

Electronic Supplementary Information (ESI)

Low-content CeO_x dually promoted $\text{Ni}_3\text{Fe}@$ CNTs electrocatalyst for overall water splitting

Mingqi Sun, Shuai Zhang, Yaru Li, Chen Yang, Ying Guo,* Lan Yang and Sailong Xu*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

*Corresponding authors. E-mail addresses: xusl@buct.edu.cn (S.X.); guoying@buct.edu.cn (Y.G.)

Fig. S1

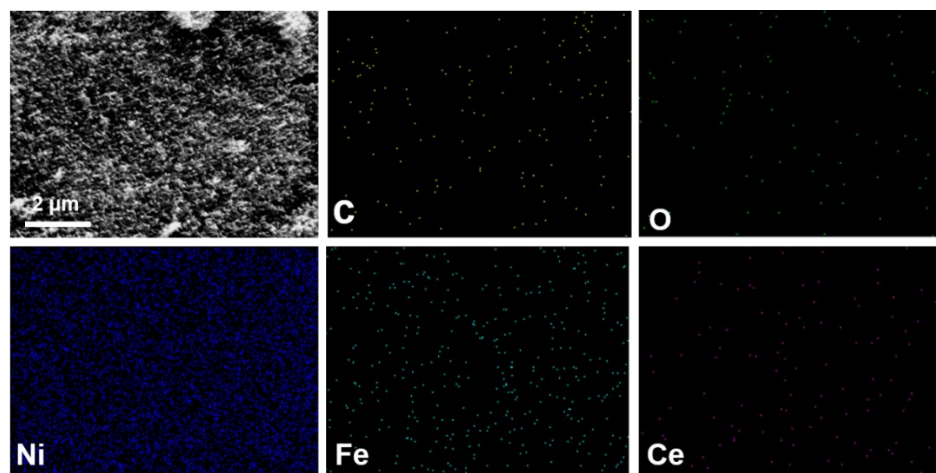


Fig. S1 SEM image of the $\text{Ni}_3\text{Fe}@$ CNTs/ CeO_x /NF composites and the corresponding EDS elements mappings of C, O, Ni, Fe and Ce elements.

Fig. S2

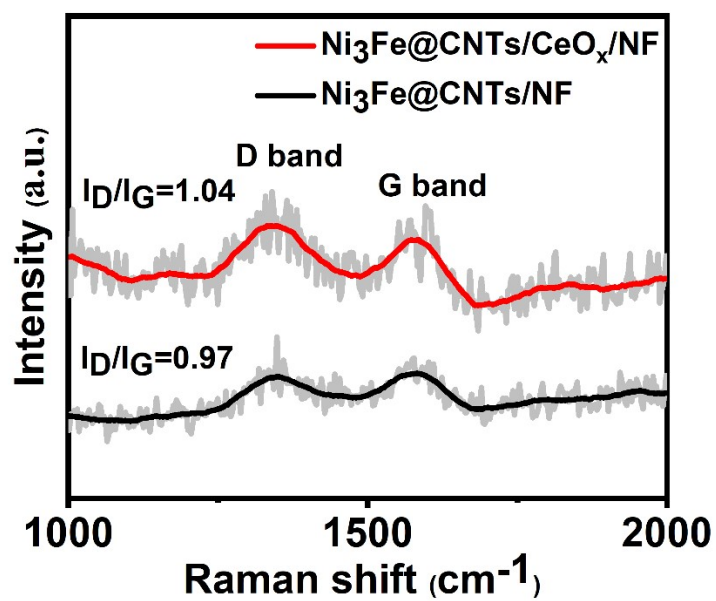


Fig. S2 Raman spectra of Ni₃Fe@CNTs/CeO_x/NF and Ni₃Fe@CNTs/NF.

