Supporting information

Hierarchical NiS$_x$/Ni$_2$P Nanotube Arrays with Abundant Interfaces for Efficient Electrocatalytic Oxidation of 5-Hydroxymethylfurfural

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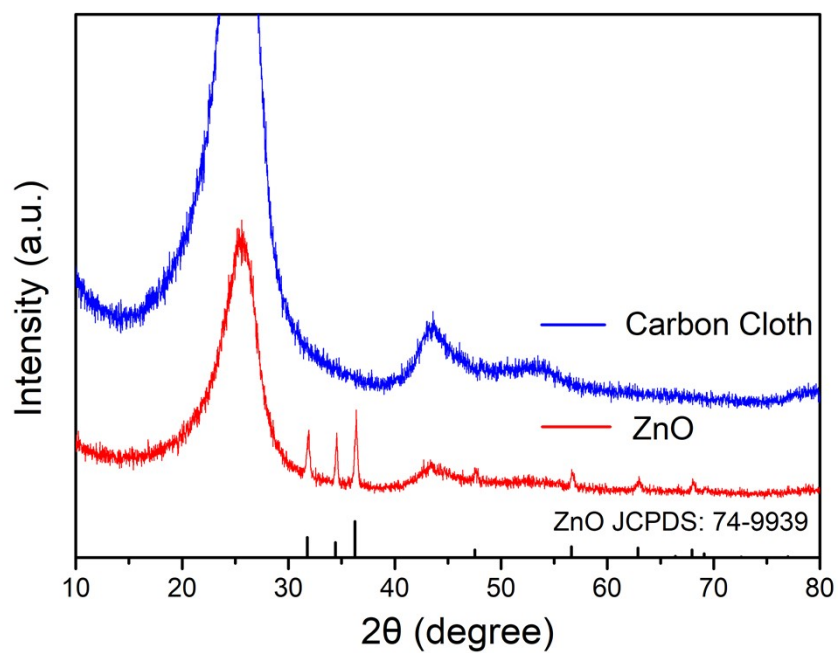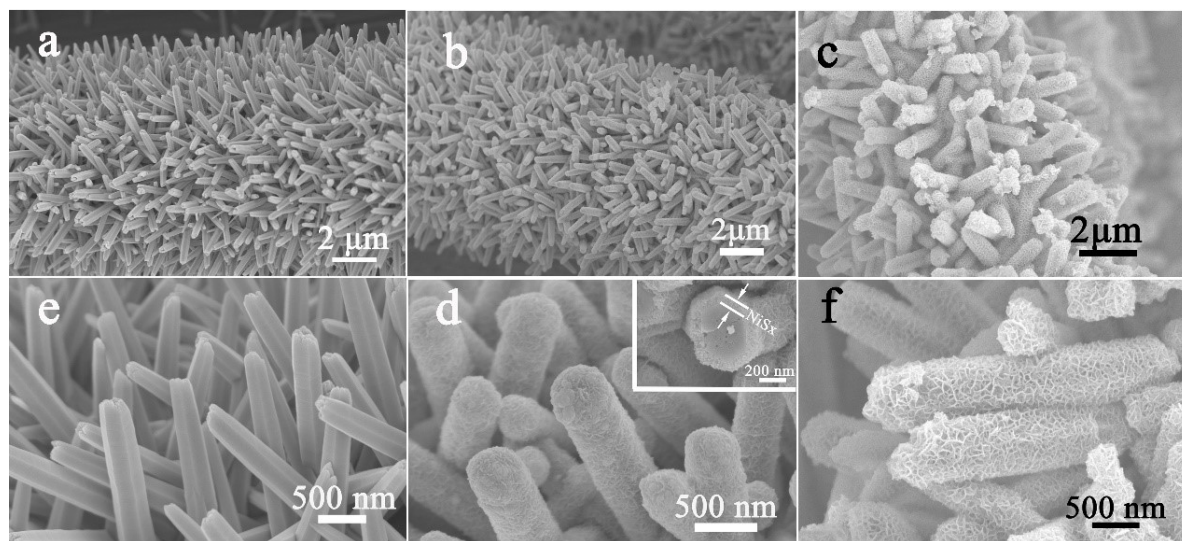
Fig. S1. The XRD pattern of ZnO and carbon cloth.

Fig. S2. SEM images of ZnO (a, e), ZnO/NiS$_x$ (b, d), ZnO/NiS$_x$/Ni(OH)$_2$ (c, f) with different magnification.
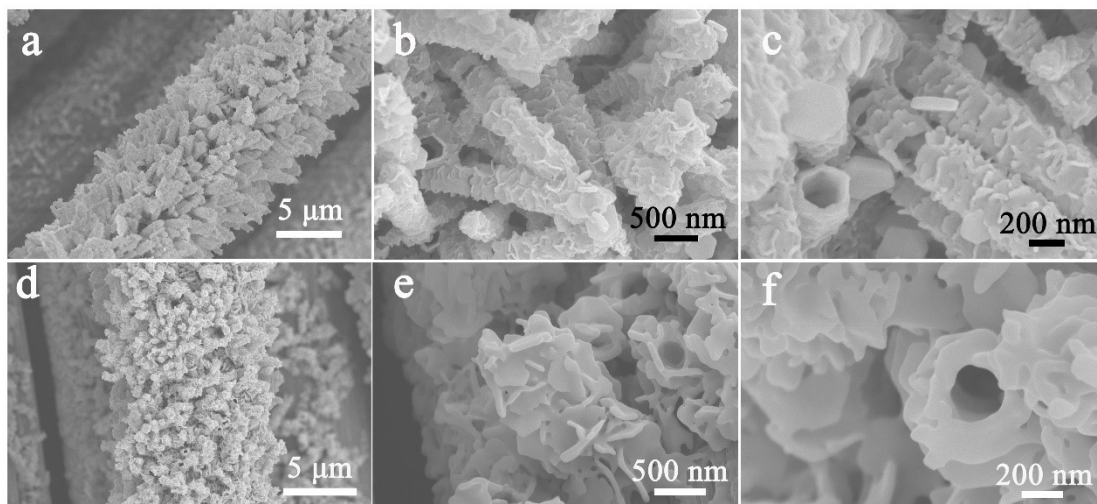
Fig. S3. SEM images of CoS_x/CoP (a, b, c) and FeS_x/FeP (d, e, f) with different magnification.
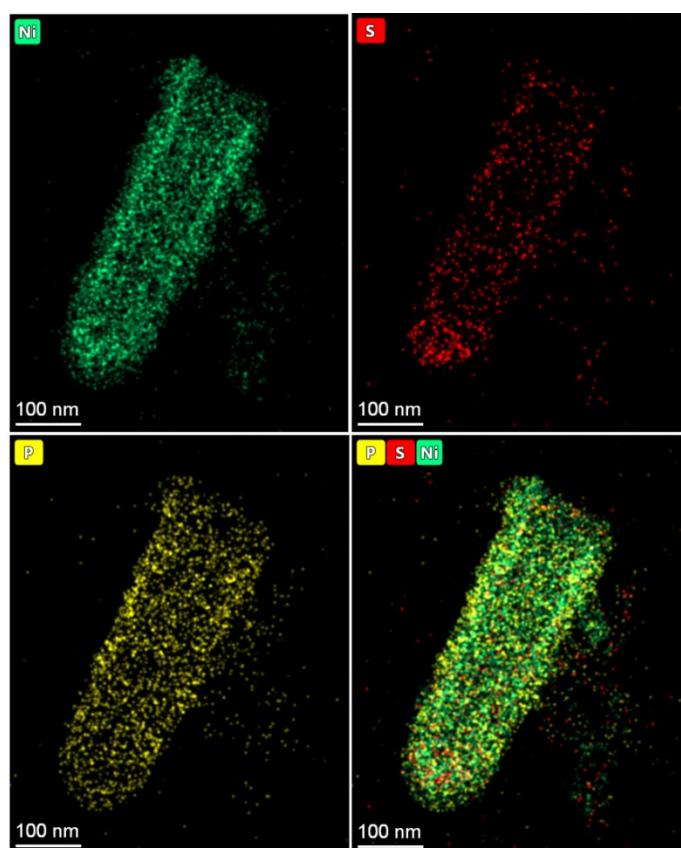

