Electronic Supplementary Information (ESI)

Electrochemically Engineered Domain: Nickel–Hydroxide/Nickel Nitride Composite for Alkaline HER Electrocatalysis

Chikaodili E. Chukwuneke,[a] Kenta Kawashima,[a] Hao Li,[b] Raul A. Marquez,[a] Yoon Jun Son,[c]

Lettie A. Smith,[a] Hugo Celio,[d] Graeme Henkelmana,[e,f,g] and C. Buddie Mullins*[a,c,d,f,g]

[a.]*Department of Chemistry, College of Natural Sciences, The University of Texas at Austin, Austin, Texas 78712, United States*

[b.]*Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan*

[c.]*McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, United States*

[d.]*Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, United States*

[e.]*Oden Institute for Computational Engineering and Sciences, The University of Texas at Austin, Austin, Texas 78712, United States*

[f.]*Center for Electrochemistry, The University of Texas at Austin, Austin, Texas 78712, United States*

[g.]*H2@UT, The University of Texas at Austin, Austin, Texas 78712, United States*

*Corresponding author.

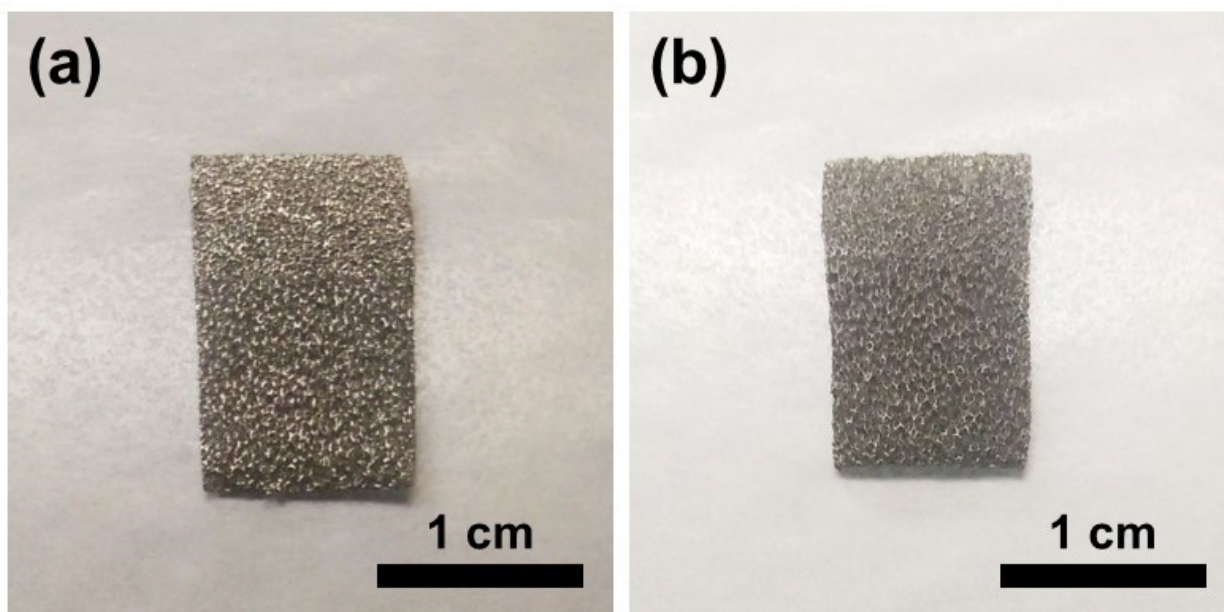E-mail address: mullins@che.utexas.edu

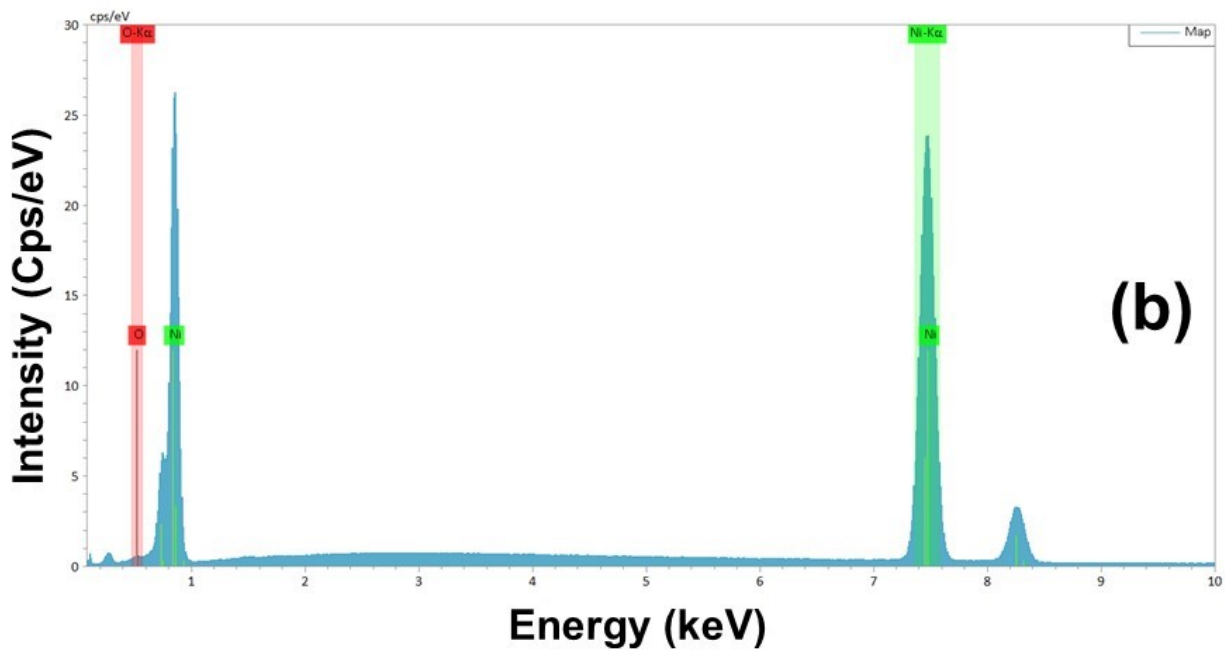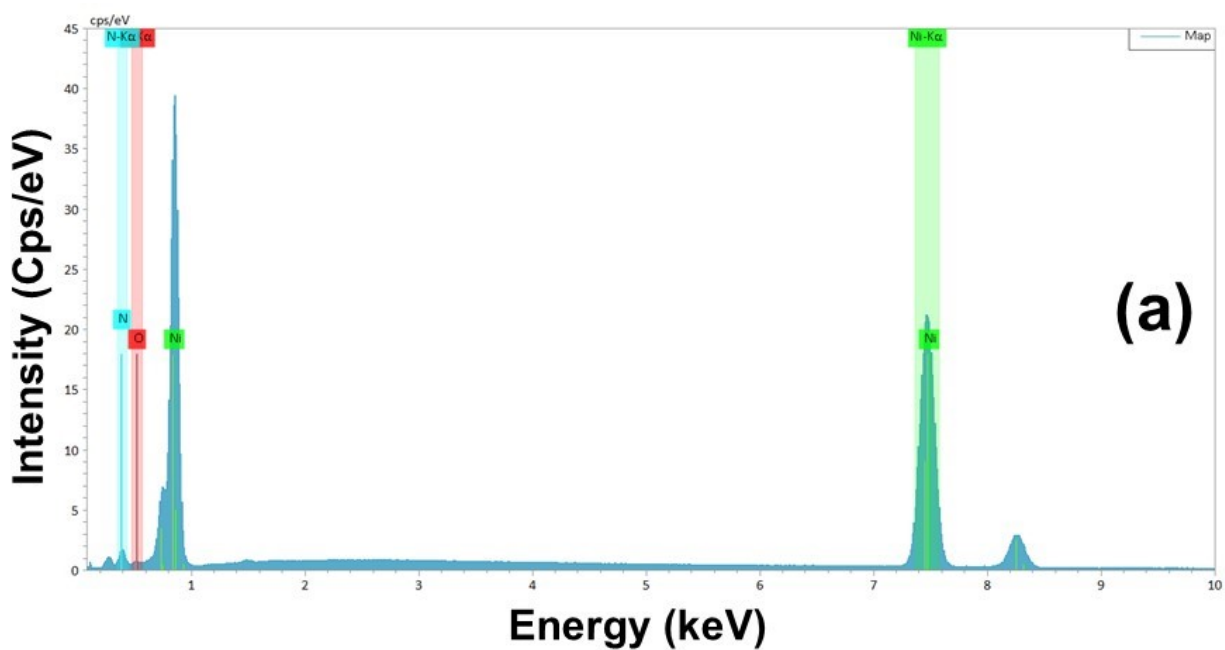**Fig. S1** Digital photographs of pristine (a) NF and (b) Ni$_3$N/NF.

