Supporting Information

Coupled W-Co_2P Hybrid Nanosheets as Robust Bifunctional Electrocatalyst for Hydrazine-Assisted Hydrogen Production

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Experimental Section

Materials: Hydrochloric acid (HCl, AR) is purchased from Country shuanglin chemical, Potassium hydroxide (KOH, AR), Sodium hypophosphite monohydrate ($NaHPO_2$, AR), Absolute ethanol (C_2H_5OH, 99.7%), Cobalt nitrate (II) hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, 98%) and Ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$, 98%) are purchased from Aladdin.

Synthesis of W@Co_2P/NF, Co_2P/NF and W/NF electrodes: In a typical synthesis process, NF (2 × 4 cm) is treated by ultrasonic cleaning in acetone, water and 3.0 M hydrochloric acid for 10 min, respectively. Then 40 ml of aqueous solution containing ($Co(NO_3)_2{\cdot}6H_2O$, 0.1 M), Ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$, 1.3 mM) and ($NaH_2PO_2{\cdot}H_2O$, 1 M) is prepared, and then 10 mL of 1 M HCl or 0.5 M H_2SO_4 is added to above solution. The NF (2 cm×1 cm) is used working electrode and immersed into 50 mL of the prepared aqueous solution. Platinum foil and saturated calomel electrode are used as counter electrode and reference electrode, respectively. The electrodeposition process is carried out at a constant voltage of -2 V for 10 minutes, then the electrodes are washed by ethanol/water mixture for three times and dried in vacuum oven. The simple W/NF and Co_2P/NF electrodes are prepared by a similar electrodeposition method by only using $(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ as solutions, respectively. In addition, the other W sources (Na_2WO_4, WCl_3, $(NH_4)_6W_7O_{24}$) are also used to prepare the W@Co_2P/NF electrodes.

Material Characterizations: The powder X-ray diffraction (PXRD) is conducted on a DX-2700 diffractometer (Dandong Haoyuan Instrument Co. Ltd. China) to analyze the phase compositions and crystal structure of catalysts. The surface morphology and composition are studied by applying a scanning electron microscope (SEM, Hitachi SU8I00) and high-resolution transmission electron microscopy (HRTEM). The X-ray photoelectron spectroscopy (XPS) is carried out on a PHI5300 instrument with monochromatic Mg Kα as the source of radiation to confirm the chemical states of elements in the samples.

Electrochemical measurements: Electrochemical measurements are performed by an electrochemical workstation (CHI660E, Chenhua Instrument, Shanghai, China) using a three-electrode configuration. The self-supported materials are used as working electrodes, while the counting electrode is a graphite rod electrode and the reference electrode is a saturated calomel electrode. Linear sweep voltammetry (LSV, scan rate of 5 mV s^{-1}) is collected to analyze the HER and OER performance in a 1.0 M KOH electrolyte, while the HzOR performance is recorded in 1.0 M KOH with 0.4 M N_2H_4

electrolyte. All the results are converted into the potential of the reversible hydrogen electrode according to the following equation: $E_{(vs.RHE)} = E_{(vs.Hg/HgCl_2)} + E^{o}_{(Hg/HgCl_2)}$ (0.241 V) + 0.059·pH. The electrochemical impedance spectroscopy (EIS) measurements is measured under an AC voltage model at a fixed overpotential in a frequency range of (10^{-2}-10^{5} Hz). The electrochemical double-layer capacitance (C_{dl}) is recorded by CV curves with the scanning rate of 20, 40, 60, 80, and 100 mV s^{-1}. All the data are presented after IR-correction.

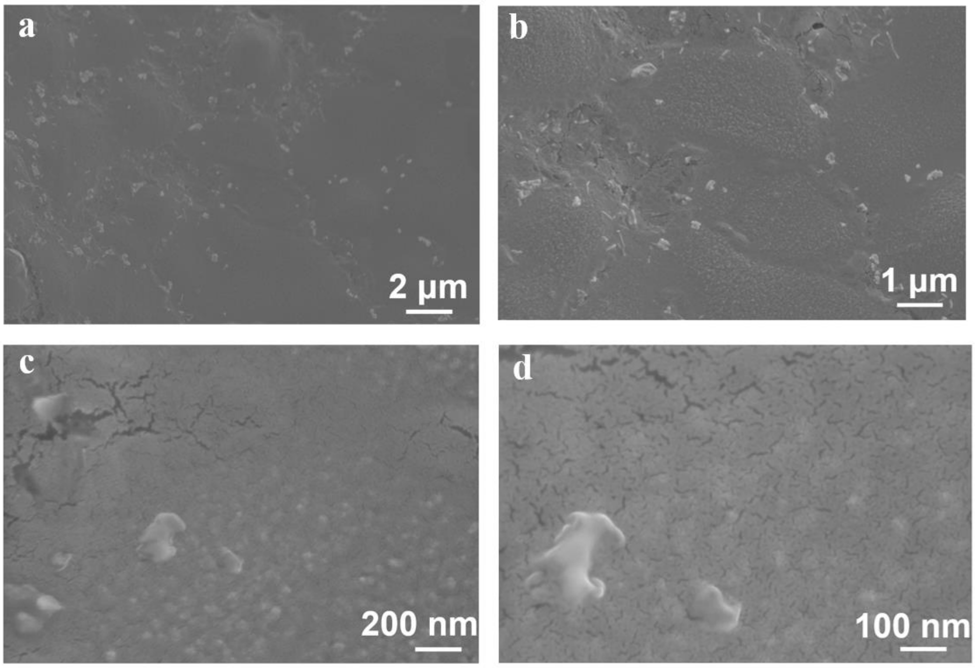

Figure S1 (a-b) SEM images of Co_2P/NF sample.

