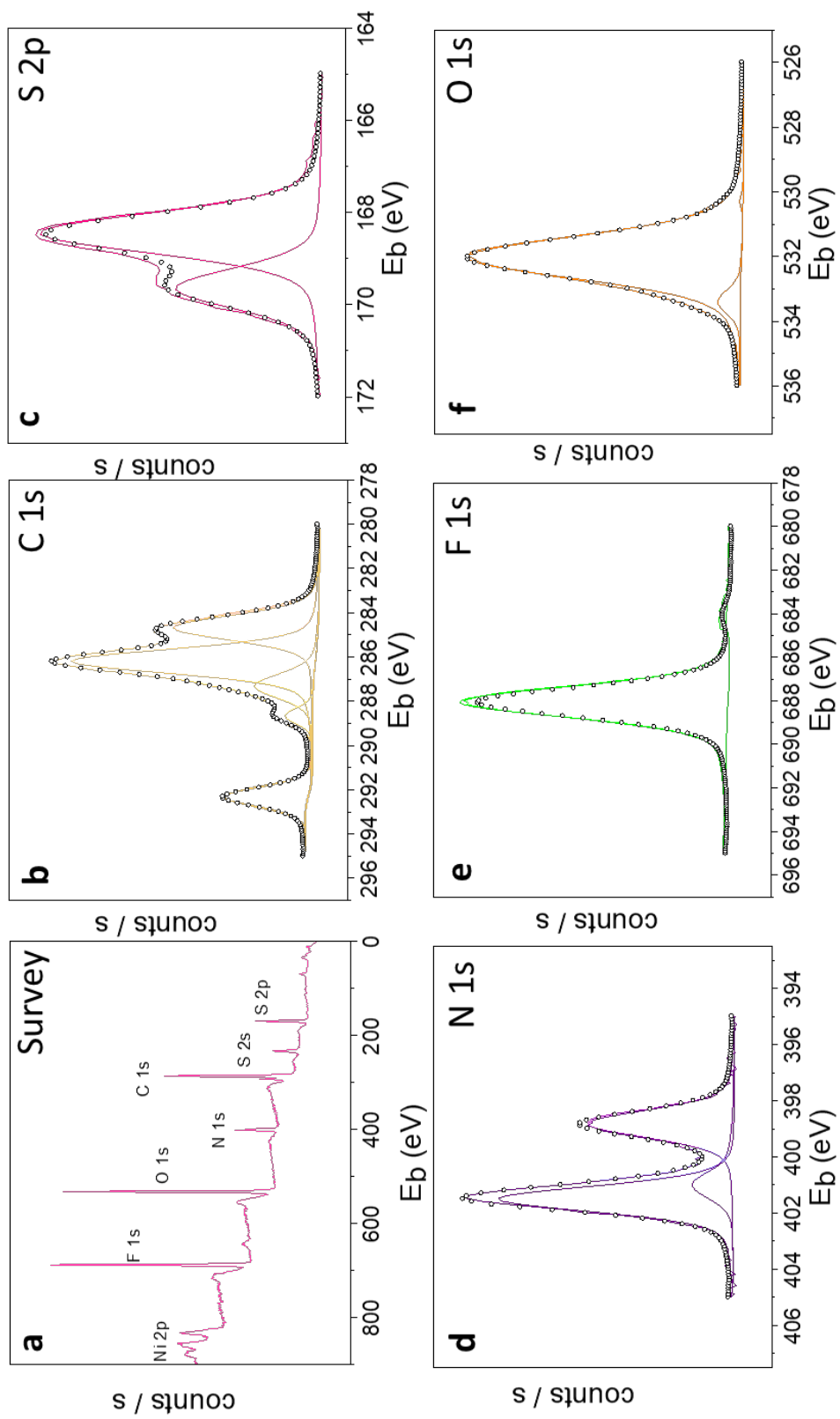


Figure S7 a) XPS survey spectrum of Ni/MME and high-resolution scan spectra of b) C 1s, c) S 2p d) N 1s, e) F 1s, and f) O 1s.

