

## Supporting information

### **Engineering Hierarchical MCo<sub>2</sub>O<sub>4</sub>/NF Nanowire Networks via Cation Substitution for High-Performance Oxygen Evolution Reaction**

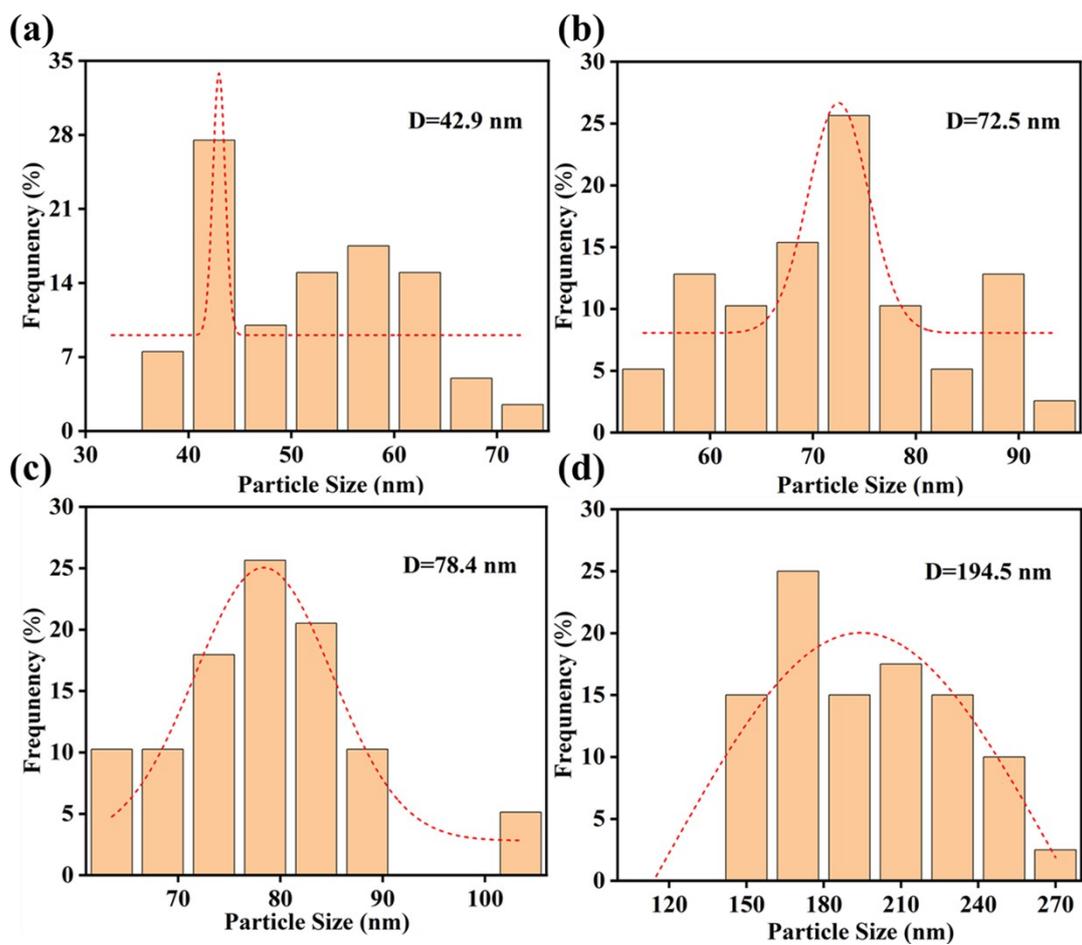
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