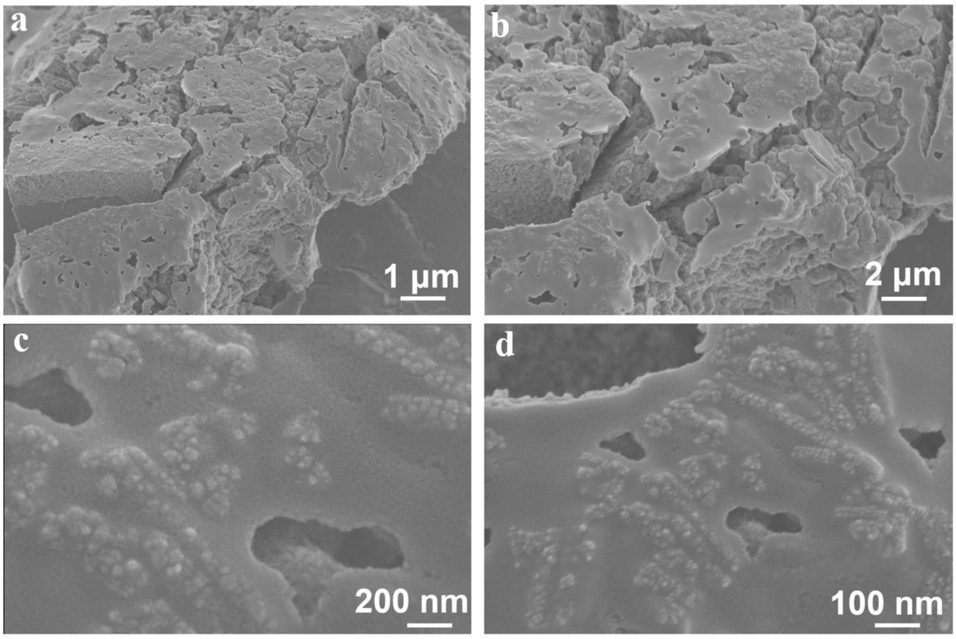

Figure S2 SEM images of W/NF sample.

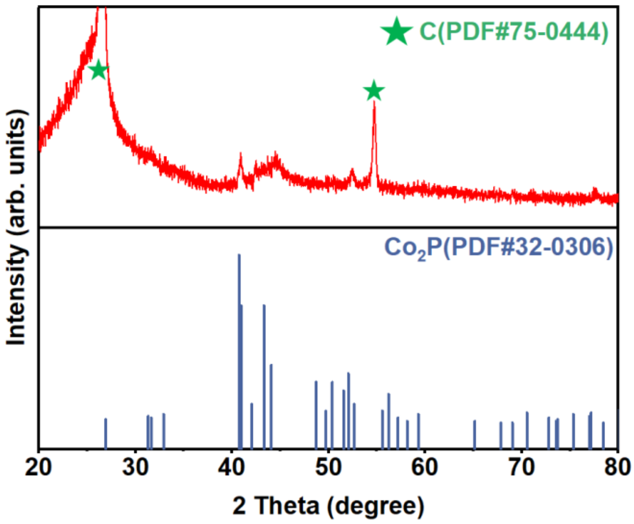

Figure S3 The XRD pattern of Co_2P/NF sample.

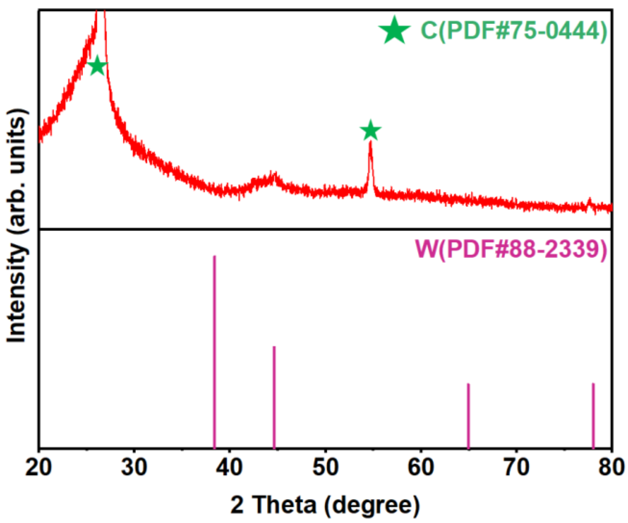

Figure S4 The XRD pattern of W/NF sample.

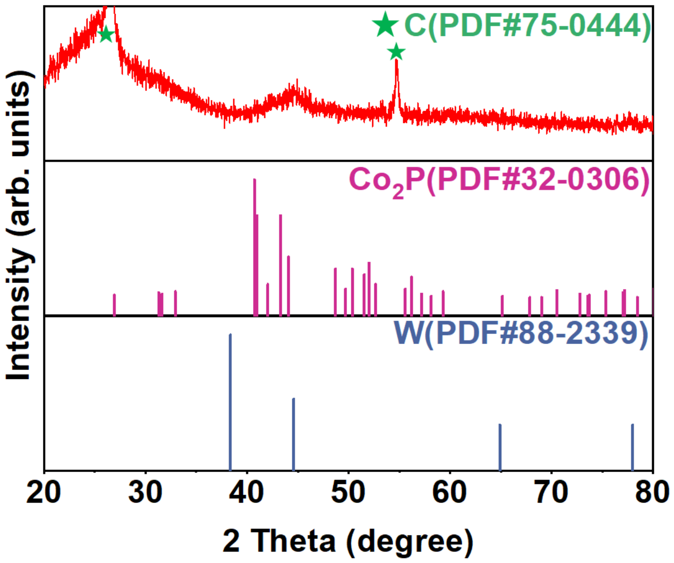

Figure S5 The XRD pattern of W@Co_2P/NF sample.

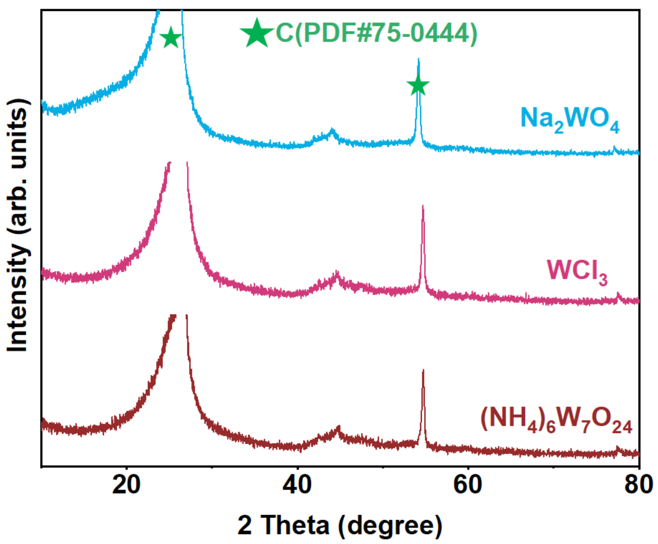

Figure S6 The XRD patterns of different W@Co_2P/NF samples by using different W sources.

