Supporting Information for

Accelerating hydrazine-assisted hydrogen production kinetics with Mn dopant modulated CoS_2 nanowires array

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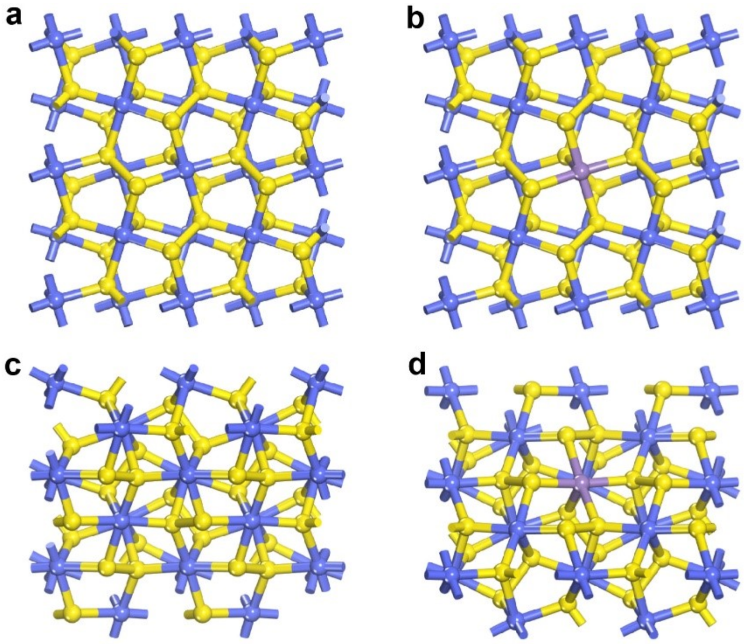

Figure S1. The different views of the optimized structural model for (a, c) CoS_2(001) and (b, d) Mn-CoS_2(001).

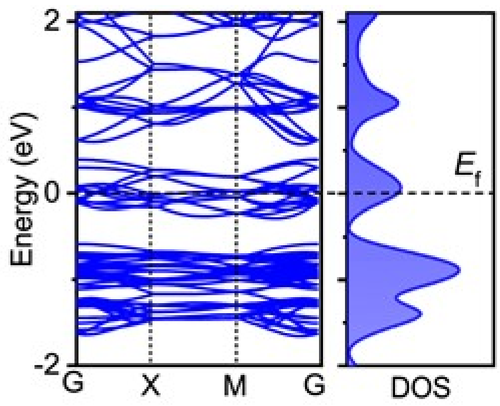

Figure S2. The calculated electronic band structure and the corresponding DOS results of the CoS_2.

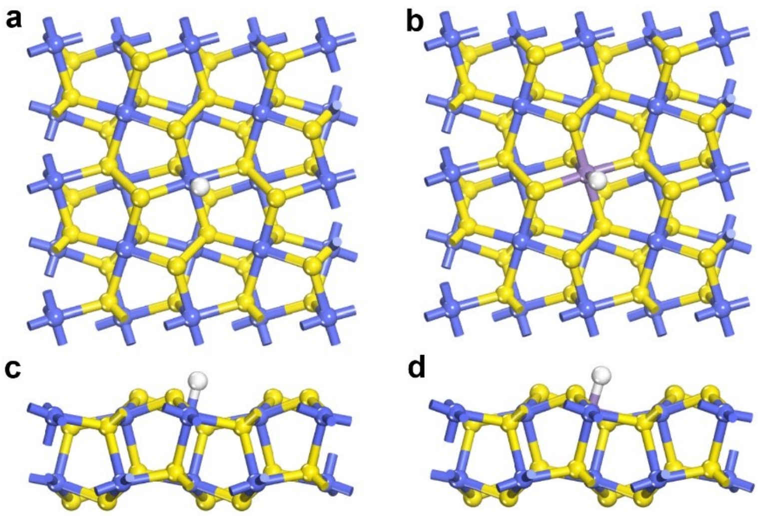

Figure S3. The different views of the optimized structural model of the adsorption of hydrogen over the surface (a, c) $CoS_2(001)$ and (b, d) Mn-$CoS_2(001)$.

