

Supplementary Information

NaBH₄ Induces High Ratio of Ni³⁺/Ni²⁺ Boosting OER Activity of the NiFe LDH Electrocatalyst†

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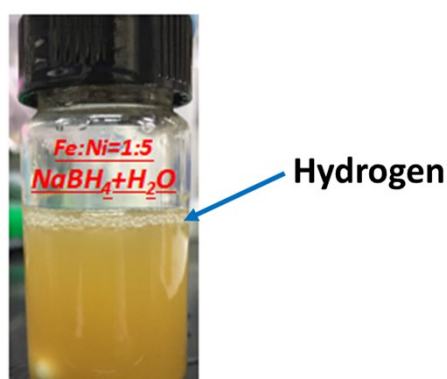


Fig. S1. The phenomenon of NiFe LDH activated by NaBH₄ treatment in aqueous solution.

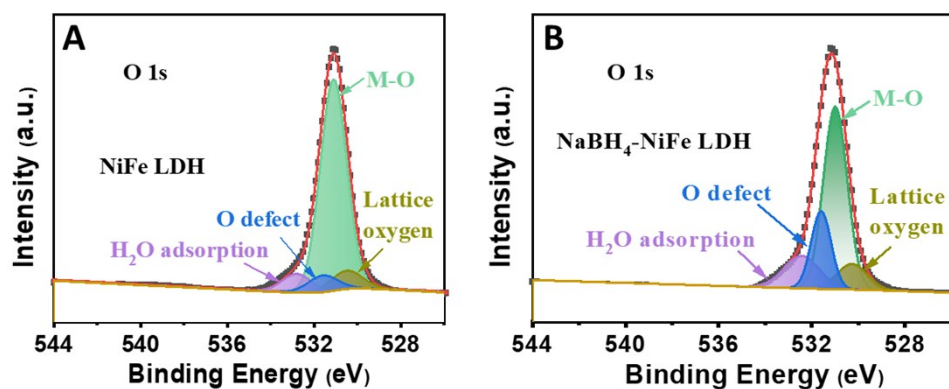


Fig. S2. High resolution XPS spectra of O1s for (A) NiFe LDH and (B) NaBH₄-NiFe LDH.

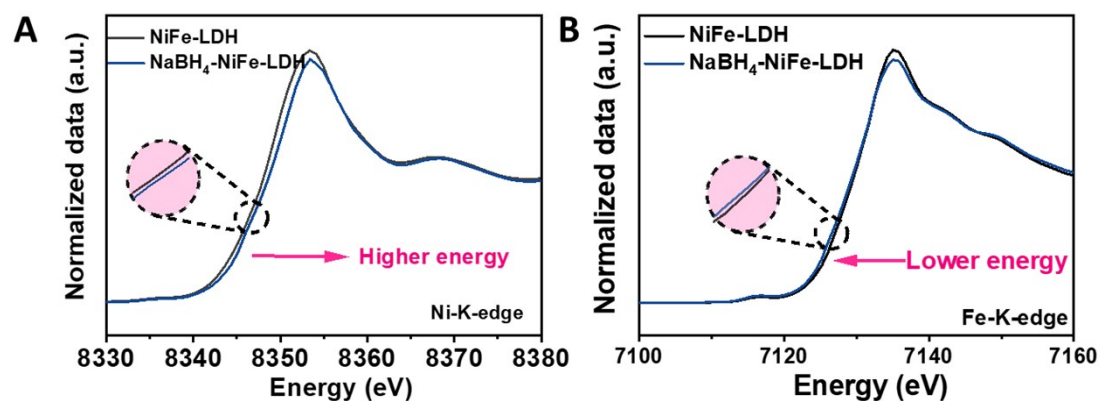


Fig. S3. (A) Ni K-edge XANES spectra, (B) Fe K-edge XANES data, the insets in A and B show magnified view of the rectangles.

