Supporting Information

Active-sites-enriched dendritic crystal Co/Fe-doped Ni_3S_2 electrocatalyst for efficient oxygen evolution reaction

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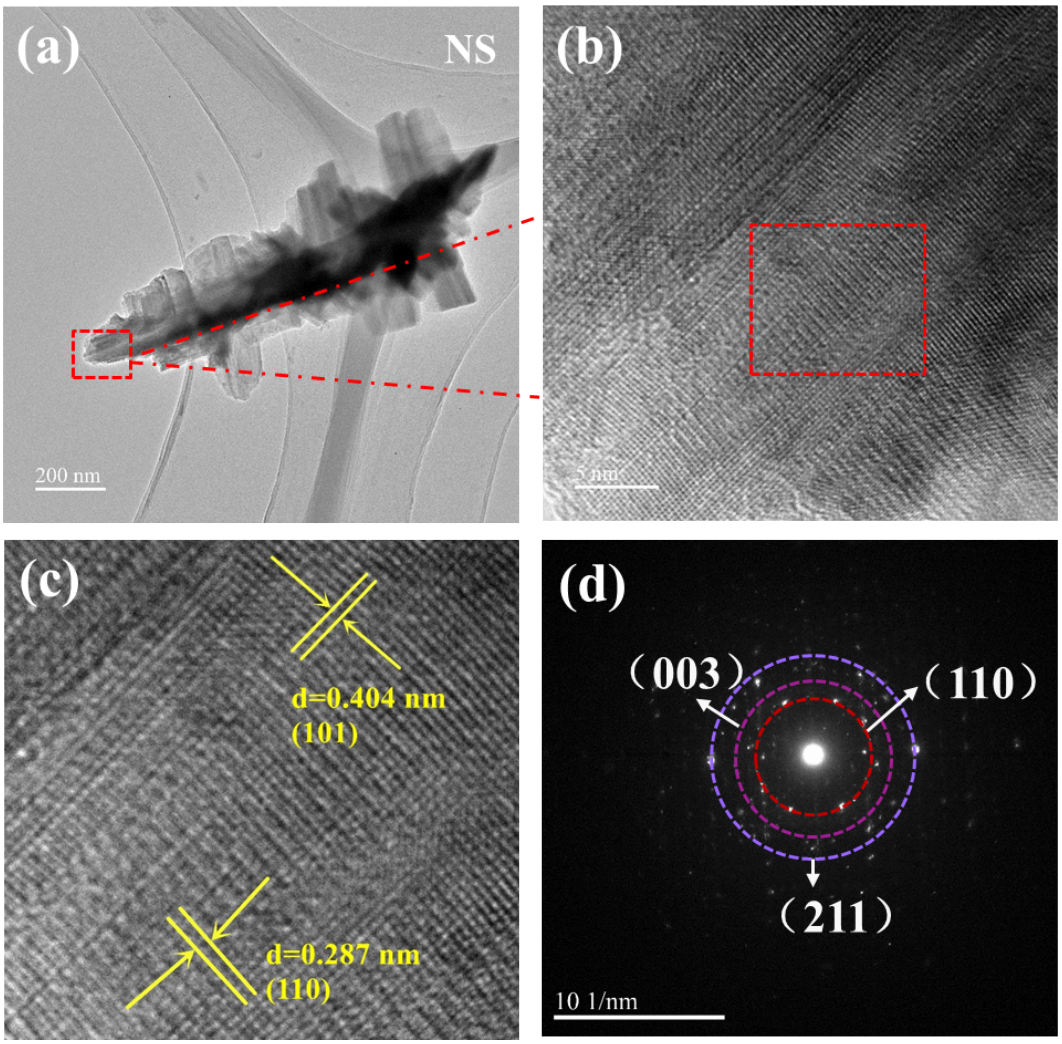

Fig. S1. (a-d) Low- and high-resolution TEM images of NS.