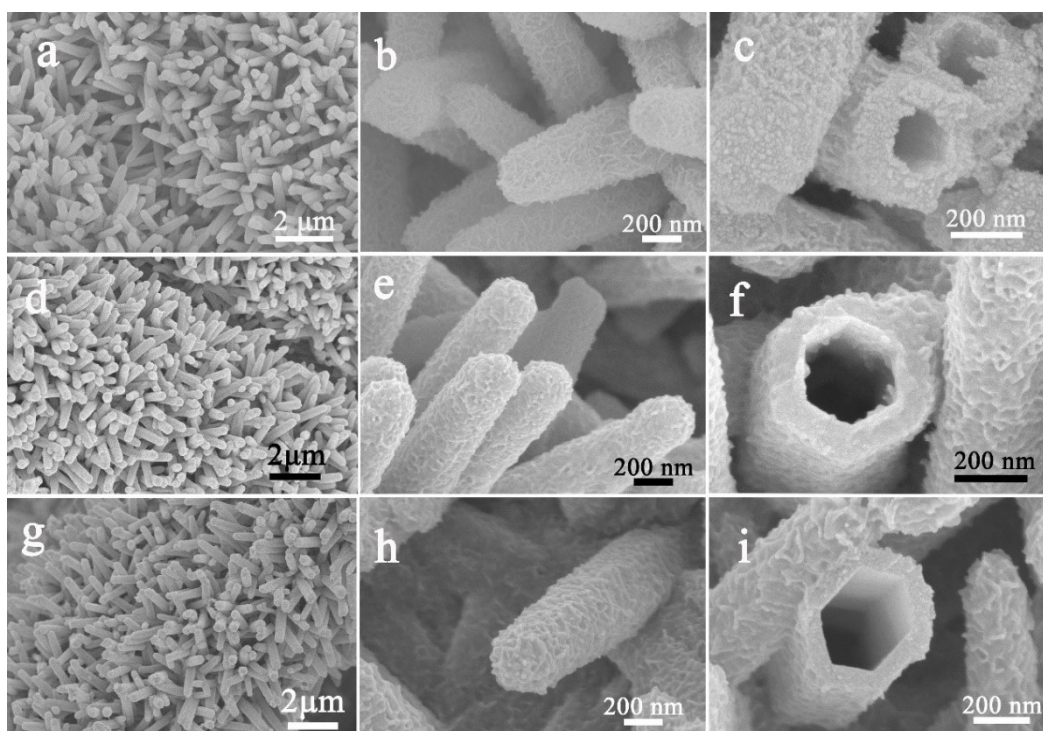**Fig. S4.** STEM-EDS elemental mapping images of SNP-2.

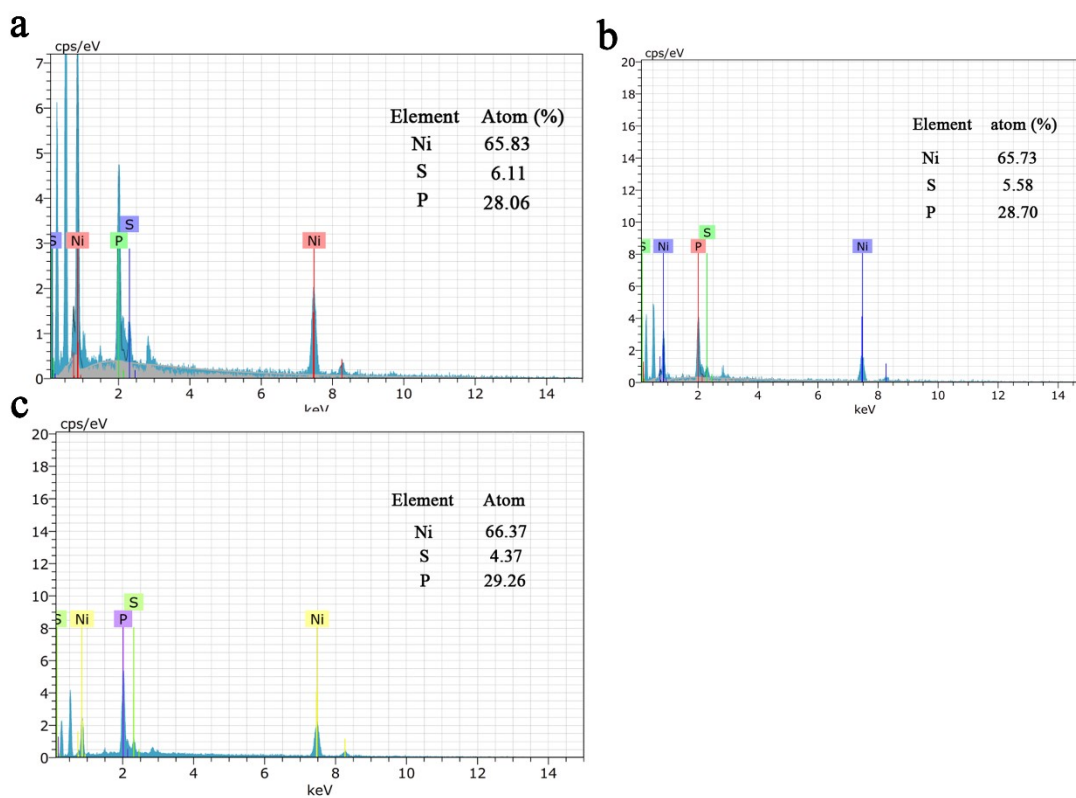**Fig. S5.** SEM images of NiS$_x$ (a, b, c), SNP-1 (d, e, f) and SNP-3 (g, h, i) with different magnification.

