Supporting Information

In-situ hierarchical self-assembly of NiFeHCF nanoparticles on nickel foam: Highly active and ultra-stable bifunctional electrocatalysts for water splitting and its environmental assessments towards green energy

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Contents

SI-I. Experimental Section

SI-II. Calculations

SI-III. Figures

SI-IV. Tables

SI-V. References

SI-I. Experimental section

Materials

Nickel (II) nitrate (Ni(NO₃)₂.6H₂O), ferric (III) nitrate Fe(NO₃)₃.9H₂O, Na₂CO₃, potassium hydroxide, isopropanol, HCl and ethanol were purchased from SDFCL chemicals and Potassium ferrocyanide trihydrate (K₄Fe(CN)₆.3H₂O) was purchased from Qualigense. Nickel foam was purchased from Vritra technologies Delhi India. These chemicals were used as received without further purification. Deionized water (DI) was used throughout this reaction.

Fabrication of NiFeHCF@NF

First, the oil stains and surface oxide layer on NF (3 cm × 2 cm) were removed using 1.0 M HCl and DI water. Next, precleaned NF was immersed in a potassium ferrocyanide solution (500 mg in 10 ml of water) for 2 hours and labelled as HCF@NF. Finally, HCF@NF was dipped in iron-nickel solution (200 mg of iron and 300 mg of nickel in 10 ml of water) for a few seconds to promote the in-situ growth of iron-nickel ferrocyanide on NF and the nickel foam was taken out, naturally dried at room temperature. Natural drying on the watch glass at room temperature, resulting in strong binding between the iron, nickel and ferrocyanide with NF. After being completely cleaned with deionised water, the sample was designated as NiFeHCF@NF with a loading of about 3.2 mg cm². Repeated the above process without adding Fe source and Ni source to obtain FeHCF@NF and NiHCF@NF. The loading of the obtained FeHCF@NF and NiHCF@NF were about 3.0 mg cm² and 3.1 mg cm², respectively.

Synthesis of NiFe-LDH@NF

Nickel-iron layered double hydroxide was prepared by following the previous report.¹ In brief, the mixture of Ni(NO₃) $2 \cdot 6H_2O$ (3 mmol) and Fe(NO₃) $_3 \cdot 9H_2O$ (1 mmol) prepared in 100 mL of water (solution A) was dropwise added into another solution B containing Na₂CO₃ (1 mmol) and NaOH (2.6 mmol) in 100 mL. The slurry was then stirred for 24 hours at 60 °C and centrifuged.

The resultant precipitate was washed with excess water and ethanol and dried in an oven at 60° C for 12 h.

Physical characterization

X-ray diffraction (XRD) of NiFeHCF@NF was recorded with Thermo XRD equinox 1000. Fourier transform infrared (FTIR) spectra of NiFeHCF@NF were recorded on Shimadzu IR Tracer-100. The morphology of NiFeHCF@NF was determined by using ZEISS Sigma 300 field emission scanning electron microscope (FESEM) operated at 20 kV and elemental mapping was carried out through energy-dispersive X-ray spectroscopy (EDX). JEM-2100 Plus was used to record high-resolution transmission electron microscope (HR-TEM) images of the nanomaterials and selected area electron diffraction (SAED) pattern was taken from JEM-2100 Plus. The elemental composition of NiFeHCF@NF was analyzed by X-ray photoelectron spectroscopy (XPS) with K α surface analysis spectrometer. The elemental content of NiFeHCF@NF was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Perkin Elmer Optima 5300 DV.

Electrocatalytic characterization

The catalytic performances of the electrodes for water splitting were studied using a threeelectrode configuration connected to a Biologic electrochemical workstation SP-200 potentiostat at room temperature. The NiFeHCF@NF was used as the working electrode. The Ag/AgCl (3 M KCl) electrode and Pt wire were used as the reference and counter electrodes, respectively. To remove the surface oxidized layer, a piece of Ni foam (0.5 cm \times 0.5 cm) was cleaned through sonication consecutively in 1.0 M HCl, ethanol, and DI water (5 min each) and dried before use as a substrate. Commercially available catalyst (Pt/C&IrO₂) and bare NF were used: about 1.0 mg/ml of commercial Pt/C&IrO₂ suspension was prepared by following a similar methodology for comparison and bare NF was used directly. The commercial Pt/C&IrO₂ catalyst has been used directly as a working electrode without further treatment. All measurements were carried out in 1.0 M KOH. The OER/HER activities of NiFeHCF@NF have been analyzed by polarization curves (LSV), electrochemical impedance spectroscopy (EIS) and chronoamperometry. The OER/HER activity of the catalyst has been made by linear sweep voltammetry (LSV) on NF electrode (scan rate: 10 mV s^{-1}). The impedance of electrocatalyst was measured by electrochemical impedance spectroscopy (EIS) over a frequency range of 100 kHz to 10 mHz with a sinusoidal perturbation amplitude of 0.4 V.