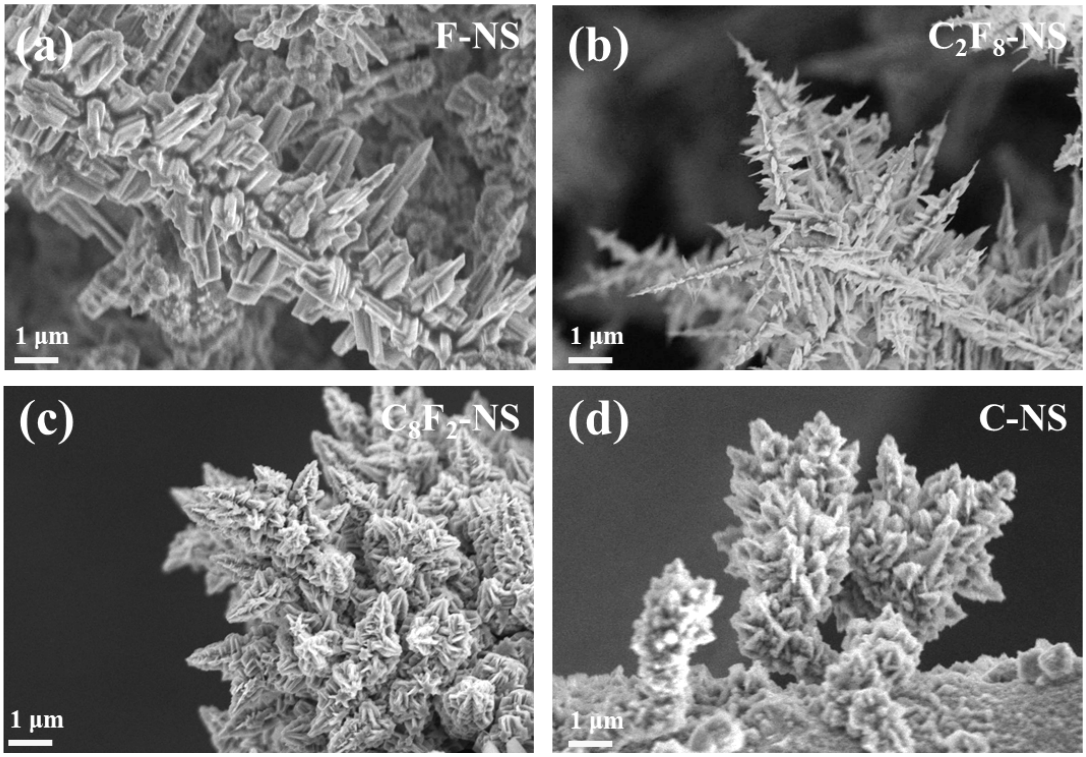

Fig. S2. (a-d) The SEM images of F-NS, C_2F_8-NS, C_8F_2-NS, and C-NS.