Fig. S2 EDX spectra of pristine (a) Ni_3N/NF and (b) NF.

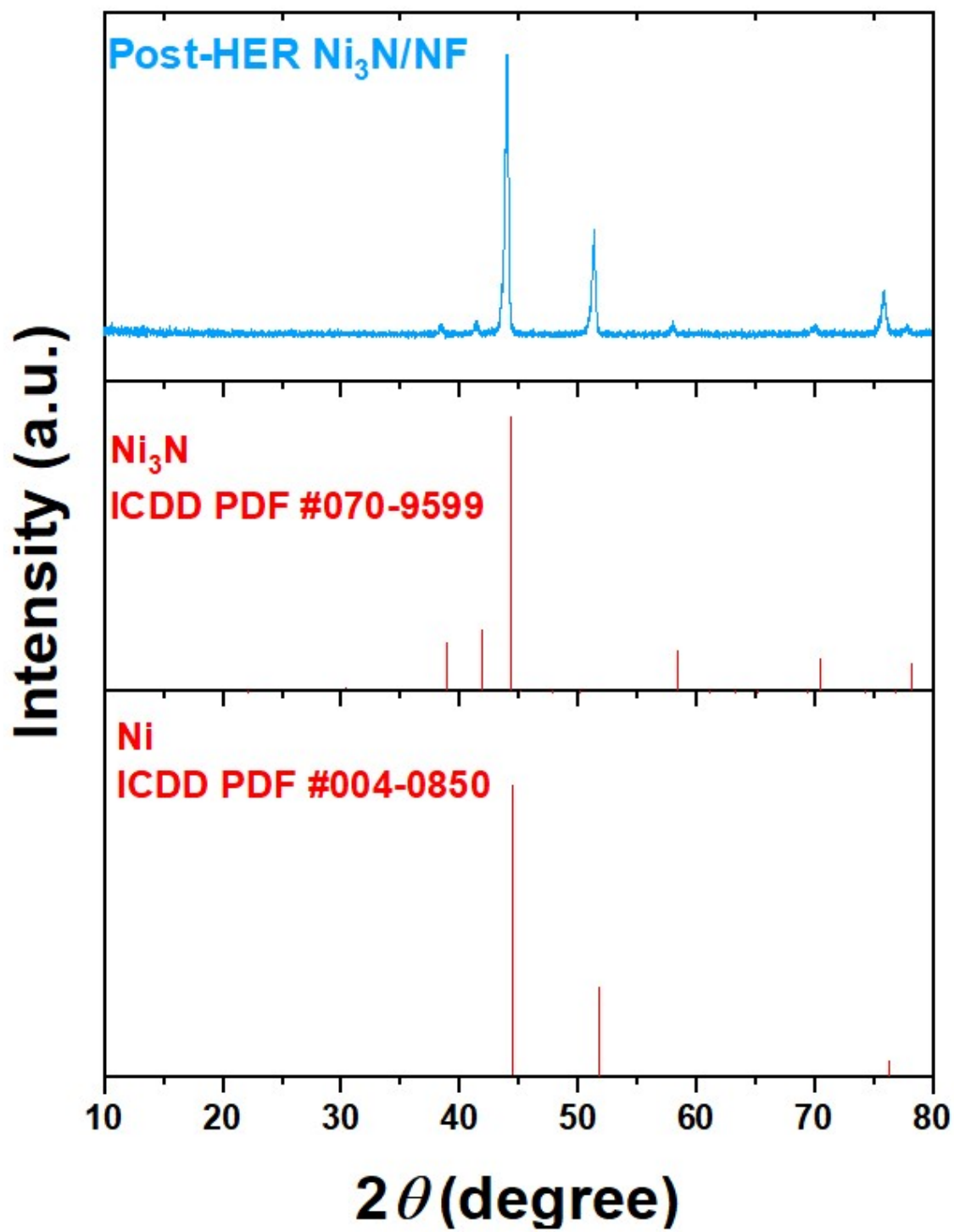**Fig. S3** XRD pattern of Ni_3N/NF after long-term HER testing.