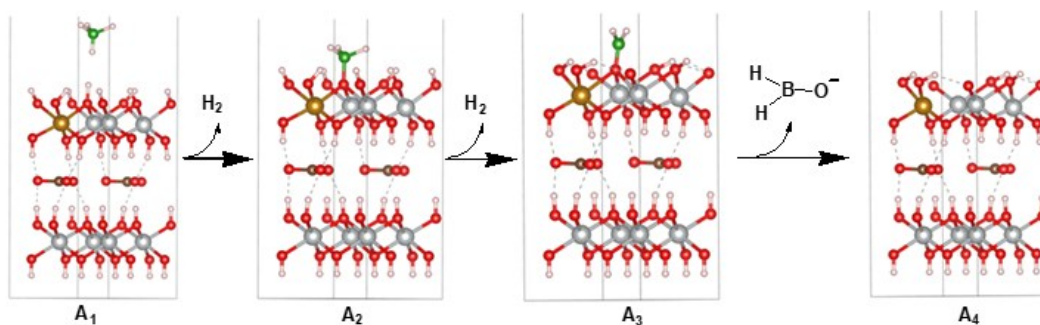


Fig. S4. Schematic illustration of the NaBH_4 -triggered electron transfer activation process of NiFe LDH via NaBH_4 treatment: atomistic models.

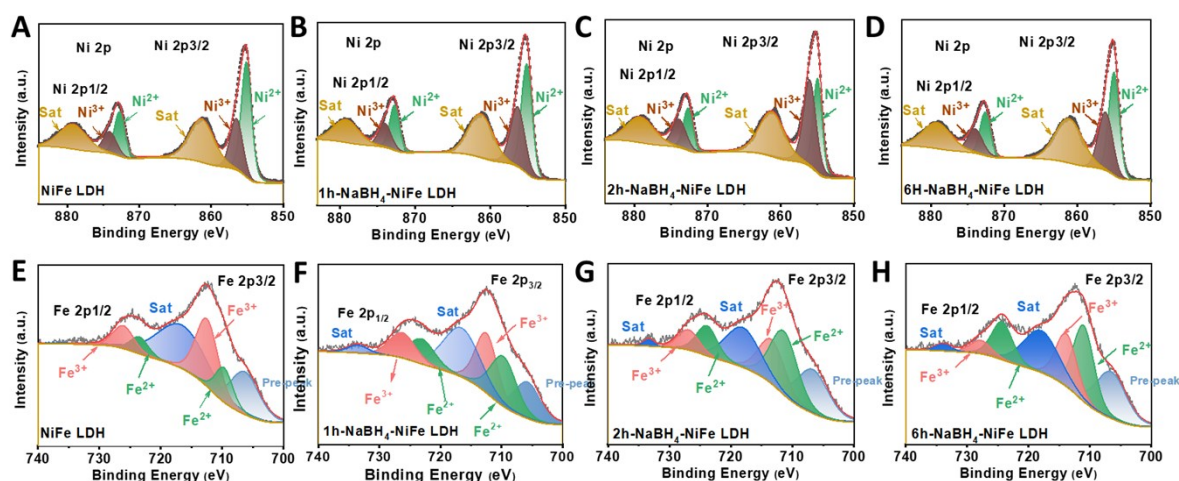


Fig. S5. Deconvoluted XPS spectra of NiFe LDH and NiFe LDH treated with NaBH_4 for 1, 2, and 6 hours in (A-D) Ni 2p spin-orbital and (E-H) Fe 2p spin-orbital.