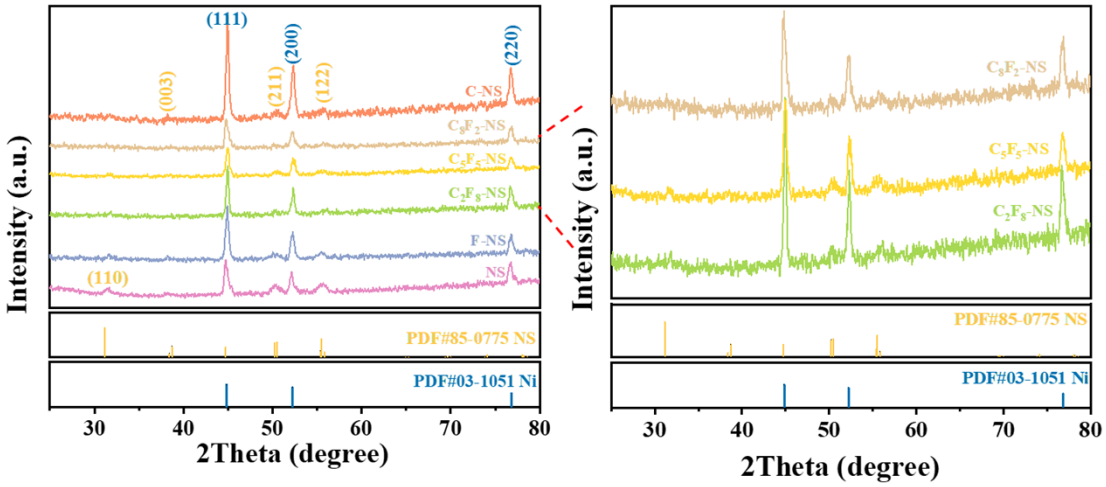

Fig. S3. XRD of NS, F-NS, C_2F_8-NS, C_5F_5-NS, C_8F_2-NS, and C-NS.

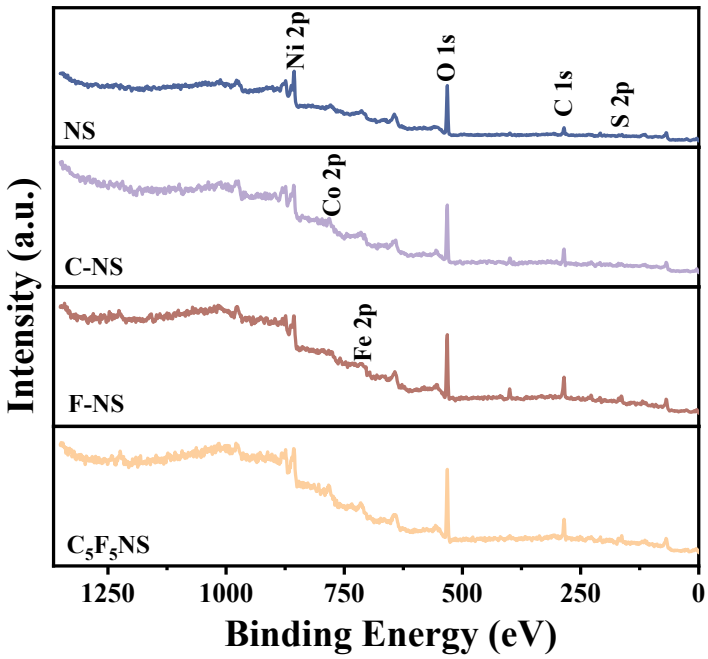

Fig. S4. XPS survey spectra of of NS, C-NS, F-NS, and C_5F_5-NS.