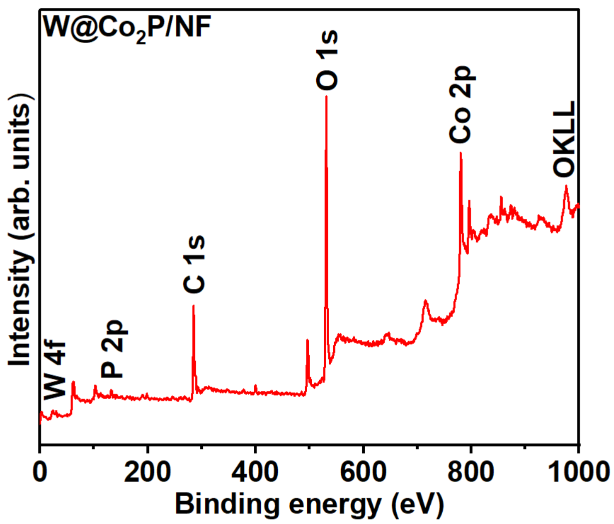

Figure S7 The XPS survey spectra of W@Co_2P/NF sample.

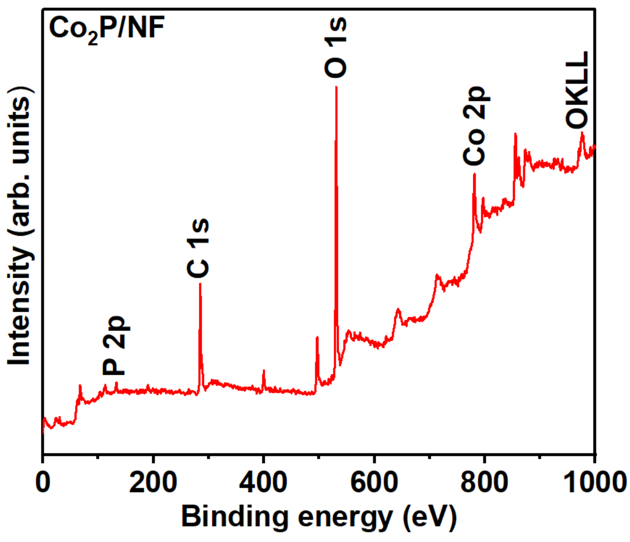

Figure S8 The XPS survey spectra of Co_2P/NF sample.

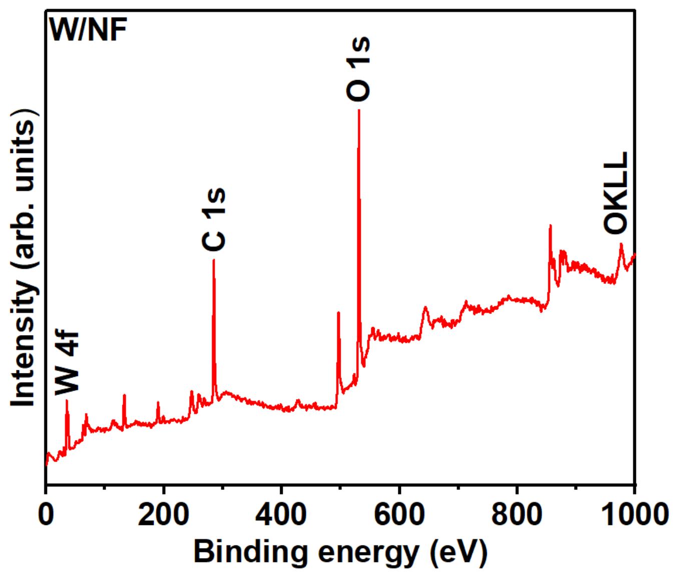

Figure S9 The XPS survey spectra of W/NF sample.

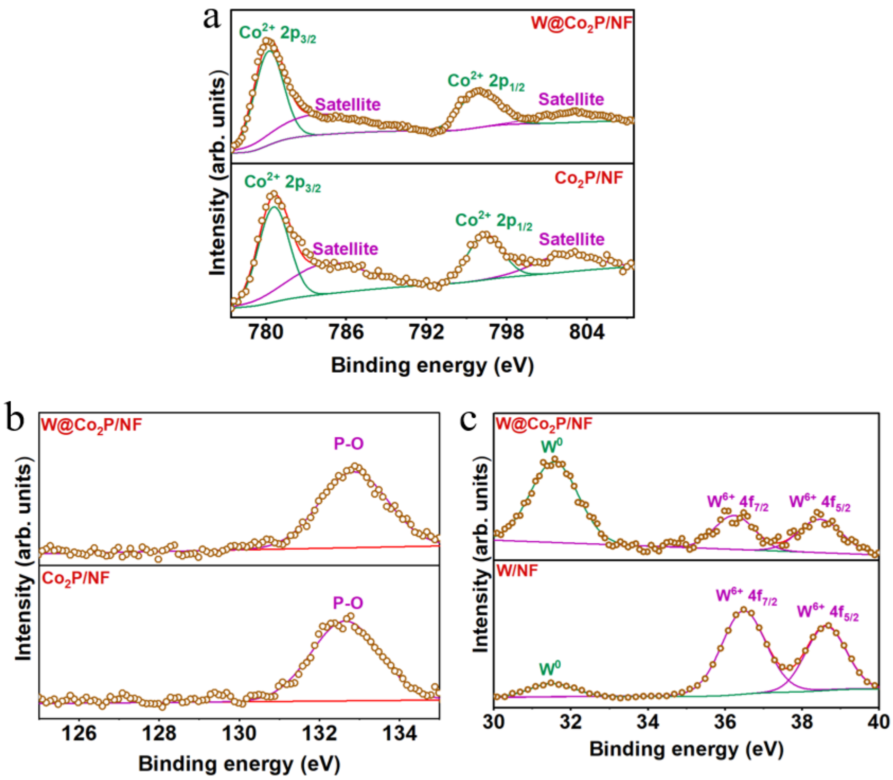

Figure S10 The high-resolution XPS spectra of (a) Co 2p, (b) P 2p and (c) W 4f for Co_2P/NF, W/NF and W@Co_2P/NF samples.