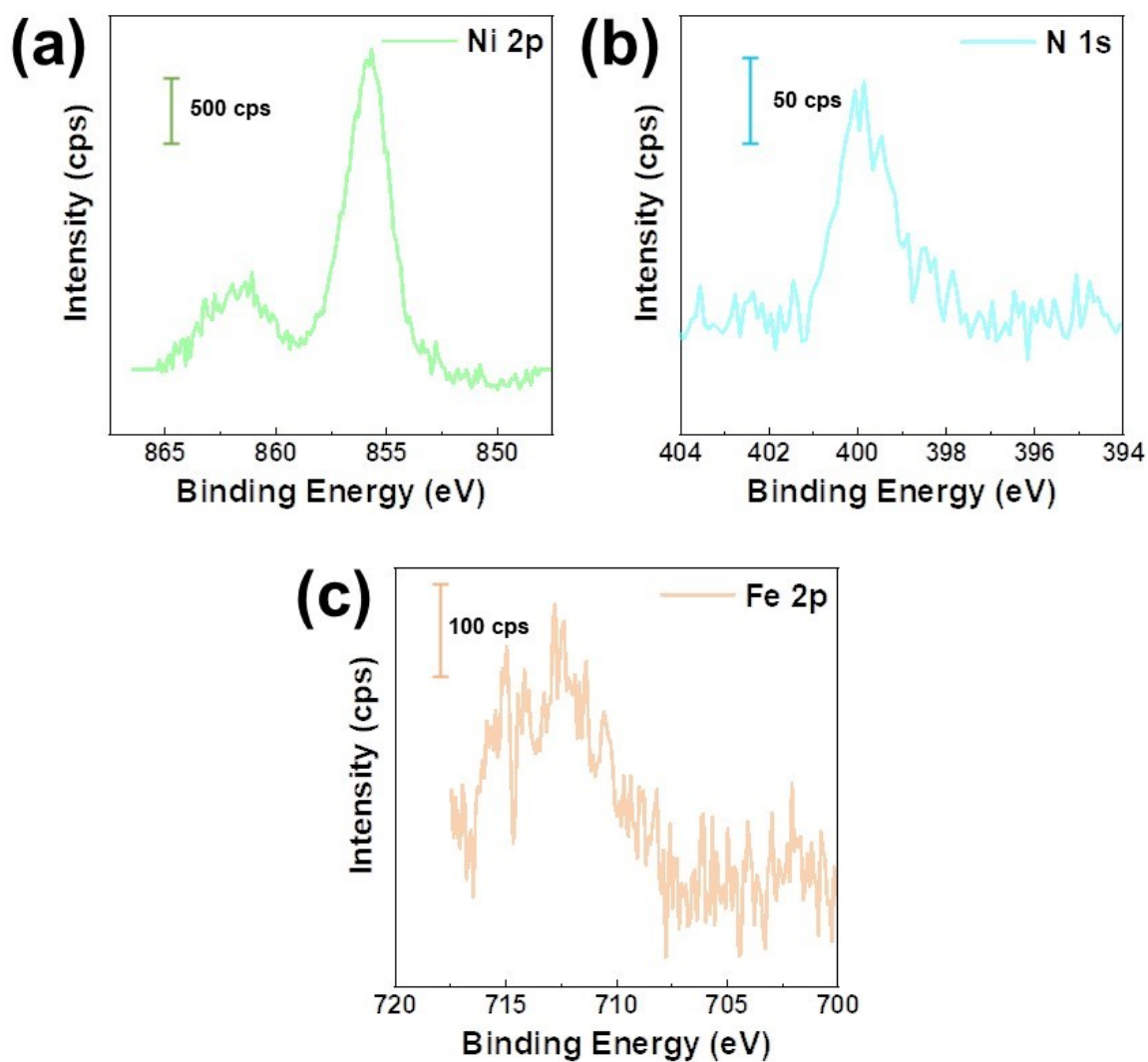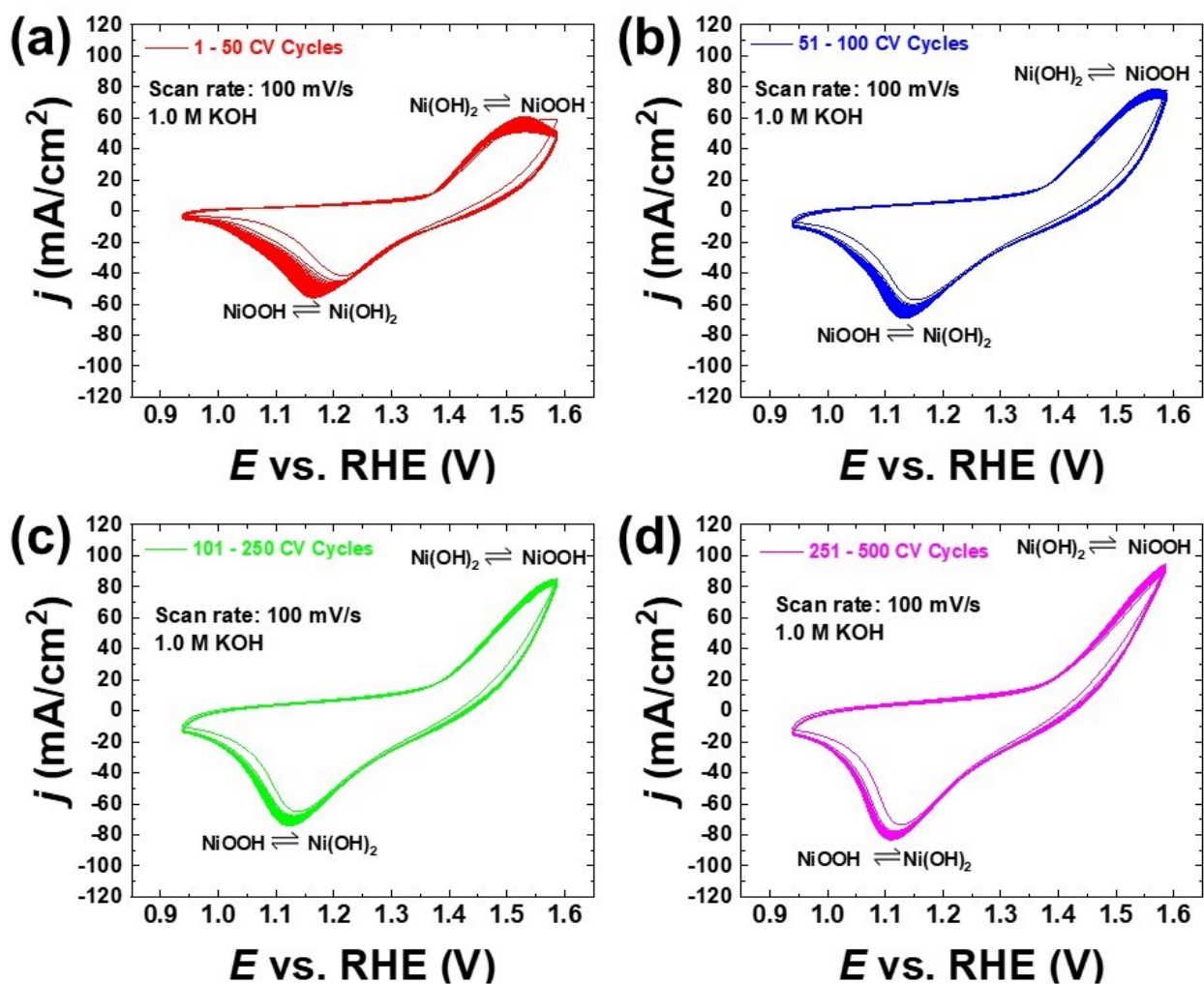**Fig. S4** (a) Ni 2p, (b) N 1s, and (c) Fe 2p XPS spectra of Ni$_3$N/NF after long-term HER testing.

Fig. S5 CV activation plots for Ni₃N/NF: (a) 1-50 CV cycles, (b) 51-100 CV cycles, (c) 101-250 CV cycles, and (d) 251-500 CV cycles.
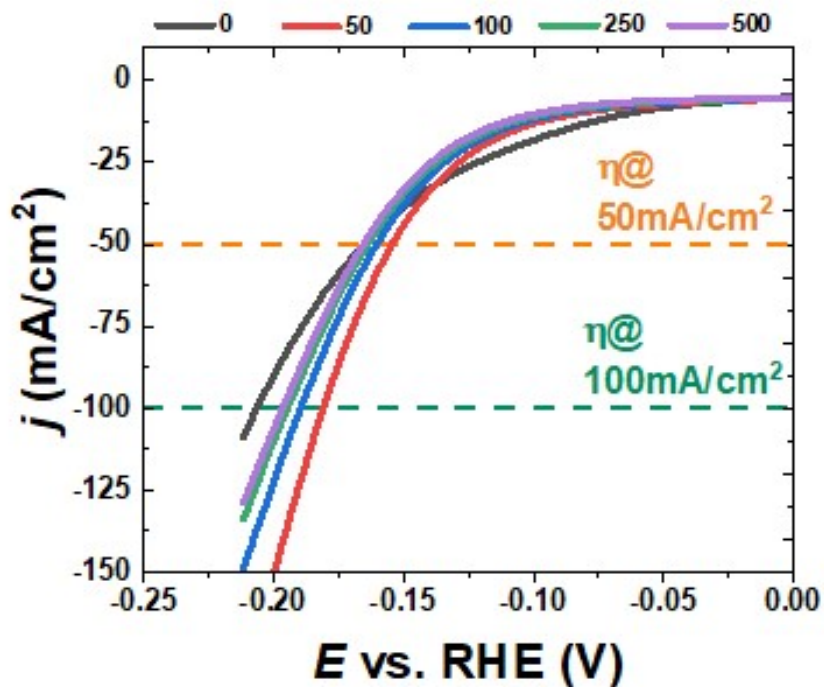
Fig. S6 LSV curves of Ni₃N/NF after CV activation with different cycle numbers: 0-500 cycles.
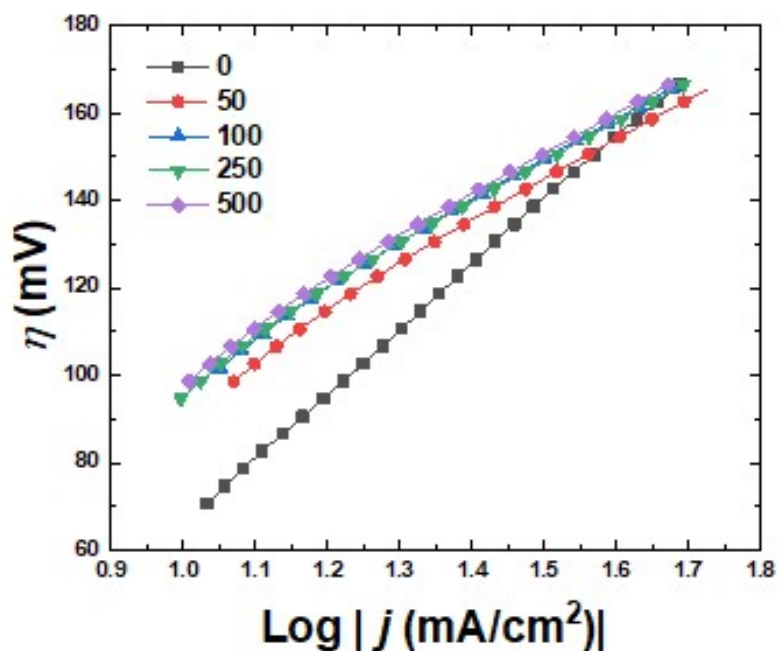