Element	Atom (%)
Ni	65.83
S	6.11
P	28.06

Element	atom (%)
Ni	65.73
S	5.58
P	28.70

Element	Atom
Ni	66.37
S	4.37
P	29.26

Fig. S6. EDS quantitative analysis of SNP-1, SNP-2 (b) and SNP-3 (c).

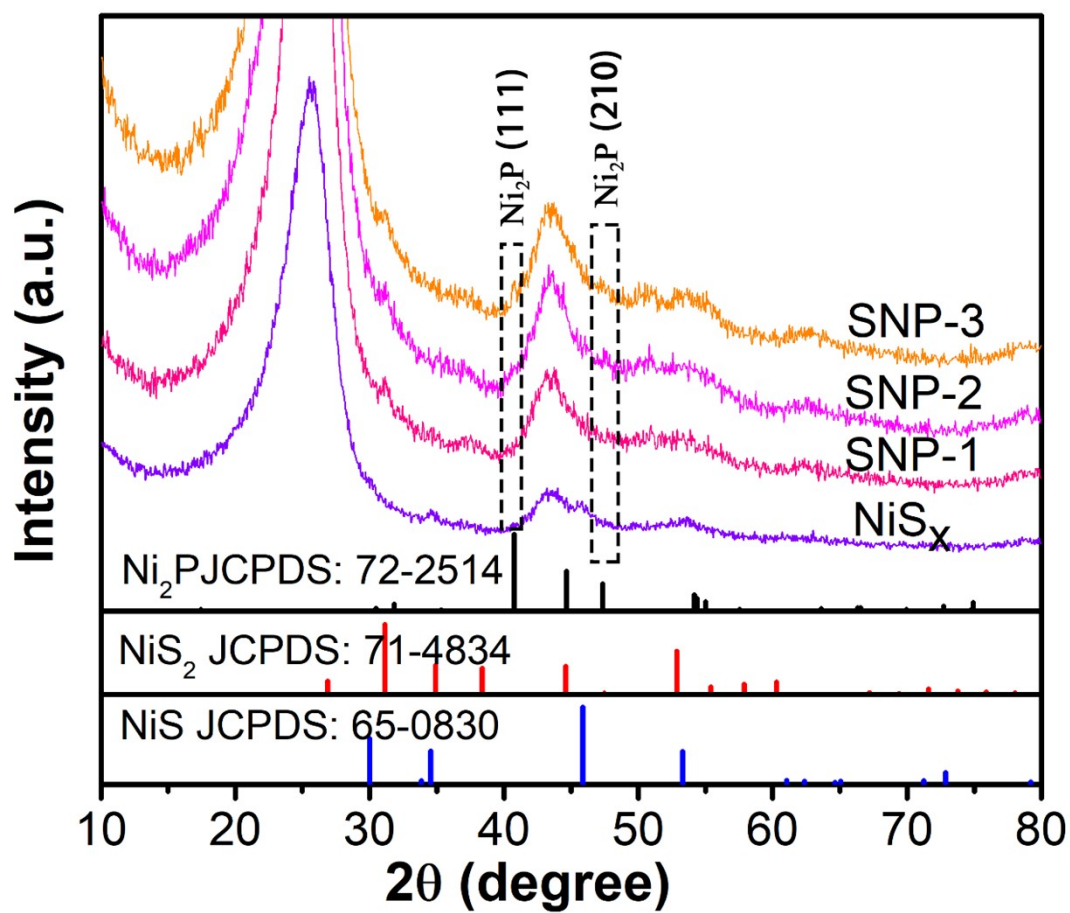**Fig. S7.** The XRD patterns of NiS_x and NiS_x/Ni_2P hybrid materials.
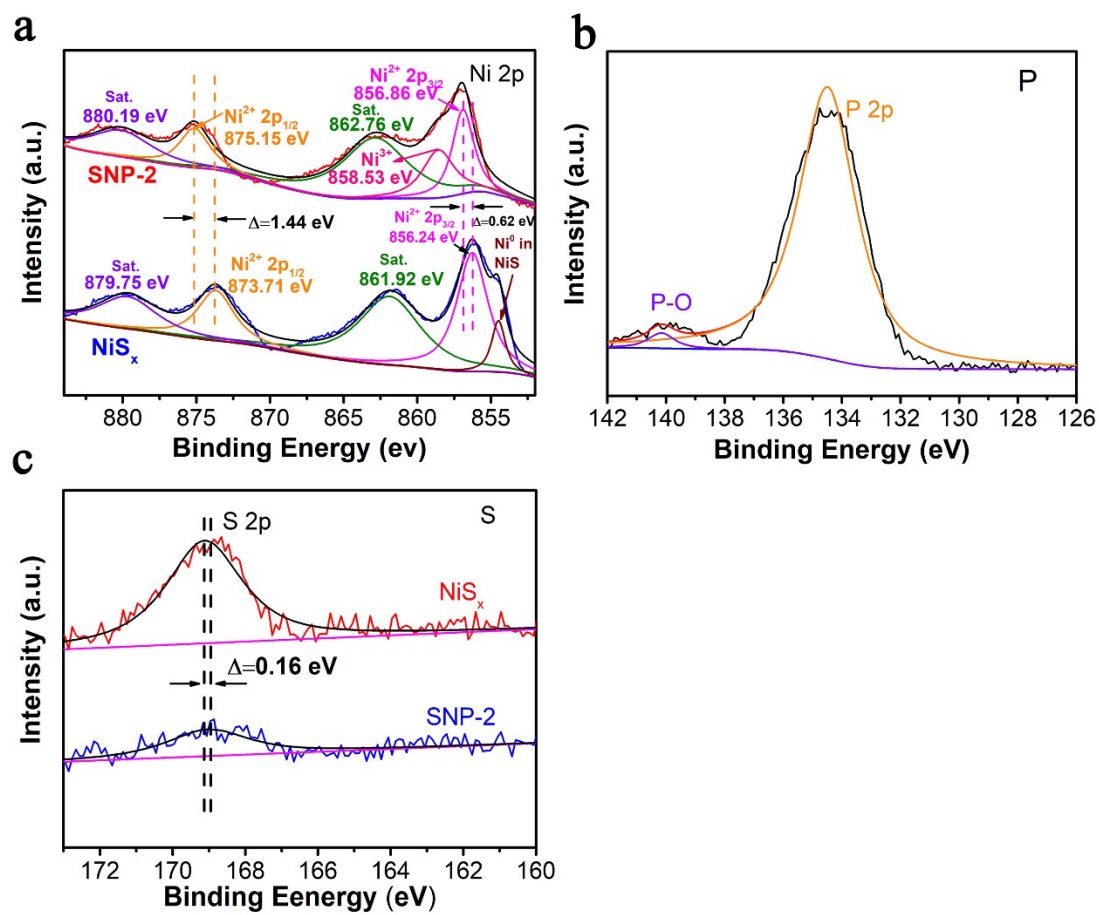
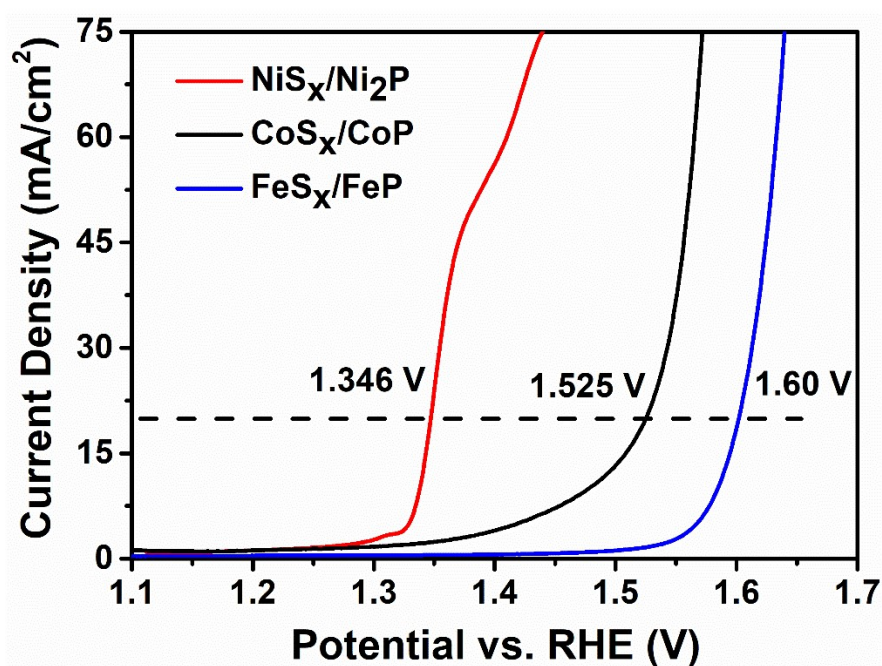**Fig. S8.** XPS spectrums of SNP-2 about Ni 2p (a), P 2p (b) and S 2p (c)