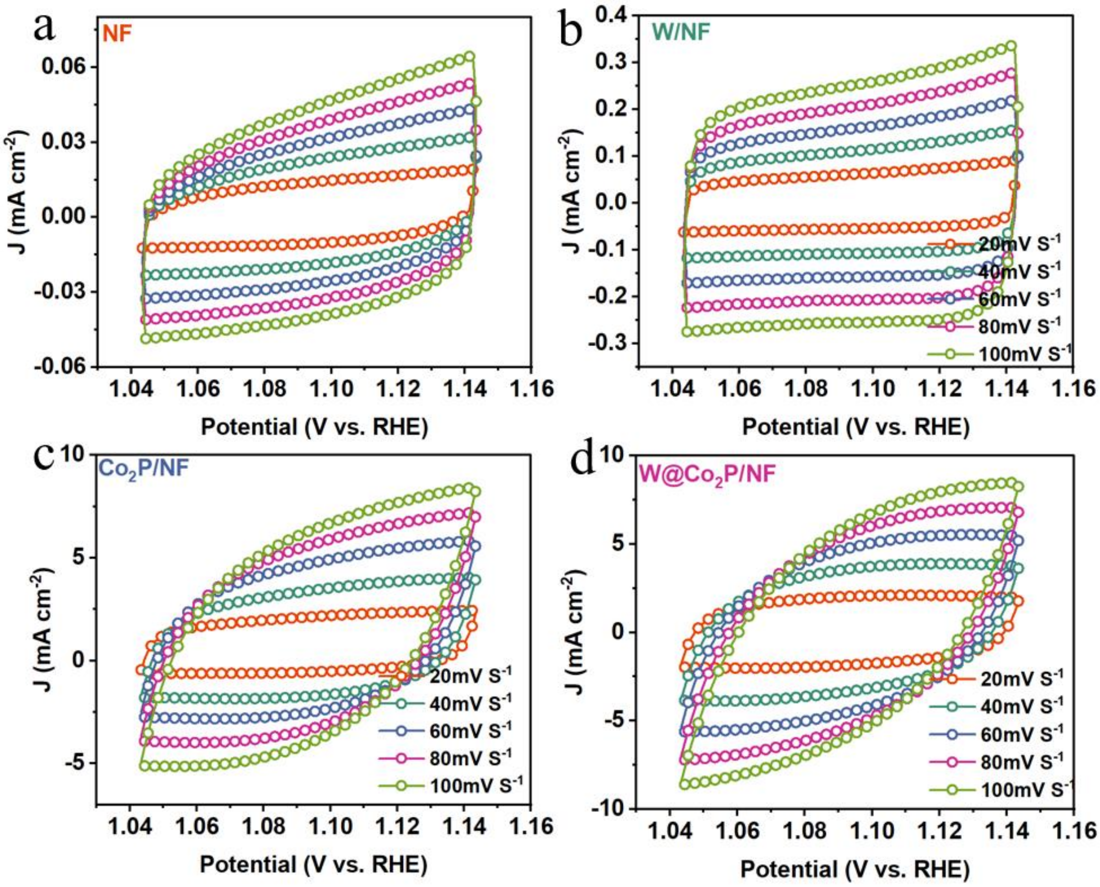

Figure S11 The cyclic voltammetry curves of (a) NF, (b) W/NF, (c) Co_2P/NF and (d) W@Co_2P/NF electrodes in 1.0 M KOH recorded at different scan rates from 20 to 100 mV s^{-1}.

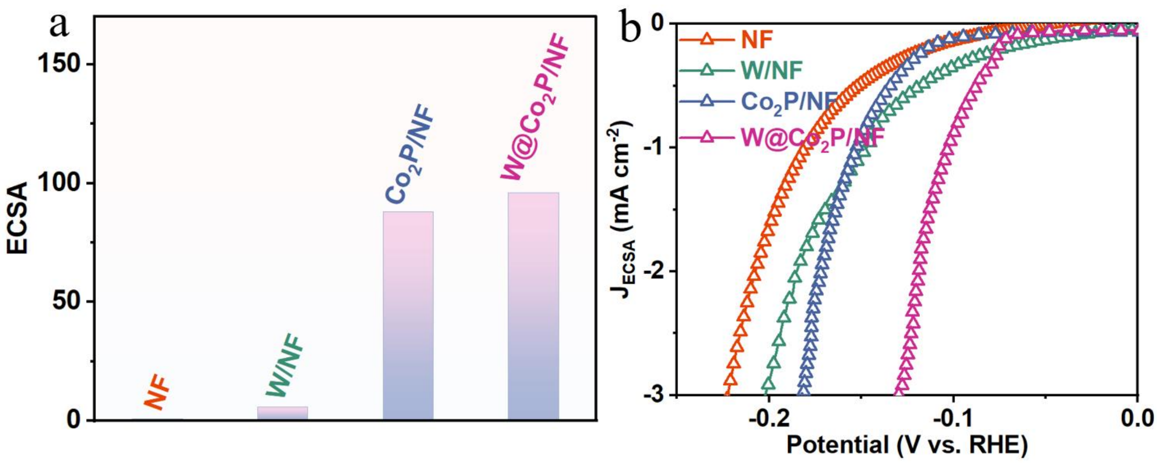

Figure S12 (a) Calculated ECSA values and (b) ECSA-normalized LSV curves of NF, W/NF, Co_2P/NF and W@Co_2P/NF.

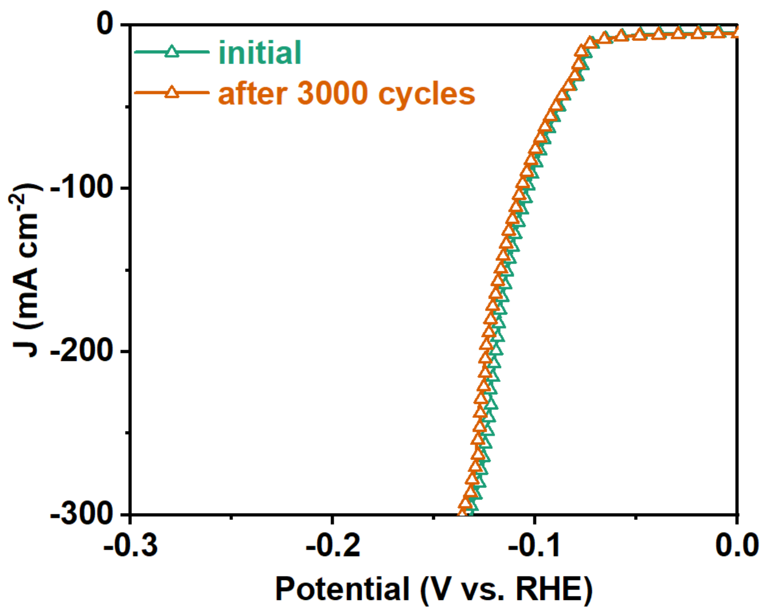

Figure S13 HER polarization curves before and after 3000 cycles of W@Co_2P/NF electrode.