SI-II. Calculations

SI-S1. Calculation of Turnover frequency.

Here, the turnover frequency (TOF) rate of evolved molecular O_2/H_2 per surface active site per second can be calculated. The overpotential used for the calculation of TOF was set at a potential of 1.6/-0.2 V vs. RHE. The TOF can be calculated using the equation:

$$\mathbf{TOF} = [\mathbf{J} \mathbf{x} \mathbf{A} / \mathbf{4} \mathbf{x} \mathbf{F} \mathbf{x} \mathbf{m}] \tag{1}$$

where, J- current density,

A- area,

F- faraday constant

m- number of moles in a catalyst.

SI-S2. Calculation of EASA.

The calculations of EASA and roughness factor (RF) are based on the following equation:

$$EASA=C_{dl}/C_{s} * S$$
⁽²⁾

RF=EASA/GSA

In eq (1), C_{dl} is the measured double layer capacitance of samples in 1.0 M KOH (mF), C_s is the specific capacitance of the catalyst ($C_s = 0.04 \text{ mF cm}^{-2}$ in 1.0 M KOH) and S is surface area (S= 0.5 cm²). In eq (2), RF is the roughness factor and GSA is the geometric surface area of the material.

(3)

SI-S3. Calculation of Faradaic Efficiency

The Faradaic Efficiency of OER/HER was estimated using the following equation:

$$FE = 4Fn_{O2}/It \times 100\% \tag{4}$$

$$FE = 2Fn_{H2}/It \times 100\%$$
(5)

Where F is Faraday constant (96485 C/mol), n_{O2} is the number of moles of experimental O_2 during the reaction (mol), n_{H2} is the number of moles of experimental H_2 during the reaction (mol), I is the current of the reaction (A), and t is the reaction time (s).²

SI-S4. Calculation of O₂/H₂ generation

Based on the displaced amount of water due to the O_2/H_2 bubbles, the amount of O_2/H_2 generated was calculated using the following equations

Amount of
$$O_2/H_2$$
 generated in 1 h = amount of water displaced in liters (6)

Amount of
$$O_2/H_2$$
 generated in $= \frac{\text{amount of water displaced (liters)}}{22.4 \text{ liters}}$ (7)

We have also calculated the O_2/H_2 generation rate from the electrical charge passed through

the electrode using the equation given below.

Current obtainedTime duration for
During water electrolysisTime duration for
ach potential= Coulomb(8) $\underline{Coulomb \ x \ F} = No. of moles of e^{-} for O_2/H_2 generation(9)96485CNo. of moles of e^{-} for O_2/H_2 generation x 1 mole of O_2/H_2 gas = Moles of O_2/H_2 generated (10)$

4/2 moles of electron

SI-S5. Environmental impact assessment

Equation S1

 $Mass Intensity = \frac{Mass of all reactents used excluding water}{Mass of product} kg/kg product$

Equation S2

Water Intensity (Wp) = $\frac{Mass \ of \ all \ water \ used}{Mass \ of \ product} kg/kg \ product$

Equation S3

Reaction Mass Efficiency (RME) = $\frac{Mass of product}{Mass of all reactents} \times 100\%$

Equation S4

 $Energy Intensity = \frac{Amount of non renewable energy used}{Mass of product} kW.h/kg$

Equation S5

 $E factor = \frac{[kg(raw material) - kg(desired product)]}{[kg(total product including water)]}$

Figure S1. Photographs of (a) Colour changes of different electrocatalysts and (b) colour change electrocatalysts after OER/HER.



Figure S2. Comparison of FE-SEM images: Bare NF (a); Fresh NiFeHCF@NF (b); After OER (c) and After HER (d).



Figure S3. XRD pattern of bare nickel foam.



Figure S4. FE-SEM elemental mapping of NiFeHCF@NF: field of view (a); carbon (b); nitrogen (c); oxygen (d); iron (e); nickel (f) and EDX spectrum (g).