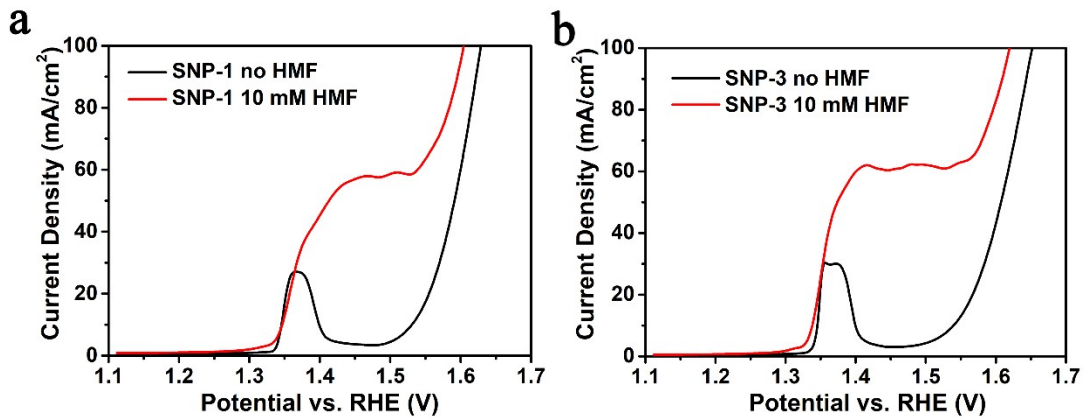**Fig. S9.** LSV curves of SNP-2, CoSx/CoP and FeSx/FeP in 1 M KOH with 10 mM HMF.

Fig. S10. LSV curves of SNP-1 (a) and SNP-3 (b) in 1 M KOH with/without HMF.
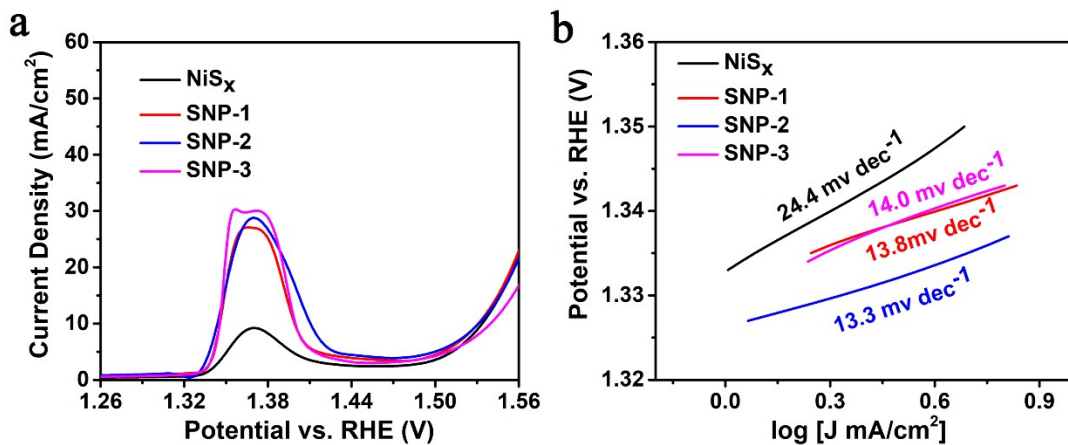