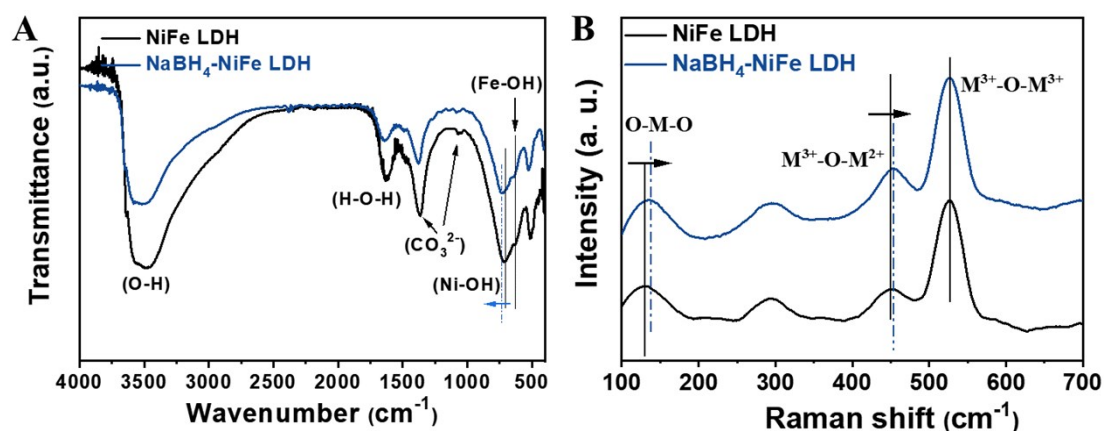


Fig. S6. FT-IR (A) and Raman (B) spectra of NiFe LDH and NaBH_4 -NiFe LDH powders.

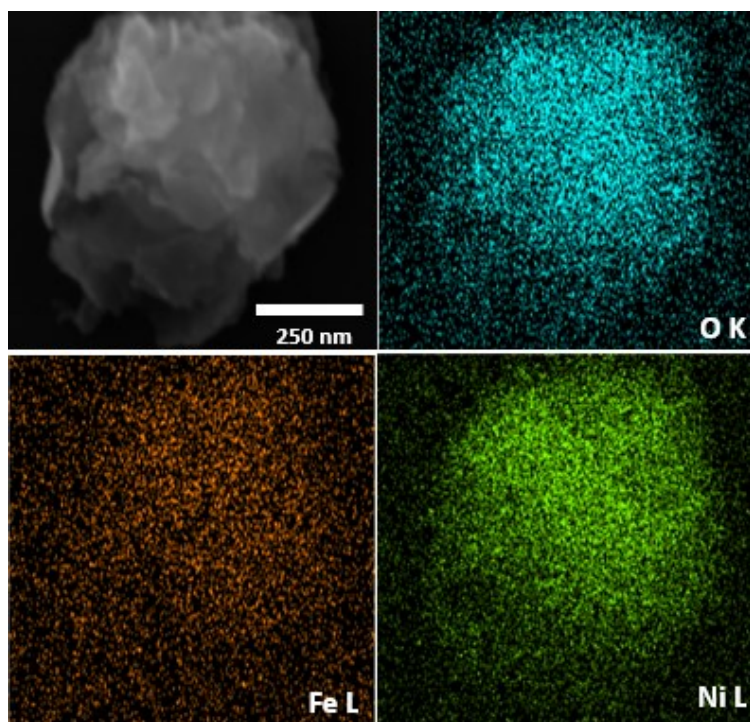


Fig. S7. Elemental mapping of NaBH₄-NiFe LDH.

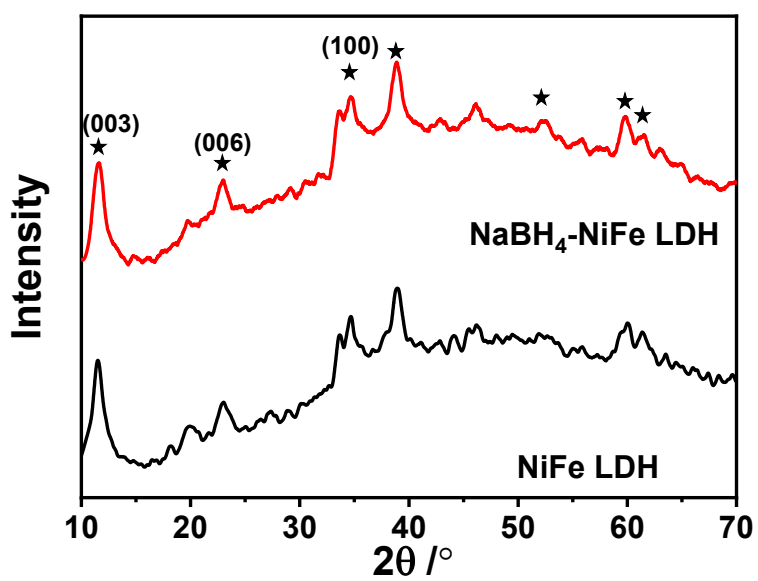


Fig. S8. XRD patterns of NiFe LDH (black curve) and NaBH₄-NiFe LDH (red curve).