Figure S5. Comparison of LSV curves before and after stability @ 10 mA/cm²: oxygen evolution reaction (a); hydrogen evolution reaction (b) and full cell (c).





Figure S6. Activity comparison LSV of *in-situ* and co-precipitation methods of NiFeHCF@NF; (a) OER and (b) HER.

Figure S7. EASA-normalized LSV curve of NiFeHCF@NF.



EASA-normalized current density = current density $\times C_s/C_{dl}$

Where $C_s = 0.04 \text{ mF/cm}^2$ in 1.0 M KOH and $C_{dl} = 5.745 \text{ mF/cm}^2$ (NiFeHCF@NF).



Figure S8. Post XRD image of NiFeHCF@NF; (a) After HER and (b) After OER.



Figure S9. IR spectrum of NiFeHCF@NF: (a) After HER and (b) After OER.

Figure S10. Post FE-SEM elemental mapping image of NiFeHCF@NF after OER: field of view (a); carbon (b); nitrogen (c); oxygen (d); iron (e); nickel (f) and EDX spectrum (g).



Figure S11. Post FE-SEM elemental mapping image of NiFeHCF@NF after HER: field of view (a); carbon (b); nitrogen (c); oxygen (d); iron (e); nickel (f) and EDX spectrum (g).









Figure S13. Calculated faradic efficiency for O_2/H_2 generation.

SI-IV. Tables

Table S1. Elemental content of NiFeHCF@NF measured by ICP-OES.

NiFeHCF@NF	Ni 231.604	57.62
	Fe 238.204	42.14

Table	S2.	Comparison	of	OER,	HER	and	overall	water	splitting	performance	of
	NiFeHCF@NF recently reported non-noble bifunctional electrocatalysts.										

S.No	Bifunctional Electrocatalyst	OER nj=10 (mV)	HER nj=10 (mV)	OWS Ej=10 (V)	Ref.
1	NiFeHCF@NF	210	125	1.56	This work
2	Fe@PSAC	231	118	1.58	[3]
3	Fe-PANI	261	155	1.64	[4]
4	Ni-Fe-P nanocubes	271	182	1.67	[5]
5	Ni (OH) ₂ /NF	350	298	1.82	[6]
6	Co _{0.85} Se/NiFe-LDH/EG	270	260	1.67	[7]
7	Co (OH)2@NCNTs	270	170	1.72	[8]
8	CTs/Co-S	301	190	1.74	[9]
9	Ni ₃ S ₂ /NF	280	223	1.76	[10]
10	Ni ₂ P/MoO ₂ @MoS ₂	280	159	1.72	[11]
11	NiCo ₂ S ₄ /CC	280	263	1.68	[12]
12	CP/CTs/Co-S	306	190	1.74	[13]
13	Co ₁ Mn ₁ CH/NF	294	180	1.68	[14]
14	Co ₂ B/CoSe ₂	320	300	1.73	[15]
15	MnMoO ₄ /PANI	410	155	1.65	[16]
16	Co(OH) ₂	281	182	1.65	[17]
17	Co ₄ Mo ₂ @NC	330	218	1.74	[18]
18	Ni/Mo ₂ C-PC	368	179	1.66	[19]
19	Co ₂ P/Mo ₂ C	368	182	1.74	[20]
20	3D-CNTA	360	185	1.68	[21]

Electrolyte: 1 M KOH

Material	Mass intensity (MI) (kg/kg)	Solvent intensity (SI) (kg/kg)	Reaction mass efficiency (RME) %	Energy consumption (kW·h/kg)	E-factor
NiFeHCF@NF	1.35	93.50	74	0	0.5
Co ₄ Fe ₆ -LDH	6.40	93.50	15.4	0	1.2
Fe-PANI	1.37	34.01	72.5	0	0.3
CNPFH	1.84	38.80	54	1.78	0.6
CMCFH	1.90	29.20	52	2.30	0.3

 Table S3. Mass-based sustainability metrics evaluation for the synthetic process comparison with recently reported works.²²⁻²⁵

