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

Hierarchical Microsphere MOF Arrays with Ultralow Ir Doping for Efficient Hydrogen Evolution Coupled with Hydrazine Oxidation in Seawater

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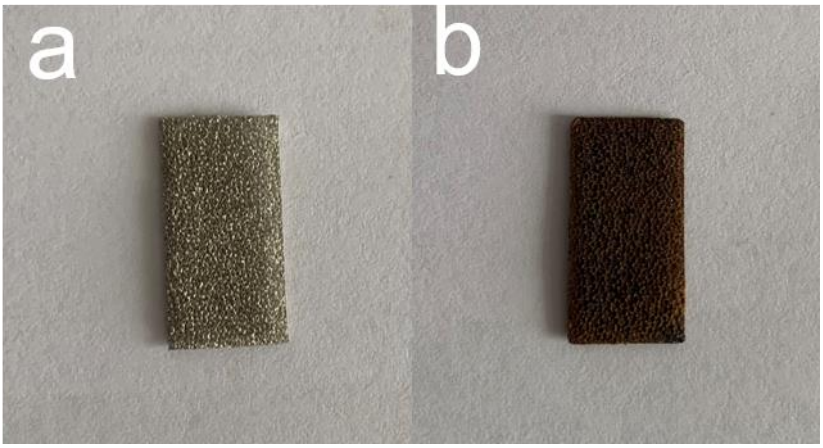


Fig. S1 Photos of (a) NF and (b) MIL-(IrNiFe)@NF.

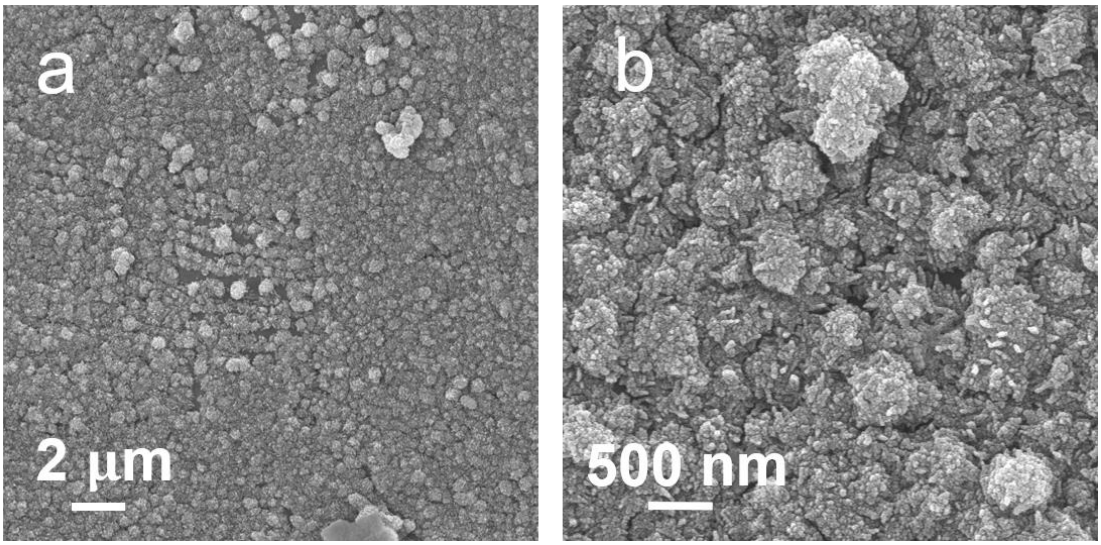


Fig. S2 (a, b) SEM images of MIL-(NiFe)@NF.