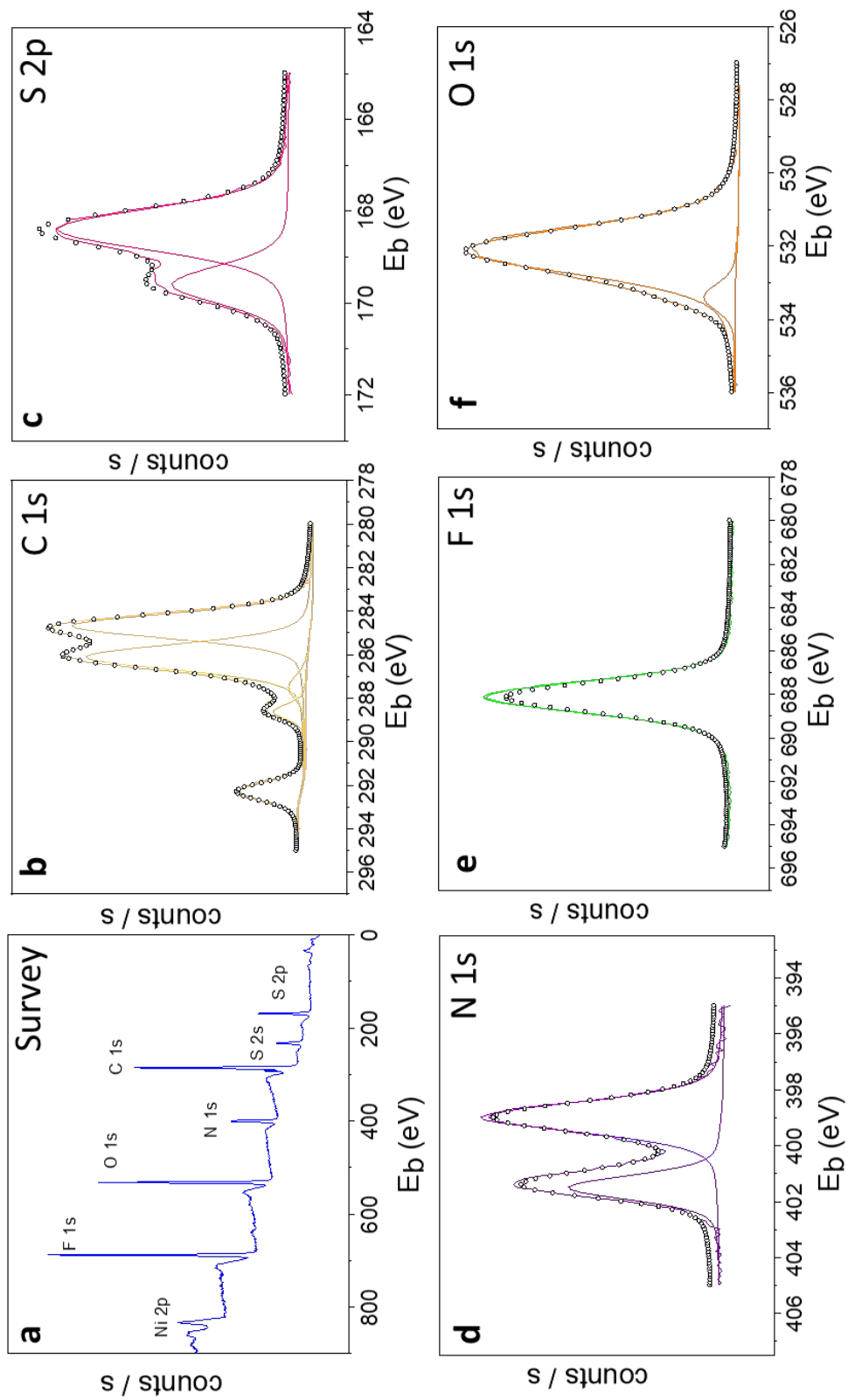


Figure S8 a) XPS survey spectrum of Ni/CN and high-resolution scan spectra of b) C 1s, c) S 2p d) N 1s, e) F 1s, and f) O 1s.

Table S1: Binding energies (eV) of C 1s for the carbon atoms in the Ni/ILs.

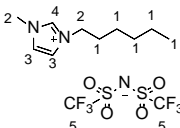
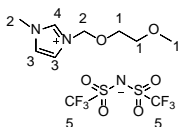
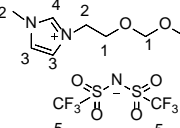
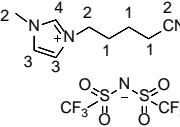
IL	Atom ^a	Binding energy Ni/FILs, E _{NiIL} (eV)	Atomic ratio (%)	FWHM (eV)
H 	C ₁	284.80	60.34	1.44
	C ₂	286.37	19.47	1.44
	C ₃	287.74	6.23	1.44
	C ₄	288.85	5.51	1.13
	C ₅	292.68	3.91	1.09
MEM 	C ₁	284.80	48.53	1.44
	C ₂	286.25	26.66	1.27
	C ₃	287.32	8.37	1.44
	C ₄	288.39	9.69	1.28
	C ₅	292.48	5.66	1.16
MME 	C ₁	284.80	43.82	1.44
	C ₂	286.21	30.71	1.34
	C ₃	287.33	8.26	1.40
	C ₄	288.50	8.46	1.23
	C ₅	292.32	7.23	1.12
CN 	C ₁	284.80	47.23	1.44
	C ₂	286.40	30.41	1.44
	C ₃	287.66	6.61	1.44
	C ₄	288.50	3.76	1.44
	C ₅	292.67	8.95	1.44

Table S2: Binding energies (eV) of the chemical states of N, S, F and O atoms in the Ni/ILs.

Element	Binding energy Ni/ILs, E_{NiIL} (eV)	Atomic ratio (%)	FWHM (eV)
H			
N 1s (anion)	399.25	37.75	1.25
N 1s (cation)	401.84	59.14	1.27
S 2p _{3/2}	168.80	67.00	1.15
S 2p _{1/2}	170.02	33.00	1.12
F 1s	688.56	100.00	1.77
O 1s (CO ₃ ²⁻)	531.33	20.07	1.66
O 1s (cation/anion)	532.28	58.37	1.37
H ₂ O _{absorbed}	533.44	21.55	1.65
MEM			
N 1s (anion)	399.05	41.17	1.44
N 1s (cation)	401.62	57.03	1.44
S 2p _{3/2}	168.58	65.50	1.25
S 2p _{1/2}	169.81	34.50	1.25
F 1s	688.33	100.00	1.86
O 1s (CO ₃ ²⁻)	530.34	2.03	1.92
O 1s (cation/anion)	532.16	77.79	1.65
H ₂ O _{absorbed}	533.44	20.18	1.52
MME			
N 1s (anion)	398.83	37.04	1.31
N 1s (cation)	401.53	46.98	1.17
S 2p _{3/2}	168.43	61.81	1.14
S 2p _{1/2}	169.64	38.19	1.27
F 1s (anion)	688.01	100.00	1.78
O 1s (CO ₃ ²⁻)	530.26	4.74	1.64
O 1s (cation/anion)	532.00	85.35	1.74
H ₂ O _{absorbed}	533.43	9.90	1.55

Element	Binding energy Ni/ILs, E_{NiIL} (eV)	Atomic ratio (%)	FWHM (eV)
CN			
N 1s (anion)	399.16	44.55	1.44
N 1s (cation)	401.77	38.63	1.39
S 2p _{3/2}	168.72	73.33	1.44
S 2p _{1/2}	170.02	26.67	1.21
F 1s	688.38	100.00	2.00
O 1s (CO ₃ ²⁻)	530.64	17.07	1.92
O 1s (cation/anion)	532.15	80.53	1.79
H ₂ O _{absorbed}	534.36	2.40	0.85

Table S3: Distribution of nickel species as a function of the Ni/ILs.

Ni/ILs	Distribution of nickel (%) ^a	
	Ni ⁰	Ni ²⁺
Ni/H	55	45
Ni/MEM	52	48
Ni/MME	51	49
Ni/CN	60	40

^a Data obtained from XPS analysis.

Ni-NiO/ILs (OT₁)

