Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Accelerating charge transfer to enhance H_2 evolution of defect-rich $CoFe_2O_4$ by constructing a Schottky junction

Experimental Section

Reagents and materials: $Co(NO_3)_2·6H_2O$, $NiCl_2·6H_2O$ were bought from Shanghai Maclean Biochemical Technology Co., Ltd. $Fe(NO_3)_3·9H_2O$ and $Zn(NO_3)_2·6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. $NaBH_4$ was bought from Tianjin Kemiou Chemical Reagent Co., Ltd. Deionized water was homemade using UPT-II-10T ultrapure water system.

Preparation of defect-rich $CoFe_2O_4$ (DCF). $CoFe_2O_4$ were synthesized at room temperature by a simple wet chemical method. Taking $Co(NO_3)_2·6H_2O$ (1 mmol), $Fe(NO_3)_3·9H_2O$ (2 mmol) dissolved in 60 mL of deionized water and stirred for 30 minutes. 20 mL of $NaBH_4$ solution (1.3 $mmol·L^{-1}$) was then added into the above mixture. After vigorously stirred at room temperature for 6 h, the deionized water/ ethanol washed sample was then dried in a vacuum drying box overnight to obtain DCF.

Preparation of FeNi/DCF/NC. The obtained $CoFe_2O_4$ (100 mg) and $Zn(NO_3)_2·6H_2O$ (0.5 mmol) dissolved in 15 mL of methanol and were stirred for 30 min to obtain solution A. 2-methylimidazole (2 mmol) dissolved in 15 mL of methanol to obtain solution B after 15 min ultrasonic treatment. After adding solution B to solution A and stirring (6 h) at room temperature, the washed sample was then dispersed with 20 mL of methanol and 75 μL $NiCl_2$ solution (100 $mg·mL^{-1}$). 2 hour's stirring later, the product was centrifuged and dried. Then, the temperature was raised to 900 °C at 5 °C/min maintaining for 2 h under N_2. The naturally cooled sample was named as FeNi/DCF/NC. FeNi/DCF/NC-5 and FeNi/DCF/NC-10 were prepared by above same method except the different volume of $NiCl_2$ solution (Table S1). Ni-NC was synthesized by the same process as FeNi/DCF/NC without using DCF.

Characterization: The X-ray diffraction (XRD) patterns were examined on a Bruker D8 Focus Diffractometer (Cu-Kα, 40kV). The morphology of the samples was characterized by a field emission scanning electron microscope (FE-SEM, Quanta 250 FEG) and Field emission transmission electron microscope (FE-TEM, FEI Tecnai G2 F20). X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Fisher Scientific K-Alpha. Raman spectrum was measured by the

Horibajylabram HR Evolution with a 532 nm excitation laser. The electron spin resonance (ESR) test was performed on JES-FA300 Electron spin resonance spectrometer.

Electrochemical tests: First, 6 mg of sample, 40 μL of Nafion membrane solution, 960 μL of ethanol were mixed and ultrasonicated for more than 1 h. Then, 25 μL of the slurry was coated on the treated carbon paper (0.5*0.5 cm) and dried at 50 °C to obtain a working electrode. Graphite rod and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The electrolyte was 1.0 M KOH. The cyclic voltammetry (CV) and linear voltammetry (LSV) were performed on an electrochemical workstation (CHI630E, Shanghai Chenhua). The potential range of CV and LSV test was -1.0 ~ -1.5 V, with a different scanning speed of 50 mV/s in CV while 2 mV/s in LSV. Electrochemical impedance spectroscopy (EIS) test was accomplished on the Admiral instruments (Squidstat Plus) at an overpotential of 100 mV in 1.0 M KOH solution. The potentials in this work were showed vs. the reversible hydrogen electrode (RHE) according to the formula of $E(RHE) = E(SCE) + 0.059\ pH + 0.242\ V$.