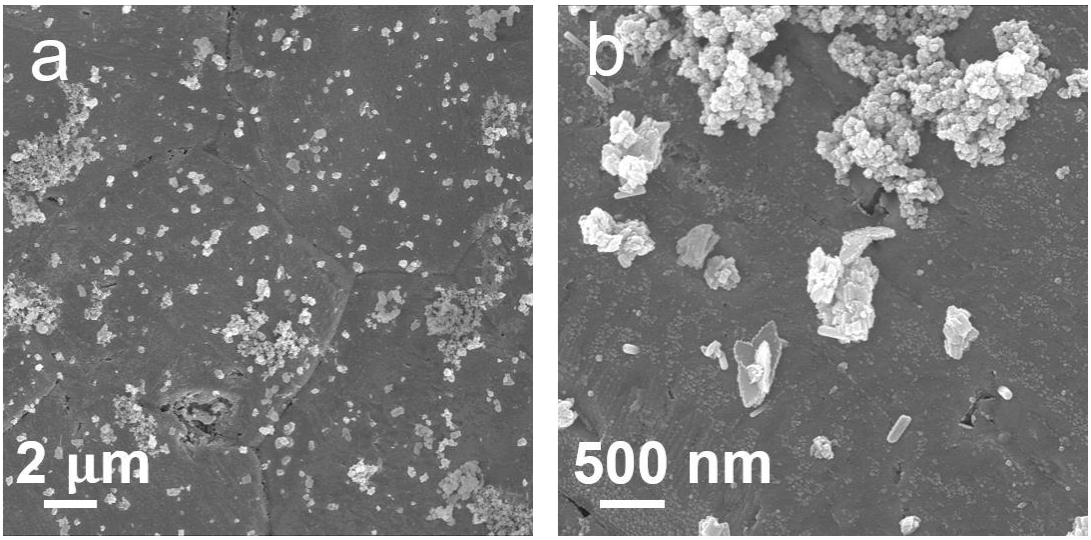


Fig. S3 (a, b) SEM images of MIL-(Fe)@NF.

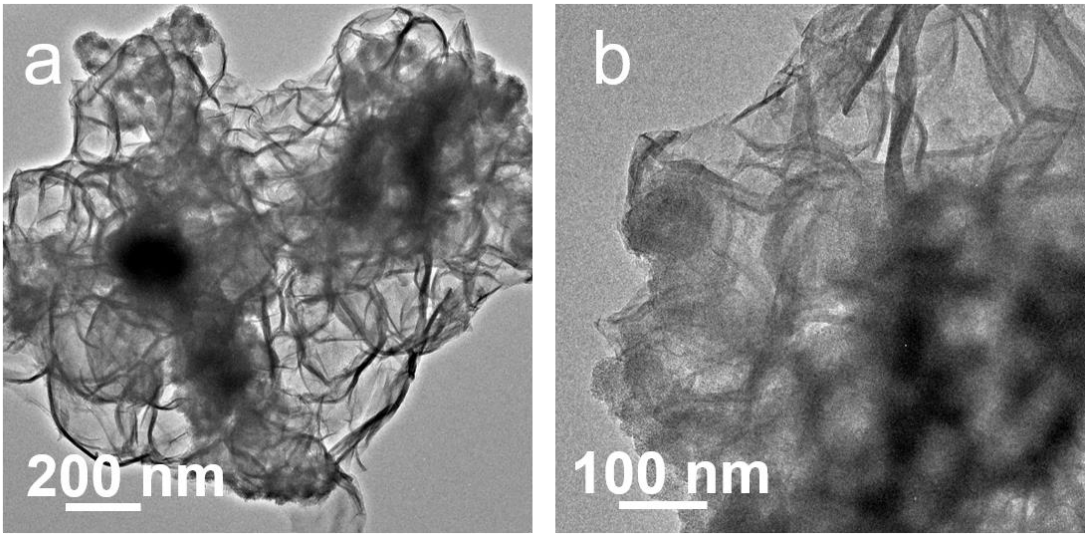


Fig. S4 (a, b) TEM image of MIL-(NiFe)@NF.