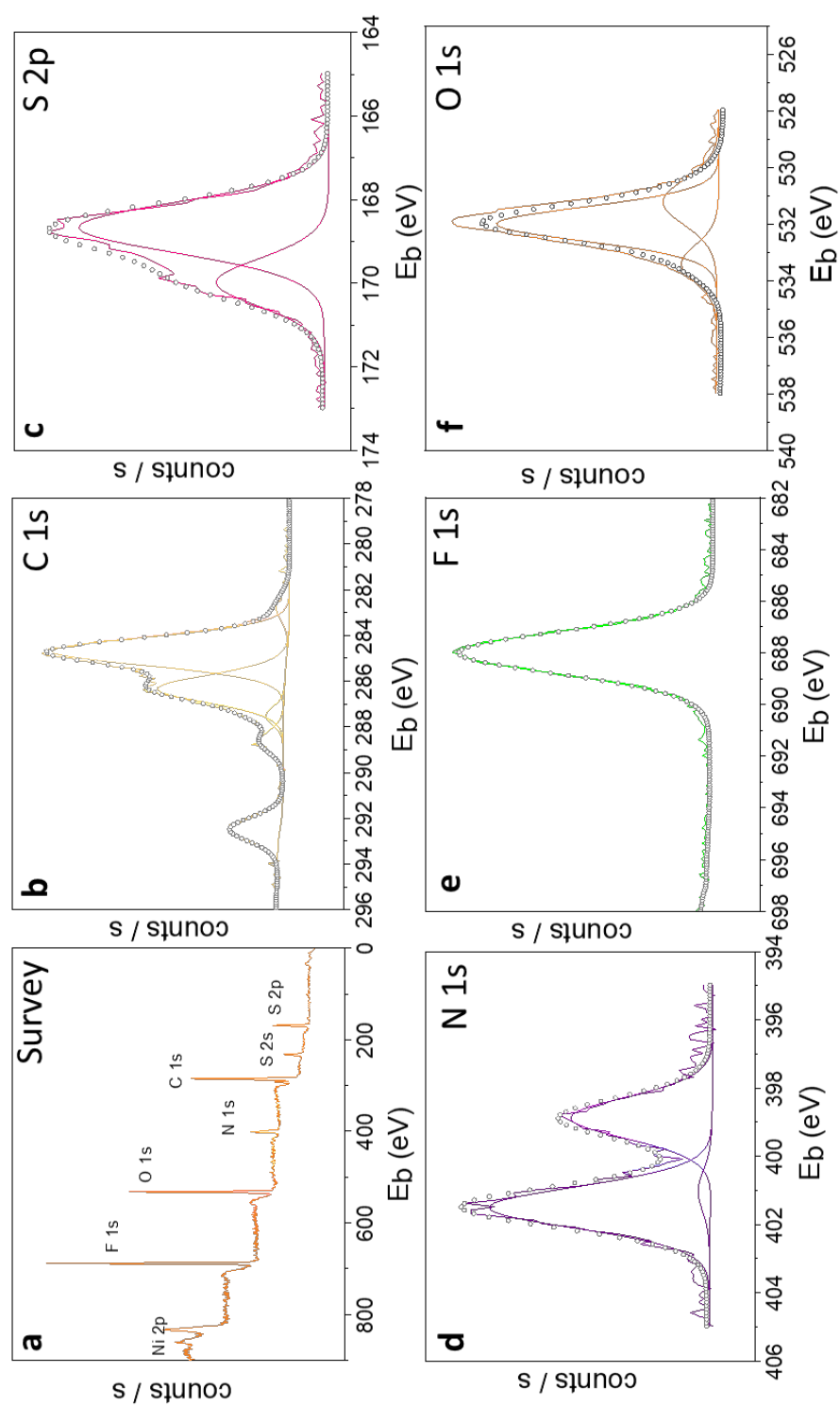


Figure S9 a) XPS survey spectrum of Ni-NiO/H and high-resolution scan spectra of b) C 1s, c) S 2p d) N 1s, e) F 1s, and f) O 1s.

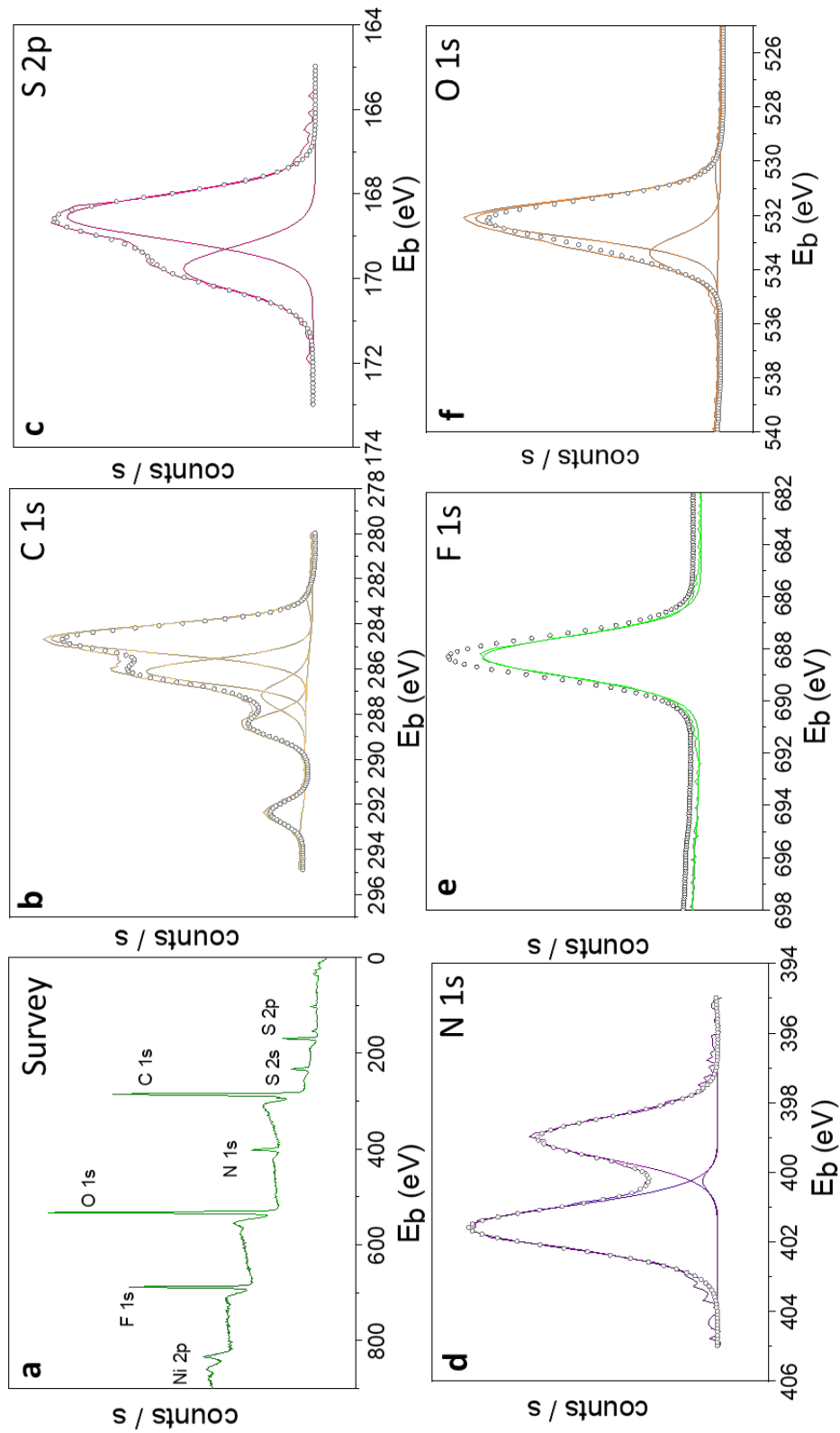


Figure S10 a) XPS survey spectrum of Ni-NiO/MEM and high-resolution scan spectra of b) C 1s, c) S 2p d) N 1s, e) F 1s, and f) O 1s.