DFT calculations

All DFT calculations were performed as implemented in the Vienna Ab Initio Simulation Package (VASP). The projector augmented wave (PAW) method with the Perdew-Burke-Ernzerhof (PBE) was used to describe the interaction between the ions and the electrons with frozen-core approximation. A cut-off energy was set to 400 eV. Stationary points were identified by the conjugate gradient method until the forces acting on each ion were smaller than 0.02 eV/Å. The convergence tolerance of the energy was set to be 10^{-4} eV. The k-points meshes of $3 \times 3 \times 1$ was used for the Brillouim zone integration.

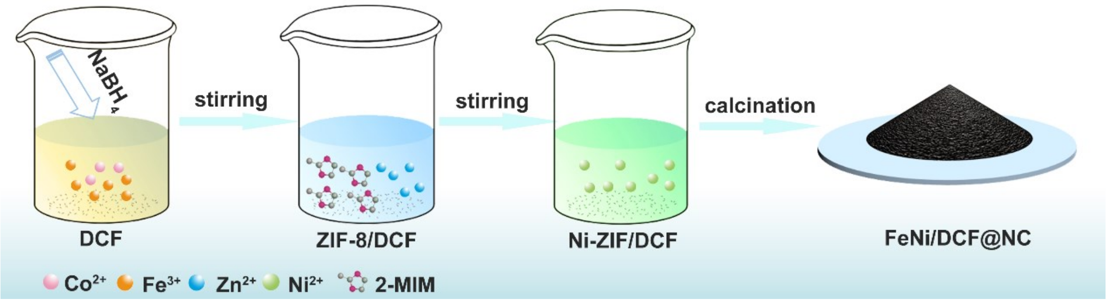

Fig. S1 Schematic illustration of the preparation of FeNi/DCF/NC.

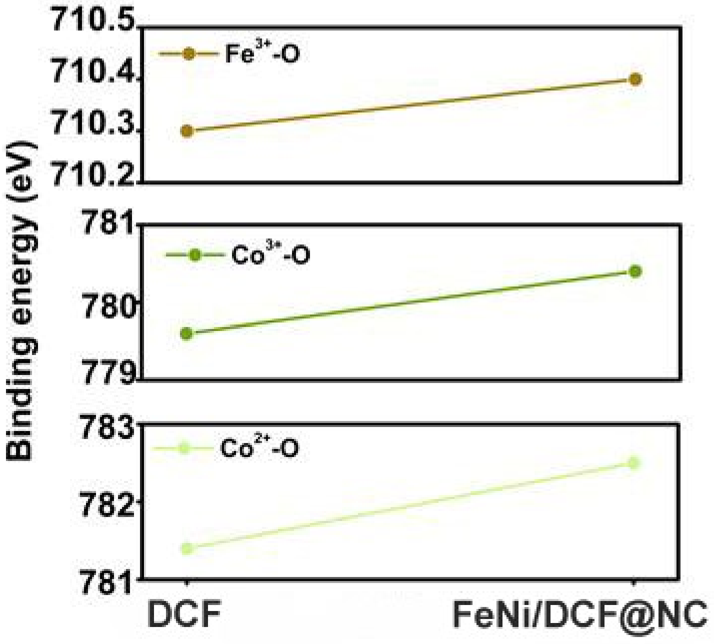

Fig. S2 Binding energy of Co-O and Fe-O peaks.