Fig. S7 Tafel slopes of Ni₃N/NF after CV activation with different cycle numbers: 0-500 cycles.
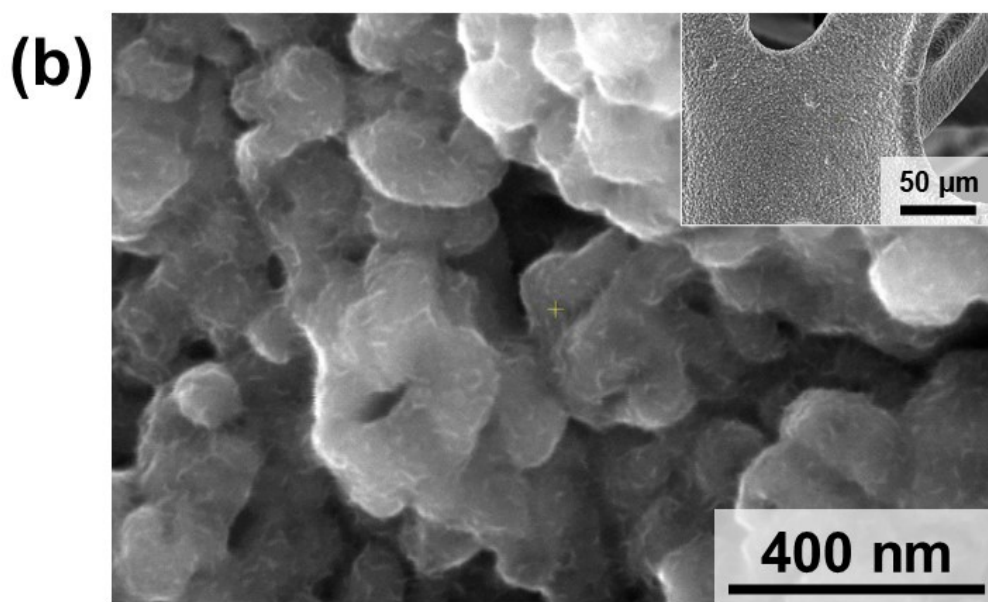
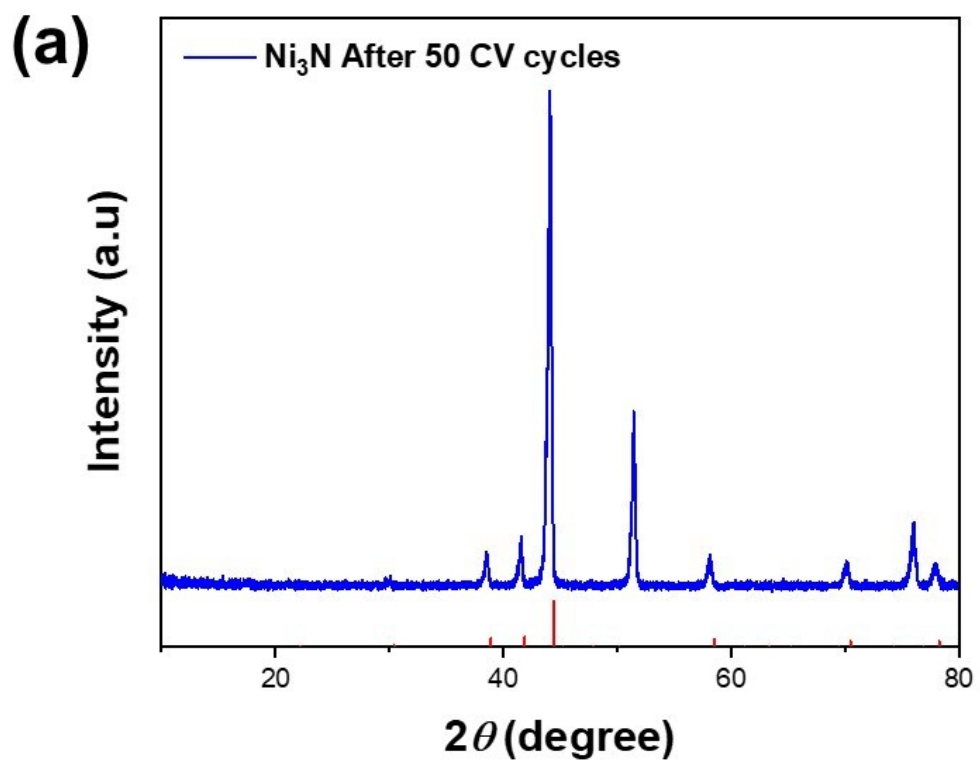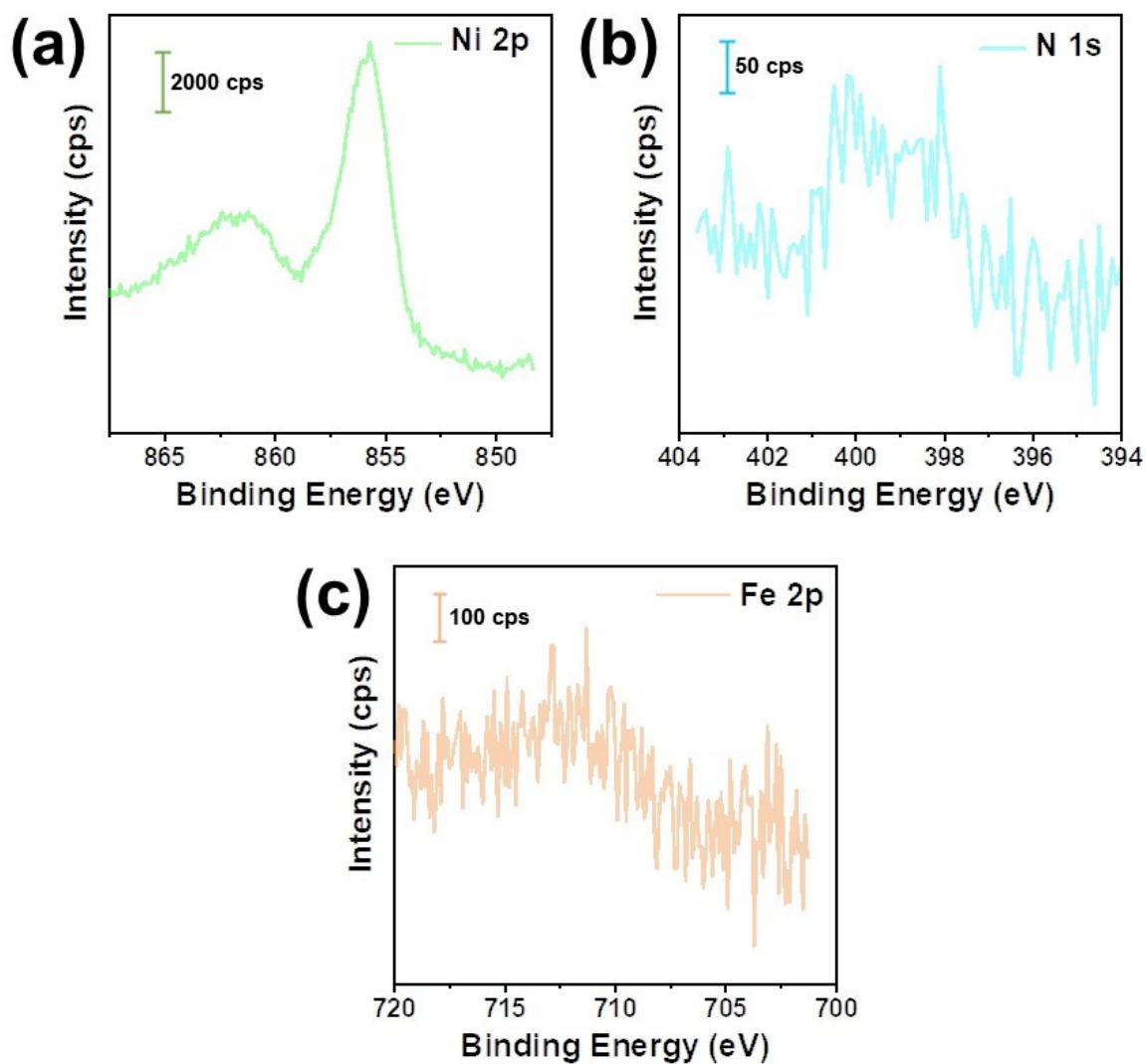**Fig. S8** (a) XRD pattern and (b) SEM images of 50 CV-activated Ni$_3$N/NF.

Fig. S9 (a) Ni 2p, (b) N 1s, and (c) Fe 2p XPS spectra of 50 CV-activated Ni$_3$N/NF.