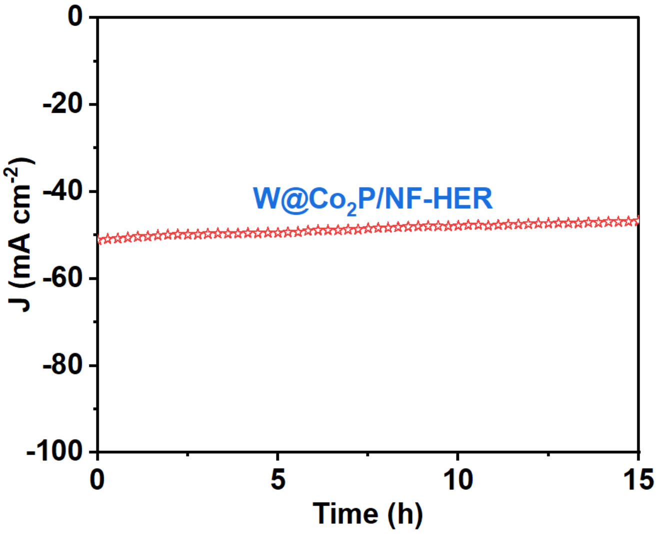

Figure S14 Chronoamperometric response of W@Co_2P/NF for HER in 1M KOH.

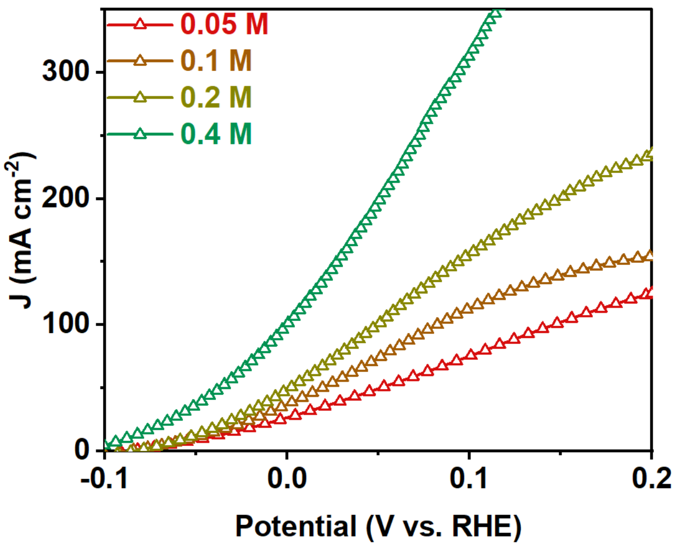

Figure S15 LSV curves in different concentrations of N_2H_4.

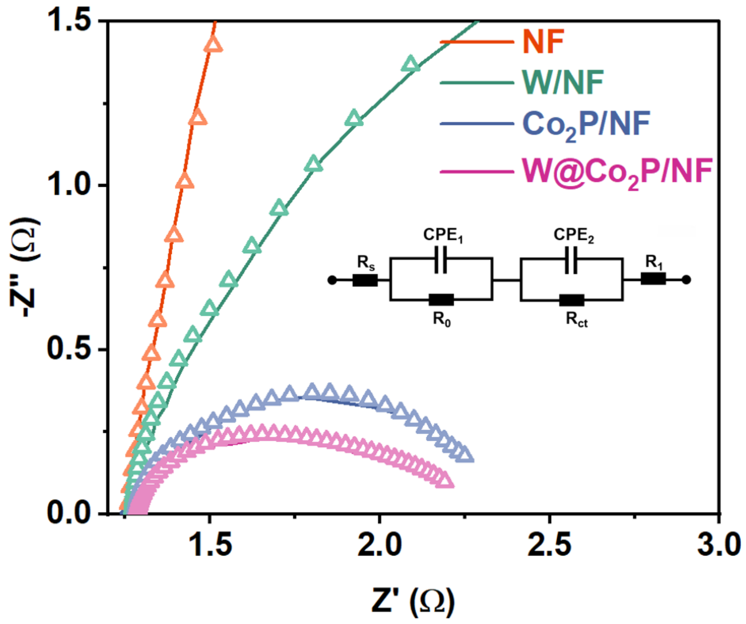

Figure S16 Nyquist plots of NF, Co_2P/NF, W/NF and W@Co_2P/NF samples.

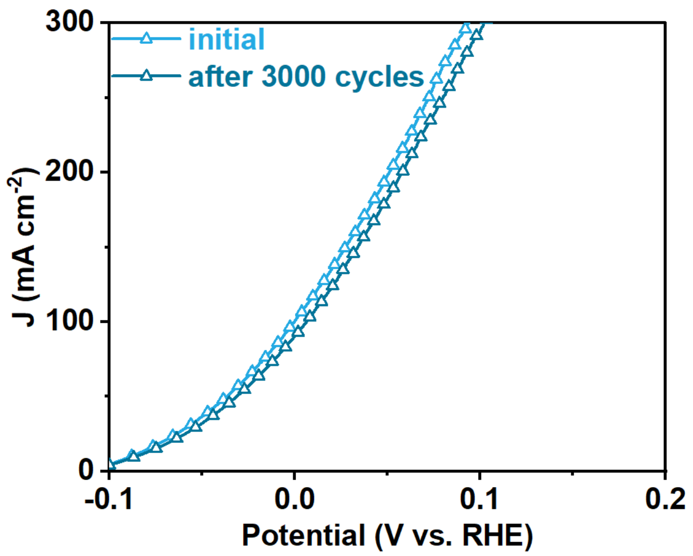

Figure S17 Polarization curves before and after 3000 cycles of W@Co_2P/NF for UOR in 1 M KOH and 0.4 M N_2H_4.

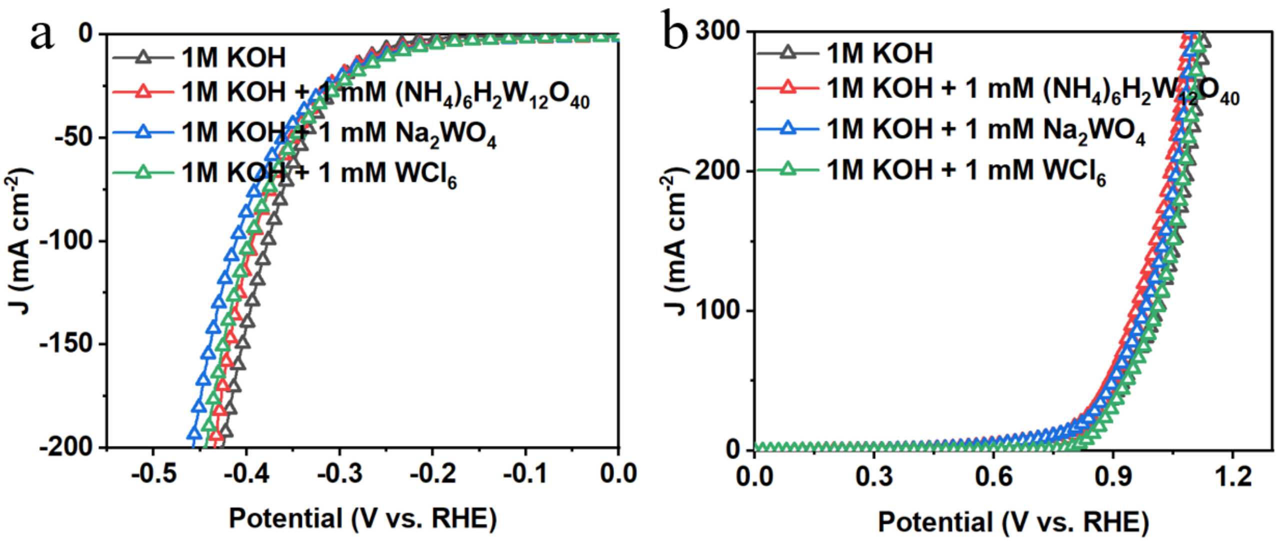

Figure S18 The polarization curves of NF for (a) HER and (b) HzOR in the electrolytes with different W sources.