SI-V. References

Reference

- E. Duquesne, S. Betelu, C. Bazin, A. Seron, I. Ignatiadis, H. Perrot, O. Sel and C. Debiemme-Chouvy, J. Phys. Chem. C, 2020, 124(5), pp.3037-3049.
- [2] X. Hou, J. Li, J. Zheng, L. Li, and W. Chu, *Dalton Trans.*, 2022, **51(36)**, pp.13970-13977.
- [3] A. Gayathri, M. Vijayarangan, M. Sangamithirai, V. Ashok, J. Jayabharathi and V. Thanikachalam, *Energy & Fuels*, 2023, 37 (24), 19812-19821.
- [4] B. Vishnu, S. Sriram and J. Jayabharathi, New J. Chem., 2023, 47(12), pp.5977-5990.
- [5] C. Xuan, J. Wang, W. Xia, Z. Peng, Z. Wu, W. Lei, K. Xia, H.L. Xin and D. Wang, ACS Appl. Mater. Interfaces, 2017, 9(31), pp.26134-26142.
- [6] J. Lee, G.H. Lim and B. Lim, Chem. Phys. Lett., 2016, 644, pp.51-55.
- [7] Y. Hou, M.R. Lohe, J. Zhang, S. Liu, X. Zhuang and X. Feng, *Energy Environ. Sci.*, 2016, 9(2), pp.478-483.
- [8] P. Guo, J. Wu, X.B. Li, J. Luo, W.M. Lau, H. Liu, X.L. Sun and L.M. Liu, *Nano Energy*, 2018, 47, pp.96-104.
- [9] M.I. Jamesh, J. Power Sources, 2016, 333, pp.213-236.
- [10]L.L. Feng, G. Yu, Y. Wu, G.D. Li, H. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, J. Am. Chem. Soc., 2015, 137(44), pp.14023-14026.
- [11] Y. Wang, T. Williams, T. Gengenbach, B. Kong, D. Zhao, H. Wang and C. Selomulya, *Nanoscale*, 2017, 9(44), pp.17349-17356.
- [12] D. Liu, Q. Lu, Y. Luo, X. Sun and A.M. Asiri, Nanoscale, 2015, 7(37), pp.15122-15126.
- [13] X.B. Zhang, J. Wang, H.X. Zhong, Z.L. Wang and F.L. Meng, ACS Nano, 2016, 10, p.2342.
- [14] X.D. Wang, H.Y. Chen, Y.F. Xu, J.F. Liao, B.X. Chen, H.S. Rao, D.B. Kuang and C.Y. Su, J. Mater. Chem. A, 2017, 5(15), pp.7191-7199.

- [15] Y. Guo, Z. Yao, C. Shang and E. Wang, ACS Appl. Mater. Interfaces, 2017, 9(45), pp.39312-39317.
- [16] M.S. Tamboli, S.A. Patil, A.M. Tamboli, S.S. Patil, N.T.N. Truong, K. Lee, C.S. Praveen, N.K. Shrestha, C. Park and B.B. Kale, *Dalton Trans.*, 2022, 51(15), pp.6027-6035.
- [17] S. Sriram, S. Mathi, B. Vishnu and J. Jayabharathi, *Energy Fuels*, 2022, 36(13), pp.7006-7016.
- [18] J. Jiang, Q. Liu, C. Zeng and L. Ai, J. Mater. Chem. A, 2017, 5(32), pp.16929-16935.
- [19]Z.Y. Yu, Y. Duan, M.R. Gao, C.C. Lang, Y.R. Zheng and S.H. Yu, Chem. Sci., 2017, 8(2), pp.968-973.
- [20] X. Li, X. Wang, J. Zhou, L. Han, C. Sun, Q. Wang and Z. Su, J. Mater. Chem. A, 2018, 6(14), pp.5789-5796.
- [21] S. Wang, J. Qin, T. Meng and M. Cao, Nano Energy, 2017, 39, pp.626-638.
- [22]B. Vishnu, S. Sriram and J. Jayabharathi, Sustainable Energy Fuels, 2023, 7(18), pp.4638-4653.
- [23] S. Mukherjee, A.A. Kumar, C. Sudhakar, R. Kumar, T. Ahuja, B. Mondal, P. Srikrishnarka,
 L. Philip and T. Pradeep, ACS Sustainable Chem. Eng., 2018, 7(3), pp.3222-3233.
- [24] S. Mukherjee, H. Ramireddy, A. Baidya, A.K. Amala, C. Sudhakar, B. Mondal, L. Philip, and T. Pradeep, ACS Sustainable Chem. Eng., 2019, 8(1), pp.139-147.
- [25]C. Jiménez-González, D.J. Constable and C.S. Ponder, Chem. Soc. Rev., 2012, 41(4), pp.1485-1498.