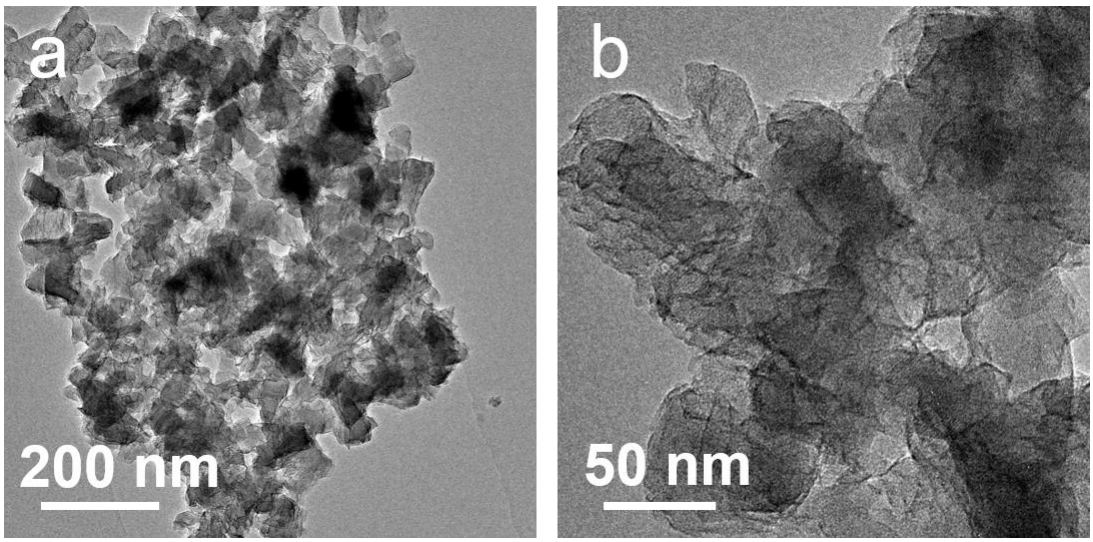
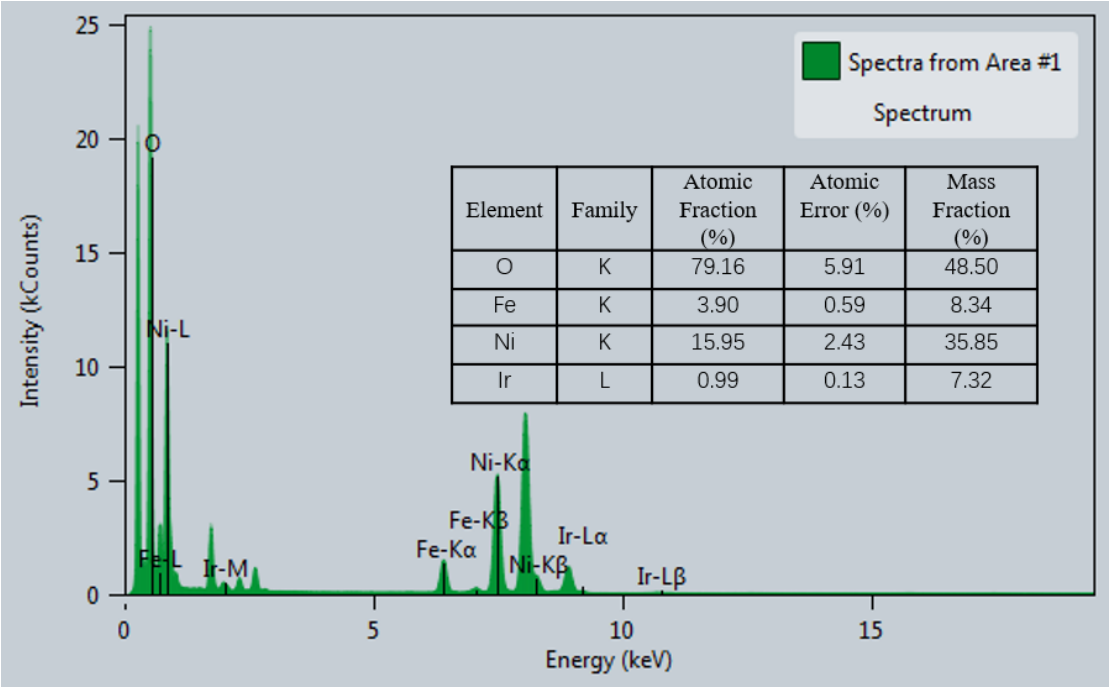


Fig. S5 (a, b) TEM images of MIL-(Fe)@NF.



Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)
O	K	79.16	5.91	48.50
Fe	K	3.90	0.59	8.34
Ni	K	15.95	2.43	35.85
Ir	L	0.99	0.13	7.32

Fig. S6 EDX of MIL-(IrNiFe)@NF catalyst.

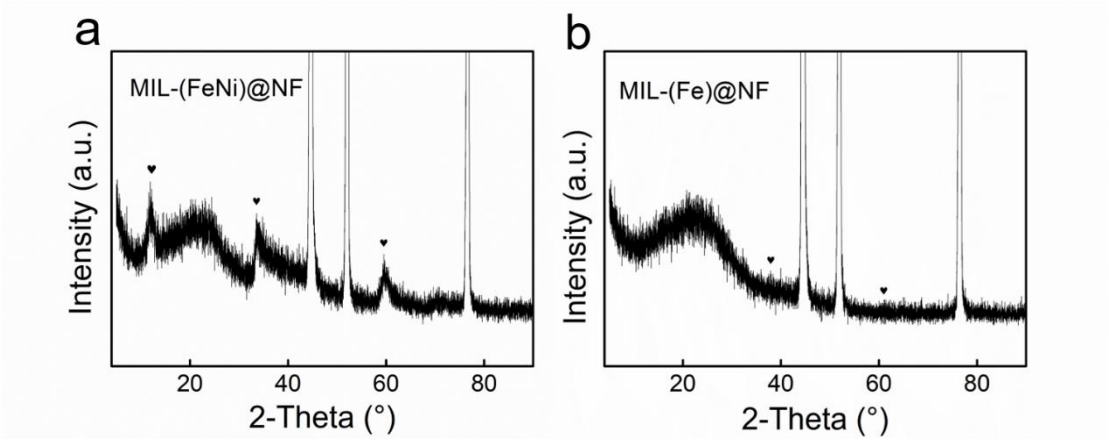


Fig. S7 XRD patterns of (a)MIL-(NiFe)@NF and (b) MIL-(Fe)@NF.

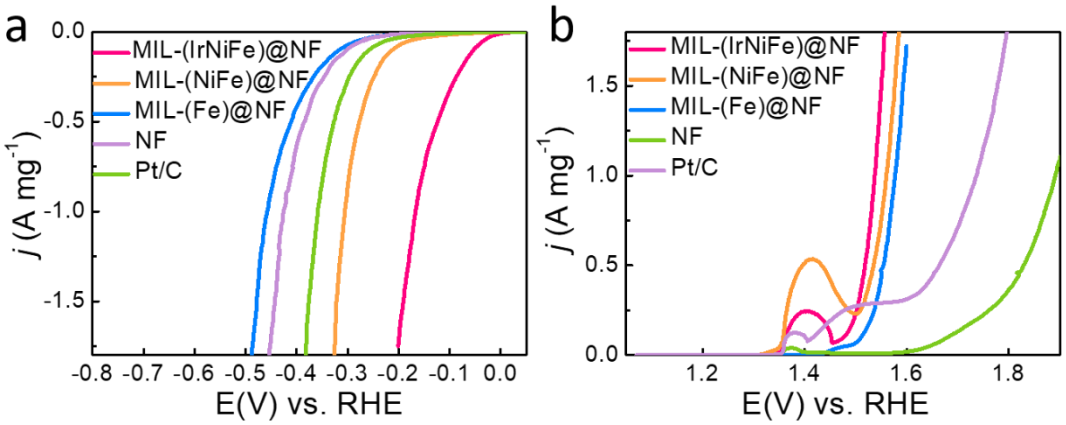


Fig. S8 Mass specific activity of (a) HER and (b) OER.

