Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

$Ni_xFe_{1-x}B$ Nanoparticles Self-Modified Nanosheets as Efficient Bifunctional Electrocatalysts for Water Splitting: Experiments and Theories

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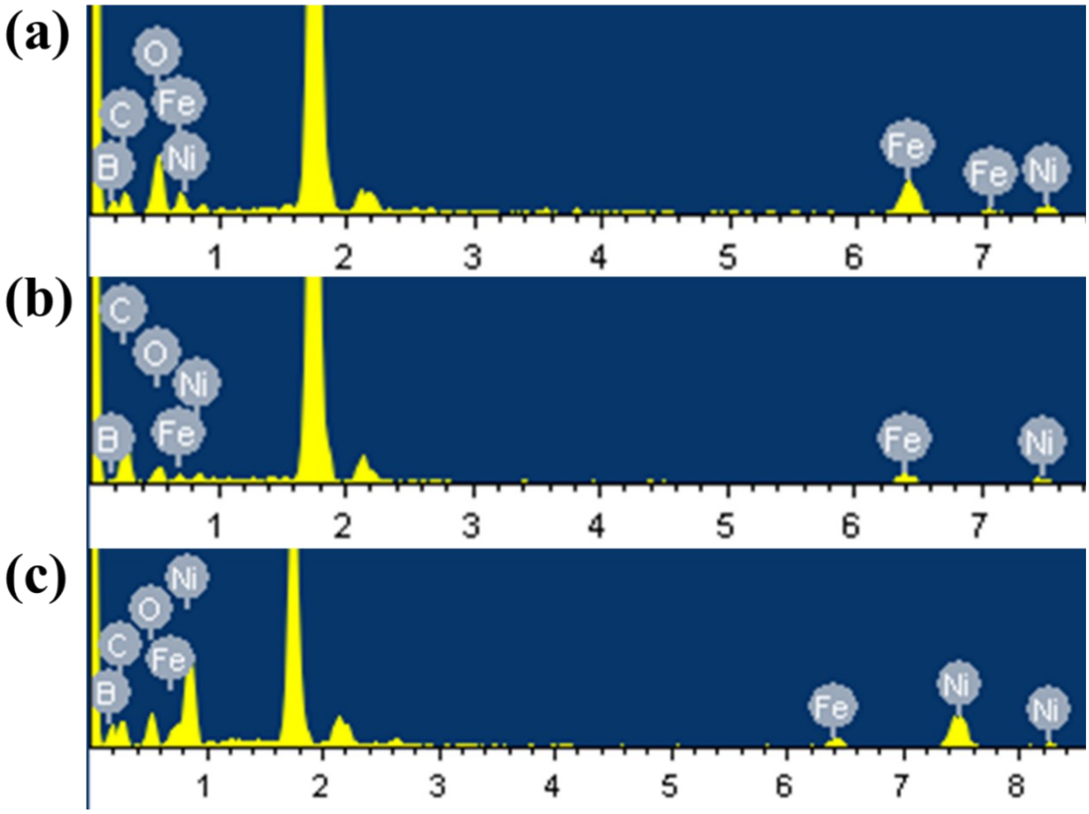

Figure S1. EDS elemental spectra of $Ni_xFe_{1-x}B$-1, $Ni_xFe_{1-x}B$-2 and $Ni_xFe_{1-x}B$-3

Table S1. The content of Fe and Ni according to EDS elemental spectra and ICP-AES analysis.

Samples	Fe (%)		Ni (%)	
	EDS	ICP-AES	EDS	ICP-AES
$Ni_xFe_{1-x}B$-1	73	68	27	32
$Ni_xFe_{1-x}B$-2	57	48	43	52
$Ni_xFe_{1-x}B$-3	13	18	87	82

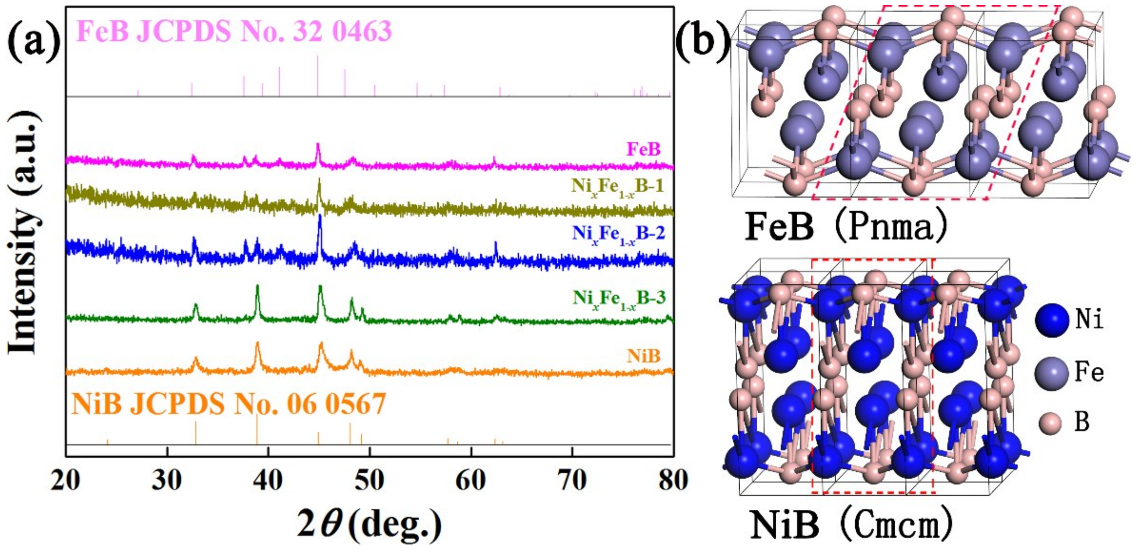

Figure S2. XRD patterns of FeB, Ni$_x$Fe$_{1-x}$B-1, Ni$_x$Fe$_{1-x}$B-2, NixFe$_{1-x}$B-3, NiB and crystal structures of FeB and NiB