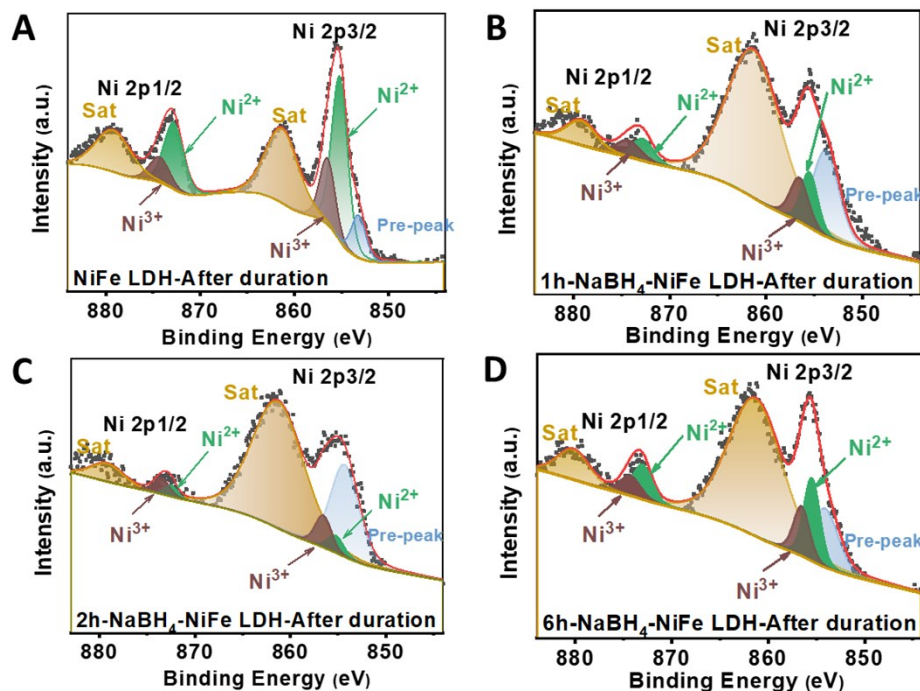


Fig. S9. Deconvoluted XPS spectra of NiFe LDH and NaBH₄-NiFe LDH for 1, 2, and 6 hours after CV duration in (A-D) Ni 2p spin-orbital.