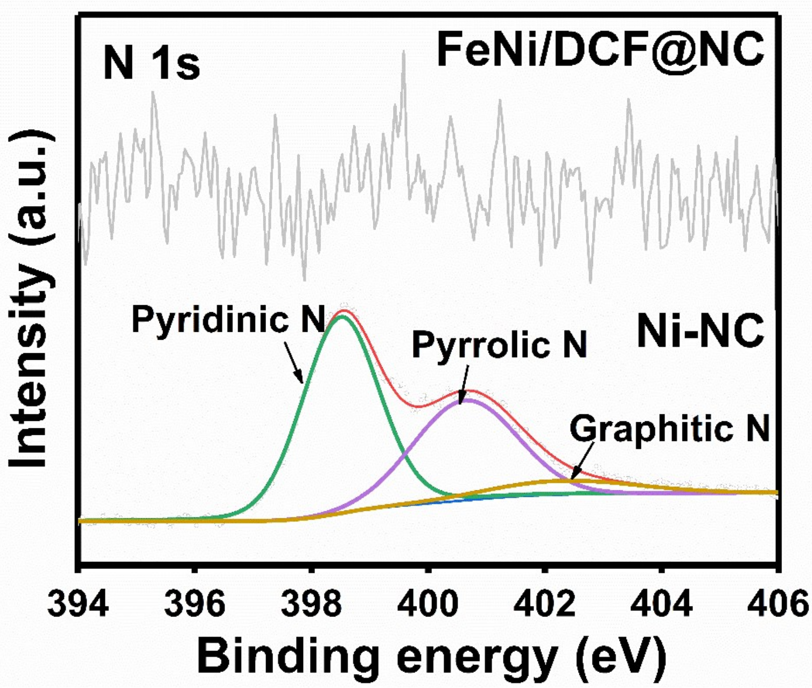

Fig. S3 The corresponding high resolution spectra of N 1s.

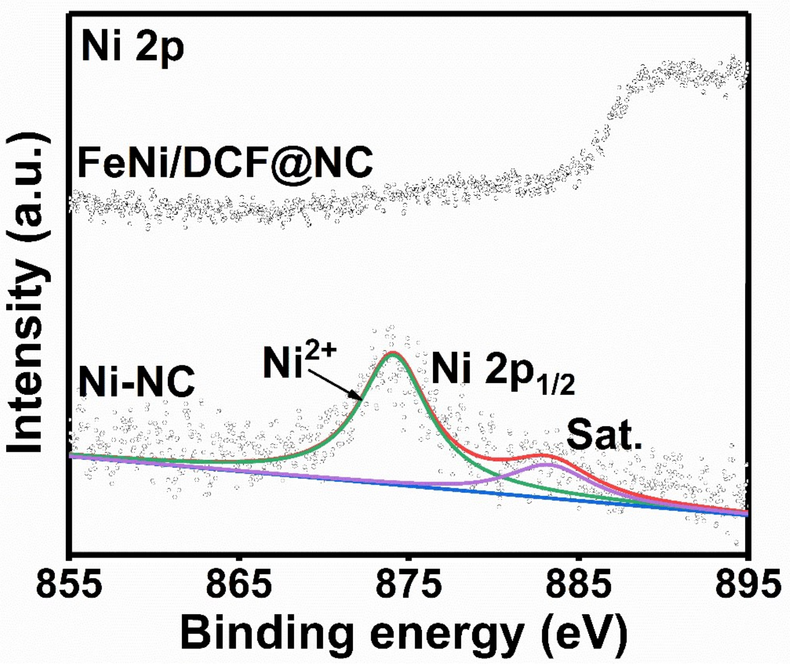

Fig. S4 The corresponding high resolution spectra of Ni 2p.