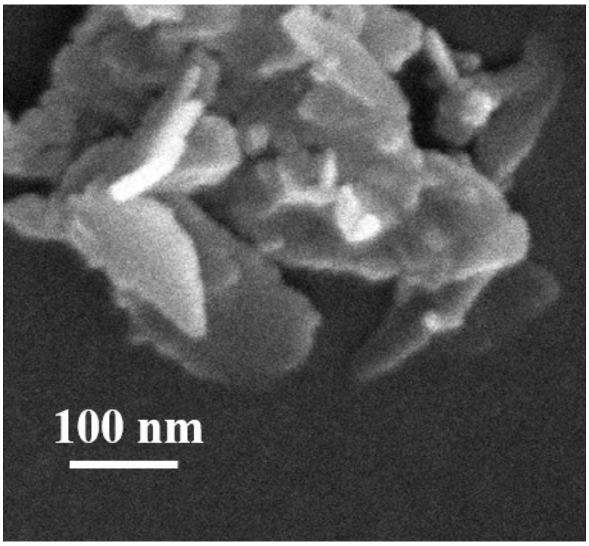

Figure S3. SEM image of $Ni_xFe_{1-x}B$-2

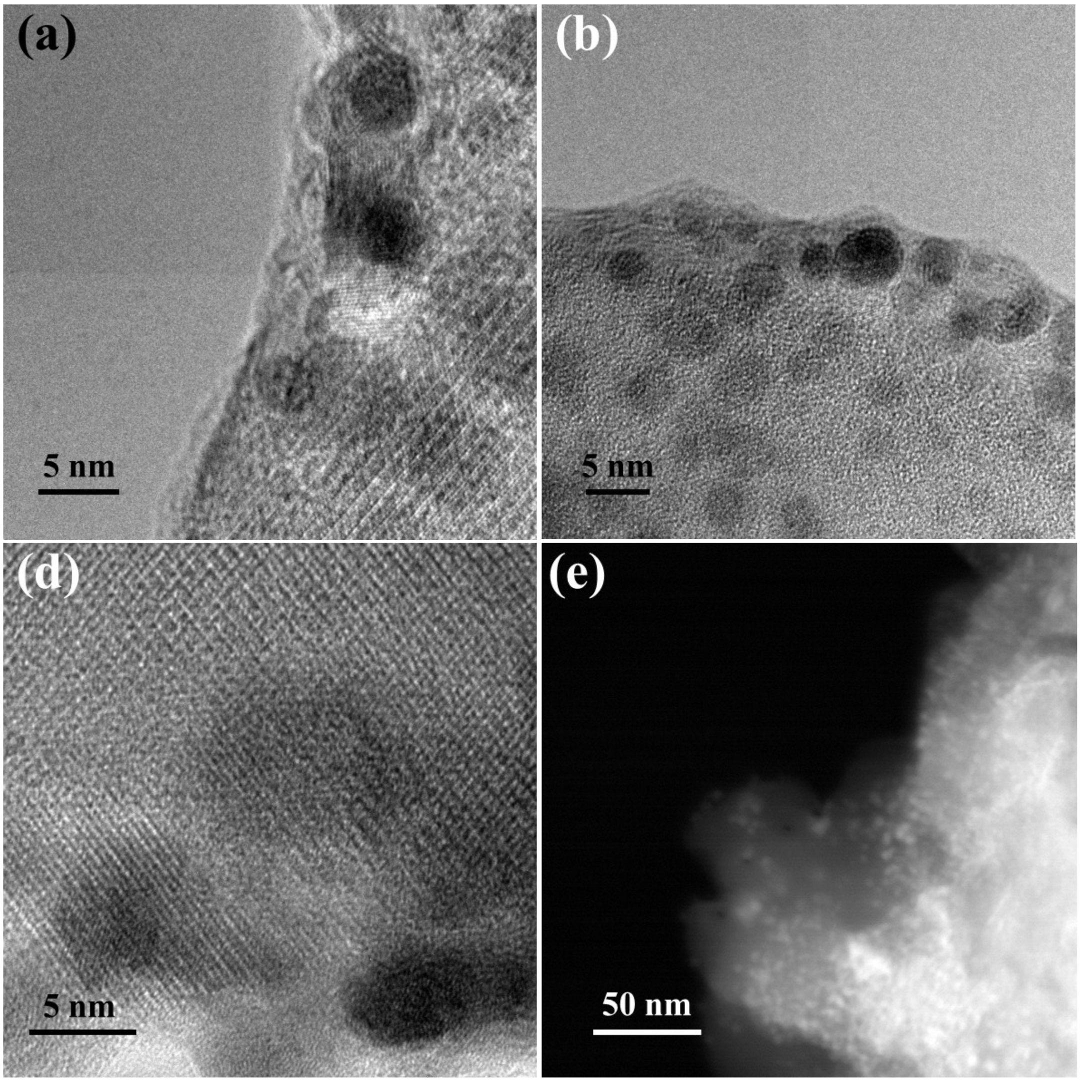

Figure S4. (a-c) TEM images and (e) HAADF image of $Ni_xFe_{1-x}B$-2

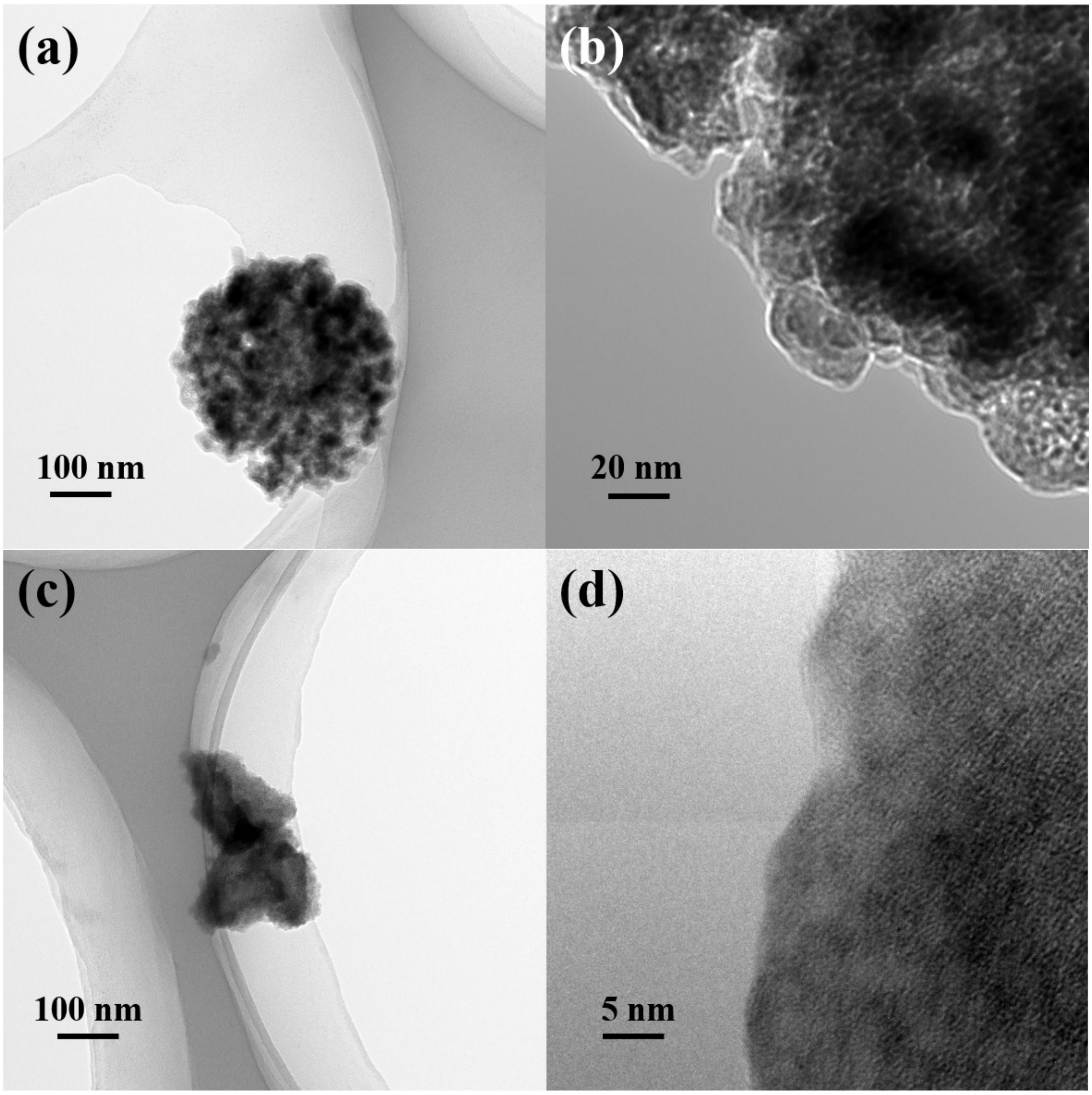

Figure S5. TEM images of (a, b) FeB and (c, d) NiB.

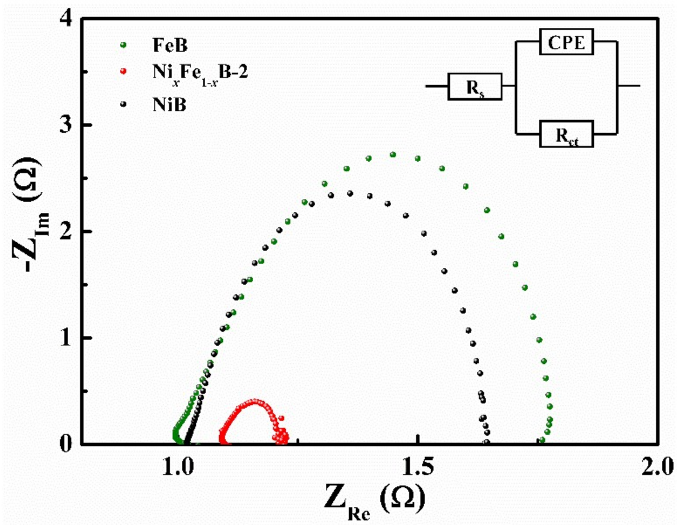

Figure S6. Nyquist plots at -0.065 V vs. RHE

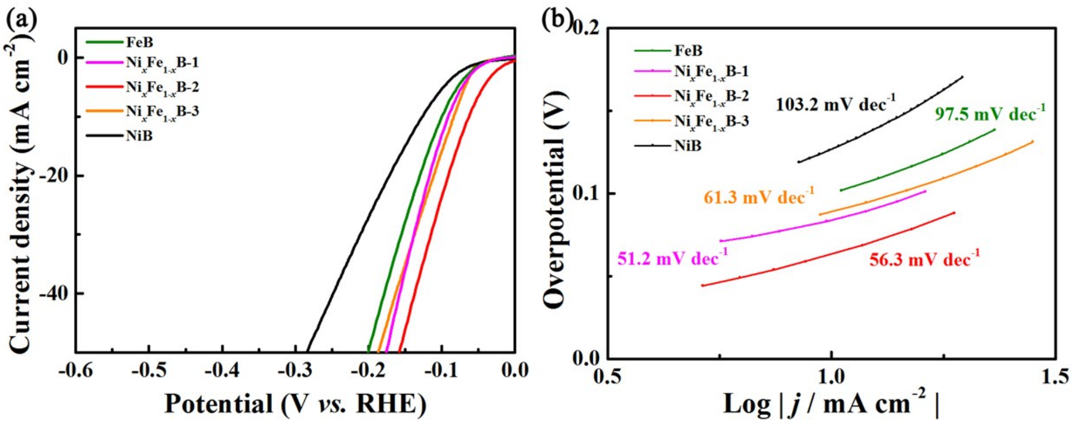

Figure S7. HER performance of FeB, NiB, $Ni_xFe_{1-x}B$ in 1.0 M KOH. (a) Polarization curves, (b) Tafel plots

Table S2. ΔG_{H*} of $Ni_xFe_{1-x}B$ (x=0, 0.25, 0.5, 0.75 and 1) with different sites and structures on (001) facet

Site	**B-top**	**Fe-top**	**Ni-top**	**Bridge**
FeB	-0.248	0.307	N/A	-0.272
$Ni_{0.25}Fe_{0.75}B$	-0.222	0.321	0.544	-0.268
$Ni_{0.5}Fe_{0.5}B$	-0.0270	0.229	0.481	-0.247
$Ni_{0.75}Fe_{0.25}B$ (*Pnma*)	-0.201	0.215	0.461	-0.285
NiB (*Pnma*)	-0.431	N/A	0.590	-0.449
$Ni_{0.75}Fe_{0.25}B$ (*Cmcm*)	-0.486	0.284	0.629	-0.635
NiB (*Cmcm*)	-0.575	N/A	0.598	-0.584