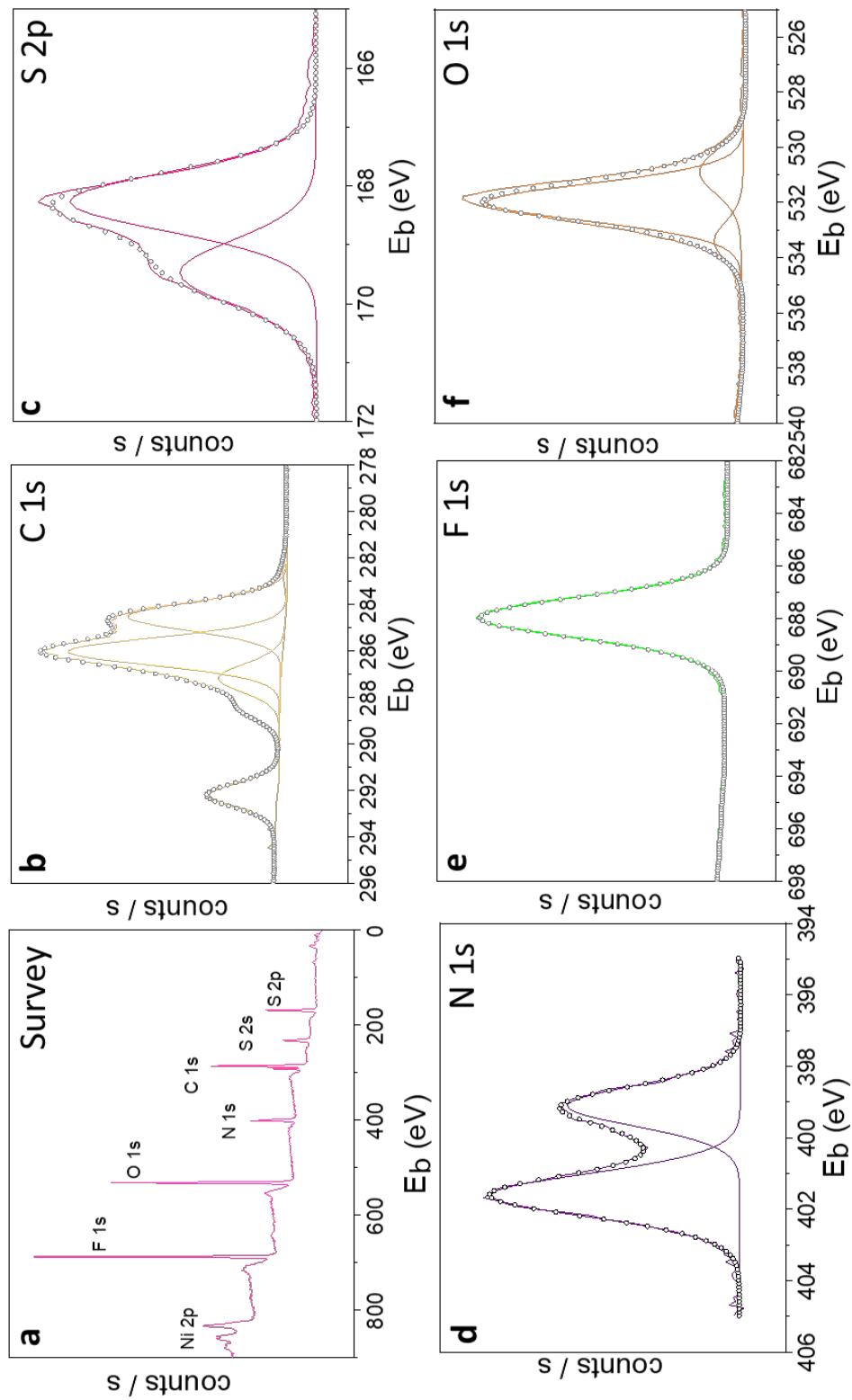


Figure S11 a) XPS survey spectrum of Ni-NiO/MME and high-resolution scan spectra of b) C 1s, c) S 2p d) N 1s, e) F 1s, and f) O 1s.