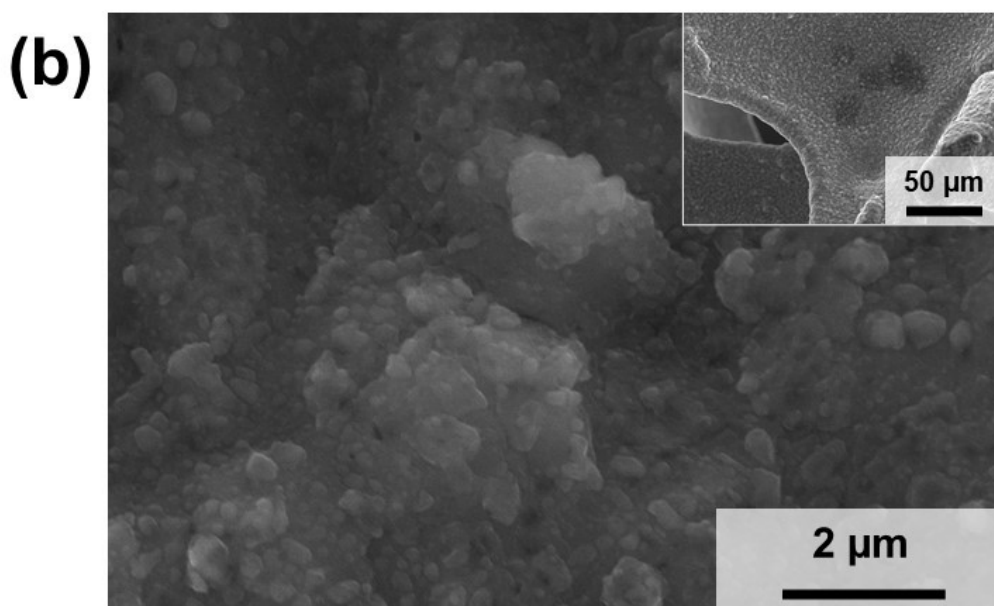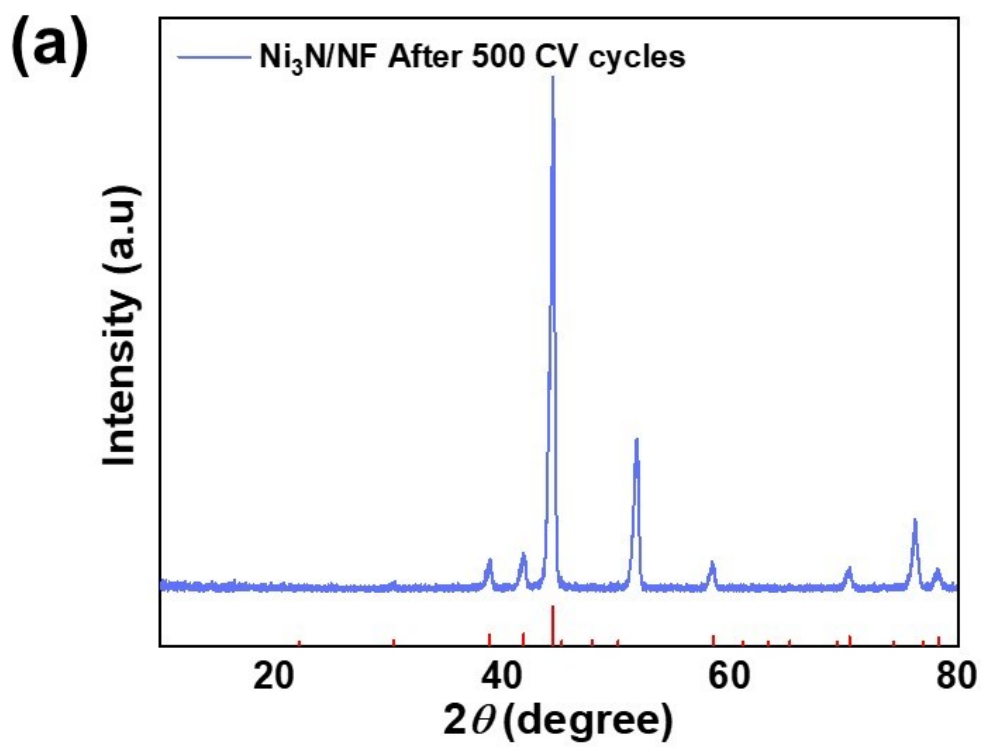**Fig. S10** (a) XRD pattern and (b) SEM images of 500 CV-activated Ni_3N/NF.
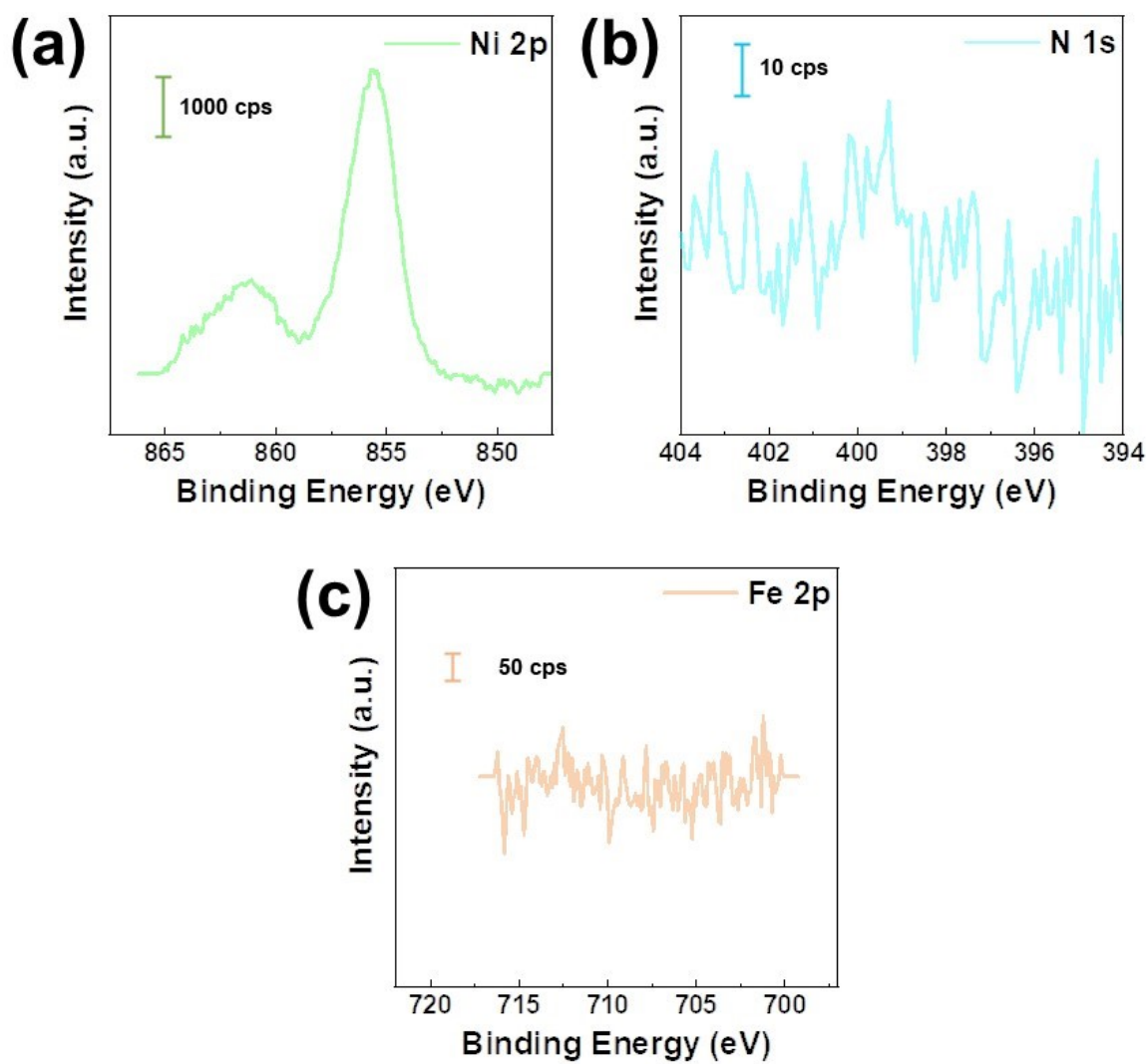
Fig. S11 (a) Ni 2p, (b) N 1s, and (c) Fe 2p XPS spectra of 500 CV-activated Ni$_3$N/NF.
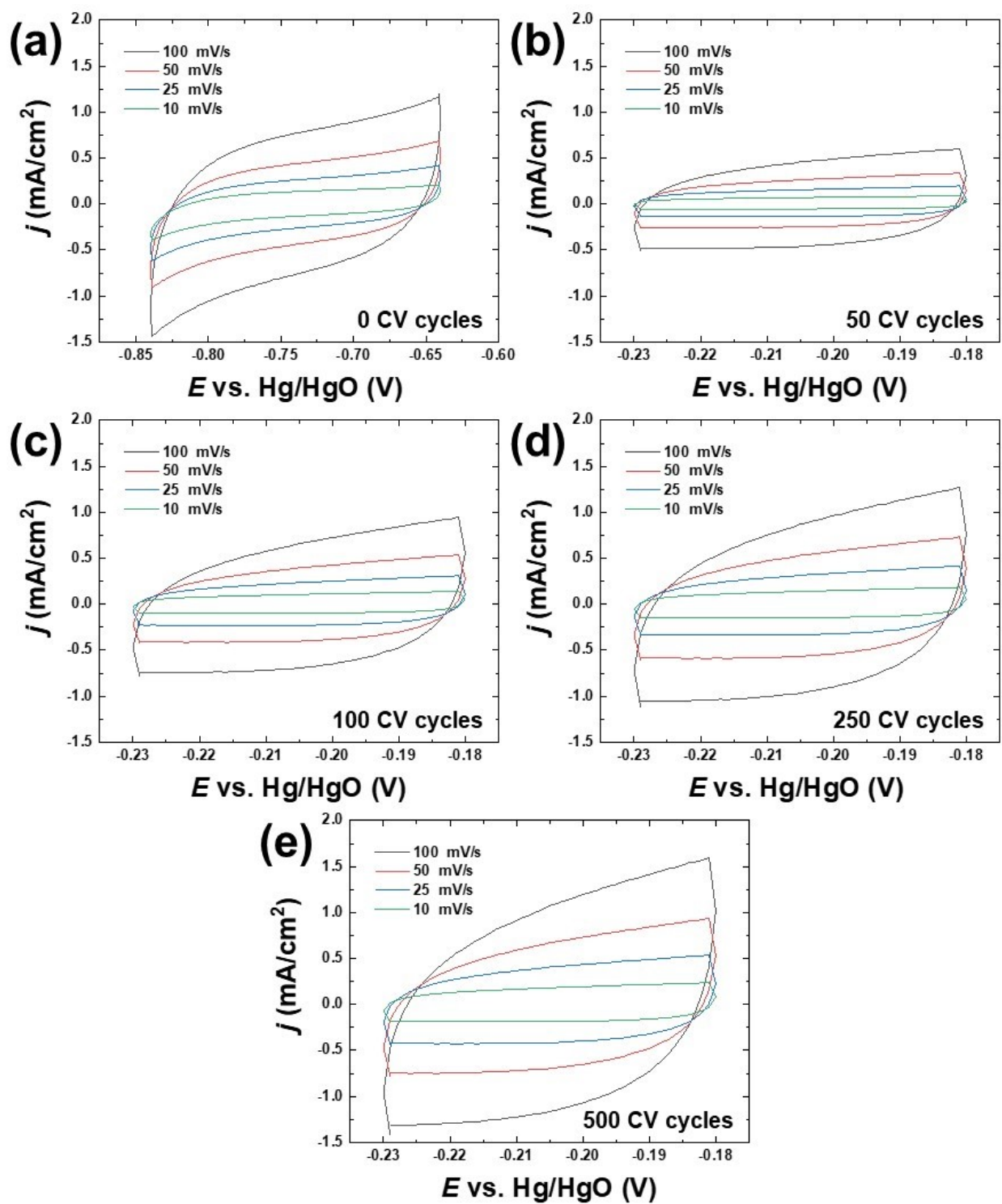
Fig. S12 Non-faradaic CV curves of (a) 0, (b) 50, (c) 100, (d) 250, and (e) 500 CV-activated Ni$_3$N/NF samples.