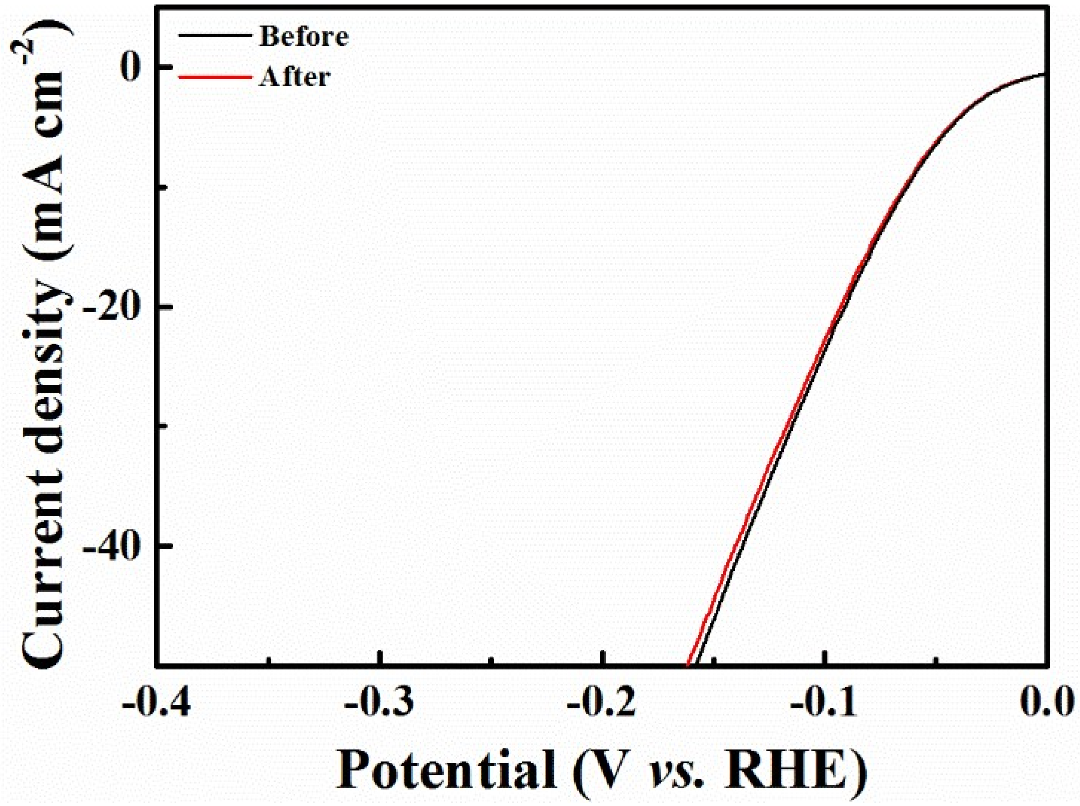

Figure S8. Polarization curve before and after 1000 cycles of a durability test in 1 M KOH

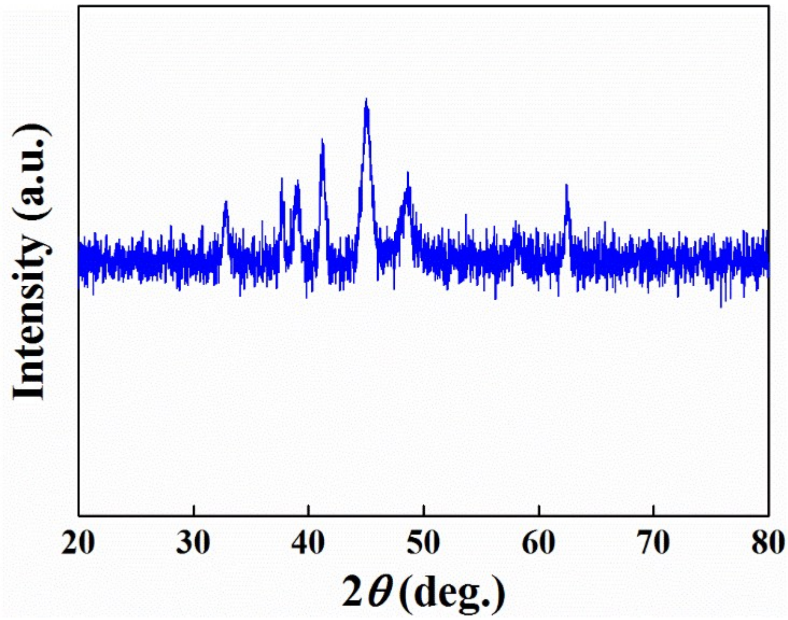

Figure S9. XRD pattern of $Ni_xFe_{1-x}B$-2 after HER.