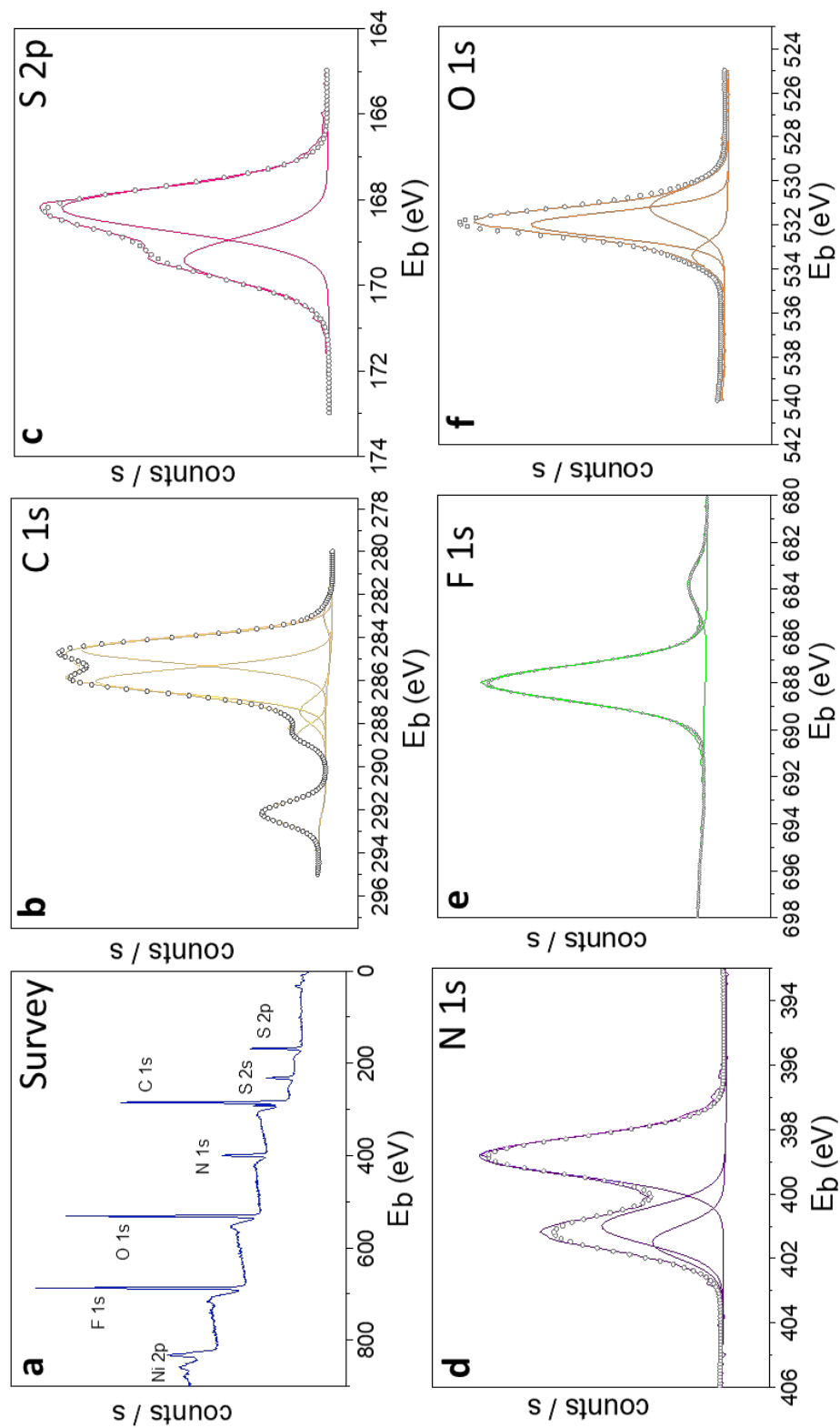


Figure S12 a) XPS survey spectrum of Ni-NiO/CN and high-resolution scan spectra of b) C 1s, c) S 2p d) N 1s, e) F 1s, and f) O 1s.

Table S4: Binding energies (eV) of C 1s for the carbon atoms in the Ni-NiO/ILs.

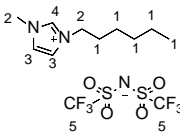
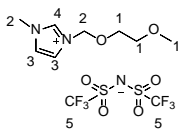
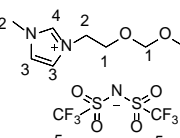
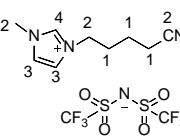
IL	Atom ^a	Binding energy Ni/FILs, E _{NiIL} (eV)	Atomic ratio (%)	FWHM (eV)
H 	C ₁	284.80	52.34	1.14
	C ₂	286.44	28.28	1.44
	C ₃	287.63	2.58	1.44
	C ₄	288.76	4.10	0.95
	C ₅	292.58	9.73	1.44
MEM 	C ₁	284.80	48.53	1.44
	C ₂	286.25	26.66	1.27
	C ₃	287.32	8.37	1.44
	C ₄	288.66	9.69	1.28
	C ₅	292.48	5.66	1.16
MME 	C ₁	284.80	30.26	1.44
	C ₂	286.02	40.26	1.41
	C ₃	287.17	11.95	1.44
	C ₄	288.50	5.35	1.22
	C ₅	292.21	11.28	1.24
CN 	C ₁	284.80	42.40	1.44
	C ₂	286.23	39.59	1.44
	C ₃	287.64	4.04	1.31
	C ₄	288.73	3.74	1.11
	C ₅	292.36	8.73	1.23

Table S5: Binding energies (eV) of the chemical states of N, S, F and O atoms in the Ni-NiO/ILs.

Element	Binding energy Ni/ILs, E_{NiIL} (eV)	Atomic ratio (%)	FWHM (eV)
H			
N 1s (anion)	398.98	37.58	1.44
N 1s (cation)	401.61	59.01	1.44
S 2p _{3/2}	168.78	70.77	1.44
S 2p _{1/2}	170.09	29.23	1.36
F 1s	688.11	100.00	1.94
O 1s (CO ₃ ²⁻)	531.33	22.32	1.92
O 1s (cation/anion)	532.11	65.84	1.43
H ₂ O _{absorbed}	533.51	11.84	1.59
MEM			
N 1s (anion)	399.05	41.17	1.44
N 1s (cation)	401.62	57.03	1.44
S 2p _{3/2}	168.58	65.50	1.25
S 2p _{1/2}	169.81	34.50	1.25
F 1s	688.33	100.00	1.86
O 1s (CO ₃ ²⁻)	530.3	2.03	1.92
O 1s (cation/anion)	532.12	77.79	1.65
H ₂ O _{absorbed}	533.4	20.18	1.52
MME			
N 1s (anion)	399.01	39.23	1.44
N 1s (cation)	401.58	61.77	1.27
S 2p _{3/2}	168.57	61.75	1.19
S 2p _{1/2}	169.78	38.25	1.33
F 1s (anion)	688.31	100.00	1.86
O 1s (CO ₃ ²⁻)	531.19	15.51	1.92
O 1s (cation/anion)	532.30	76.34	1.61
H ₂ O _{absorbed}	533.70	8.15	1.63

Element	Binding energy Ni/ILs, E_{NiIL} (eV)	Atomic ratio (%)	FWHM (eV)
CN			
N 1s (anion)	399.05	57.88	1.44
N 1s (cation)	401.73	14.38	1.24
S 2p _{3/2}	168.44	63.97	1.23
S 2p _{1/2}	169.64	36.03	1.28
F 1s	688.22	91.00	1.86
O 1s (CO ₃ ²⁻)	531.51	17.07	1.92
O 1s (cation/anion)	532.23	80.53	1.37
H ₂ O _{absorbed}	533.63	2.40	1.21

Table S6: Distribution of nickel species as a function of the Ni-NiO/ILs.

Ni-NiO/ILs	Distribution of nickel (%) ^a	
	Ni ⁰	Ni ²⁺
Ni-NiO/H	55	45
Ni-NiO/MEM	42	58
Ni-NiO/MME	44	54
Ni-NiO/CN	60	40

^a Data obtained from XPS analysis.

3. Solubility tests of 2-cyclohexen-1-one in ILs



Figure S13 Pictures of the solutions obtained after addition of 2-cyclohexen-1-one (2 mL) to the H, MEM, MME, CN ILs (0.5 mL).

4. Hydrogenation of 2-cyclohexen-1-one (CH-enon) with Ni/ILs at different temperatures

Table S7: Hydrogenation of CH-enon with the four Ni/ILs.^a

Catalyst system	Temperature (°C)	Conversion (%) ^b	Selectivity (%) ^b		
			CH-non	CH-ol	CH-enol
Ni/H	150	>99	98	3	0
	170	>99	96	4	0
Ni/MEM	150	>99	>99	0	0
	170	>99	>99	0	0
Ni/MME	150	>99	>99	0	0
	170	>99	>99	0	0
Ni/CN	150	>99	>99	0	0
	170	>99	>99	0	0

^a Reaction conditions: 0.01 mmol of Ni, 1 mmol of 2-cyclohexen-1-one (CH-enon), 0.3 mmol of octane (internal standard), 150/170 °C, 10 bar H₂, 1 h, 1200 rpm. ^b Determined by GC using internal standard technique.

5. Calculation of TOFs for the Ni/ILs

Table S8: Calculation of TOFs for the Ni/ILs.