Fig. S11 LSV curves of different catalysts in 1.0 M KOH electrolyte and Tafel slopes of derived from LSVs
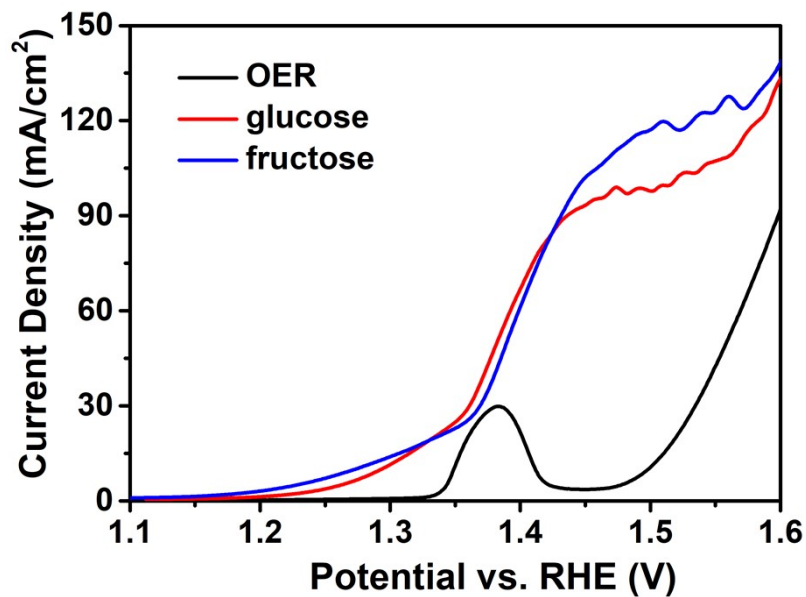
Fig. S12. LSV curves of SNP-2 in 1.0 M KOH electrolyte with 10 mM glucose (red line) and 10 mM fructose (blue line).
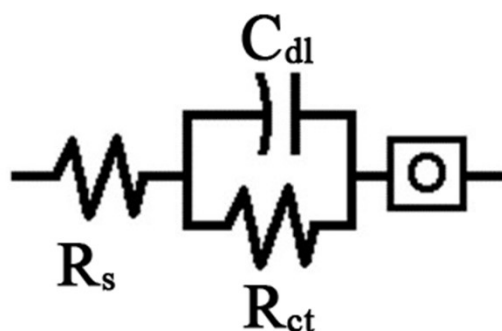
Fig. S13. Equivalent circuit applied to analyze the electrochemical impedance spectroscopy