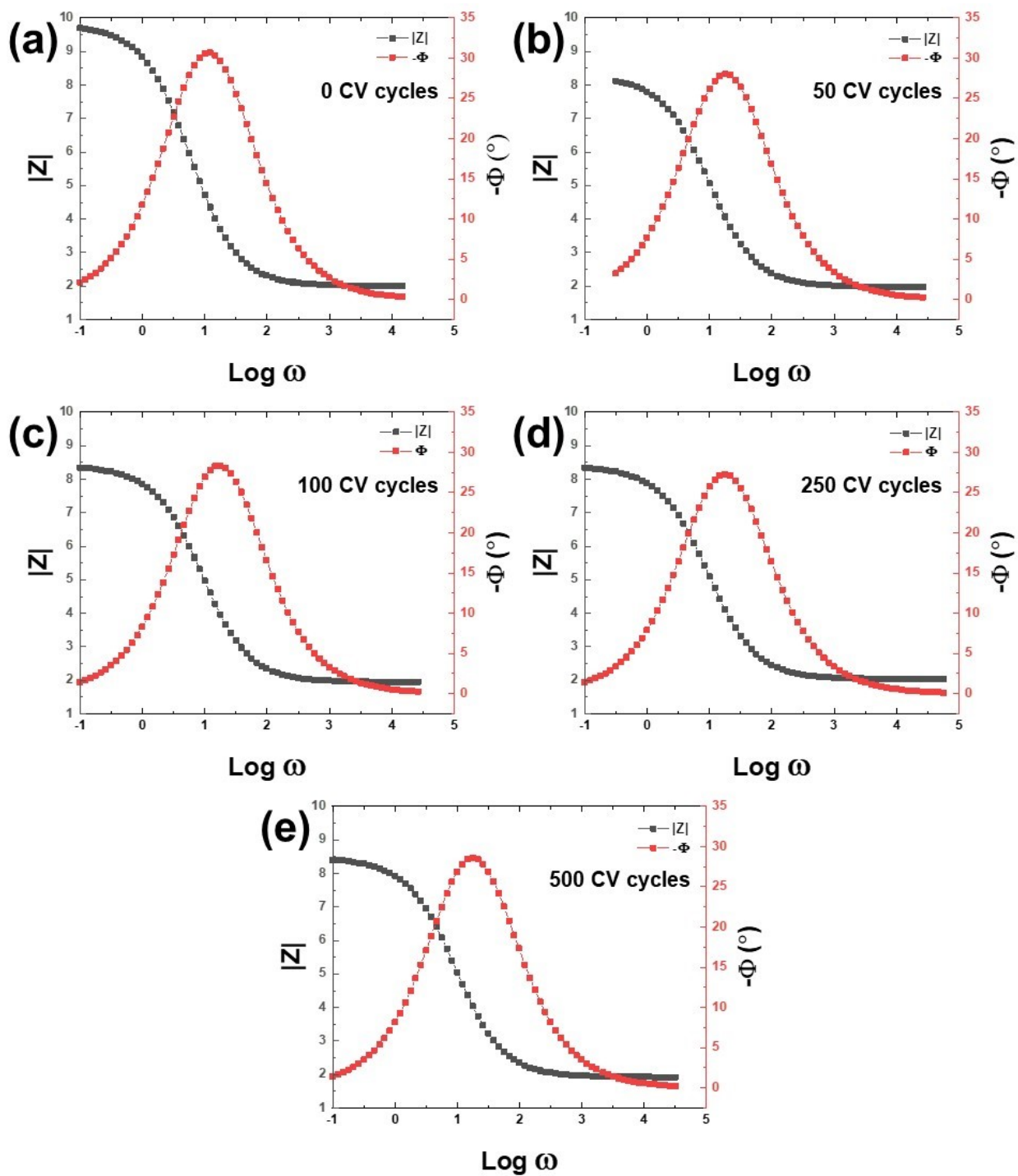
Fig. S13 Bode plots of (a) 0, (b) 50, (c) 100, (d) 250, and (e) 500 CV-activated Ni_3N/NF samples.
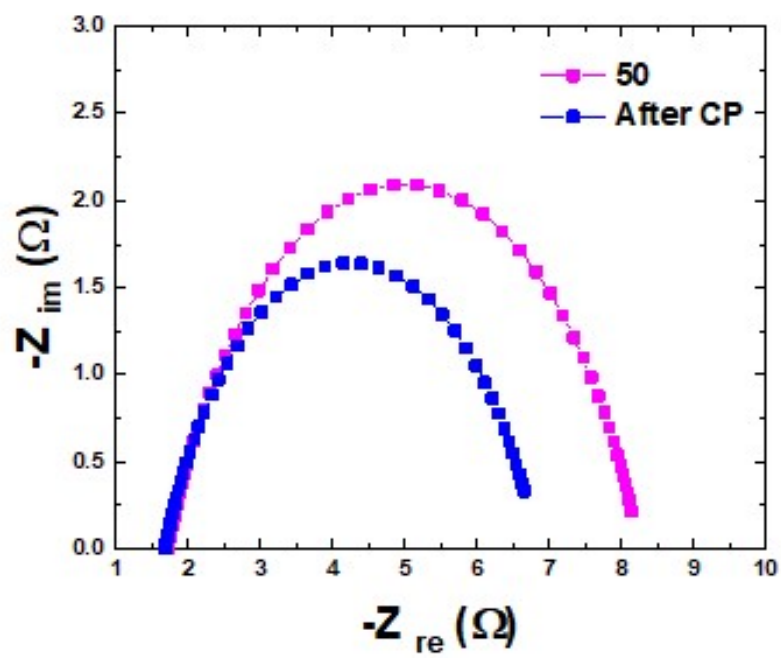
Fig. S14 Nyquist plots for 50 CV-activated Ni$_3$N/NF before and after long-term HER testing.
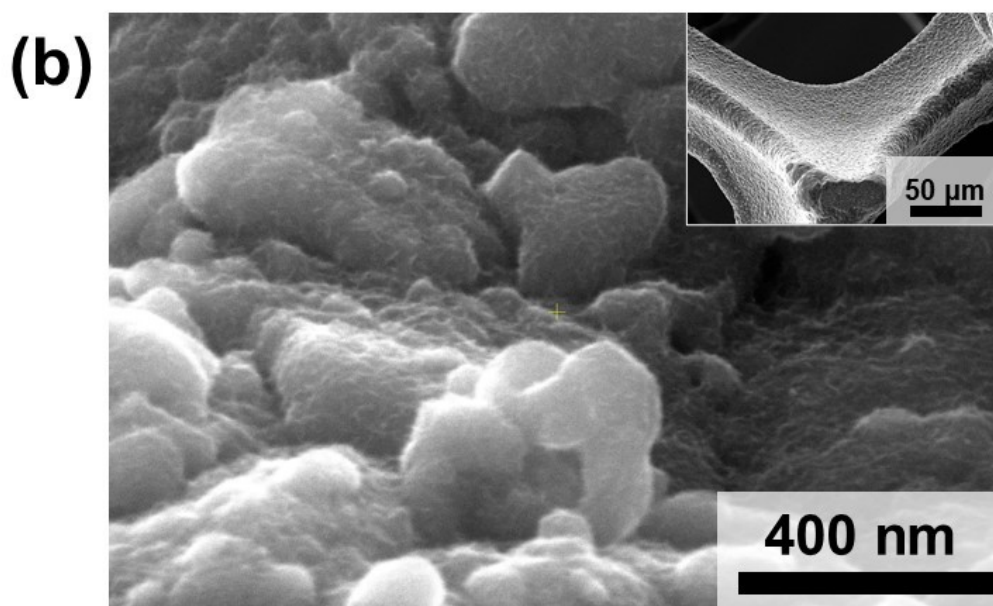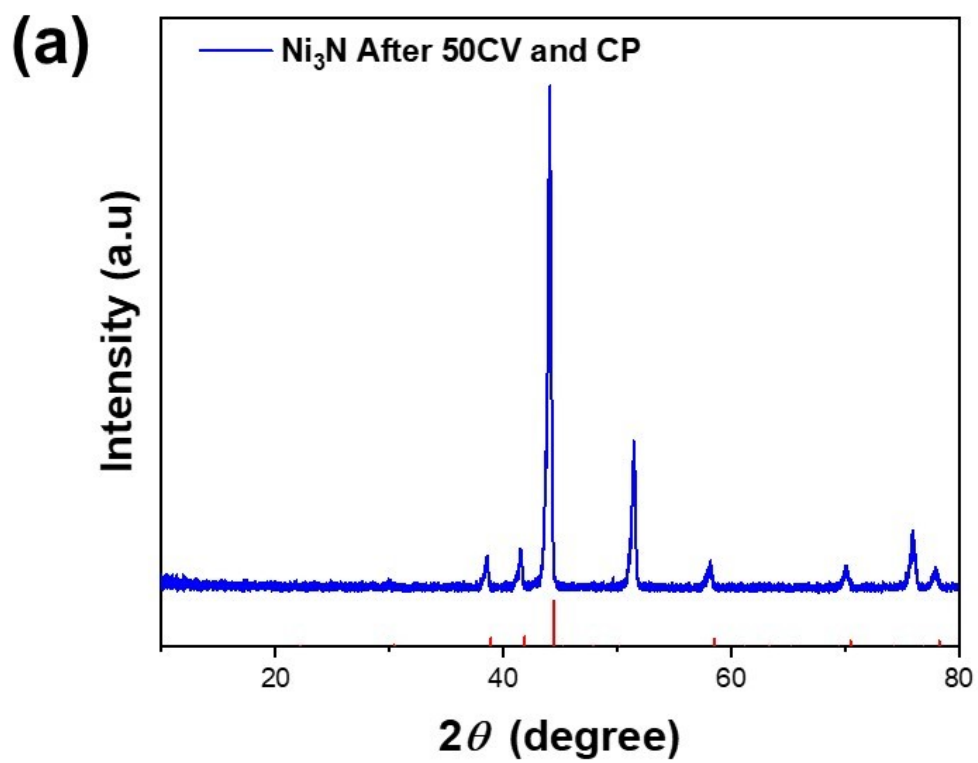
Fig. S15 (a) XRD pattern and (b) SEM images of 50 CV-activated Ni₃N/NF after long-term HER testing.