Fig. S3

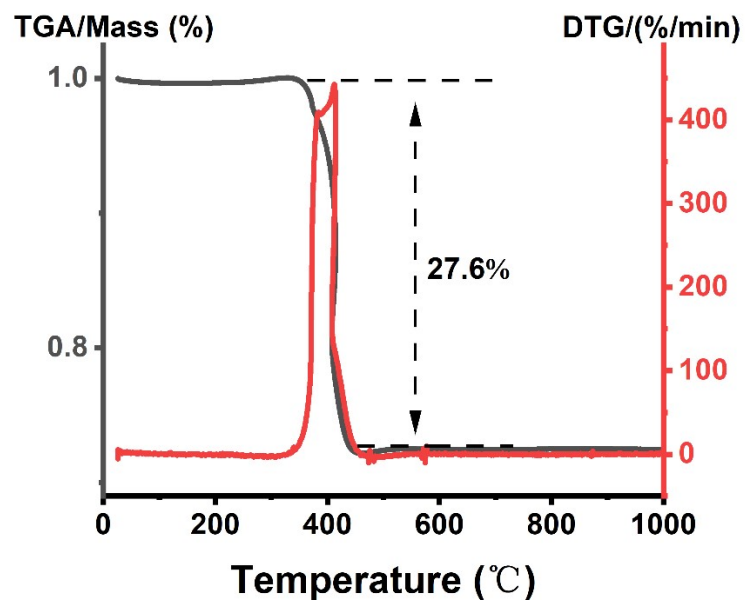


Fig. S3 Thermogravimetric analysis and derivative thermogravimetry (TGA/DTG) of the Ni₃Fe@CNTs/CeO_x/NF composite.

Fig. S4

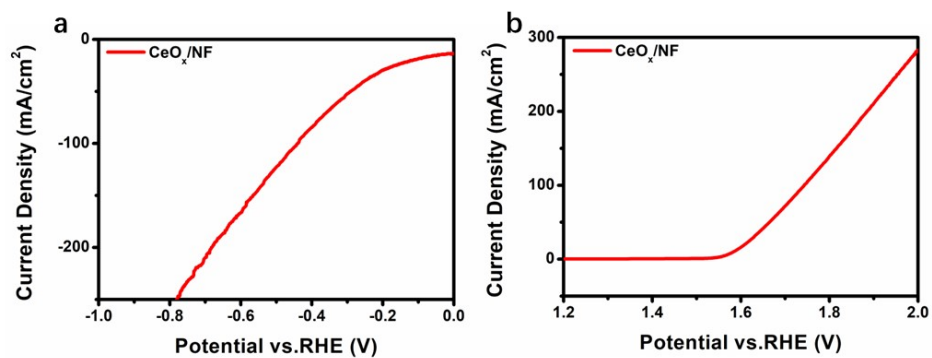


Fig. S4 LSV curve for CeO_x/NF : (a) The HER performance (b) The OER performance

Fig. S5

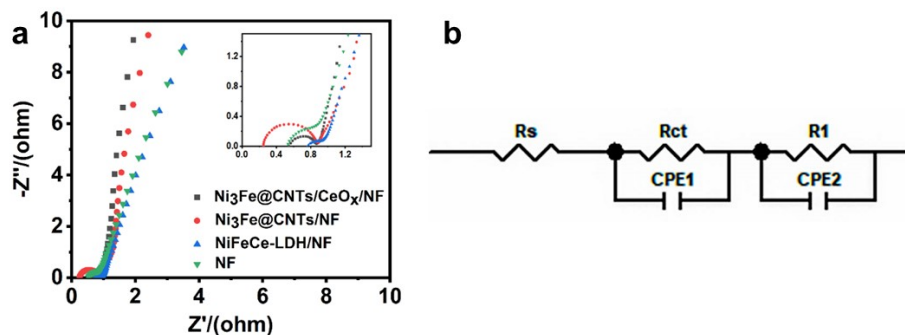


Fig. S5 (a) Electrochemical impedance spectra for the OER between $Ni_3Fe@CNTs/CeO_x/NF$, $Ni_3Fe@CNTs/NF$, together with $NiFeCe-LDH/NF$ and NF for comparison; (b) the equivalent circuit diagram of $Ni_3Fe@CNTs/CeO_x/NF$.