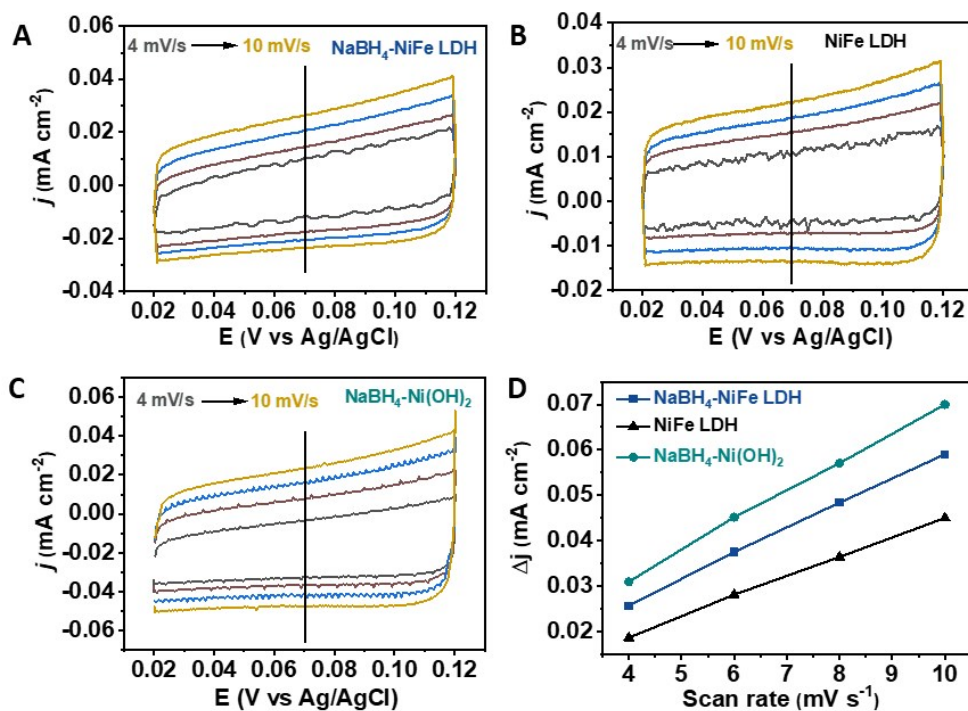


Fig. S10. The CV curves of (A) NaBH₄-NiFe LDH, (B) initial NiFe LDH and (C) NaBH₄-Ni(OH)₂ nanosheets with various scan rates, and (D) the capacitive current density differences plotted against scan rates.

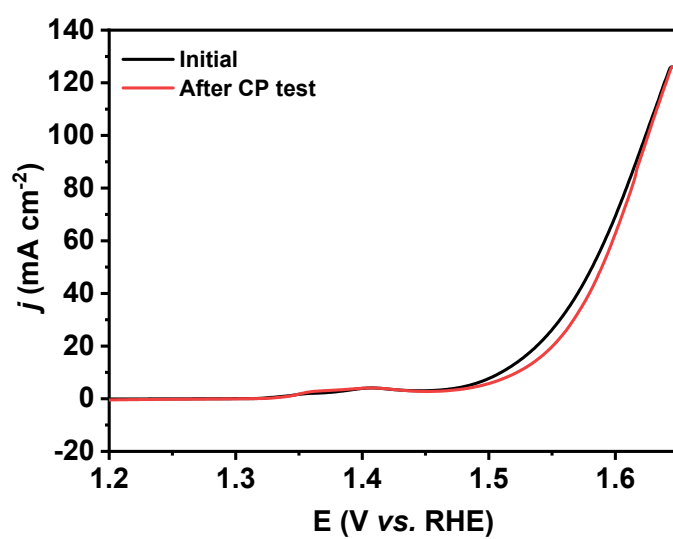


Fig. S11. LSV curves of initial NaBH_4 -NiFe LDH nanosheets (black curve) and that after the CP testing at 50 mA cm^{-2} for 12 h (red curve).

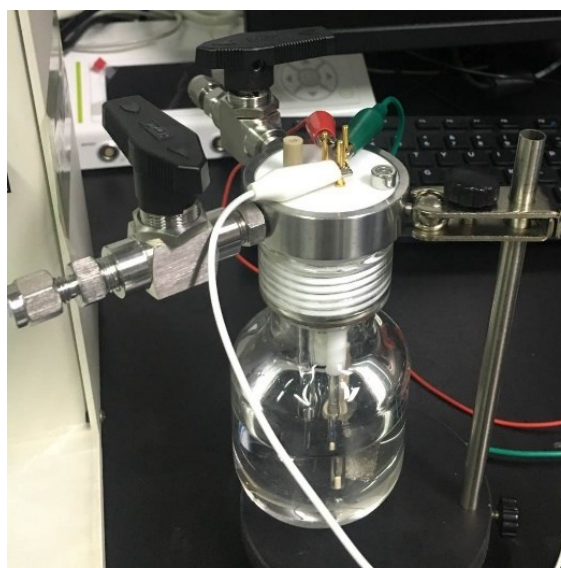


Fig. S12. The schematic diagram of OER equipment for FE measurement.