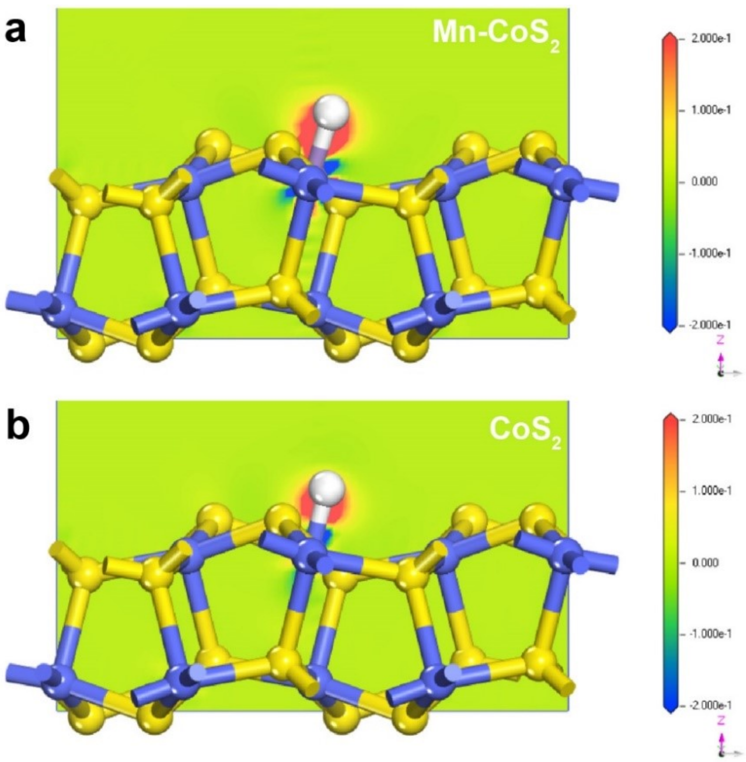

Figure S4. The charge density difference contour plot in the Co-H and Mn-H region, the red and blue colors represent the accumulation and depletion of electrons, respectively.

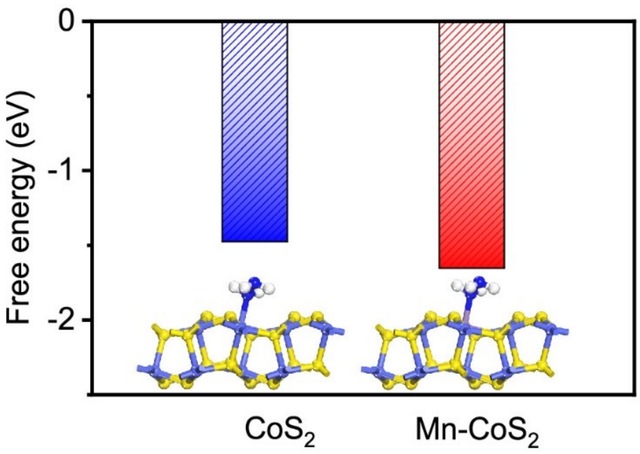

Figure S5. The adsorption energy for the N_2H_4 molecule over the surface of the catalyst. The inset is the corresponding structural optimization model.

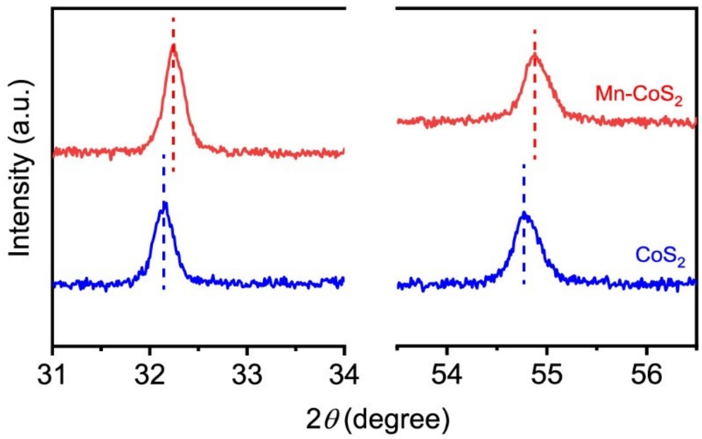

Figure S6. The XRD enlarged pattern corresponds to Figure 3a.