Fig. S6

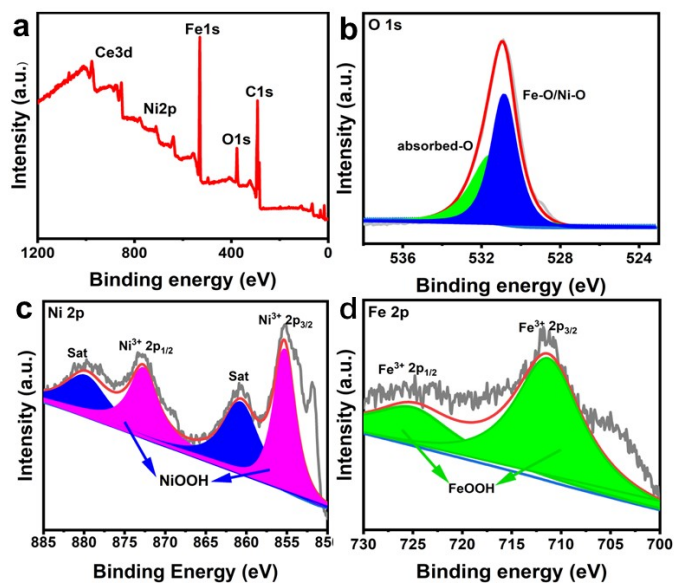


Fig. S6 XPS spectra of the $\text{Ni}_3\text{Fe@CNTs/CeO}_x/\text{NF}$ composite after the OER testing:

(a) a full spectrum, (b) O 1s, (c) Ni 2p, and (d) Fe 2p.

Fig. S7

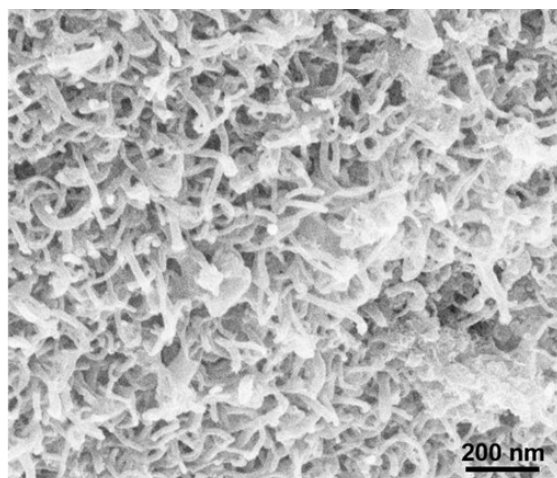


Fig. S7 SEM of Ni₃Fe@CNTs/CeO_x/NF after OER test.