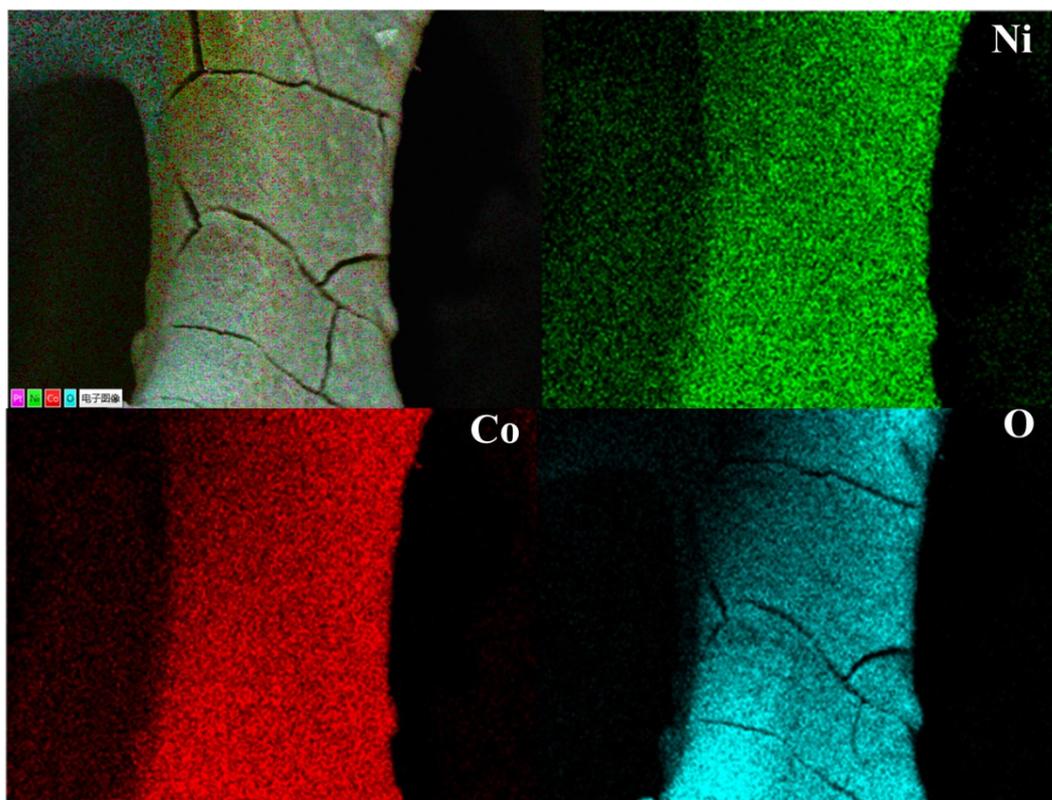
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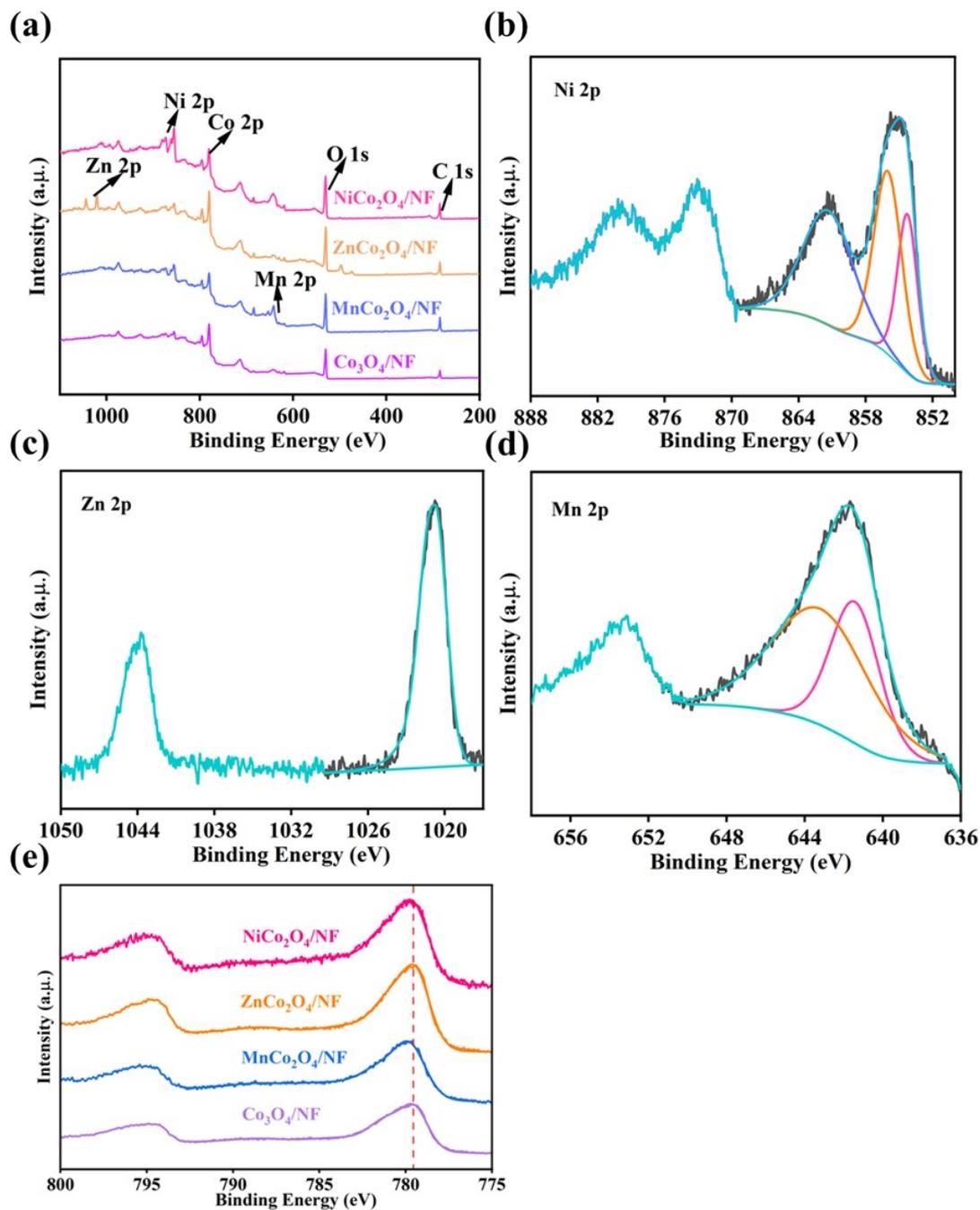
E-mail addresses: sanxiaoguang@syuct.edu.cn (X. San), mengdan@syuct.edu.cn (D. Meng), taokai@ebu.edu.cn (K. Tao).