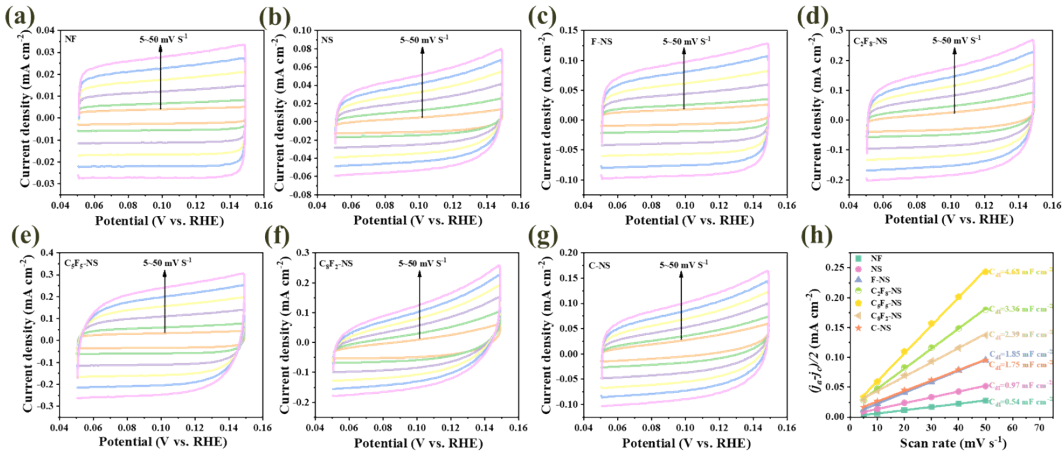

Fig. S5. (a-g) Cyclic voltammograms of NF, NS, F-NS, C_2F_8-NS, C_5F_5-NS, C_8F_2-NS, and C-NS. (h) Estimation of C_{dl} by plotting the current density variation vs. scan rate to fit a linear regression of NF, NS, F-NS, C_2F_8-NS, C_5F_5-NS, C_8F_2-NS, and C-NS.

The ECSA of the samples can be calculated by Eq. (S1) [1]:

$$ECSA = \frac{C_{dl}}{C_s} \cdot S \tag{S1}$$

where S represents the geometric area of the working electrode (in this work, S = 1 cm^2) and C_s is the specific capacitance of the sample or the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions. We used general specific capacitances of C_s = 0.040 mF cm^{-2} in 1 M KOH based on typical reported values [2].

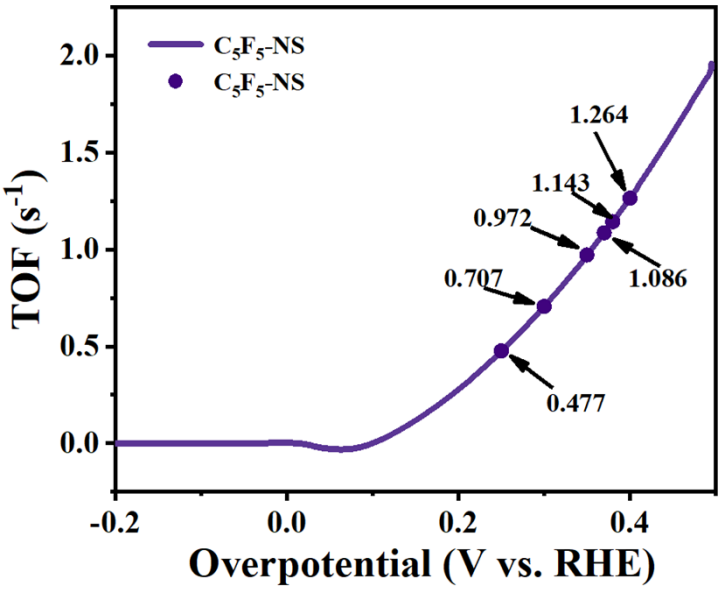

Fig. S6. The TOF values of C_5F_5-NS.

For OER, the TOF values can be obtained by Eq. (S2):

$$TOF = \frac{I}{4nF} \tag{S2}$$

where I is the current during the LSV measurement in 1 M KOH solution, F is the Faraday constant, and n is the molar number of active sites for the electrocatalyst. n was obtained in 1 M PBS solution using the CV method (the potential range was -0.2 to 0.6 V (vs. RHE) and scan rate was 50 mV/s) [3]. With a given geometric area A, the

number of active sites "n" is proportional to the charge Q, which can be calculated from the obtained CV curve by integrating. Therefore, substituting $Icv = Jcv \cdot A$ and $t = \frac{Ucv}{v}$, we derived the following Eq. (S3) [3]:

$$Q = \frac{1}{2}\int d(Icvt) = A/2v \int d(UcvIcv) = \frac{SA}{2v} \quad \text{S3}$$

Because the charge Q of surface active sites (n) can be described by $Q = nF$, therefore,

$$n = \frac{SA}{2vF} \quad \text{S4}$$

where I_{cv}, J_{cv}, U_{cv} are the current, current density, and potential obtained from CV curve, v is the scan rate (50 mV/s in this work), S is the integrated area of CV curve [3].