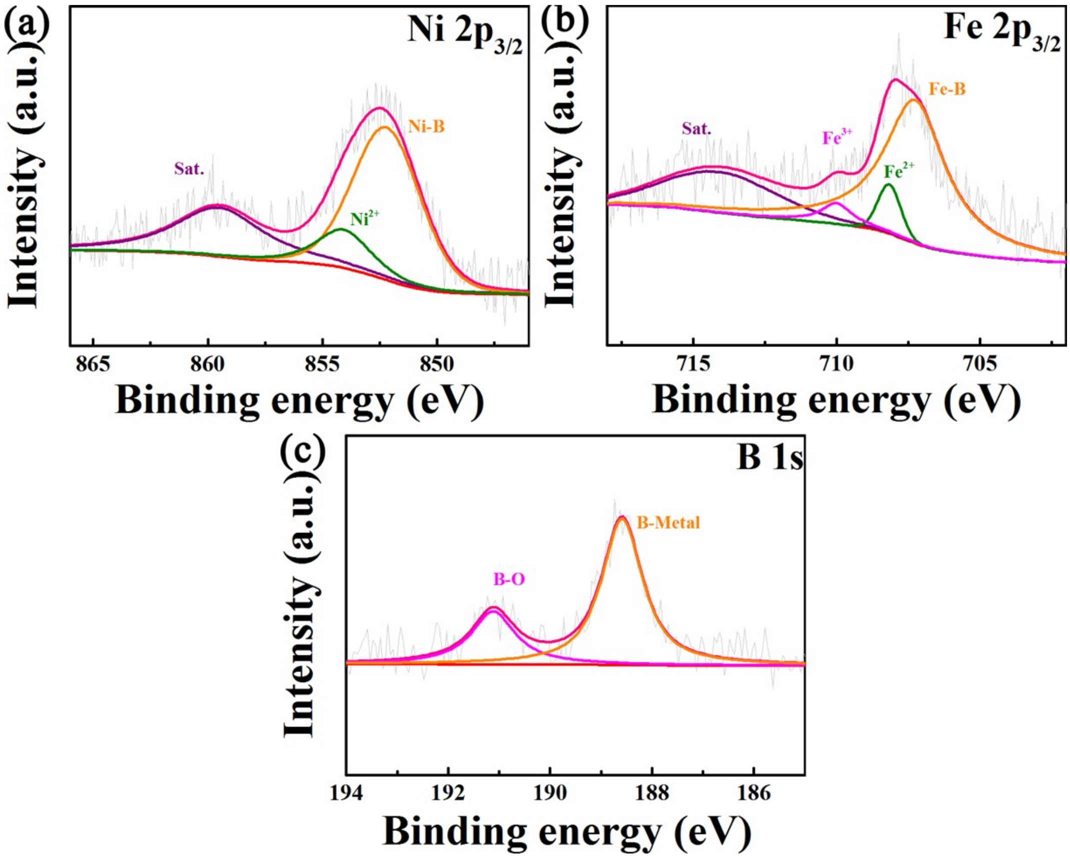

Figure S10. High resolution XPS spectra of (a) Ni $2p_{3/2}$, (b) Fe $2p_{3/2}$, (c) B 1s of $Ni_xFe_{1-x}B$-2 after HER.

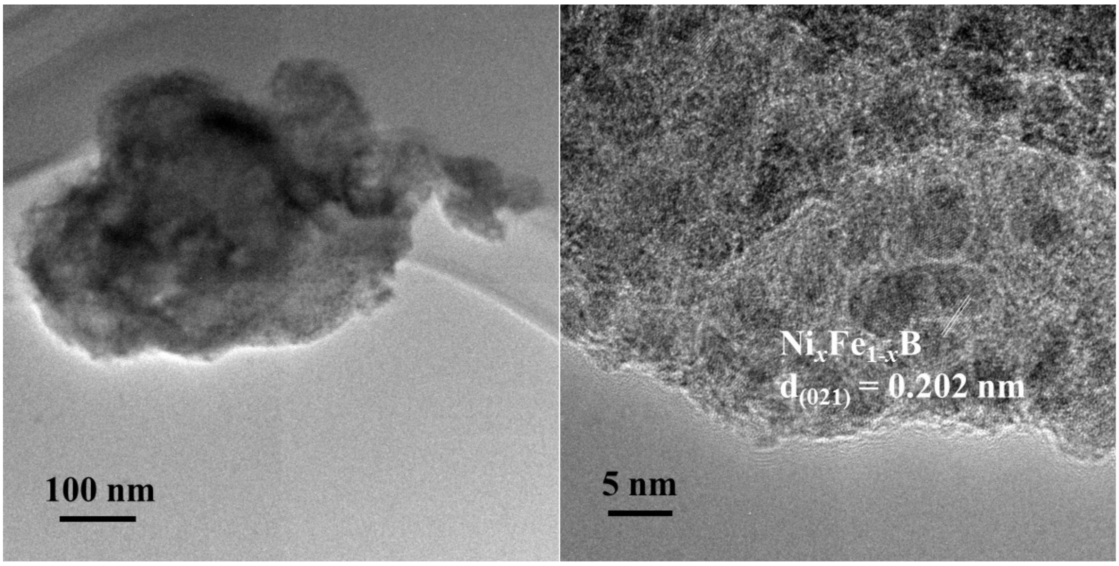

Figure S11. TEM images of $Ni_xFe_{1-x}B$-2 after HER.

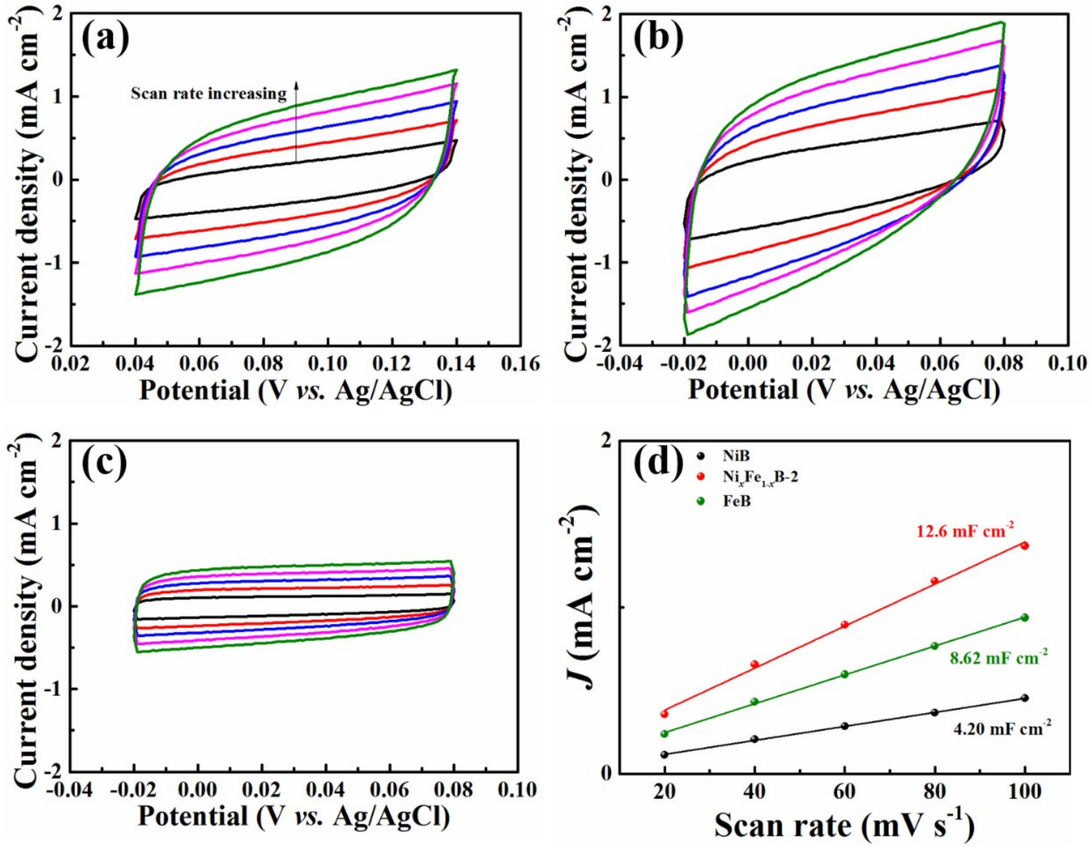

Figure S12. Electrochemical capacitance measurements to determine the surface area of the obtained electrodes in 1 M KOH. The capacitive current density on (a) FeB, (b) $Ni_xFe_{1-x}B$-2, (c) NiB from double layer charging can be measured from cyclic voltammograms with the scan rates of 20, 40, 60, 80, and 100 mV/s in a potential range where no Faradic reaction occur. d) The measured capacitive current plotted as a function of scan rate.