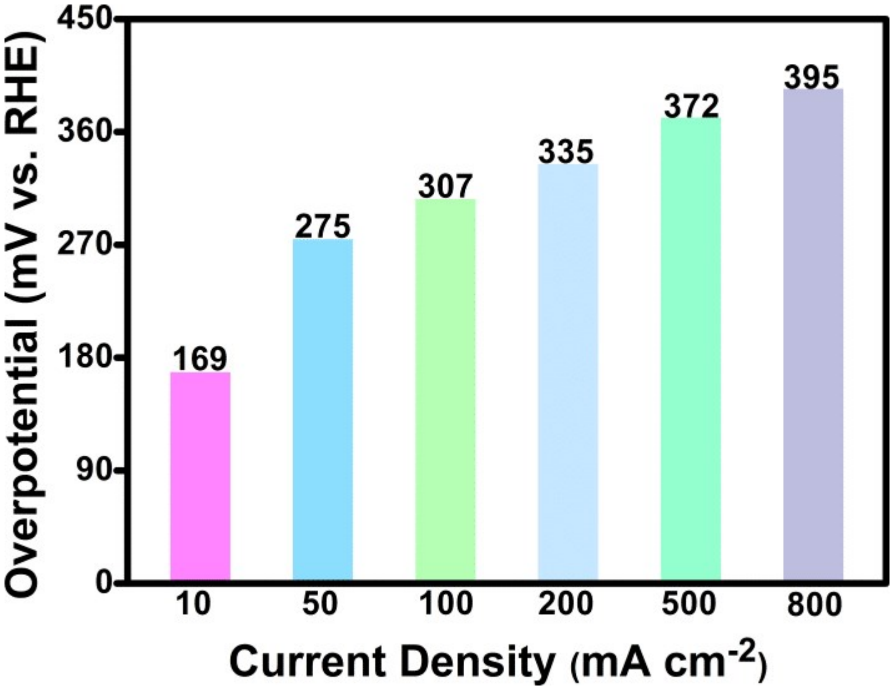

Fig. S5 The overpotential of FeNi/DCF/NC at different current density.

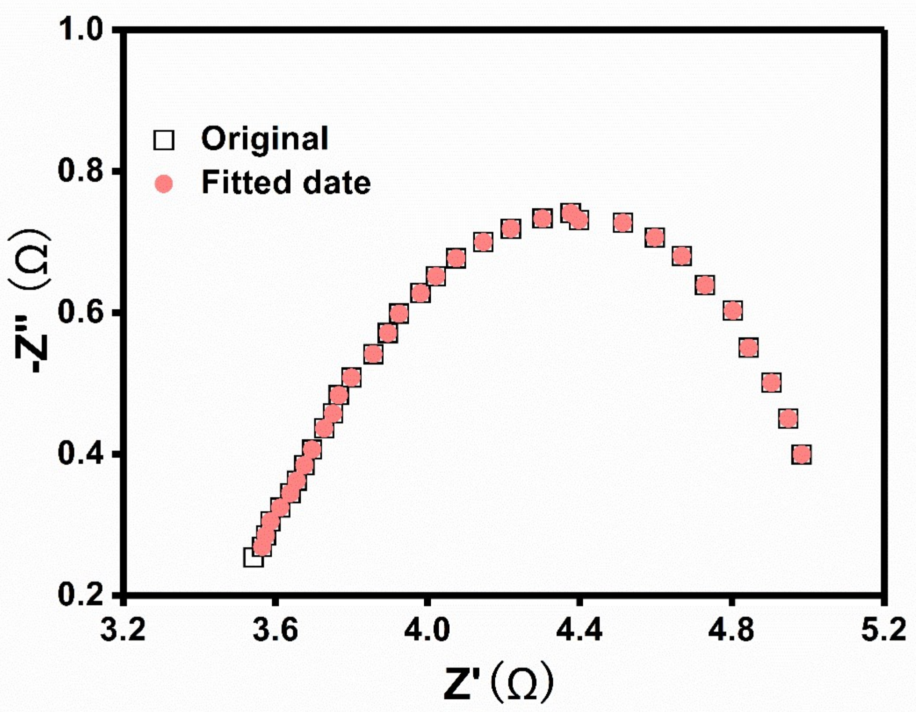

Fig. S6 The equivalent circuit diagram of FeNi/DCF/NC.

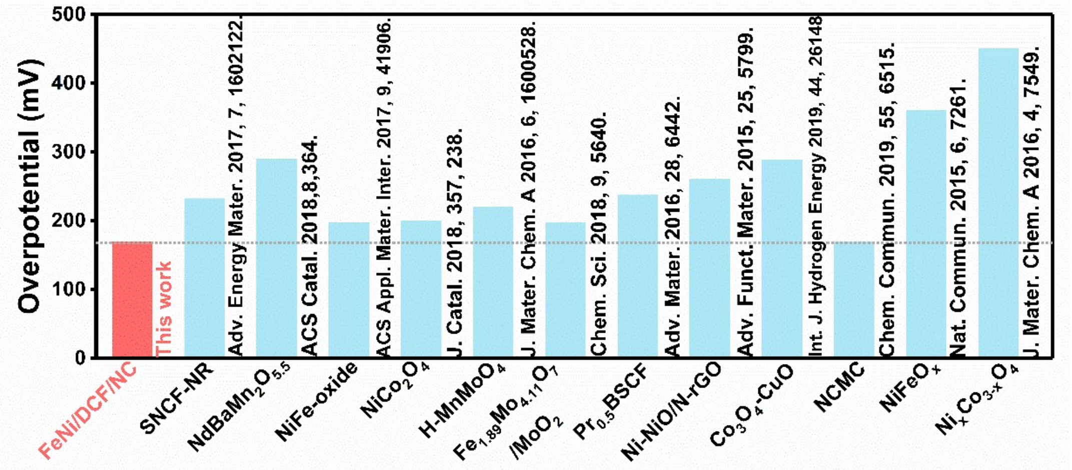

Fig. S7 The overpotentials of recent reported oxides delivered at 10 mA cm^{-2} in 1.0 M KOH.