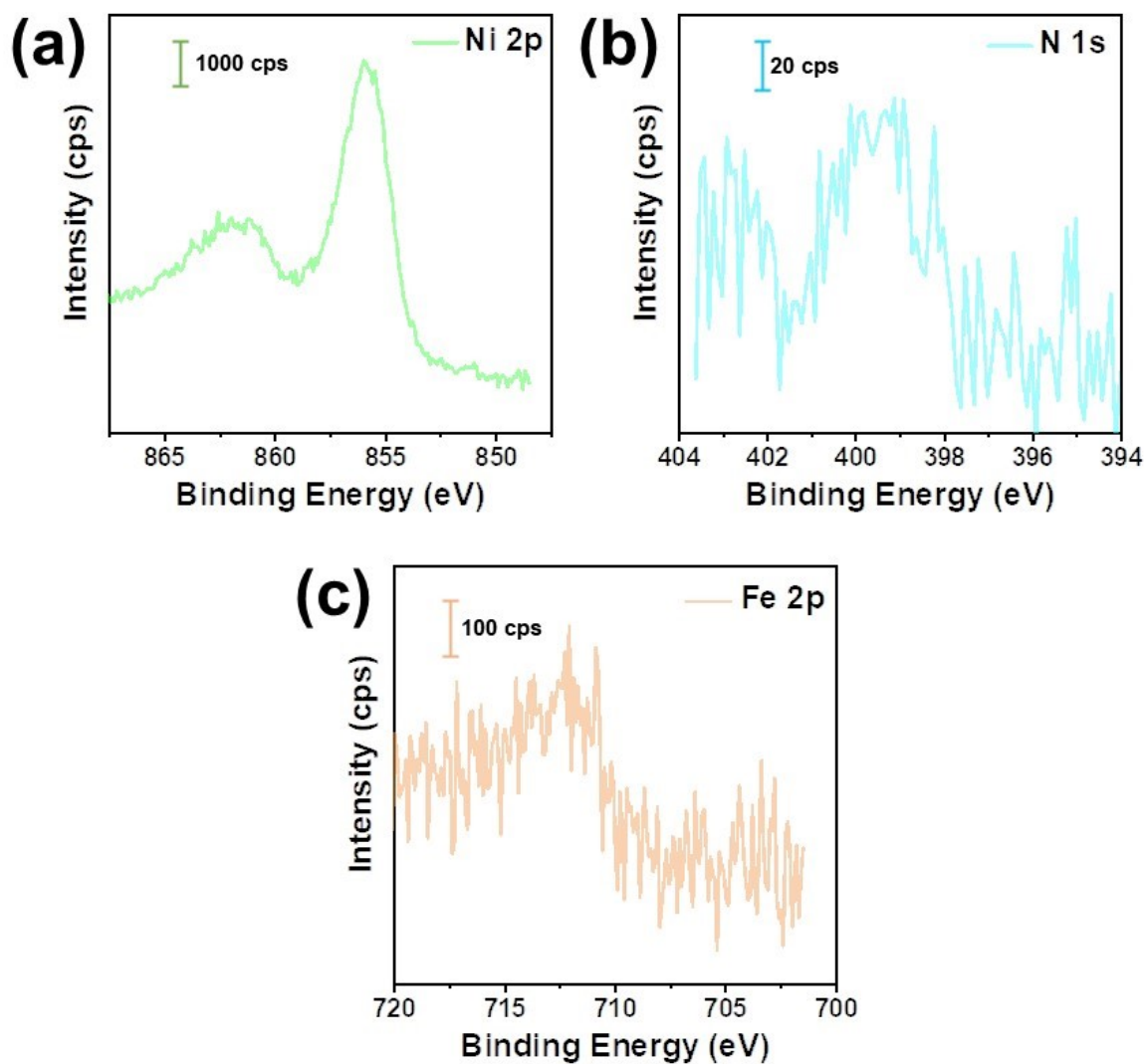
Fig. S16 (a) Ni 2p, (b) N 1s, and (c) Fe 2p XPS spectra of 50 CV-activated Ni_3N/NF after long-term HER testing.
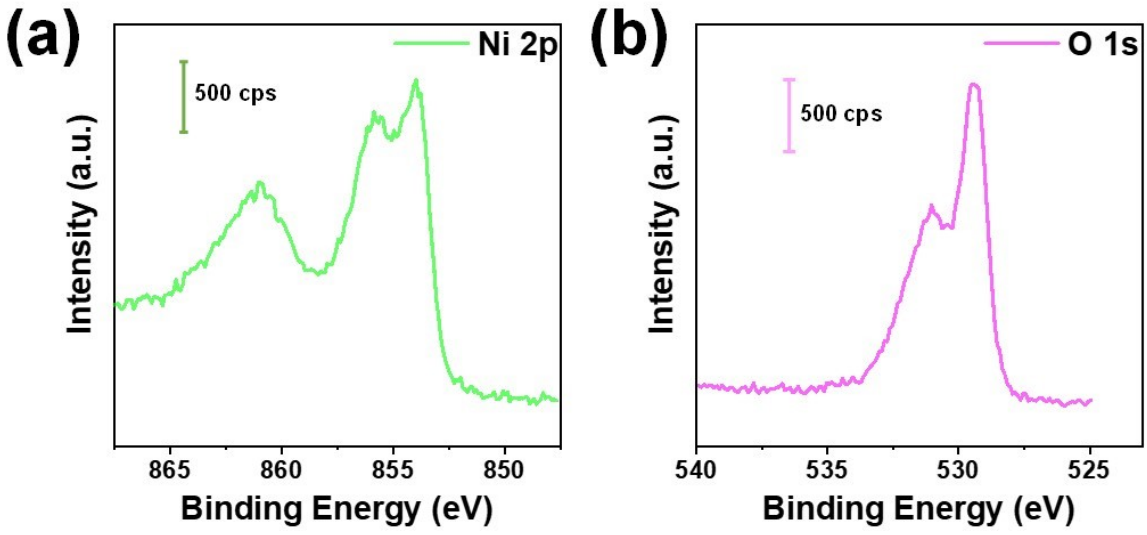
Fig. S17 (a) Ni 2p and (b) O 1s XPS spectra of NiO/NF.
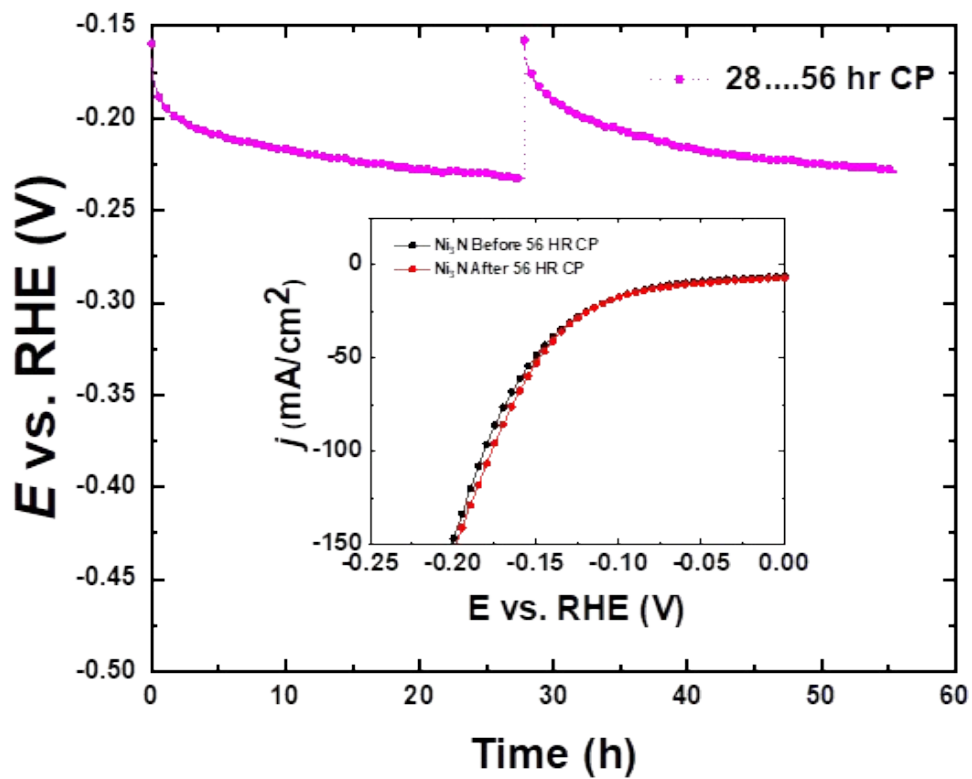
Fig. S18 ~56 h HER chronopotentiometry tests at -20 mA/cm^2 for Ni(OH)$_2$-Ni$_3$N/NF and LSV curves before and after the chronopotentiometry (inset).