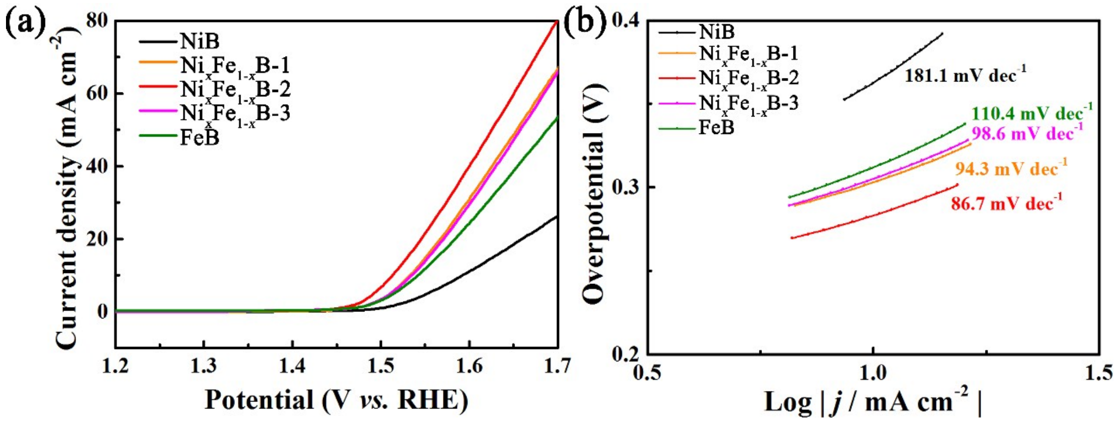

Figure S13. OER performance of FeB, NiB, Ni$_x$Fe$_{1-x}$B in 1.0 M KOH. (a) Polarization curves, (b) Tafel plots

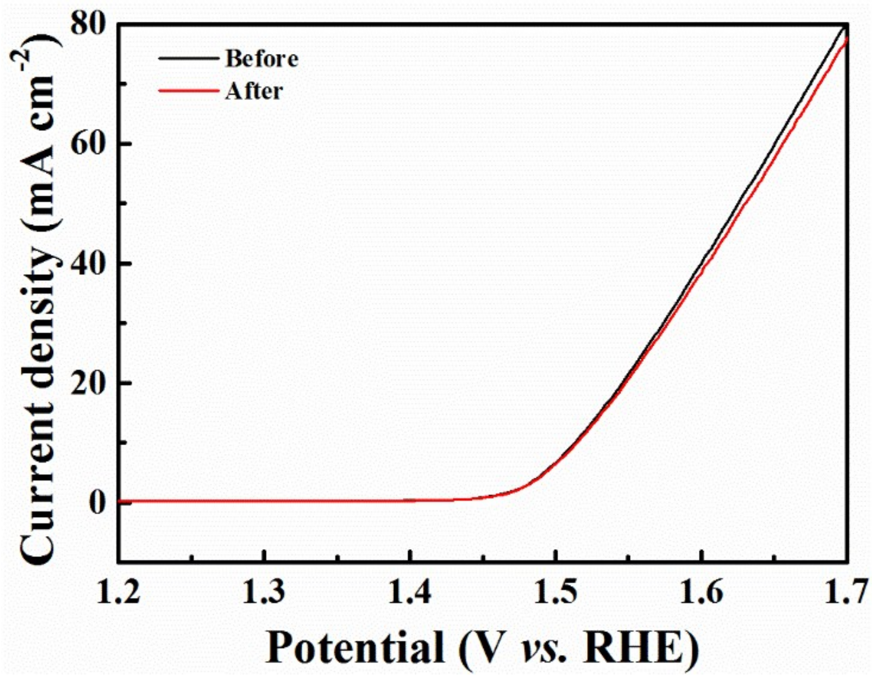

Figure S14. Polarization curve before and after 1000 cycles of a durability test in 1 M KOH

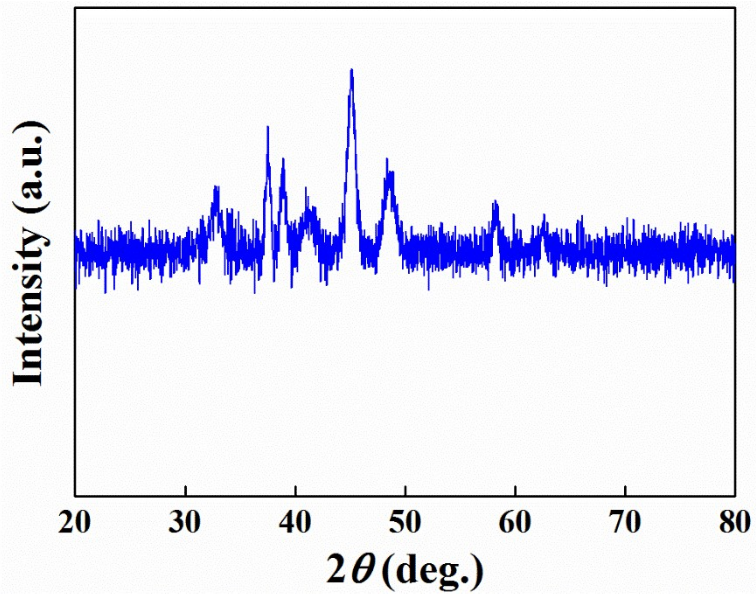

Figure S15. XRD pattern of $Ni_xFe_{1-x}B$-2 after OER.