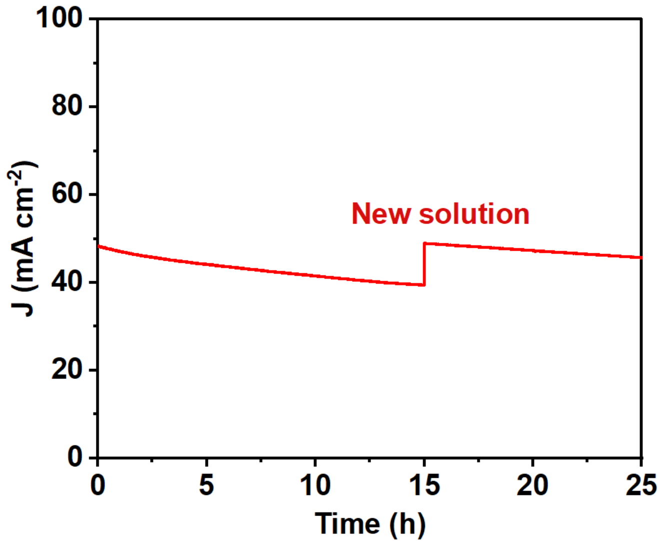

Figure S19 Chronoamperometric response of W@Co_2P/NF for UOR in 1 M KOH and 0.4 M N_2H_4.

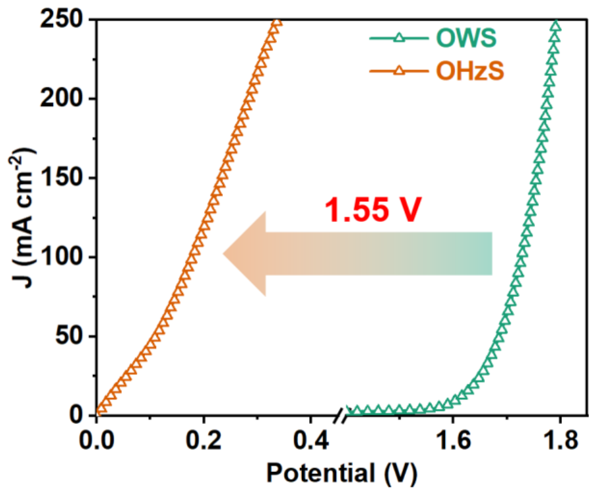

Figure S20 LSV curves of W@Co_2P/NF-based electrolyzer in 1 M KOH electrolyte with and without 0.4 M N_2H_4.

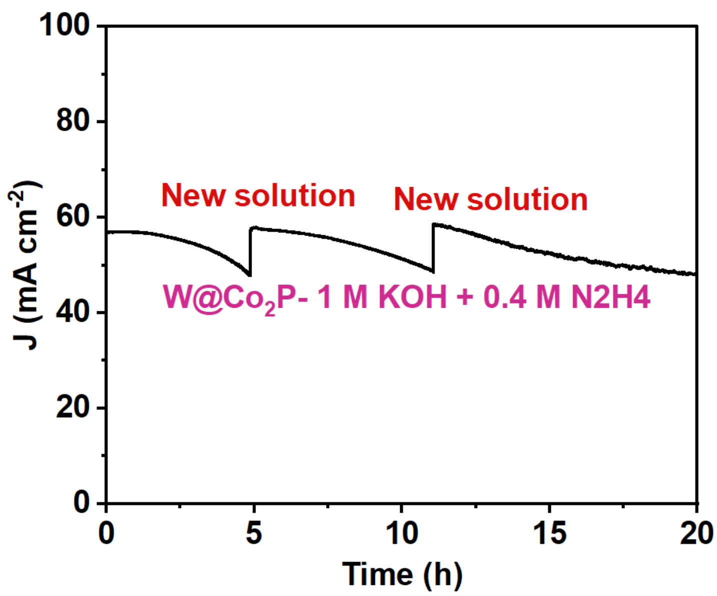

Figure S21 Chronoamperometric response of W@Co_2P/NF-based electrolyzer.

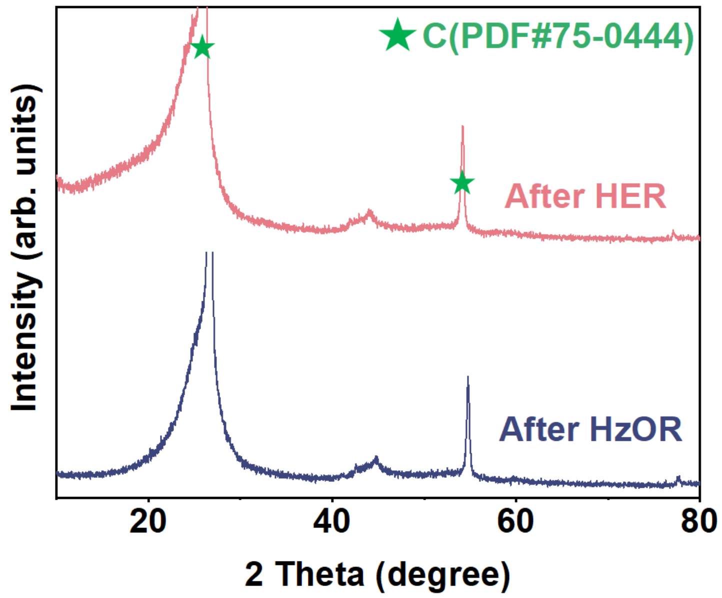

Figure S22 The post-XRD patterns of W@Co_2P/NF sample after a long time tests of HER and HzOR.