Ni/ILs	NP mean size (nm) ^a	Ni atoms in NP ^b	Ni atoms in core ^c	Ni atoms in outer layer ^d	Ratio of Ni atoms at NP surface ^e	TOF (h ⁻¹) ^f
Ni/H	5.6 ± 0.3	8397	6909	1487	0.17	677
Ni/MEM	4.4 ± 0.4	4073	3170	902	0.22	814
Ni/MME	6.5 ± 0.3	13131	11109	2022	0.15	627
Ni/CN	2.8 ± 0.3	1049	701	348	0.33	712

^a Mean size of Ni/IL NPs were determined from analysis of TEM images by considering at least 200 individual nanoparticles. Number of atoms in Ni NPs were calculated as follows: the number of Ni atoms in *fcc* cell (N) is 4. The shell thickness is assumed as the half of the lattice constant, for Ni is 0.176 nm. The volume of Ni cell is 0.0438 nm³. R_{np} represents the radius of NP. The volume of all Ni atoms in the outer layer of NP: $V_{\text{shell}} = V_{\text{total}} - V_{\text{core}} = 4/3 \cdot \pi \cdot R_{\text{np}}^3 - 4/3 \cdot \pi \cdot (R_{\text{np}} - R_{\text{Ni}})^3$, V_{total} means the volume of one Ni NP, V_{core} corresponds to the volume of NP excluded the outer layer of atoms. ^b The total number of Ni atoms N_{total} = N · V_{total}/0.0438. ^c The number of metal atoms in the core N_{core} = N_{total} - N_{shell}. ^d The number of metal atoms on the shell N_{shell} = N · V_{shell}/0.0438. ^e The ratio of Ni atoms on the surface of NP = N_{shell}/N_{total}. ^f TOFs have been calculated at 15 min with respect to the surface Ni atom ratio.

6. XPS analyses of Ni-NiO/MEM (after catalytic hydrogenation)

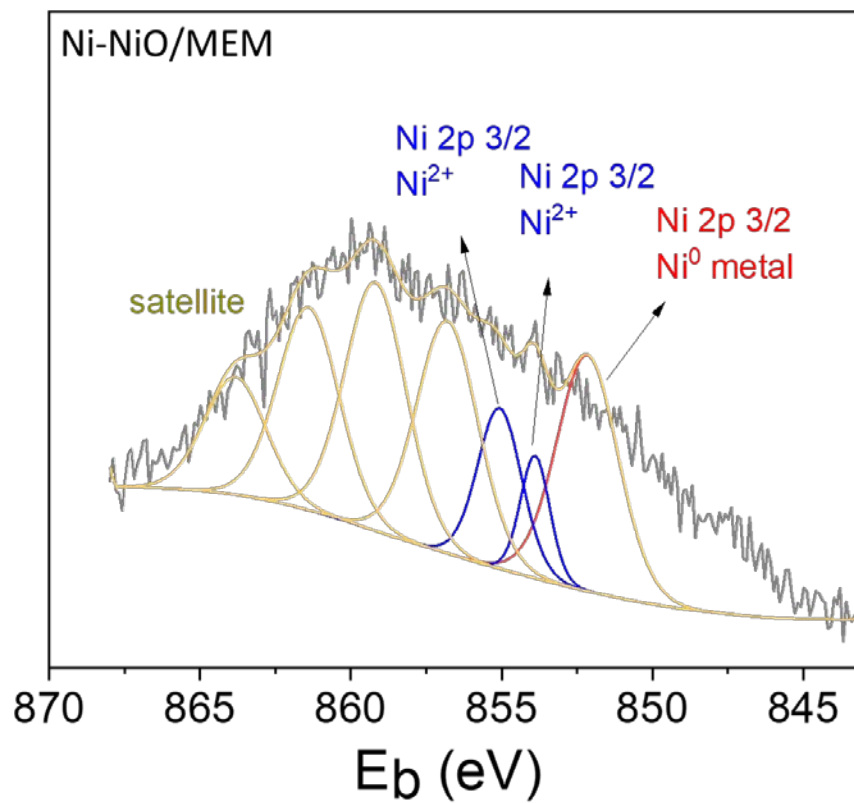


Figure S14 High-resolution XPS scan spectrum of Ni 2p for the Ni-NiO/MEM.