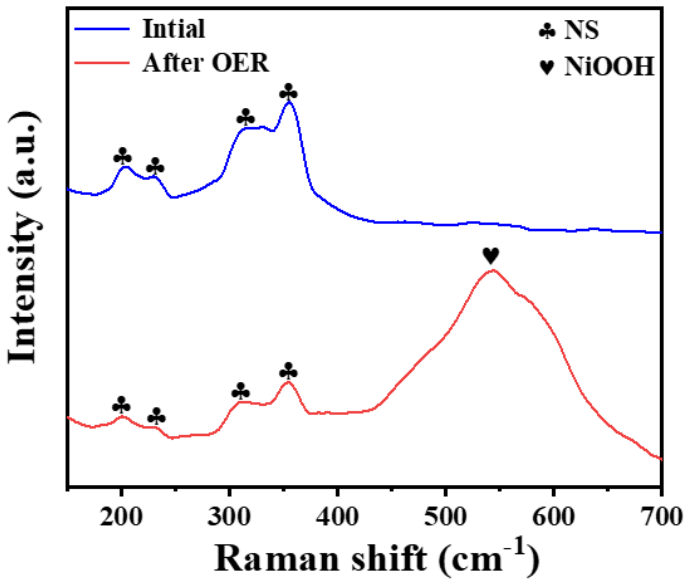

Fig. S7. Raman spectra of C_5F_5-NS before and after durability tests for OER.