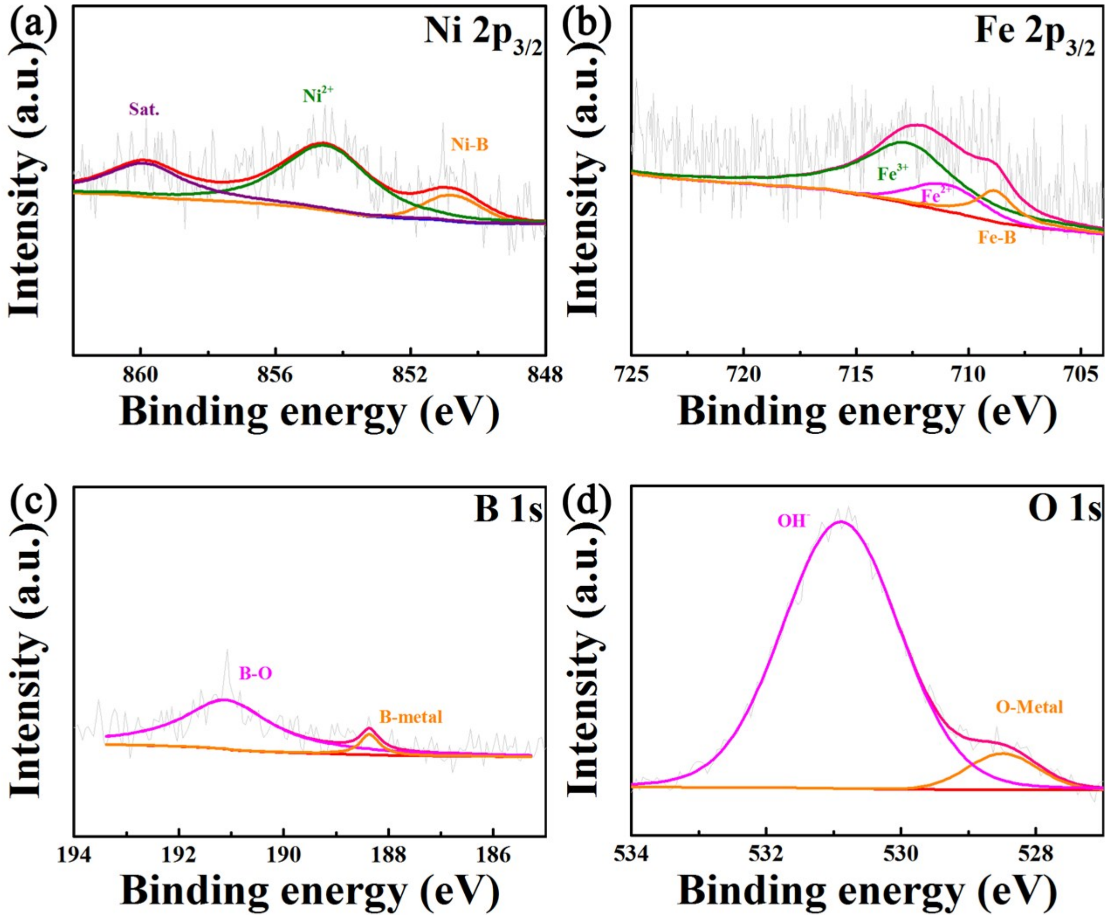

Figure S16. High resolution XPS spectra of (a) Ni $2p_{3/2}$, (b) Fe $2p_{3/2}$, (c) B 1s (d) O 1s of $Ni_xFe_{1-x}B$-2 after OER.

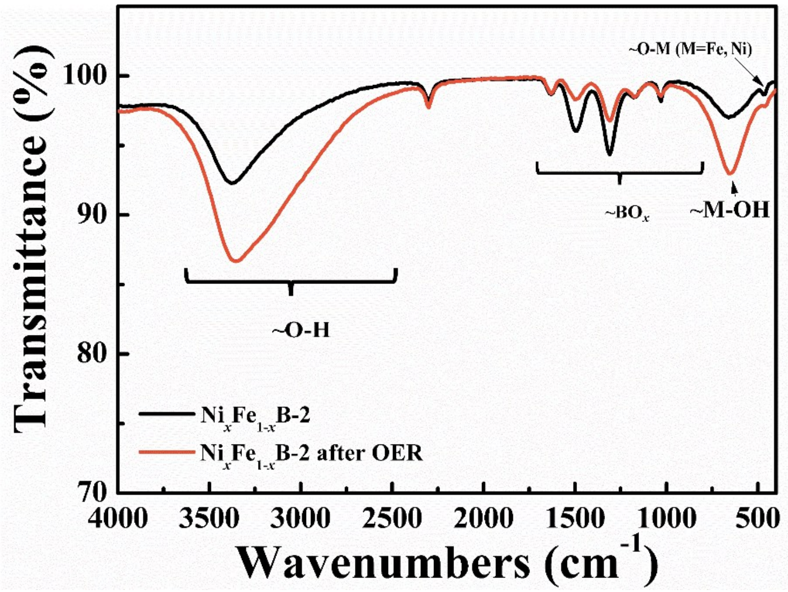

Figure S17. FTIR of Ni$_x$Fe$_{1-x}$B-2 and Ni$_x$Fe$_{1-x}$B-2 after OER.

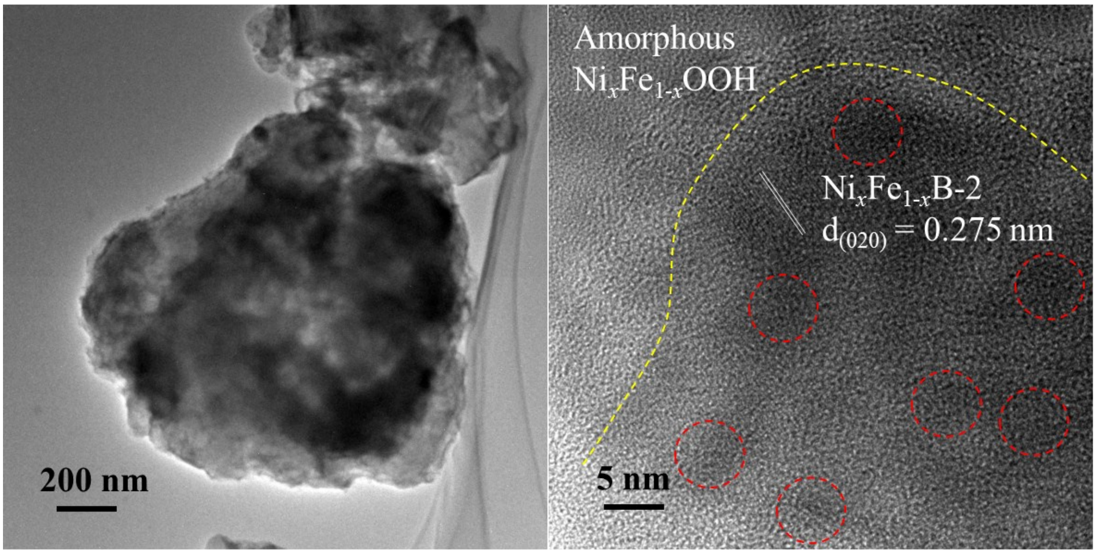

Figure S18. TEM images of $Ni_xFe_{1-x}B$-2 after OER.