Rs stands for the solution resistance, C_{dl} represents double layer capacitance, R_{ct} has contact with the interfacial charge transfer reaction, O stands for finite layer diffusion impedance of a planar electrode.
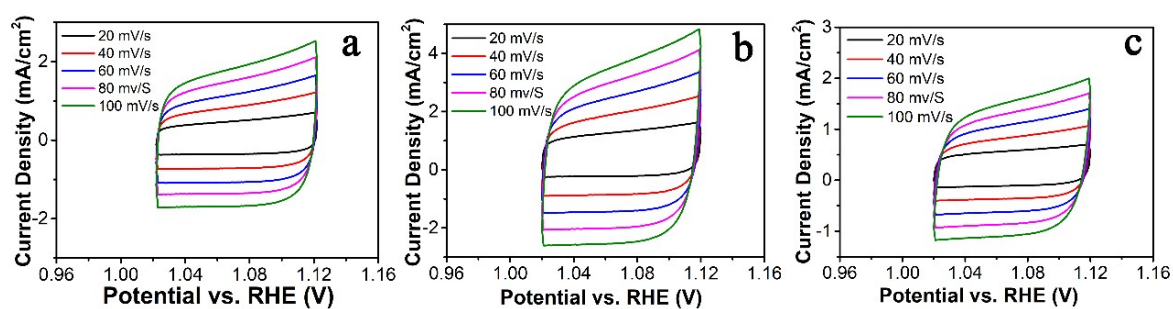
Fig. S14. The polarization curves of NiS_x (a), SNP-2 (b) in 1 M KOH with 10 mM HMF and without HMF (c) at different scan rates from 20 to 100 mV/s.
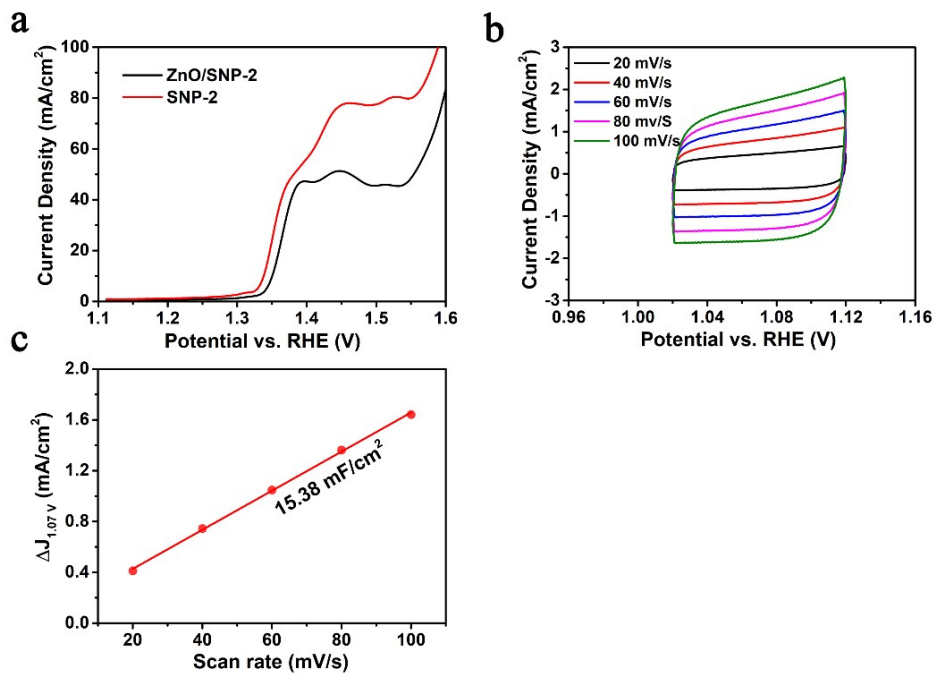
Fig. S15. (a) LSV curves of SNP-2 and ZnO/SNP-2 in 1 M KOH with10 mM HMF. (b) The polarization curves of ZnO/SNP-2 in 1 M KOH with 10 mM HMF at different scan rates from 20 to 100 mV/s. (c) Change of current density plotted against for the scan rate at 1.07 V vs RHE for ZnO/SNP-2.
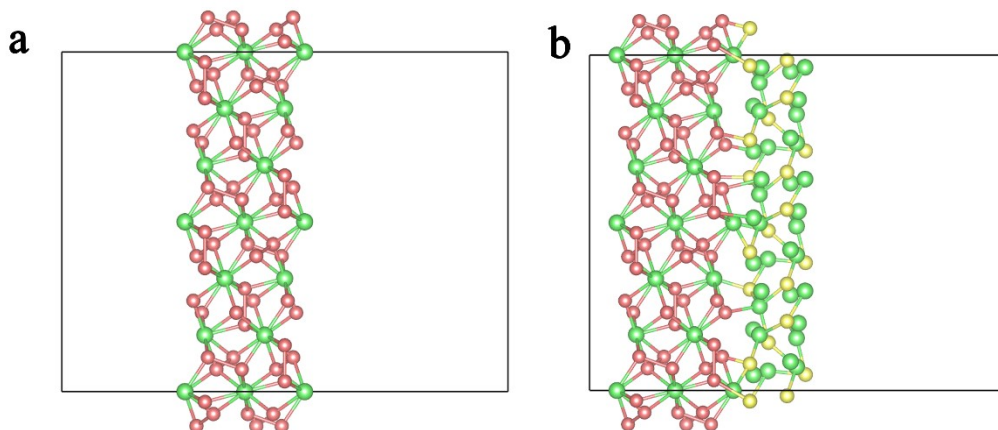
Fig. S16. a) The side view of NiS$_2$ (211) (Ni atom in green, S atom in red). b) The side view of the SNP-2 (Ni atom in green, S atom in red, P atom in yellow).
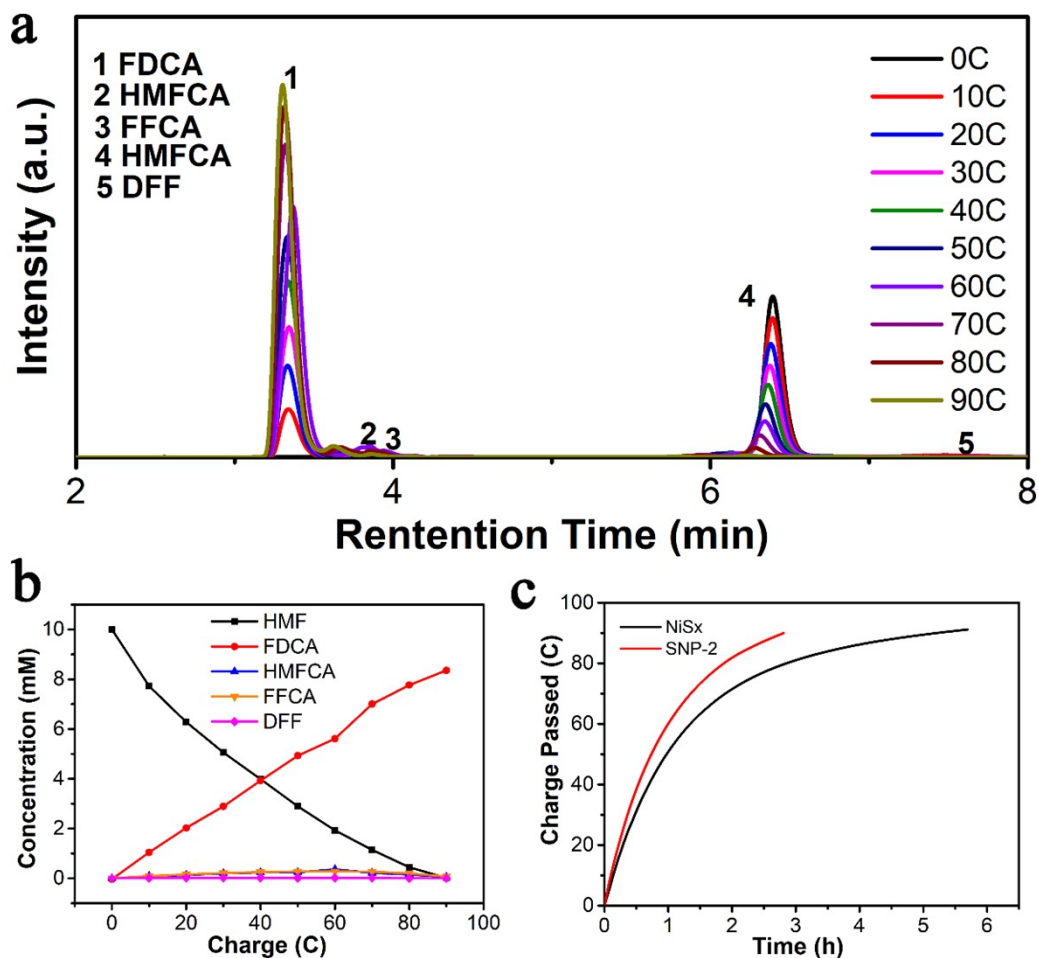