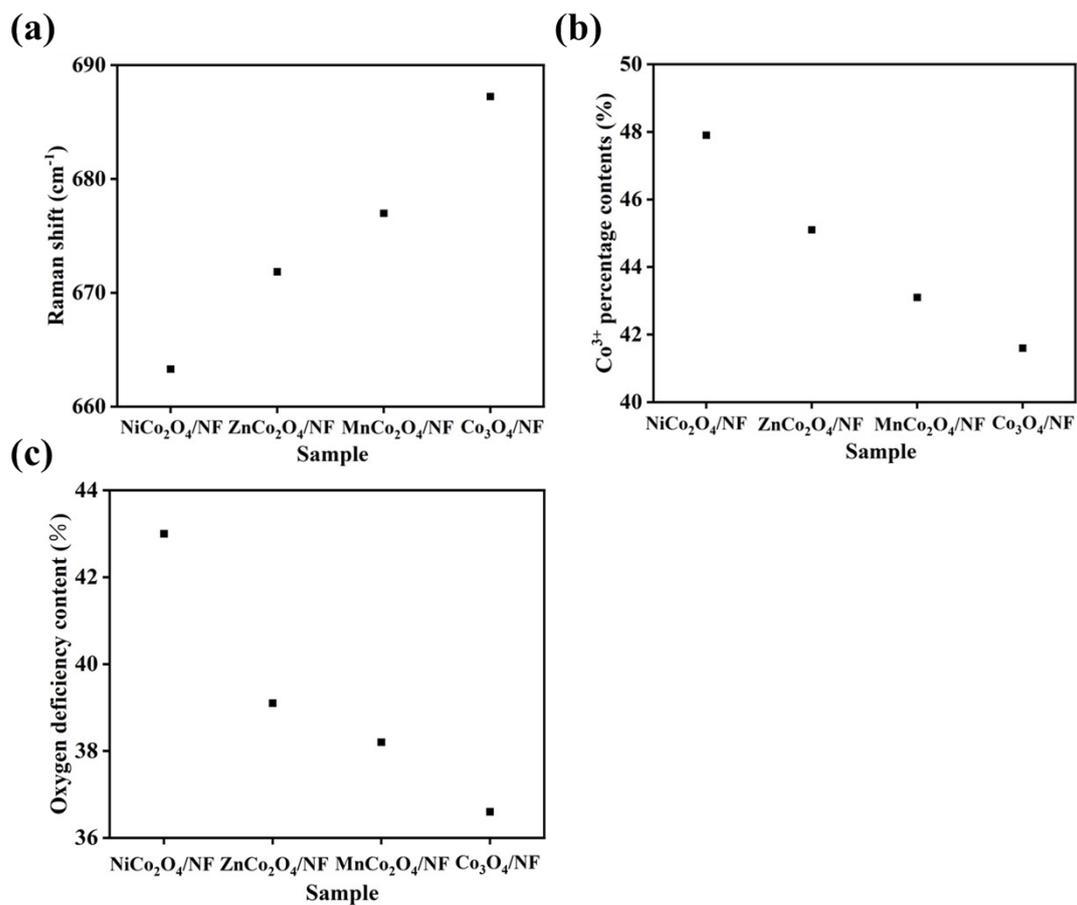
**Fig. S1** Statistical analysis of the diameter distribution of MCo<sub>2</sub>O<sub>4</sub>/NF: (a) NiCo<sub>2</sub>O<sub>4</sub>/NF, (b) ZnCo<sub>2</sub>O<sub>4</sub>/NF, (c) MnCo<sub>2</sub>O<sub>4</sub>/NF and (d) Co<sub>3</sub>O<sub>4</sub>/NF.