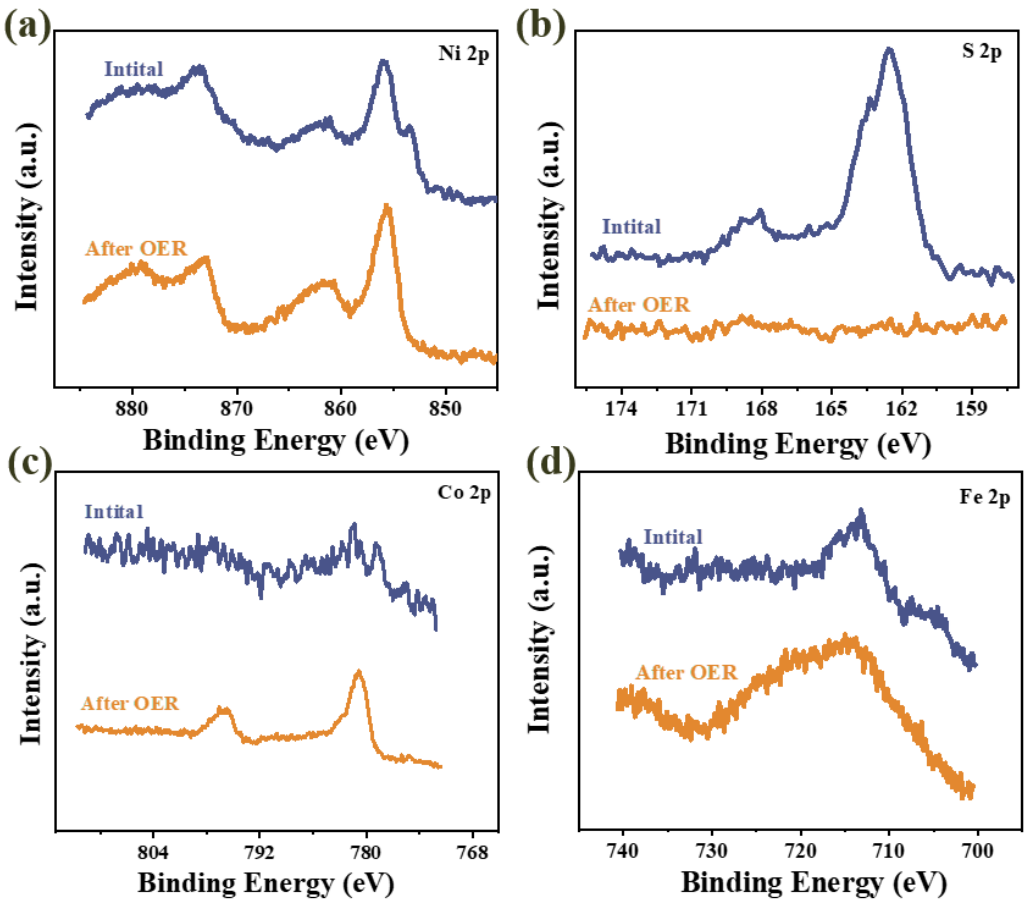

Fig. S8. (a) Ni 2p, (b) S 2p, (c) Co 2p and (d) Fe 2p high-resolution XPS spectra of C_5F_5-NS before and after durability tests for OER in the 1.0 M KOH electrolyte.

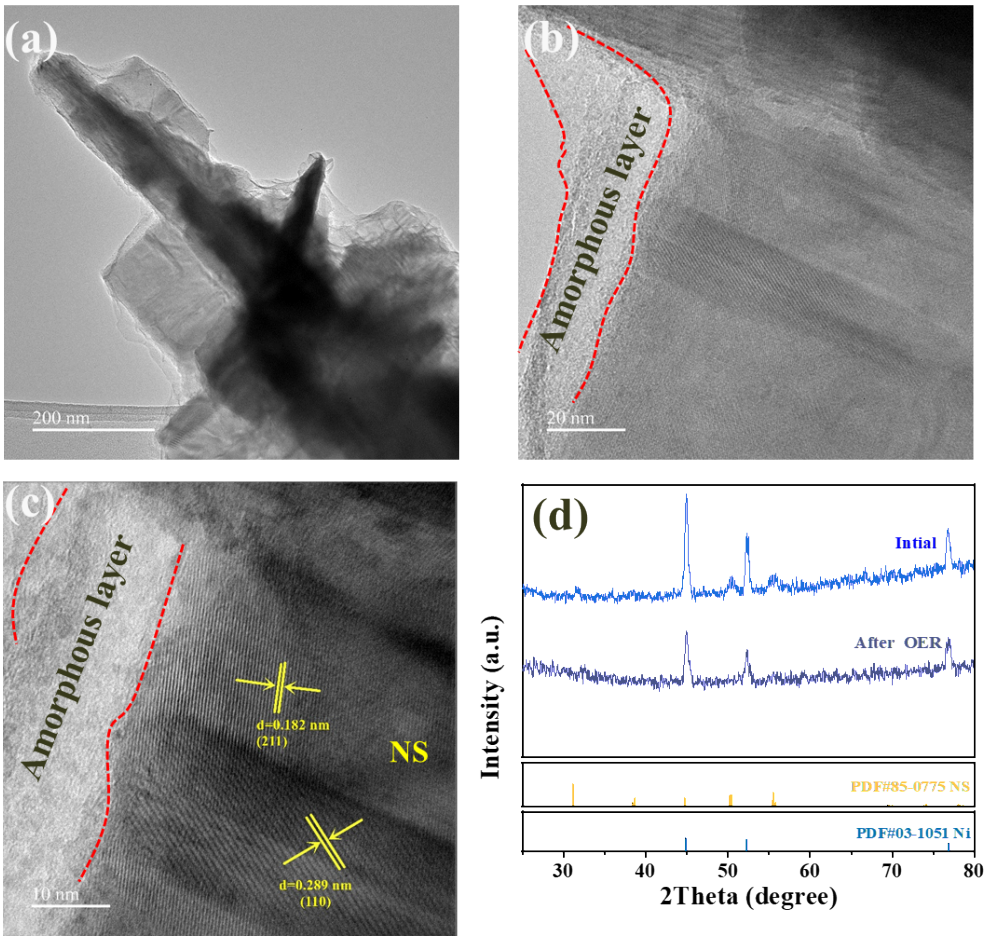

Fig. S9. (a-c) TEM images of C_5F_5-NS after durability tests and (d) XRD of C_5F_5-NS before and after durability tests for OER in the 1.0 M KOH electrolyte.