Fig. S17. HPLC traces of electrolysis of HMF oxidation catalyzed by NiS_x at 1.46 V vs RHE in 15 mL, 1 M KOH with 10 mM HMF. b) Conversion or yield of HMF and its oxidation products catalyzed by NiS_x during electrolysis. c) charge-time transients of NiS_x and SNP-2 during the electrochemical oxidation of HMF.
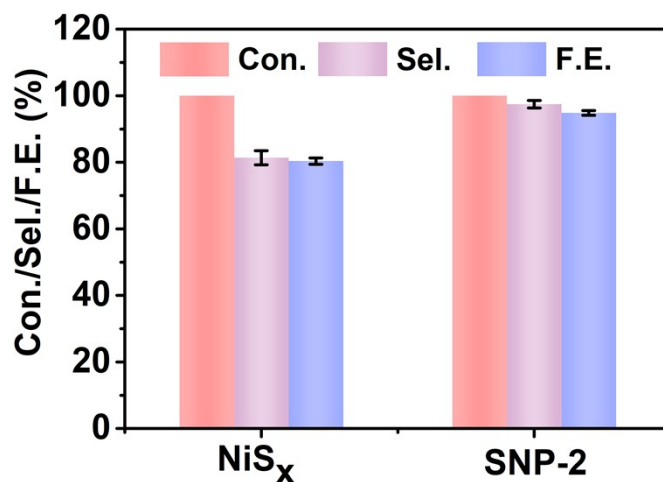
Fig. S18. Comparation of the conversion efficiency, yield and FE between SNP-2 and NiS_x.
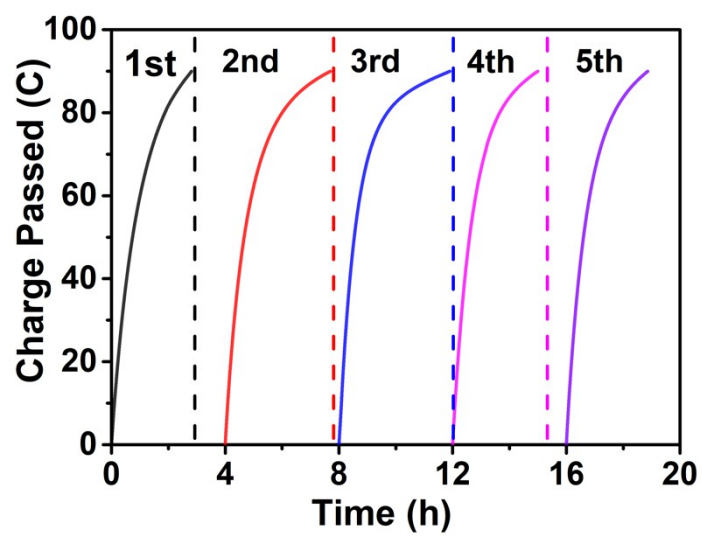
Fig. S19. charge-time transients during the electrochemical oxidation of HMF.
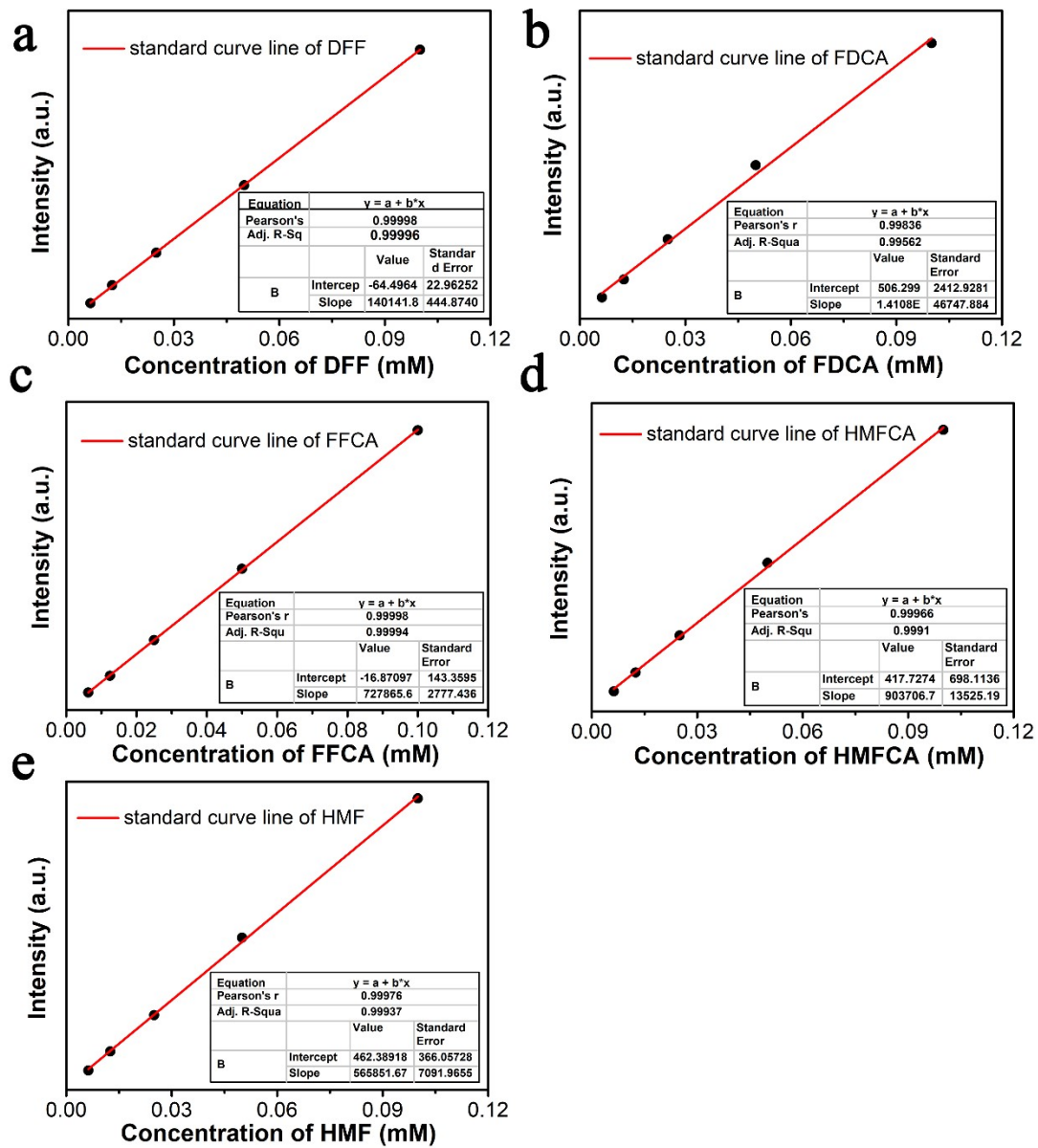
Fig. S20. Calibration of the HPLC for DFF (a), FDCA (b), FFCA (c), HMFCA (d), HMF (e).
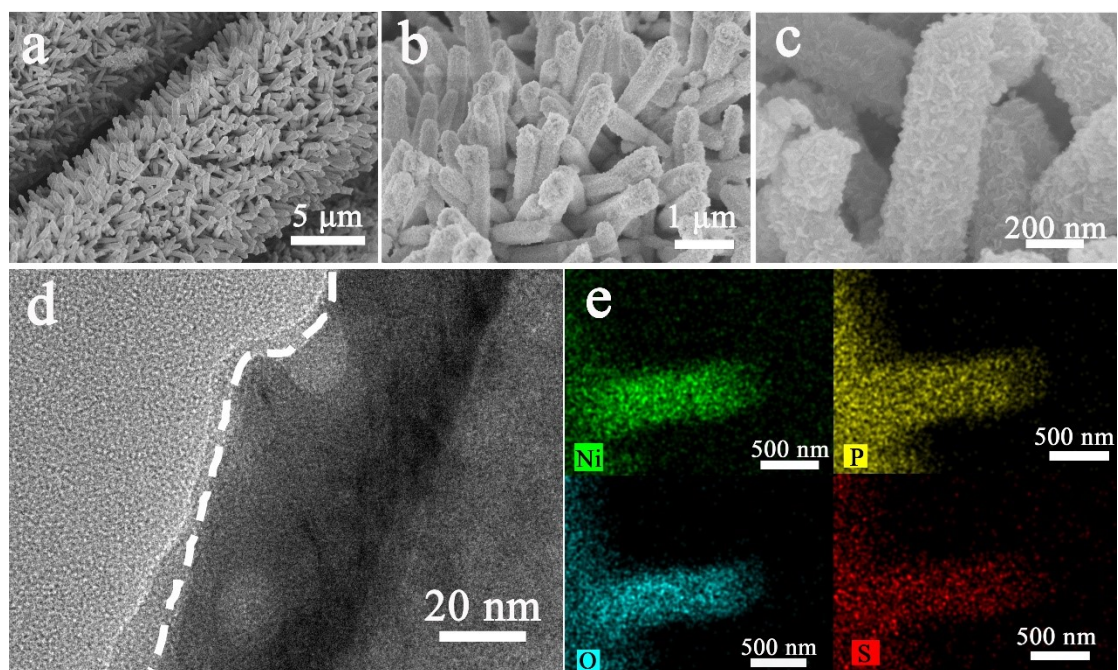
Fig. S21. SEM images of post-SNP-2 (a, b, c) with different magnification. d) TEM images of post-SNP-2. e) EDX elemental mapping of post-SNP-2.
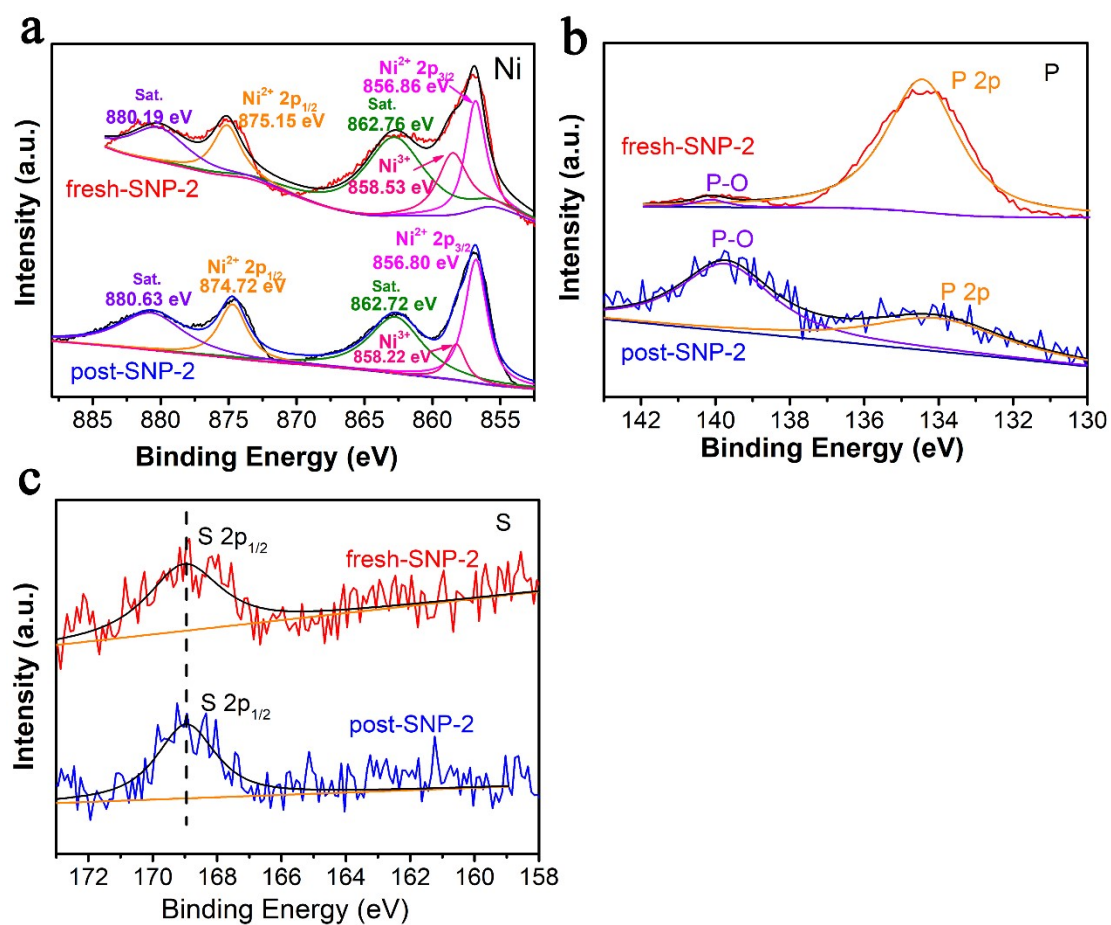
Fig. S22. XPS spectrums of Ni 2p, P 2p and S 2p of pos-SNP-2 and fresh-SNP-2.