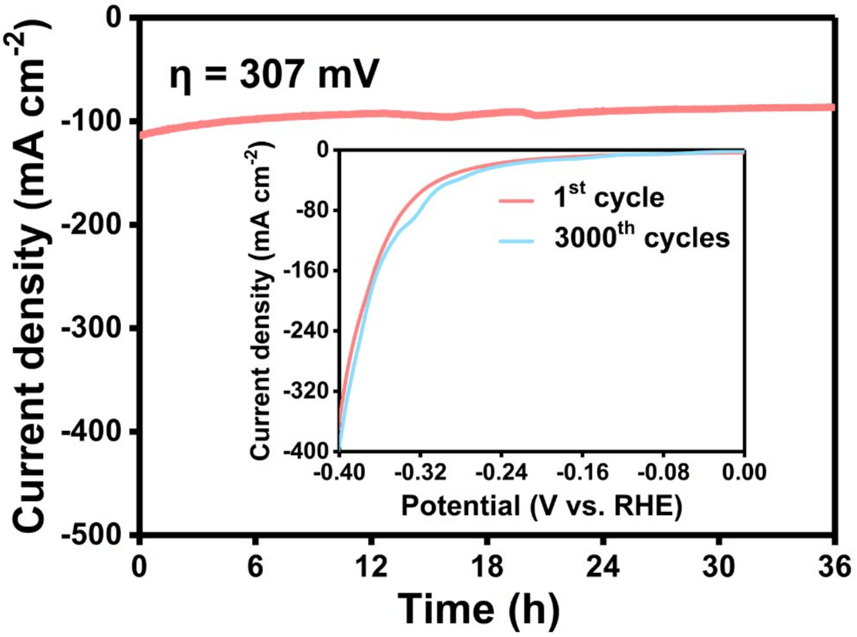

Fig. S8 The time-dependent current density curve, inset shows the polarization curve of FeNi/DCF/NC.

Table S1 The amount of raw materials (mmol) used to prepare samples.

Precursor sample	$Co(NO_3)_2 \cdot 6H_2O$	$Fe(NO_3)_3 \cdot 9H_2O$	$NiCl_2 \cdot 6H_2O$
FeNi/CF/NC	1	2	0.06
$CoFe_2O_4$-V_O	1	2	0
FeNi/CF/NC-5	1	2	0.04
FeNi/CF/NC-10	1	2	0.08
Ni-NC	0	0	0.06

Note: $Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), 2-methylimidazole (2 mmol)**.**

Table S2 Corresponding structure of XRD peaks in FeNi/DCF/NC.

2θ (degree)	Corresponding structure	PDF card
18.3	$CoFe_2O_4$	22-1086
30.1		
35.4		
43.1		
53.4		
57.0		
62.6		
39.6	Ni	89-7129
44.6		
43.6	$Fe_{0.64}Ni_{0.36}$	47-1405
50.8		
74.7		

Table S3 The assignment of the major Raman peaks of FeNi/DCF/NC.

Raman shift (cm^{-1})	Corresponding structure	Refs.
215	Ni-Fe	Nat. Mater. 2009, 8, 882.
287	Ni-Fe	Nat. Mater. 2009, 8, 882.
326	NiFe-O	Adv. Energy Mater. 2017, 1701347.
385	Fe-O	J. Nanomater. 2019, 5394325.
480	$CoFe_2O_4$	Adv. Funct. Mater. 2019, 1900030.
666	$CoFe_2O_4$	Adv. Funct. Mater. 2019, 1900030.
1313	D-band	ACS Energy Lett. 2018, 3, 1183.
1408	C	J. Raman Spectrosc. 2007, 38, 704.