Fig. S8

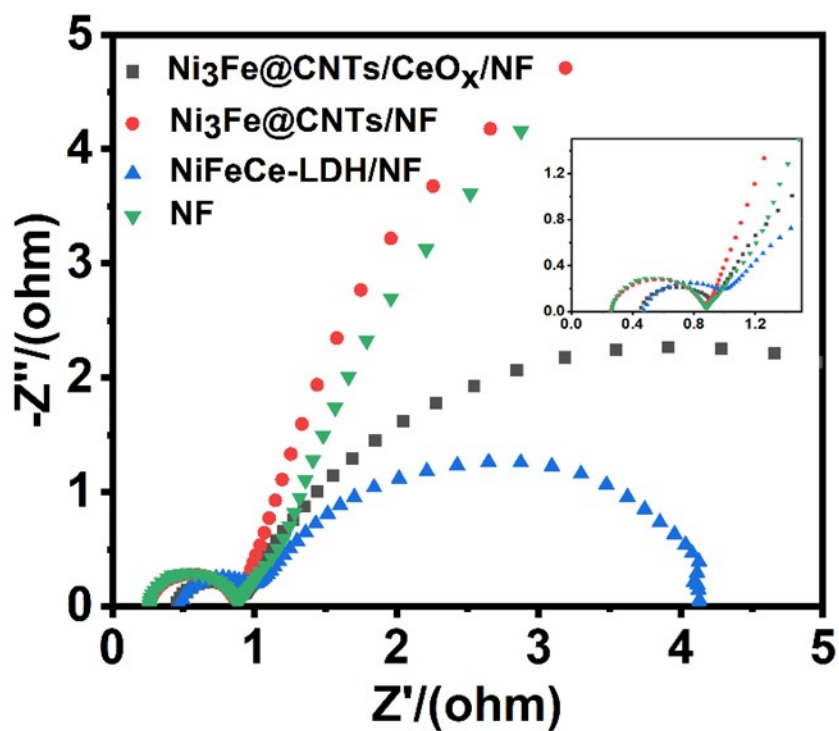


Fig. S8 Electrochemical impedance spectra of $\text{Ni}_3\text{Fe@CNTs/CeO}_x/\text{NF}$ and $\text{Ni}_3\text{Fe@CNTs/NF}$ for the HER, together with NiFeCe-LDH/NF and NF for comparison.

Fig. S9

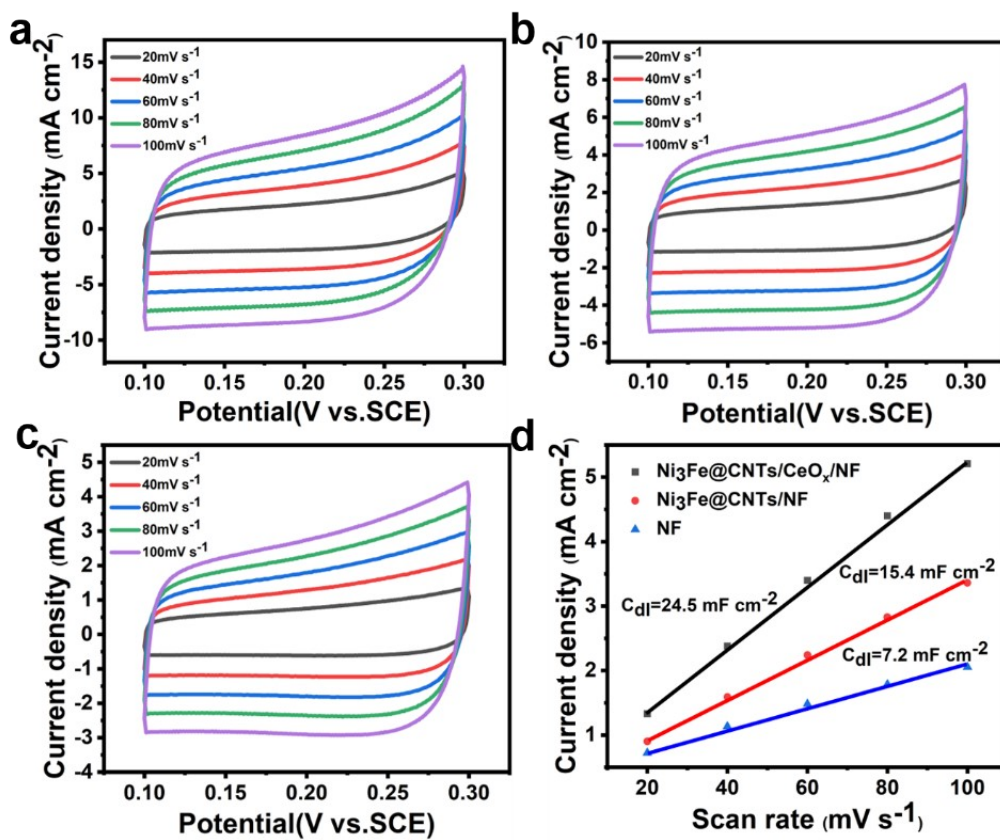


Fig.S9 Cyclic voltammograms (CVs) for (a) Ni₃Fe@CNTs/CeO_x/NF, (b) Ni₃Fe@CNTs/NF, (c) NF measured at sweep speeds from 20 to 100 mV s⁻¹ and (d) the current densities at 0.15 V vs. SCE plotted as a function of scan rates.