7. TEM analyses of the Ni/ILs after five catalytic runs

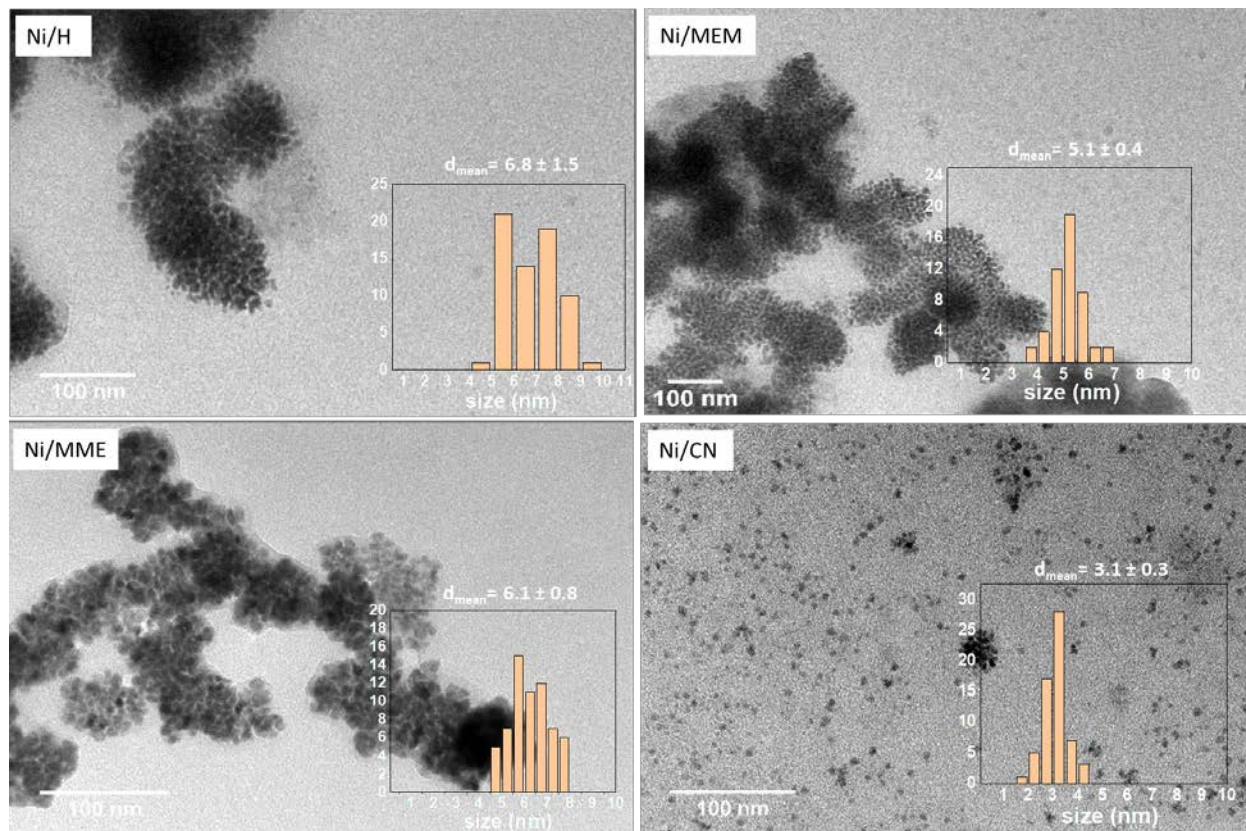


Figure S15 TEM images of the Ni/ILs after five catalytic runs with their corresponding size distributions a) Ni/H, b) Ni/MEM, c) Ni/MME, and d) Ni/CN.

8. XPS analyses of Ni-NiO/ILs (OT₃)

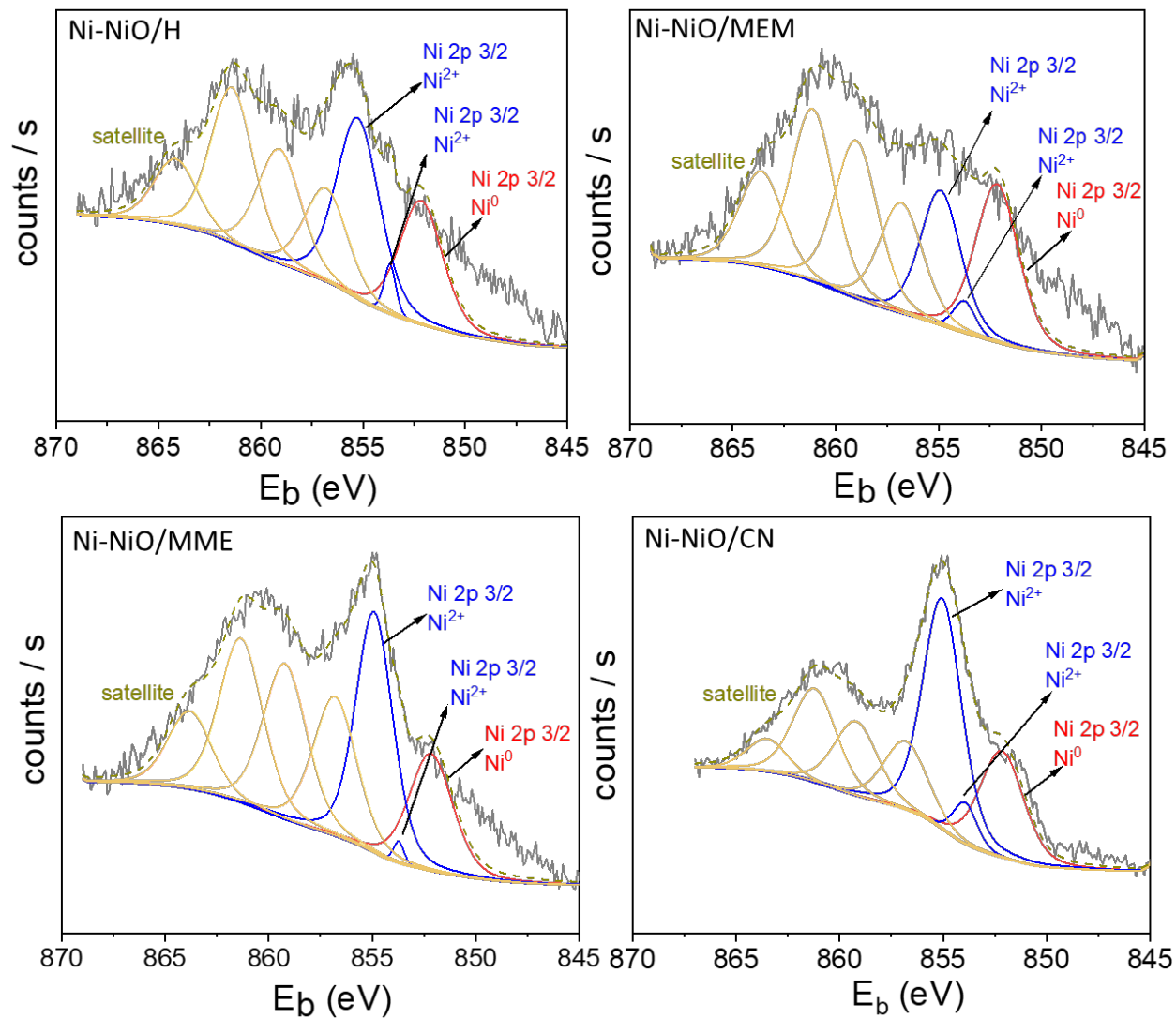


Figure S16 High-resolution XPS scan spectra of Ni 2p for the Ni-NiO/ILs (OT₃).

Table S9: Distribution of nickel species as a function of the Ni-NiO/ILs.

Ni-NiO/ILs	Distribution of nickel (%) ^a	
	Ni ⁰	Ni ²⁺
Ni-NiO/H	49	50
Ni-NiO/MEM	56	44
Ni-NiO/MME	49	50
Ni-NiO/CN	70	30

^a Data obtained from XPS analysis.