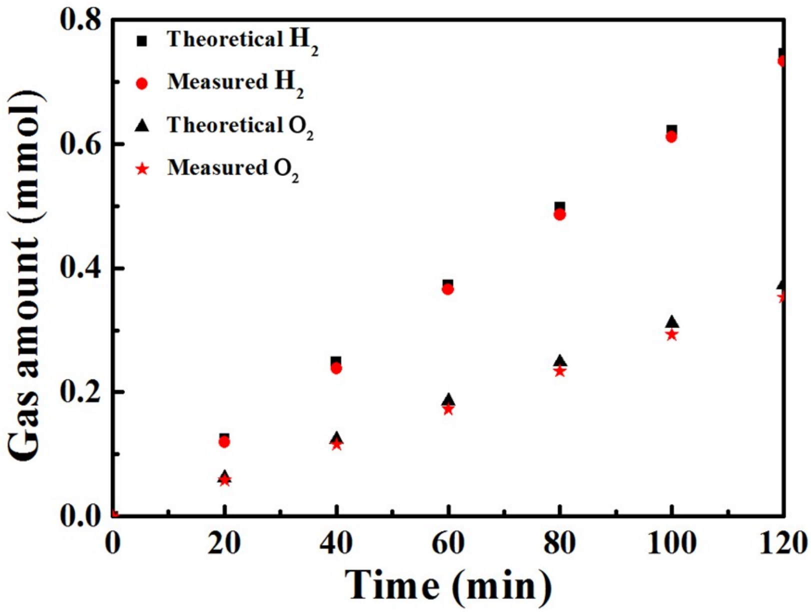

Figure S19. The amount of H_2 theoretically calculated and experimentally measured versus time in 1 M KOH.

Table S3 Comparison of overpotentials for HER at 10 mA cm^{-2} (η_{10}) in alkaline electrolyte (1 M KOH) for $Ni_xFe_{1-x}B$ with other recently published highly active HER electrocatalysts

Catalyst	η_{10} (mV)	Tafel slopes (mV dec^{-1})	Ref.
FeB_2	61	87.5	*Adv. Energy Mater. DOI:10.1002/aenm.201700513*
Ni_3S_2/VS_4 nanohorn arrays	177	139	*Appl. Catal. B: Environ. DOI:10.1016/j.apcatb.2019.117899*
Plasma-doping NiCo LDHs	100	123	*Catal. Today DOI:10.1016/j.cattod.2019.04.017*
$Ni_2P/Ni(PO_3)_2$/N,S-carbon nanosheet	88	65	*Electrochimica Acta DOI: 10.1016/j.electacta.2019.134579*
Co-E_x-MoS_2	89	53	*ACS Nano. 2018, 12, 4565.*
$Ni_{0.51}Co_{0.49}P$ film	82	43	*Adv. Funct. Mater. 2016, 26, 7644*
$Ni_{0.89}Co_{0.11}Se_2$ MNSN/NF	85	52	*Adv. Mater. 2017, 29, 1606521.*
Ni_3S_2-Ni_2P/NF	130	77.6	*Dalton Trans. 2019,48, 13466*
CoP/CN@MoS_2	149	88	*ACS Appl. Mater. Interfaces DOI:10.1021/acsami.9b11859*
CoFeP NFs/NPCNT	132	*62.9*	Nanoscale, 2019,11, 17031
$Ni_xFe_{1-x}B$	63.5	56.3	This work

Table S4 Comparison of overpotentials for OER at 10 mA cm^{-2} (η_{10}) in alkaline electrolyte (1 M KOH) for $Ni_xFe_{1-x}B$ with other recently published highly active HER electrocatalysts

Catalyst	η_{10} (mV)	Tafel slopes (mV dec^{-1})	Ref.
FeB_2	296	52.4	*Adv. Energy Mater. DOI:10.1002/aenm.201700513*
$Ni_2P/Ni(PO_3)_2$/N,S-carbon nanosheet	190	46	*Catal. Today DOI:10.1016/j.cattod.2019.04.017*
Plasma-doping NiCo LDHs	273	96	*Electrochimica Acta DOI: 10.1016/j.electacta.2019.134579*
$Ni_{0.51}Co_{0.49}P$	239	45	*Adv. Funct. Mater. 2016, 26, 7644*
NiCoP/NF	280	87	*Nano Lett. 2016, 16, 7718*
Co_2B-500	380	45	*Adv. Energy Mater. 2016,6,1502313*
Ni_3Se_2-GC	310	79.5	*Energy Environ. Sci. 2016, 9, 1771*
Mo-CoP	305	56	*Nano Energy. 2018, 48, 73*
FeCoP UNSAs	260	63	*Nano Energy. 2017, 41, 583*
CoP/CN@MoS_2	289	69	*ACS Appl. Mater. Interfaces DOI:10.1021/acsami.9b11859*
CoFeP NFs/NPCNT	278	*39.5*	Nanoscale, 2019,11, 17031
$Ni_xFe_{1-x}B$	282	86.7	This work

Table S5 Comparison of overpotentials for electrochemical water splitting at 10 mA cm^{-2} (η_{10}) in alkaline electrolyte (1 M KOH) for $Ni_xFe_{1-x}B$ with other recently published highly active HER electrocatalysts

Catalyst	$E_{j=10}$ (mV)	Ref.
FeB_2	1.57	*Adv. Energy Mater. DOI:10.1002/aenm.201700513*
Ni_3S_2/VS_4 nanohorn arrays	1.57	*Appl. Catal. B: Environ. DOI:10.1016/j.apcatb.2019.117899*
$Ni_2P/Ni(PO_3)_2$/(N/S)-carbon NS	1.63	*Electrochimica Acta DOI: 10.1016/j.electacta.2019.134579*
Co_2B-500-NG	1.66	*ACS Catal.2017,7,469*
$CoSe_2$-CC	1.63	*Adv. Mater.2016,28,7527*
NiCoP-NF	1.58	*Nano Lett. 2016,16,7718*
Ni_3S_2-Ni_2P/NF	1.58	*Dalton Trans. 2019,48, 13466*
CoP/CN@MoS_2	1.61	*ACS Appl. Mater. Interfaces DOI:10.1021/acsami.9b11859*
CoFeP NFs/NPCNT	1.56	*Nanoscale, 2019,11, 17031*
$Ni_xFe_{1-x}B$	1.57	This work