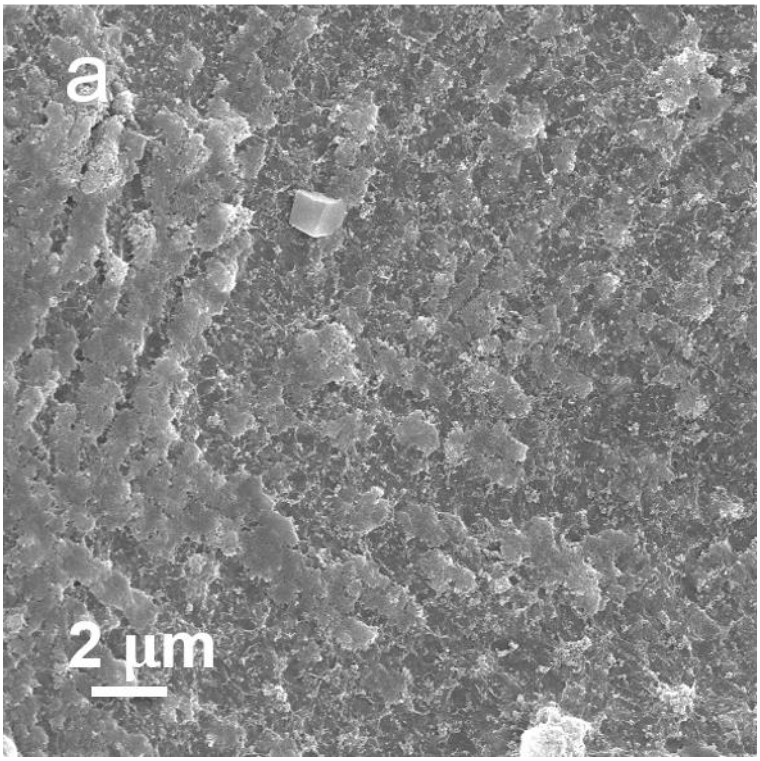


Fig. S9 SEM image of MIL-(IrNiFe)@NF after stability test for OER.

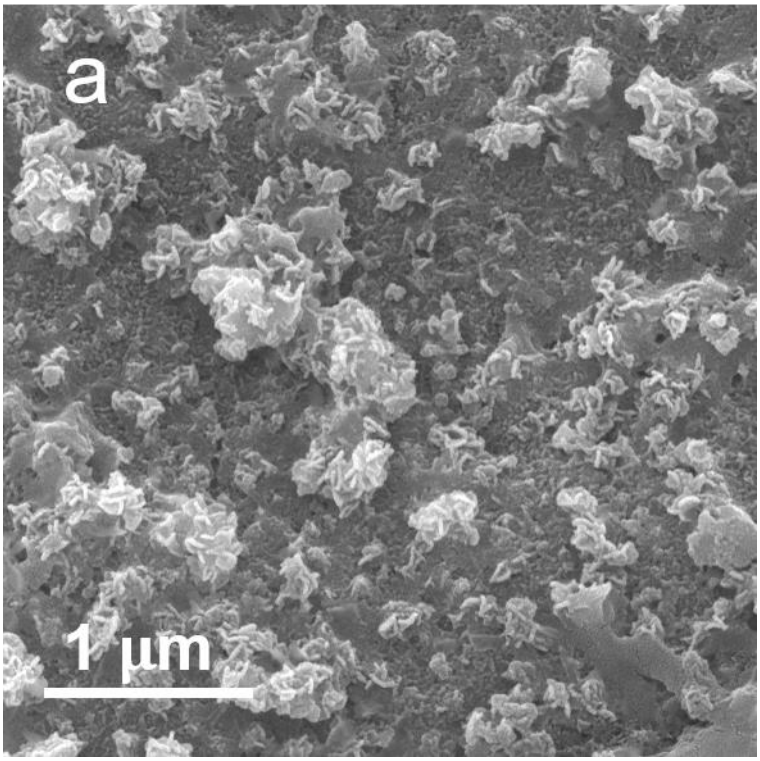


Fig. S10 SEM image of MIL-(IrNiFe)@NF after stability test for HER.