9. XPS analyses of Ni/ILs and Ni-NiO/ILs (OT₂).

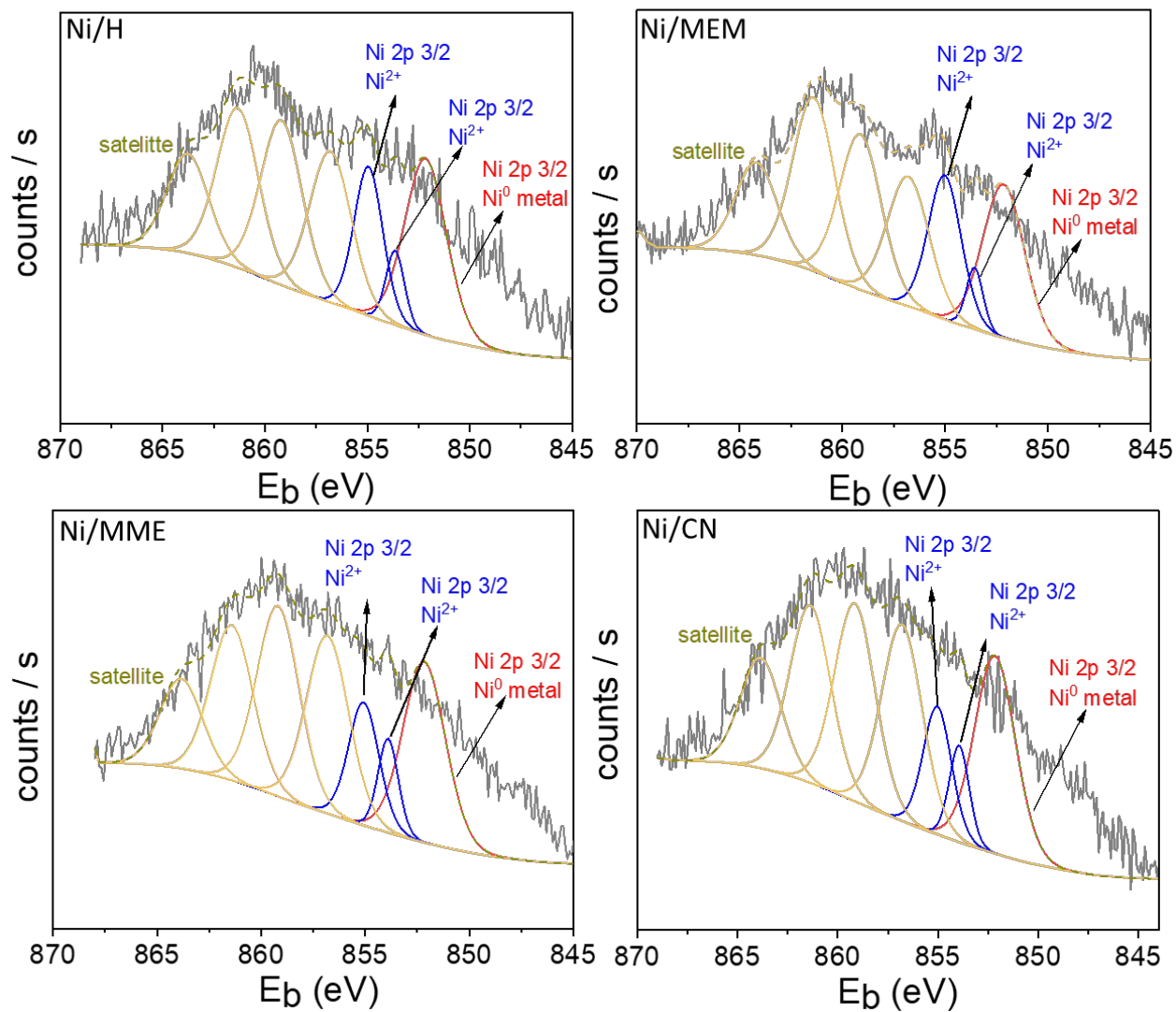


Figure S17 High-resolution XPS scan spectra of Ni 2p for the Ni/ILs.

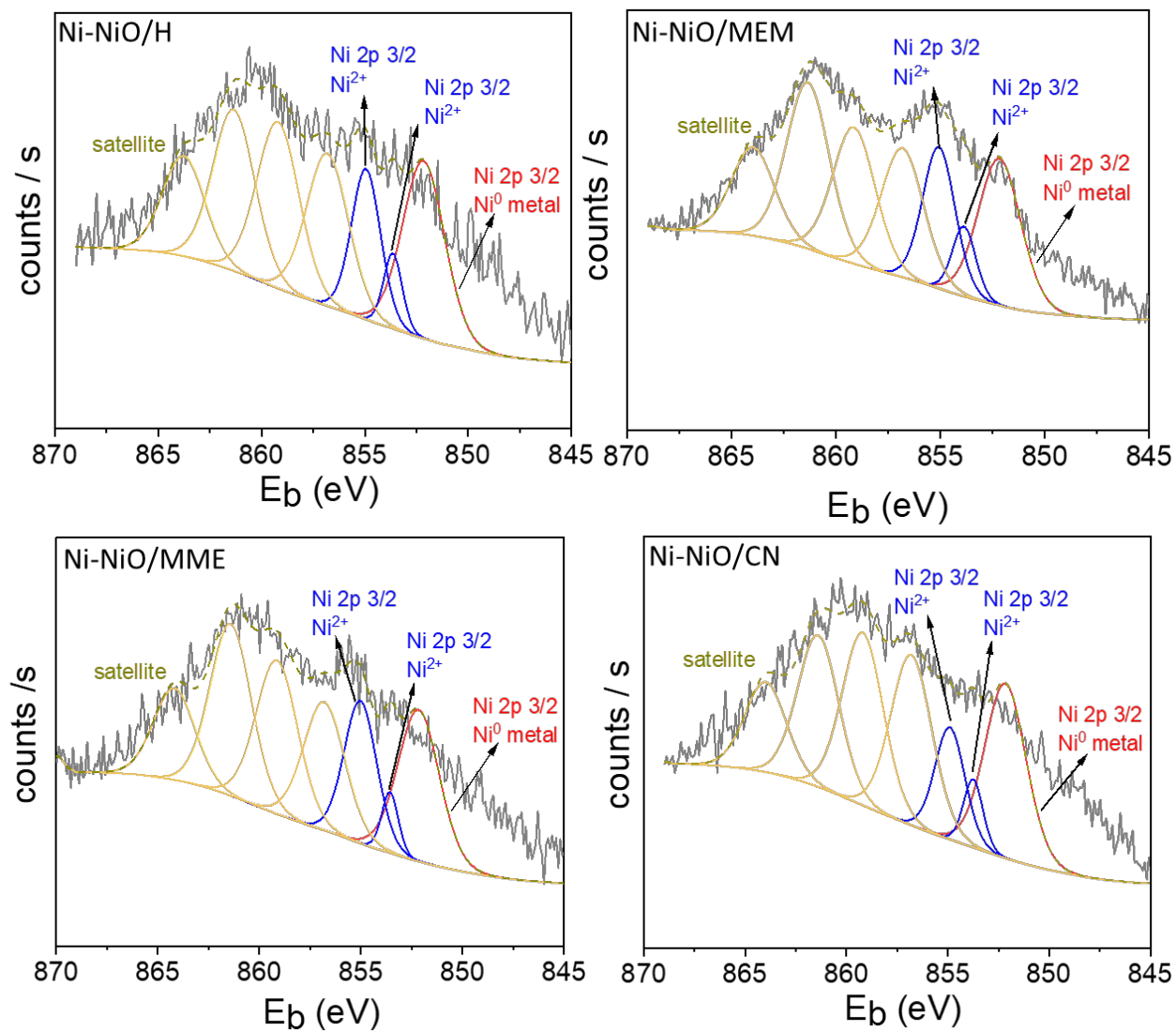


Figure S18 High-resolution XPS scan spectra of Ni 2p for the Ni-NiO/ILs.