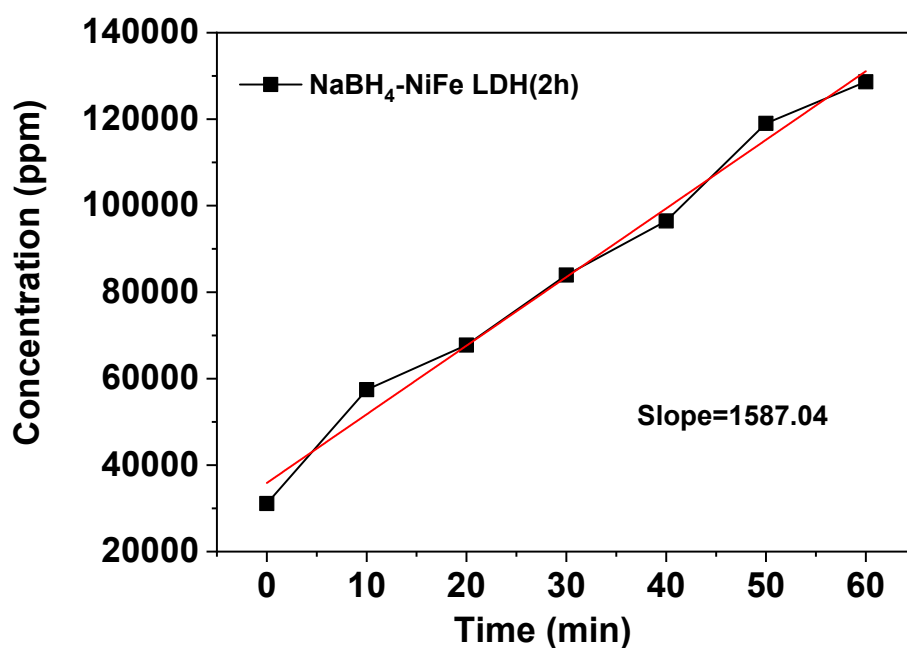


Fig. S13. The obtained concentration of O_2 from the GC analysis on $NaBH_4$ -NiFe LDH (2h) under a constant oxidation current of 50 mA conducted by chrompotentiometry (CP) plotted against time injections. The volume of the sample injection is 1ml gaseous product.

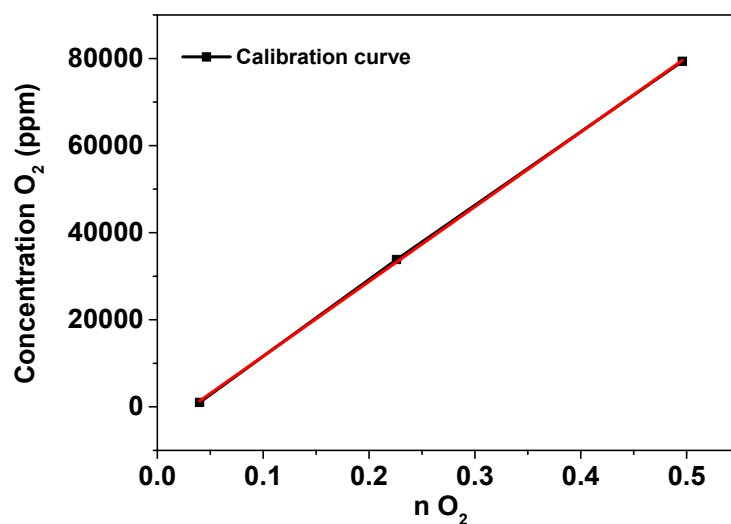


Fig. S14. The calibration curve prepared by injecting three calibrating gases with known concentrations of H_2 and O_2 into GC. The volume of the injection is 1 ml.