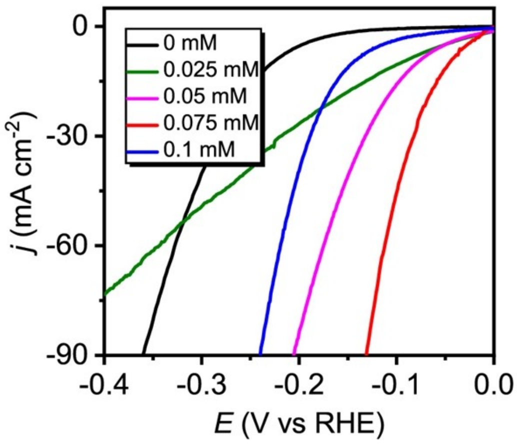

Figure S7. HER polarization curves of the Mn-CoS_2 catalyst with different addition content of Mn precursor ($MnCl_2 \cdot 4H_2O$) in 0.1 M KOH aqueous solution.

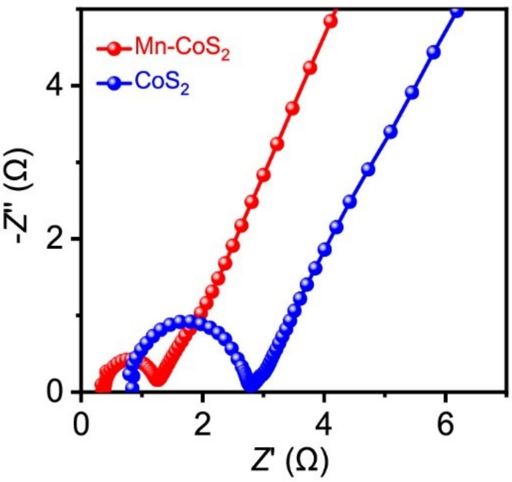

Figure S8. Nyquist plots of the CoS_2 and Mn-CoS_2. Obviously, the Mn-CoS_2 electrode exhibits an enhanced electron transfer rate and faster catalytic kinetics during the electrochemical process.

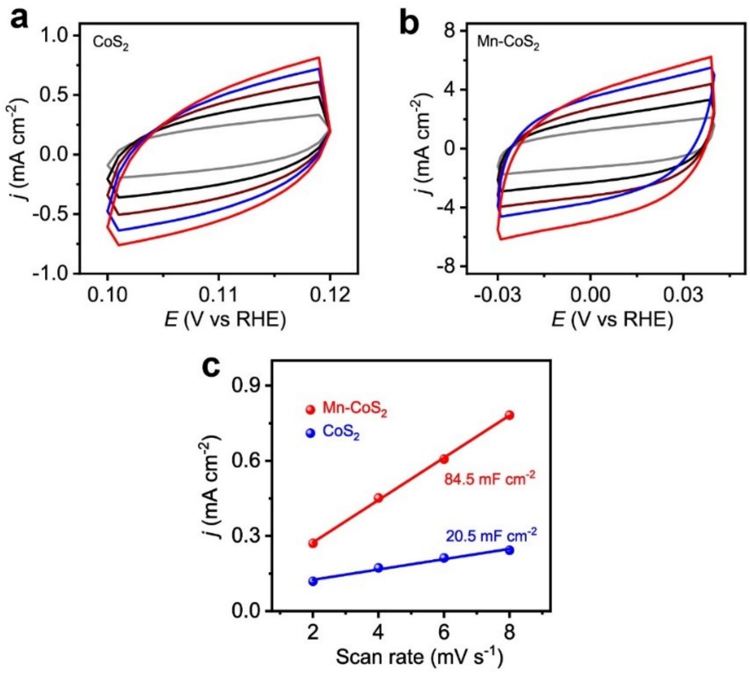

Figure S9. The CV curves (a) CoS_2 and (b) Mn-CoS_2 with different scan rates of 2, 4, 6, and 8 mV s^{-1}. (b) The capacitive current densities as a function of scan rate for the catalysts.