Fig. S10

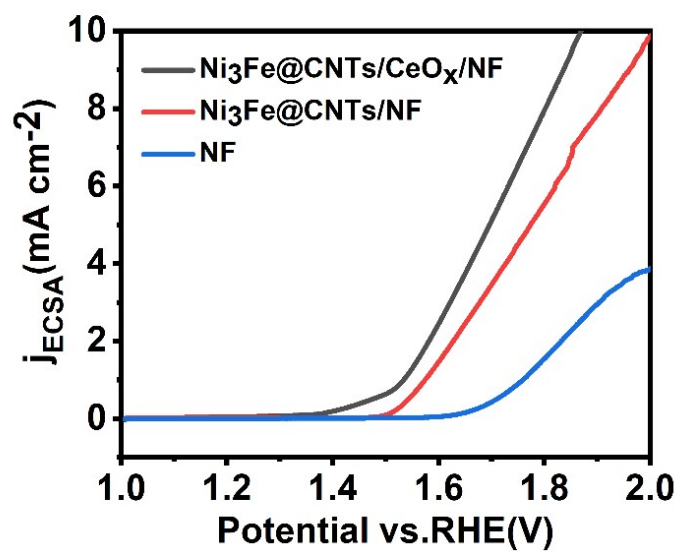


Fig. S10 The OER LSV curves normalized by ECSA for Ni₃Fe@CNTs/CeO_x/NF, Ni₃Fe-CNTs/NF, and NF.

Table S1

The ICP-OES result of Ni, Fe and Ce in the Ni₃Fe/CeO_x-CNTs.

Element	Mass fraction (wt.%)	Mole fraction
Ni	19.29	3.28
Fe	5.33	0.95
Ce	1.34	0.09

Table S2

Comparison R_{ct} between $\text{Ni}_3\text{Fe@CNTs/CeO}_x/\text{NF}$, $\text{Ni}_3\text{Fe@CNTs/NF}$, and NF for the OER.

Catalyst	$\text{Ni}_3\text{Fe@CNTs/CeO}_x/\text{NF}$	$\text{Ni}_3\text{Fe@CNTs/NF}$	NF
R_{ct} / Ω	0.27	0.60	1.73

Table S3

Comparison of OER performance at 10 mA cm⁻² between the Ni₃Fe@CNTs/CeO_x composite and those Ni₃Fe-based electrocatalysts reported previously (in 1.0 M KOH solution).

Catalysts	Overpotential (mV)	Long-term stability (h)	References
Ni ₃ Fe-NC/NF	203	110	<i>J. Mater. Chem. A</i> , 2023, 11, 6452
Fe ₄ Ni-Se/NF	207	70	<i>J. Electroanal. Chem.</i> , 2022, 906, 116014
Hollow FeNi ₃ N	210	30	<i>J. Mater. Chem. A</i> , 2021, 9, 7750
Fe _{0.2} Ni _{0.8} /NC	270	12	<i>Chem. Eng. J.</i> , 2020, 394, 124977
Fe-enriched-FeNi ₃ /NC	300	3000 cycles	<i>J. Colloid Interface Sci.</i> , 2021, 582, 977
Ni ₃ Fe@B-doped carbon	280	20	<i>J. Alloys Compd.</i> , 2020, 835, 155267
Ni ₃ FeN/Ni ₃ Fe	250	2000 cycles	<i>J. Mater. Chem. A</i> , 2021, 9, 4036
Ni ₃ Fe/N-C	330	10	<i>Carbon</i> , 2021, 174, 475
FeNi ₃ @NC	277	20	<i>Appl. Catal. B</i> , 2020, 268, 118729
Ni ₃ Fe-CW	237	50	<i>Chem. Eng. J.</i> , 2022, 439, 135722
Ni ₃ Fe@CNTs/CeO _x	195	100	This work

x

Table S4

Comparison of HER performance at 10 mA cm⁻² between the Ni₃Fe@CNTs/CeO_x composite and those Ni₃Fe-based electrocatalysts reported previously (in 1.0 M KOH solution).