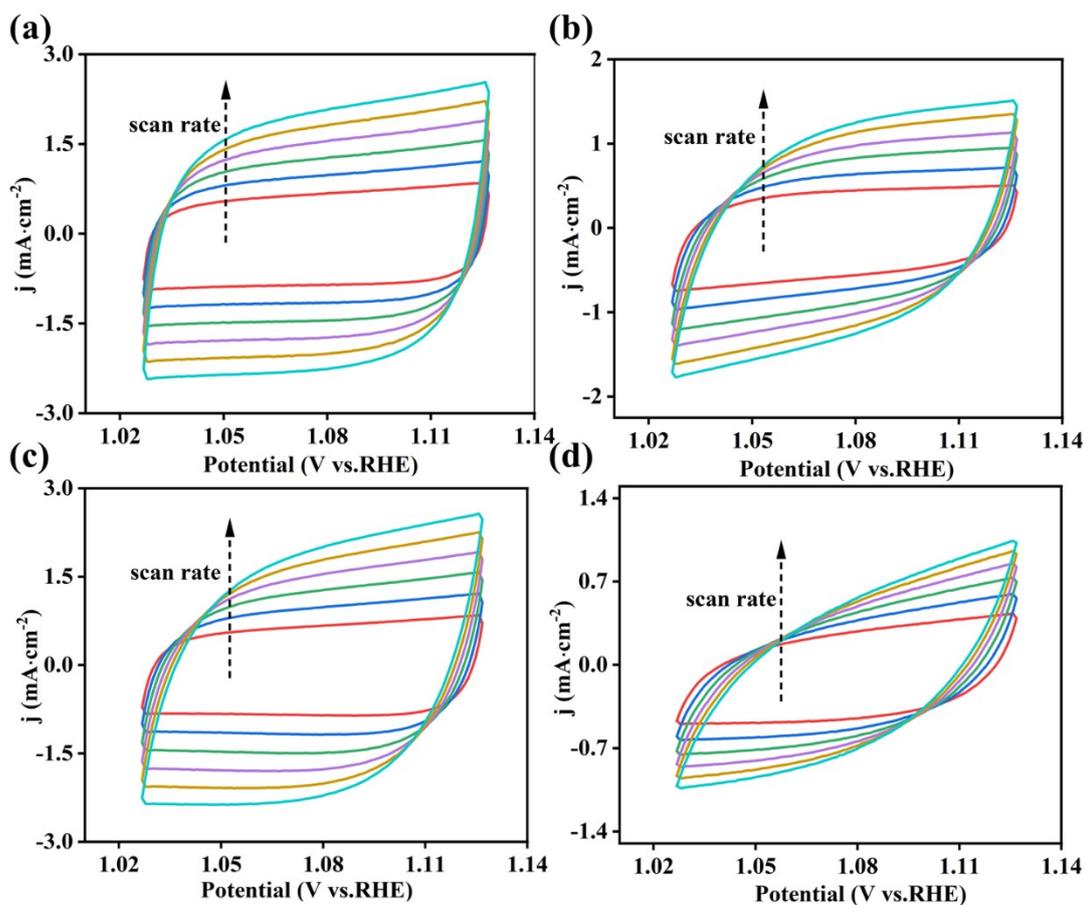
**Fig. S2.** Energy dispersive X-ray spectroscopy (EDS) elemental mapping of NiCo<sub>2</sub>O<sub>4</sub>/NF