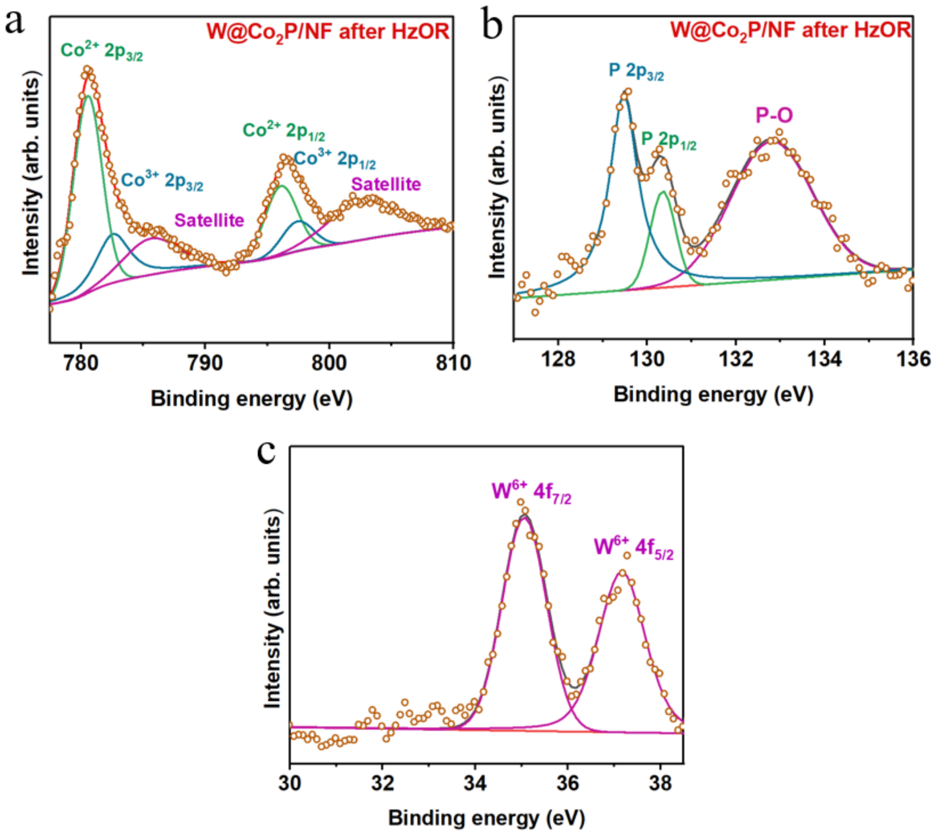

Figure S23 The post-XPS spectra of W@Co_2P/NF sample after a long time test of HzOR, (a) Co 2p, (b) P 2p and (c) W 4f.

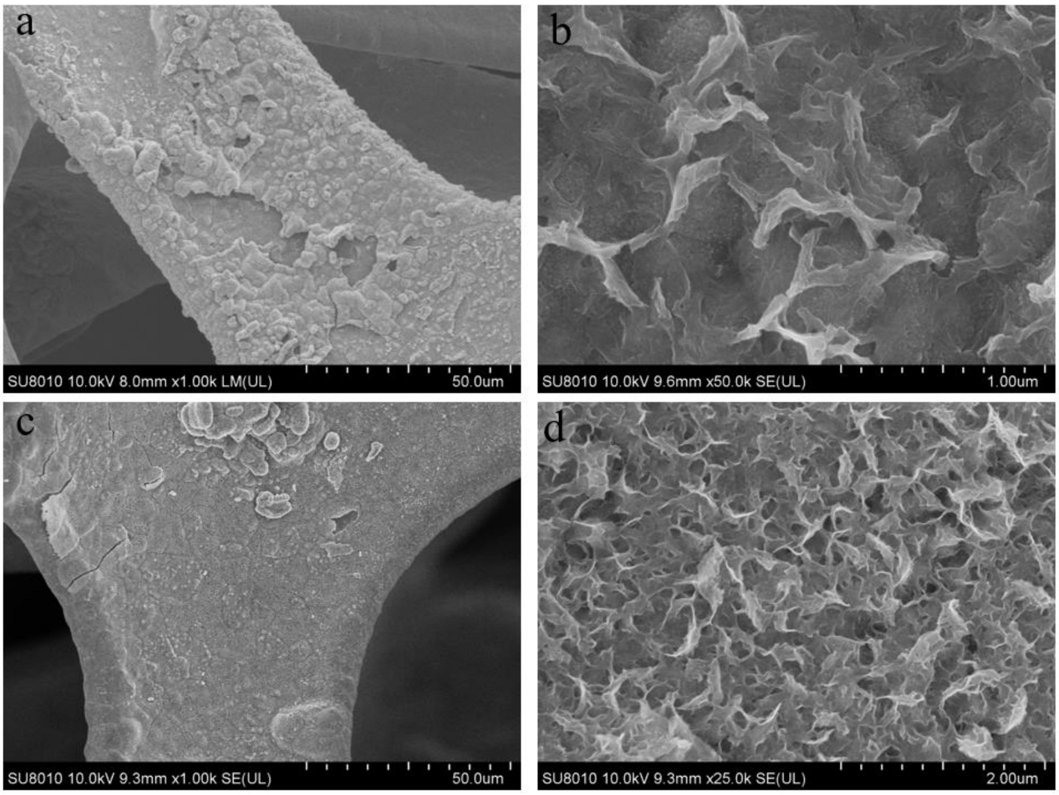

Figure S24 The post-SEM images of W@Co_2P/NF sample after a long time test of HzOR.

Table S1 Performance comparison of W@Co_2P/NF with various kinds of reported electrocatalysts for HER.

Electrocatalyst	η_{100} (mV)	η_{200} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	References
W@Co_2P/NF	100	118	39	1.0 M KOH	This work
PW-Co_3N NWA/NF	130	170	40	1.0 M KOH	[1]
Cu_1Ni_2-N	200	250	71	1.0 M KOH	[2]
Fe-$CoSe_2$	100	150	32	1.0 M KOH	[3]
$CoSe_2$	180	240	84	1.0 M KOH	[4]
Ni(Cu)	203	254	/	1.0 M KOH	[5]
Ni_2P	250	290	/	1.0 M KOH	[6]
CoSe/CP	320	390	96	1.0 M KOH	[7]
$Ni_{0.5}Co_{0.5}Se_2$/CC	150	200	56.5	1.0 M KOH	[8]
NiCo-$MoNi_4$	170	210	67.5	1.0 M KOH	[9]
Ru-FeP_4/IF	100	200	51	1.0 M KOH	[11]
Ni_2P-HNTs/NF	190	250	84	1.0 M KOH	[12]
NiS_2/TiM	250	350	\	1.0 M KOH	[13]
Mo-Ni_3N/Ni/NF	170	220	\	1.0 M KOH	[14]
Ni_2P/NF	200	290	\	1.0 M KOH	[15]
Ni(Cu)@NiFeP/NM	105	160	57	1.0 M KOH	[16]

Table S2 Performance comparison of W@Co_2P/NF with other well-developed catalytic materials for HzOR.