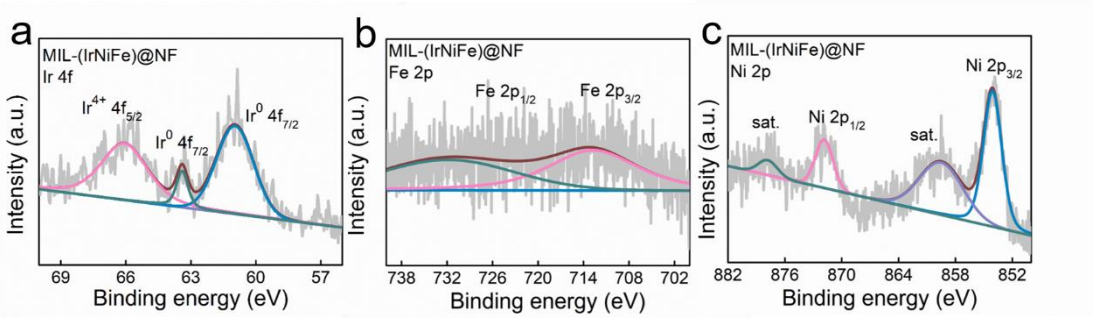


Fig. S11 (a) Ir 4f spectra, (b) Fe 2p spectra, and (c) Ni 2p spectra of MIL-(IrNiFe)@NF after stability test for HER.

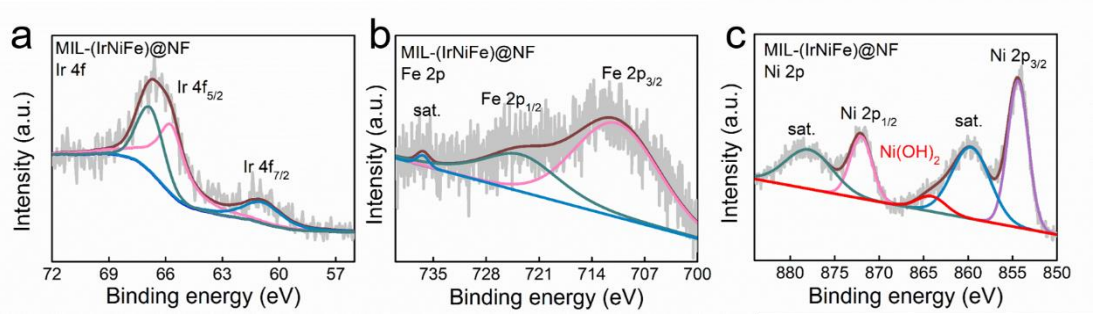


Fig. S12 (a) Ir 4f spectra, (b) Fe 2p spectra, and (c) Ni 2p spectra of MIL-(IrNiFe)@NF after stability test for HzOR.

Table S1. Comparison of HER activity between MIL-(IrNiFe)@NF and recently reported MOF-based electrocatalysts in a wide pH range.