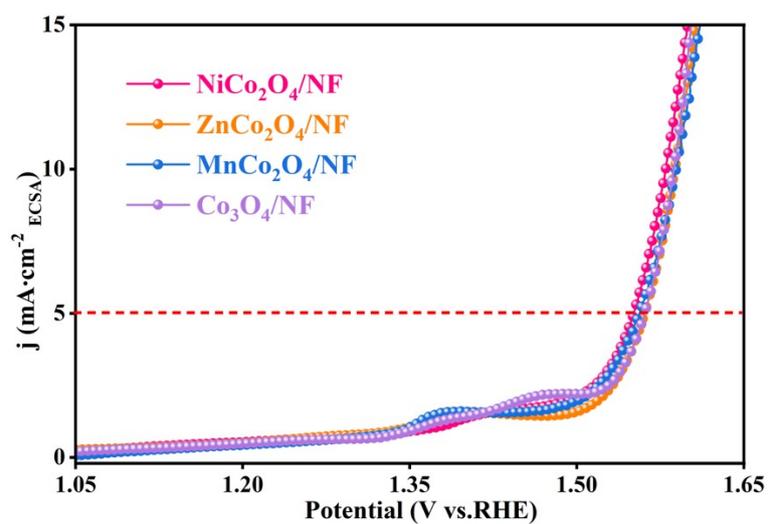
**Fig. S3** (a) The overall XPS spectra; (b) Ni 2p spectra of NiCo<sub>2</sub>O<sub>4</sub>/NF; (c) Zn 2p spectra of ZnCo<sub>2</sub>O<sub>4</sub>/NF; (d) Mn 2p spectra of MnCo<sub>2</sub>O<sub>4</sub>/NF, (e) Co 2p spectra of MnCo<sub>2</sub>O<sub>4</sub>/NF.



**Fig. S4** (a) Raman shift, (b) Co<sup>3+</sup> percentage content and (c) oxygen defect content of MCo<sub>2</sub>O<sub>4</sub>/NF.



**Fig. S5** Cyclic voltammograms of (a) NiCo<sub>2</sub>O<sub>4</sub>/NF, (b) ZnCo<sub>2</sub>O<sub>4</sub>/NF, (c) MnCo<sub>2</sub>O<sub>4</sub>/NF and (d) Co<sub>3</sub>O<sub>4</sub>/NF.



**Fig. S6** The ECSA-normalized LSV curves of NiCo<sub>2</sub>O<sub>4</sub>/NF, ZnCo<sub>2</sub>O<sub>4</sub>/NF, MnCo<sub>2</sub>O<sub>4</sub>/NF and Co<sub>3</sub>O<sub>4</sub>/NF.

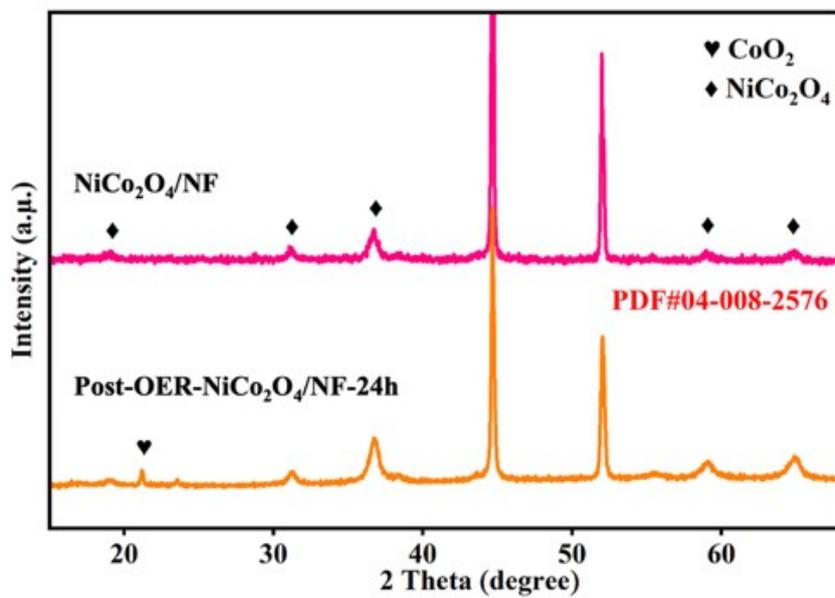


Fig. S7 XRD patterns of  $\text{NiCo}_2\text{O}_4/\text{NF}$ , and  $\text{post-OER-NiCo}_2\text{O}_4/\text{NF-24h}$

**Table S1** The average particle size of (111), (220), (311), (511), (440) crystal planes of  $M\text{Co}_2\text{O}_4/\text{NF}$  and the interplanar spacing of the highest diffraction peak (311) crystal plane.