Table S4 The assignment of the major XPS peaks of FeNi/DCF/NC.

Element	Binding energy (eV)	Corresponding structure	Refs.
Co	779.9	Co 2p $_{3/2}$ (Co^{3+})	J. Am. Chem. Soc. 2019, 141, 10417.
	781.9	Co 2p $_{3/2}$(Co^{2+})	
	794.9	Co 2p $_{1/2}$(Co^{3+})	
	796.8	Co 2p $_{1/2}$(Co^{2+})	
	786	Satellite peak	
	802.6	Satellite peak	
Fe	710.4	Fe 2p $_{3/2}$	Adv. Energy Mater. 2017, 1701347.
	712.4	Fe^{3+}	
	724.4	Fe 2p $_{1/2}$	
	718.4	Fe^{3+}	
	733.8	Fe^{3+}	Nano Energ. 2017, 41, 327.
O	529.8	O^{2-}	Adv. Energy Mater. 2017, 1701347.
	531.1	OH^{-} and O^{-} or O^{2-}	
	532.5	adsorbed water	Appl. Catal. B Environ. 2019, 244, 1096.
C	284.8	C-C	Adv. Mater. 2017, 1605957.
	286	C-N	
	288.4	C=O	

Table S5 The element contents of FeNi/DCF/NC from XPS test.

Element	Atomic %
C	30.76
N	1.04
O	42.79
Fe	17.93
Co	6.52
Ni	0.94

Table S6 The element contents of Ni/NC from XPS test.

Element	Atomic %
C	89.49
N	10.36
Ni	0.15

Table S7 The element contents of DCF from XPS test.

Element	Atomic %
Co	11.31
Fe	21.24
O	47.24

Table S8 EIS calculation parameters of FeNi/DCF/NC and reference samples obtained by fitting the Nyquist plots of Fig. 3f.

Sample	**R1 (Ω cm^{-2})**	**R2 (Ω cm^{-2})**	**R3 (Ω cm^{-2})**	**C1 (F)**	**C2 (F)**
FeNi/DCF/NC	3.498	1.443	0.158	0.0013	0.0025
DCF	3.497	22.021	2.214	0.0001	0.0002
Ni/NC	3.073	57.455	4.273	0.0034	0.0033

Table S9 HER performance of FeNi/CF/NC and other electrocatalysts reported recently in 1.0 M KOH.

Catalysts	**η_{10} (mV)**	**Tafel slope (mV dec^{-1})**	**Refs.**
FeNi/DCF/NC	169	98	This work
$NdBaMn_2O_{5.5}$	290	87	ACS Catal. 2018,8,364.
$Fe_{1.89}Mo_{4.11}O_7/MoO_2$	197	79	Chem. Sci. 2018, 9, 5640.
NCMC	169.5	119	Chem. Commun. 2019, 55, 6515.
SNCF-NR	232	103	Adv. Energy Mater. 2017, 7, 1602122.
$NiFeO_x$ nanoparticles	360	N/A	Nat. Commun. 2015, 6, 7261.
NiFe-oxide	197	130	ACS Appl. Mater. Inter. 2017, 9, 41906.
$NiCo_2O_4$	200	71.2	J. Catal. 2018, 357, 238.
Co_3O_4–CuO	288	65	Int. J. Hydrogen Energ. 2019, 44, 26148.
$Pr_{0.5}$BSCF	237	45	Adv. Mater. 2016, 28, 6442.
H-$MnMoO_4$	~220	36	J. Mater. Chem. A 2016, 6, 1600528.
Ni-NiO/N-rGO	260	67	Adv. Funct. Mater. 2015, 25, 5799.
$Ni_xCo_{3-x}O_4$	450	123	J. Mater. Chem. A 2016, 4, 7549.

Table S10 Summary table of level (eV).

	NC	**FeNi**	**DCF**
Work function	5.23	4.34	4.17
Bandgap	0.32	0	0
Fermi	-2.05	-0.34	-1.70
E vacuum	3.18	4	2.47