Electrocatalysts	*j* (mA cm^{-2})	*η* (mV)	Electrolyte solution	Refs.
MIL-(IrNiFe)@NF	10	12	1.0 M KOH	This work
MIL-53(Ru-NiFe)@NF	10	27	1.0 M KOH	1
NiFe-MOF/NF	10	134	1.0 M KOH	2
NFN-MOF/NF	10	87	1.0 M KOH	3
MNF-MOFs/NF	10	79	1.0 M KOH	4
NiFe/$NiCo_2O_4$/NF	10	270	1.0 M KOH	5
S-$NiFe_2O_4$/NF	10	138	1.0 M KOH	6
Ni_3FeN/r-GO-NF	10	94	1.0 M KOH	7
Ni-Co-P HNBs on NF	10	107	1.0 M KOH	8
FeMnP/GNF	10	84	1.0 M KOH	9
CoFePO@NF	10	87.5	1.0 M KOH	10
MoS_2-Ni_3S_2 HNRs/ NF	10	98	1.0 M KOH	11
$FeSe_2$/NF	10	178	1.0 M KOH	12
FeB_2-NF	10	69	1.0 M KOH	13

Table S2. Comparison of OER activity between MIL-(IrNiFe)@NF and recently reported MOF-based electrocatalysts in a wide pH range.

Electrocatalysts	*j* (mA cm^{-2})	*η* (mV)	Electrolyte solution	Refs.
MIL-(IrNiFe)@NF	50	230	1.0 M KOH	This work
MIL-53(Ru-NiFe)@NF	50	210	1.0 M KOH	1
NiFe-MOF/NF	10	240	1.0 M KOH	2
NFN-MOF/NF	10	240	1.0 M KOH	3
MNF-MOFs/NF	50	235	1.0 M KOH	4
NiFe/$NiCo_2O_4$/NF	60	270	1.0 M KOH	5
S-$NiFe_2O_4$/NF	10	267	1.0 M KOH	6
Ni_3FeN/r-GO-NF	10	270	1.0 M KOH	7
Ni-Co-P HNBs on NF	10	270	1.0 M KOH	8
FeMnP/GNF	10	280	1.0 M KOH	9
CoFePO@NF	10	274.5	1.0 M KOH	10
MoS_2-Ni_3S_2 HNRs/ NF	10	249	1.0 M KOH	11
$FeSe_2$/NF	10	245	1.0 M KOH	12
FeB_2-NF	10	296	1.0 M KOH	13

Table S3. Comparison of overall water splitting solution performance of MIL-(IrFeNi)@NF and other recently reported electrocatalysts in alkaline seawater. E_{10} and E_{100} are the working voltage at 10 mA cm^{-2} and 100 mA cm^{-2} in the two-electrode system.

Electrocatalysts	E_{10} (V)	E_{100} (V)	Electrolyte solution	Refs.
MIL-(IrFeNi)@NF	1.4	1.67	1.0 M KOH +Seawater+ 0.5 M N_2H_4	This work
Ni_2P-Fe_2P/NF	1.56	1.68	1.0 M KOH	14
S-(Ni,Fe)OOH		1.66	1.0 M KOH + Seawater	15
Co–Se1//Co–Se4	1.8		1.0 M KOH + Seawater	16
Ni_3FeN@C/NF//Ni_3N@C/NF		1.69	1.0 M KOH	17

Table S4. Comparison of overall water splitting coupled with HzOR of MIL-(IrFeNi)@NF and other recently reported electrocatalysts. E_{10}, E_{100}, and E_{500} are the working potential at 10, 100, and 500 mA cm^{-2} in the two-electrode system.

Electrocatalysts	E_{10} (V)	E_{100} (V)	E_{500} (V)	Electrolyte solution	Refs.
MIL-(IrFeNi)@NF	0.03	0.15	0.39	1.0 M KOH +Seawater+ 0.5 M N_2H_4	This work
Mo-Ni_3N/Ni/NF	0.05	0.26		1.0 M KOH + 0.1 M N_2H_4	18
PW-Co3N NWA/NF	0.028			1.0 M KOH + 0.1 M N_2H_4	19
Fe_2O_3/ECP-15‖FeP/ ECP-15	0.93			1.0 M KOH + 0.1 M N_2H_4	20
Ni_2P/NF			1.00	1.0 M KOH + 0.1 M N_2H_4	21

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