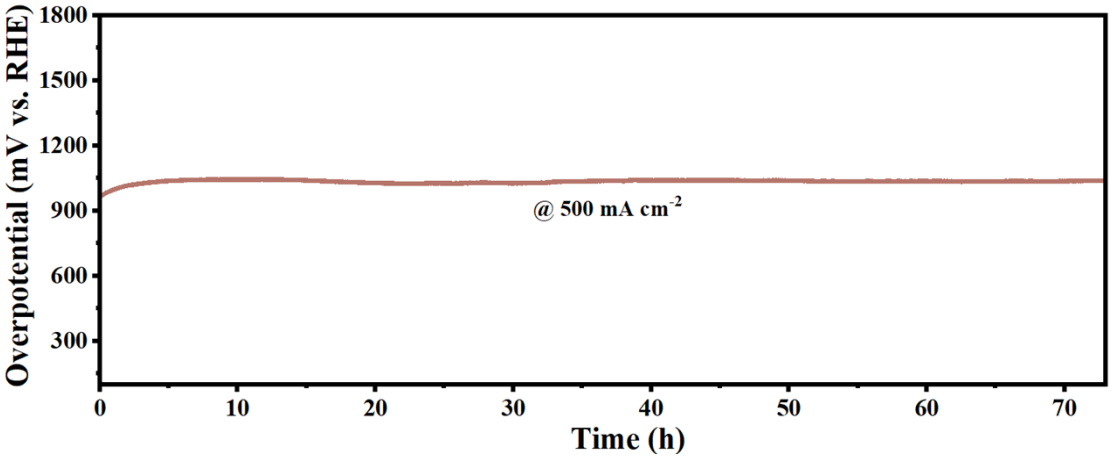

Fig. S10. The v-t curves at 500 mA cm^{-2} of C_5F_5-NS toward OER in 1.0 M KOH electrolyte.

Table S1. The element atomic content of the as-obtained electrocatalysts via ICP analysis.

Catalysts	Ni (%)	Co (%)	Fe (%)
C-NS	59	12.6	-
F-NS	58.5	-	11.8
C_2F_8-NS	58	2.76	10.6
C_5F_5-NS	58.4	6.97	6.3
C_8F_2-NS	58.1	11	2.7

Table S2. The element atomic content of Ni^{3+} in the as-obtained electrocatalysts via XPS analysis.

Element	NS (%)	C-NS (%)	F-NS (%)	C5F5-NS (%)
Ni^{3+}	36.02	38.97	44.81	47.89

Table S3. The TOF values of the as-obtained C_5F_5-NS electrocatalyst for OER in comparison with reported electrocatalysts.