Table S1. The proposed equivalent circuit

Samples	NiS_x	SNP-2	SNP-2
Electrolyte	1.0 M KOH + 50 mM HMF	1.0 M KOH + 50 mM HMF	1.0 M KOH
R_s	1.649	1.681	1.658
C_{dl}	0.0045	0.2845	0.7335
R_{ct}	4.21	2.9	58.88
O	1.23	0.8193	7.363

Table S2. The calculated charge values (Q, q) in the case of HMF adsorbing on NiS_x and SNP-2 surfaces, respectively.

| Samples	Q (Ni)	Q (S)	Q (P)	Q (HMF)
NiS_x	-14.45	14.38	0	0.065
SNP-2	-18.96	14.69	4.18	0.081

Table S3. HMF electrocatalytic performance of non-noble metal catalysts.

Catalyst	E_{onset} (V vs. RHE)	$E_{j = 20\ mA/cm2}$ (V	FDCA	Ref.
NiS_x/Ni_2P	1.25	1.346	98.5	This work
Ni_3S_2/NF	~1.35	~1.36	98.0	1
Ni_2P NPA/NF	~1.35	~1.37	100.0	2
$NiP-Al_2O_3/NF$	~1.38	~1.41	99.6	3
Ni_xB	~1.38	~1.41	98.5	4
Ni_3N/C	1.25	1.36	98	5
NiCoBDC-NF	~1.38	~1.60	99.0	6
$Ni(OH)_2/NF$	~1.25	1.33	96.0	7
$NiSe@NiO_x$	~1.25	1.35	99.0	8

om-Co$_3$O$_4$	1.30	~1.45	>99.8	9
NiCo$_2$O$_4$	~1.23	>1.6	90.8	10
CoO-CoSe	1.30	1.38	99.0	11
CuNi(OH)$_2$/C	1.38	1.75	93.0	12
VN	1.34	1.37	96.0	13
MoO$_2$/FeP	1.35	1.38	98.6	14
NiFe LDH	1.25	1.32	98.0	15
NiCoFe LDH	1.23	1.51	84.9	16
Ni(NS)/CC	1.25	1.47	>99.0	17
t-Ni1Co1-MOF	1.25	1.28	100.0	18
Pt/Ni(OH)$_2$	1.36	1.42	98.7	19

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