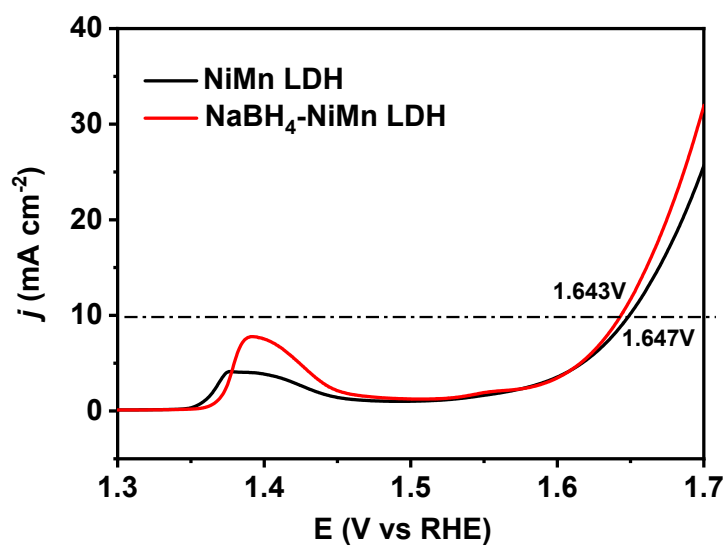


Fig. S15. Linear sweep voltammetry (LSV) curves of the NiMn and NaBH₄-NiMn LDHs

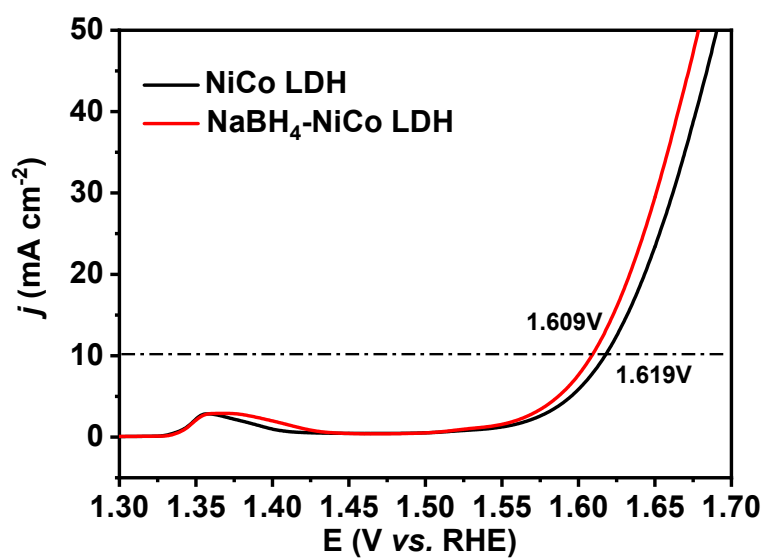


Fig. S16. Linear sweep voltammetry (LSV) curves of the NiCo and NaBH₄-NiCo LDHs

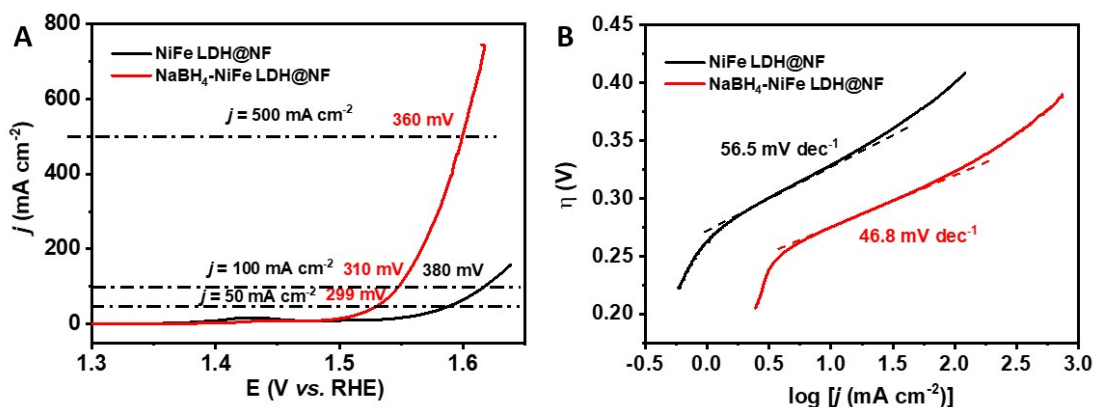


Fig. S17. Electrocatalytic performance characterizations of the catalysts. (A) Linear sweep voltammograms (LSV). (B) Tafel plots.

Table S1. The summarized data from XPS showing the atomic ratios of Ni (III) to Ni (II) and Fe (II) to Fe (III) with various activated time by NaBH₄ treatment. NaBH₄-NiFe LDH mentioned in the manuscript refers to NiFe LDH treated for 2h, if not otherwise indicated.

Species	Ratio of Ni (III) to Ni (II)	Ratio of Fe (II) to Fe (III)
NiFe LDH	0.39	0.40
1h	0.78	0.99
2h	1.32	1.49
6h	0.75	1.51

Table S2. Local structure parameters around Ni estimated by EXAFS analysis.