Catalysts	TOF_{250} (s^{-1})	TOF_{300} (s^{-1})	TOF_{350} (s^{-1})	TOF_{370} (s^{-1})	TOF_{380} (s^{-1})	TOF_{400} (s^{-1})	References
C_5F_5-NS	**0.477**	**0.707**	**0.972**	**1.086**	**1.143**	**1.264**	**This work**
FeNi-1/2-600/Ni	0.11	-	-	-	-	-	[4]
CoCu-MOF NBs	-	0.326	-	-	-	-	[5]
NiP_c-$NiFe_x$ MOFs	-	0.194	-	-	-	-	[6]
r-CoFe	-	0.151	-	-	-	-	[7]
CoO-NiFe LDH/NF	-	-	0.590	-	-	-	[8]
$Ni_{0.81}Fe_{0.19}O$	-	0.100	0.480	-	-	-	[9]
$Co_{0.5}V_{0.5}$-COF-SO_3	-	0.098	-	-	-	-	[10]
Hollow CoP OCHs	-	0.072	-	-	-	-	[11]
CoOOH	-	0.040	-	-	-	-	[12]
Co-MnO_2/$MnCo_2O_{4.5}$	-	0.034	-	-	-	-	[13]
NiO/Fe^{trace}	-	0.030	-	-	-	-	[14]
α-$Co_4Fe(OH)_x$	-	0.027	-	-	-	-	[15]
$Co_{0.4}Fe_{0.6}$LDH/ g-CN_x	-	-	0.250	-	-	-	[16]
Pd_{180}	-	-	0.200	-	-	-	[17]
β-$Ni(OH)_2$ ultrathin nanomeshes	-	-	0.078	-	-	-	[18]
NiP nanocoatings	-	-	0.05	-	-	-	[19]
Fe-NS	-	-	0.021	-	-	-	[20]
{($Ni(L_1)(TA)(H_2O)_2$)·2 H_2O}$_n$	-	-	-	0.600	-	-	[21]
$Cr_{0.2}Co_{1.8}P$/CB	-	-	-	0.585	-	-	[22]
Co QD/rGO	-	-	-	0.181	-	-	[23]
CoNi hydroxide UNSs	-	-	-	-	0.160	-	[24]
MWCNT-bpyRutpy	-	-	-	-	-	0.583	[25]
$Co_3O_{3.87}F_{0.13}$	-	-	-	-	-	0.042	[26]
EK-b	-	-	-	-	-	0.012	[27]

Note: TOF_x (x = 250, 300, 350, 370, 380 and 400) represents the TOF at x mV.

Table S4. The OER activity of the as-obtained C_5F_5-NS electrocatalyst in comparison with reported electrocatalysts.

Catalysts	η_{10} (mV)	Tafel slope (mV dec^{-1})	Stability (h)	References
C_5F_5-NS	**146**	**26**	**86**	**This work**
NiS/G	300	55.8	72	[28]
FeNi-1/2-600/Ni	200	30	20	[4]
FeS_2/C	291	65.6	15	[29]
Ni-P alloys	335	70	12	[19]
NF@NiMoCo	277	87.0	24	[30]
EK-b	378	60	12	[27]
Co_9S_8/NOSC-900	340	68.0	10	[31]
O-doped Co_2P/CuO NWs/CF	270	74.4	30	[32]
Ni_3S_2/Ni	310	80.1	30	[33]
Ni_3S_2 films	400	51.0	24	[34]
Ni_3S_2/NF	296	65.1	50	[35]
ANF/NW	382	103.0	20	[36]
MoS_2/NiS_2	278	91.7	24	[37]
$ZnCo_2S_4$	278	64.3	25	[38]
MoS_2/NiS	350	108.0	24	[39]
Co-NC/Mo_2C	347	61.0	20	[40]
$Ni_{12}P_5/Ni_3(PO_4)_2$	318	51.7	10	[41]
Fe_7S_8	270	43.0	24	[42]
NiVB/rGO	267	44.0	12	[43]
6-FP-Co-OMC-1	355	67	11	[44]
$Co_2P@Co_3O_4$	335	60.0	8	[45]

Note: η_{10} represents the overpotential at 10 mA cm^{-2}.

Table S5. The mass activities of the as-obtained electrocatalysts for OER.

Catalysts	Electrolyte	η_{10} (mV)	Mass activities (mA mg^{-1})
NS	1.0 M KOH	333	0.94 (η = 0.27 V)
F-NS	1.0 M KOH	244	7.72 (η = 0.27 V)
C_2F_8-NS	1.0 M KOH	181	18.48 (η = 0.27 V)
C_5F_5-NS	**1.0 M KOH**	**146**	**21.79 (η = 0.27 V)**
C_8F_2-NS	1.0 M KOH	216	8.61 (η = 0.27 V)
C-NS	1.0 M KOH	257	4.92 (η = 0.27 V)

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