Table S1 An alkaline HER activity comparison (at a cathodic current density of 50 mA/cm^2) of pristine Ni$_3$N/NF and electrochemically engineered Ni(OH)$_2$-Ni$_3$N/NF (after 50 CV cycles) in this work with previously reported similar electrocatalysts

| This work pristine Ni$_3$N η@50 mA/cm^2 = 171.93 ± 3.8 mV		
After 50 CV cycles η@50 mA/cm^2 = 164 ± 1.2 mV		
Sample Name	η@50 mA/cm^2 (mV)	Reference
Ni$_3$N/NF	~210	1
Ni$_3$N/NF	~220	2
Ni$_3$N$_{1-x}$/NF	~240	3
Ni$_3$N/NF	~200	4
Ni-S/NF	~350	5
Ni-S-OH/NF	~270	5
Ni$_3$N	~300	6
Ni$_3$N/NF	~210	7

Table S2 A alkaline HER activity comparison (at a cathodic current density of 100 mA/cm^2) of pristine Ni$_3$N/NF and electrochemically engineered Ni(OH)$_2$-Ni$_3$N/NF (after 50 CV cycles) in this work with previously reported similar electrocatalysts

This work pristine Ni$_3$N η@ 100mA/cm^2 = 207.27 ± 3.06 mV		
After 50 CV cycles η@ 100mA/cm^2 = 192.27 ± 1.53 mV		
Sample Name	η@100 mA/cm^2 (mV)	Reference
Ni$_3$N/NF	~300	1
Ni$_3$N/NF	~250	2
Ni$_3$N$_{1-x}$/NF	~350	3
Ni$_3$N/NF	~300	7
Ni-S/NF	~410	5
Ni-S-OH/NF	~310	5
Ni$_3$N	~350	6

References

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