Sample	Shell	N ^[a]	R [Å] ^[b]	σ ² [Å ²] ^[c]	Δ E ₀ (eV)	R factor
NiFe-LDH	Ni-O	6.0	2.06	0.0059	-2.1	0.0078
	Ni-Ni	7.6	3.12	0.0087		
	Ni-Fe	1.5	3.06	0.0087		
NaBH ₄ -NiFe-LDH	Ni-O	5.9	2.05	0.0060	-4.4	0.0086
	Ni-Ni	6.8	3.12	0.0096		
	Ni-Fe	1.4	3.06	0.0096		

[a] *N* = coordination number; [b] *R* = distance between absorber and backscatter atoms; [c] σ₂ = Debye-Waller factor

Table S3. Local structure parameters around Fe estimated by EXAFS analysis.

Sample	Shell	N ^[a]	R [Å] ^[b]	σ^2 [Å ²] ^[c]	ΔE_0 (eV)	R factor
NiFe-LDH	Fe-O	6.0	2.01	0.0047	-1.7	0.0009
	Fe-Ni	7.4	3.10	0.0070		
	Fe-Fe	2.2	2.95	0.0070		
NaBH ₄ -NiFe-LDH	Fe-O	5.6	1.99	0.0062	-0.7	0.0012
	Fe-Ni	5.8	3.09	0.0086		
	Fe-Fe	2.1	2.91	0.0086		

[a] N = coordination number; [b] R = distance between absorber and backscatter atoms; [c] σ^2 = Debye-Waller factor

Table S4. The summarized data from XPS showing the atomic ratios of Ni (III) to Ni (II) of various NaBH₄-NiFe LDH samples before and after CV duration.

Species	Ratio of Ni (III) to Ni (II) (Before)	Ratio of Ni (III) to Ni (II) (After)
NiFe LDH	0.39	0.40
1h	0.78	0.91
2h	1.32	1.50
6h	0.75	0.76

Table S5. The summarized data from XPS showing the ratios of M₁/M₂ in LDHs and NaBH₄-TM LDHs.

Species	Mn (II)/Mn (III)	Ni (III)/Ni (II)
NiMn LDH	0.79	0.5
NaBH₄-NiMn LDH	1.53	1.01
	Co (II)/Co (III)	Ni (III)/Ni (II)
NiCo	0.76	0.45
NaBH₄-NiCo	1.42	1.20
	Fe(II)/Fe(III)	Ni (III)/Ni (II)
NiFe	0.40	0.39
NaBH₄-NiFe	1.49	1.32

Table S6. Comparison of the catalysts and their OER activity in alkaline medium

Catalyst	Substrate	Medium	$\eta(\text{mV})$ for OER @10 mA cm^{-2})	$\eta(\text{mV})$ for OER @20 mA cm^{-2})	$\eta(\text{mV})$ for OER @ 100 mA cm^{-2})	$\eta(\text{mV})$ for OER @ 500 mA cm^{-2})	Tafel slope (mV dec ⁻¹)	Ref.
3D NiFe LDH/graphene	Au RDE	1 M KOH	259			-	39	1
NiFe LDH/carbon quantum dots	bare GC	1 M KOH	235			-	35	2
Fe₂O₃@Ni₂P/Ni(PO₃)₂	NF					340		3
3D NiFe-LDH HMS			290				51	4
Au/NiFe LDH	Ti mesh	1M KOH	237				36	5
NiFeSe-LDH	nickel foam	1M KOH	244				32	6
3D-NiFe-LDH	nickel foam	0.1M KOH	256				50	7
NiFe nanoplatelet arrays	nickel foam	1M KOH	224				52.8	8
NiFeZn-LDH	nickel foam	1M KOH		298			63.8	9
NiFeAl-LDH	nickel foam	1M KOH		310			69.6	9
D-NiFeAl-LDH	nickel foam	1M KOH		270			46.1	9
NiFe-LDH array	nickel foam	1 M NaOH	~295				57	10
Ni₃S₂ nanorod@NiFe LDH nanofilms	nickel foil	1M KOH	245				35	11
NiFeMn LDH nanosheets	Ni Foam	1M KOH		289			47	12
Our work NaBH₄-NiFe LDH@NF	Ni Foam	1M KOH	250	270	310	368	47	

Au RDE: Au rotating disk electrode

HMS : hollow microsphere