Electrocatalyst	η_{50} (mV)	η_{200} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	References
W@Co_2P/NF	310	390	9.8	1.0 M KOH+0.4 M N_2H_4	This work
PW-Co_3N NWA/NF	300	357	14	1.0 M KOH+0.4 M N_2H_4	[1]
Cu_1Ni_2-N	410	730	44	1.0 M KOH+0.4 M N_2H_4	[2]
Fe-$CoSe_2$	430	500	48	1.0 M KOH+0.4 M N_2H_4	[3]
$CoSe_2$	390	680	\	1.0 M KOH+0.4 M N_2H_4	[4]
Ni(Cu)	400	500	51	1.0 M KOH+0.4 M N_2H_4	[5]
Ni_2P	315	335	55	1.0 M KOH+0.4 M N_2H_4	[6]
CoSe/CP	490	520	\	1.0 M KOH+0.4 M N_2H_4	[7]
$Ni_{0.5}Co_{0.5}Se_2$/CC	350	520	\	1.0 M KOH+0.4 M N_2H_4	[8]
NiCo-$MoNi_4$	345	430	\	1.0 M KOH+0.4 M N_2H_4	[9]
$FeWO_4$-WO_3/NF	350	400	36	1.0 M KOH+0.4 M N_2H_4	[10]
Ru-FeP_4/IF	330	420	\	1.0 M KOH+0.4 M N_2H_4	[11]
Ni_2P-HNTs/NF	400	650	\	1.0 M KOH+0.4 M N_2H_4	[12]
NiS_2/TiM	400	490	22	1.0 M KOH+0.4 M N_2H_4	[13]
Mo-Ni_3N/Ni/NF	360	400	48	1.0 M KOH+0.4 M N_2H_4	[14]
Ni_2P/NF	260	350	55	1.0 M KOH+0.4 M N_2H_4	[15]

Table S3 Performance comparison of W@Co_2P/NF-based electrolyzers with other reported bifunctional electrodes.

Electrodes	Cell voltage (V) at 50 mA cm^{-2}	Cell voltage (V) at 200 mA cm^{-2}	References
W@Co_2P/NF	0.1	0.3	This work
PW-Co_3N NWA/NF	0.11	0.31	[1]
Cu_1Ni_2-N	0.85	1.2	[2]
Fe-$CoSe_2$	0.43	0.75	[3]
$CoSe_2$	0.1	0.3	[4]
Ni(Cu)	0.28	0.6	[5]
Ni_2P	0.4	0.6	[6]
CoSe/CP	0.5	0.75	[7]
NiCo-$MoNi_4$	0.2	0.45	[9]
$FeWO_4$-WO_3/NF	0.2	0.42	[10]
Ru-FeP_4/IF	0.2	0.35	[11]
Ni_2P-HNTs/NF	0.15	0.35	[12]
NiS_2/TiM	0.55	0.95	[13]
Mo-Ni_3N/Ni/NF	0.2	0.35	[14]
Ni(Cu)@NiFeP/NM	0.35	0.75	[15]
Ni_3N-Co_3N/NF	0.25	0.5	[16]

References

[1] Y Liu , J Zhang , Y L, Q Qian, Z L, Y Zhu and G Zhang. *Nat. Commun*, 2020, **11(1)**: 1-13.

[2] Z Wang, L Xu, F Huang, L Qu, J Li, K Owusu, Z Liu, Z Lin, B Xiang, X Liu, K Zhao, X Liao, W Yang, Y Cheng and L Mai. *Adv. Energy Mater*, 2019, **9(21)**: 1900390.

[3] X Liu, J He, S Zhao, Y Liu, Z Zhao, J Luo, G Hu, X Sun and Y Ding. *Nat. Commun*, 2018, **9(1)**: 1-10.

[4] J Zhang, H Wang, Y Tian, Y Yan, Q Xue, T He, H Liu, C Wang, Y Chen and B Xia. *Angew. Chem*, 2018, **130**: 7775-7779.

[5] Q Sun , L Wang, Y Shen, M Zhou, Y Ma, Z Wang and C Zhao. *Acs sustain chem eng*, 2018, **6(10)**: 12746-12754.

[6] C Tang, R Zhang, W Lu, Z Wang, D Liu, S Hao, G Du, A Asiri and X Sun. *Angew. Chem. Int. Ed*, 2017, **56(3)**: 842-846.

[7] Z Pu, I Amiinu, F Gao, Z Xu, C Zhang, W Li, G Li and S Mu. *Journal of Power Sources*, 2018, **401**: 238-244.

[8] G Wang, J Chen, P Cai, J Jia and Z Wen. *J. Mater. Chem. C*, 2018, **6(36)**: 17763-17770.

[9] Z Wang, L Xu, F Huang, L Qu, J Li, K Owusu, Z Liu, Z Lin, B Xiang, X Liu, K Zhao, X Liao, W Yang,Y Cheng and L Mai. *Adv. Energy Mater*, 2019, **9(21)**: 1900390.

[10] F Shen, Z Wang, Y Wang, G Qian, M Pan, L Luo, G Chen, H Wei and S Yin. *Nano Research*, 2021, **14(11)**: 4356-4361.

[11] T Cui, J Chi, J Zhu, X Sun, J Lai, Z Li and L Wang. *Appl. Catal. B*, 2022, **319**: 121950.

[12] T Wang, G Xu, H Sun, H Huang, F Li, P Chen and Y Chen. *Nanoscale*, 2020, **12(21)**: 11526-11535.

[13] J Wang, X Ma, T Liu, D Liu, S Hao, G Du, R Kong, A Asiri and X Sun. *Mater. Today Phys*, 2017, **3**: 9-14.

[14] Y Liu, J Zhang, Y Li, Q Qian, Z Li and G Zhang. *Adv funct mater*, 2021, **31(35)**: 2103673.

[15] H Zhang, J Wang, F Qin, H Liu and C Wang. *Nano Res.*, 2021, **14(10)**: 3489-3496.

[16] Q Qian, J Zhang, J Li, Y Li, X Jin, Y Zhu, Y Liu, Z Li, A Harairy, C Xiao, G Zhang and Y Xie. *Angew. Chem. Int. Ed*, **2021**, 133(11): 6049-6058.