Catalysts	Overpotential (mV)	Long-term stability (h)	References
Fe ₄ Ni-Se/NF	93	70	<i>J. Electroanal. Chem.</i> , 2022, 906, 116014
(Ni, Fe)S ₂ @MoS ₂	130	44	<i>Appl. Catal. B Environ.</i> , 2019, 247, 107
Hollow FeNi ₃ N	185	30	<i>J. Mater. Chem. A</i> , 2021, 9, 7750
Ni ₃ Fe/NiFe ₂ O ₄ NPs@CNT	128	40	<i>ACS Appl. Mater. Interfaces</i> 2020, 12, 50, 55782
Fe-Ni@NC-CNTs	202	11	<i>Angew. Chem. Int. Ed.</i> , 2018, 57, 8921
Ni ₃ Fe@BC	330	20	<i>J. Alloys Compd.</i> , 2020, 835, 155267
Ni ₃ FeN/Ni ₃ Fe	125	2000 cycles	<i>J. Mater. Chem. A</i> , 2021, 9, 4036
Ni ₃ Fe(OH) ₉ /Ni ₃ Fe	217	12	<i>ACS Appl. Energy Mater.</i> 2018, 1, 3, 986-992
Ni ₃ Fe-CW	76	50	<i>Chem. Eng. J.</i> , 2022, 439, 135722
Ni ₃ Fe-NC/NF	98	110	<i>J. Mater. Chem. A</i> , 2023, 11, 6452
Ni ₃ Fe@CNTs/CeO _x	125	100	This work

Table S5

Comparison of electrocatalytic performance as the electrolyzer at 10 mA cm⁻² between the Ni₃Fe@CNTs/CeO_x composite and those Ni₃Fe-based electrocatalysts reported previously (in 1.0 M KOH solution).

Catalysts	Overall voltage (V)	References
Ni ₃ Fe-NC/NF	1.49	<i>J. Mater. Chem. A</i> , 2023, 11, 6452
S-Fe-Ni/NF	1.49	<i>J. Mater. Chem. A</i> , 2023, 11, 4661–4671
Fe ₄ Ni-Se/NF	1.55	<i>J. Electroanal. Chem.</i> , 2022, 906, 116014
Hollow FeNi ₃ N	1.63	<i>J. Mater. Chem. A</i> , 2021, 9, 7750
Ni ₃ Fe/NiFe ₂ O ₄ NPs@CNT	1.62	<i>ACS Appl. Mater. Interfaces</i> 2020, 12, 50, 55782
Ni ₃ FeN/Ni ₃ Fe	1.61	<i>J. Mater. Chem. A</i> , 2021, 9, 4036
Fe-enriched-FeNi ₃ /NC	1.59	<i>J. Colloid Interface Sci.</i> , 2021, 582, 977
Ni ₃ Fe-CW	1.54	<i>Chem. Eng. J.</i> , 2022, 439, 135722
Ni ₃ Fe-FeV ₂ O ₄ @C/NF	1.51	<i>ACS Sustainable Chem. Eng.</i> 2021, 9, 24, 8249
Ni ₃ Fe/Co-N-C	1.54	<i>Chem. Eng. J.</i> , 2020, 395, 125151
Ni ₃ Fe@CNTs/CeO _x	1.641	This work

Table S6

Comparison of exchange current densities for the OER between Ni₃Fe@CNTs/CeO_x/NF, Ni₃Fe@CNTs/NF, NF and IrO₂.

Catalyst	Ni ₃ Fe@CNTs/CeO _x /NF	Ni ₃ Fe@CNTs/NF	NF	IrO ₂
Exchange current densities (mA/cm ²)	5.16×10 ⁻³	1.83×10 ⁻³	2.85×10 ⁻⁴	1.38×10 ⁻⁴

Table S7

Comparison of exchange current densities for the HER between Ni₃Fe@CNTs/CeO_x/NF, Ni₃Fe@CNTs/NF, NF, and Pt.

Catalyst	Ni ₃ Fe@CNTs/CeO _x /NF	Ni ₃ Fe@CNTs/NF	NF	Pt
Exchange current densities (mA/cm ²)	3.65×10 ⁻⁷	1.79×10 ⁻⁷	6.7×10 ⁻⁷	1.95×10 ⁻³