Composition	Interplanar distance (nm)	Grain size (nm)
$\text{NiCo}_2\text{O}_4/\text{NF}$	0.2446	13.8
$\text{ZnCo}_2\text{O}_4/\text{NF}$	0.2449	10.7
$\text{MnCo}_2\text{O}_4/\text{NF}$	0.2447	17.1
$\text{Co}_3\text{O}_4/\text{NF}$	0.2434	25.6

**Table S2** The Co2p content of MCo<sub>2</sub>O<sub>4</sub>/NF samples was calculated by XPS.

<b>Composition (%)</b>	<b>Co<sup>3+</sup></b>	<b>Co<sup>2+</sup></b>	<b>Sat.(Co<sup>3+</sup>)</b>	<b>Sat.(Co<sup>2+</sup>)</b>	<b>Co<sup>3+</sup>/Co<sup>2+</sup></b>
NiCo <sub>2</sub> O <sub>4</sub> /NF	47.9	26.4	16.8	8.9	1.83
ZnCo <sub>2</sub> O <sub>4</sub> /NF	45.1	33.0	13.1	8.8	1.39
MnCo <sub>2</sub> O <sub>4</sub> /NF	43.1	35.4	12.2	9.3	1.24
Co <sub>3</sub> O <sub>4</sub> /NF	41.6	36.1	13.2	9.1	1.21

**Table S3.** Fitting parameters of the O1s XPS spectra of Co<sub>3</sub>O<sub>4</sub>/NF and MCo<sub>2</sub>O<sub>4</sub>/NF.

Sample		O <sub>L</sub>	O <sub>V</sub>	O <sub>H<sub>2</sub>O</sub>
NiCo <sub>2</sub> O <sub>4</sub> /NF	Position(eV)	529.4	531.3	533.0
	FWHM(eV)	1.30	1.77	1.77
	Aera%	45.2	43.0	11.8
ZnCo <sub>2</sub> O <sub>4</sub> /NF	Position(eV)	529.3	531.2	532.8
	FWHM(eV)	1.26	1.79	1.79
	Aera%	52.6	39.1	8.3
MnCo <sub>2</sub> O <sub>4</sub> /NF	Position(eV)	529.6	531.2	532.8
	FWHM(eV)	1.21	1.65	1.65
	Aera%	52.7	38.2	9.1
Co <sub>3</sub> O <sub>4</sub> /NF	Position(eV)	529.5	531.2	532.8
	FWHM(eV)	1.15	1.62	1.62
	Aera%	55.3	36.6	8.1

**Tabel S4** Comparison of the OER performance of NiCo<sub>2</sub>O<sub>4</sub>/NF with other recently reported Co-based electrocatalysts in 1.0 M KOH electrolyte

Catalysts	Electrolyte	$\eta_{10}$ (mV)	Ref.	References
NiCo <sub>2</sub> O <sub>4</sub> /NF	1M KOH	277	This work	[1] Cheng
P-NiCo <sub>2</sub> O <sub>4</sub> /NF	1M KOH	279	[1]	L, Zhang R,
P-NiCo <sub>2</sub> O <sub>4</sub> -V	1M KOH	280	[2]	Lv W, et al.
Fe-NiCo <sub>2</sub> O <sub>4</sub> /NiO@P-rGO	1M KOH	293	[3]	Surface
Ni <sub>1.25</sub> Ru <sub>0.75</sub> P	1M KOH	340	[4]	phosphatio
NP-NiCo <sub>2</sub> O <sub>4</sub>	1M KOH	360	[5]	n of 3D
NiCo <sub>2</sub> O <sub>4</sub> /MXene	1M KOH	360	[6]	NiCo <sub>2</sub> O <sub>4</sub>
NiCo <sub>2</sub> O <sub>4</sub> @MoS <sub>2</sub>	1M KOH	313	[7]	nanowires
NiCoO/NiCo@C	1M KOH	329	[8]	grown on
NiO/Co <sub>3</sub> O <sub>4</sub>	1M KOH	330	[9]	Ni foam as

bifunctional catalyst for water splitting[J]. Nano, 2020, 15(02): 2050024.

[2] Wen T, Yang M, Zou J, et al. Localized phosphorization synthesis of vacancy-rich NiCo<sub>2</sub>O<sub>4</sub>/NiCoP urchin-like heterojunction for alkaline electrocatalytic water splitting[J]. Industrial & Engineering Chemistry Research, 2025, 64(18): 9209-9216.

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