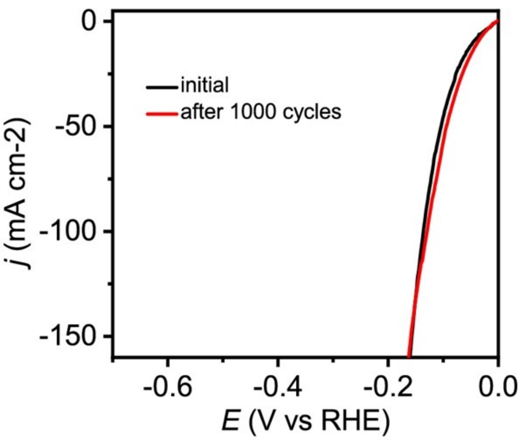

Figure S10. HER polarization curves of the Mn-CoS_2 catalyst before and after 1000 CV cycles.

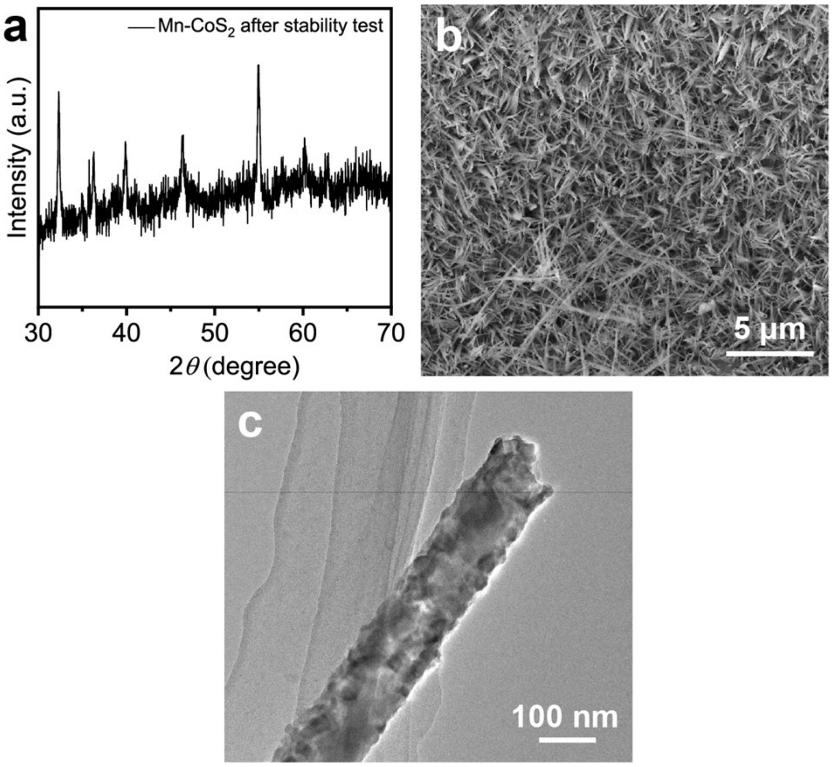

Figure S11. XRD pattern, SEM, and TEM images of the Mn-CoS_2 catalyst after the 54-h HER cycling stability measurement.

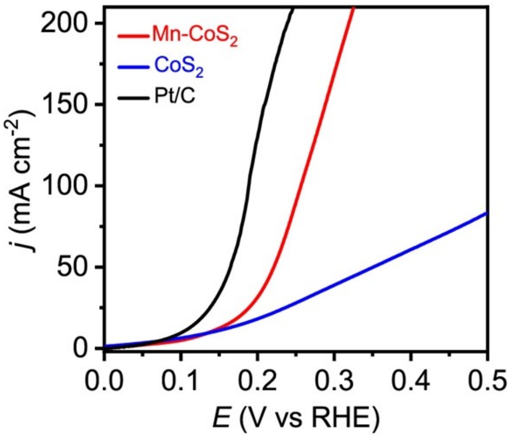

Figure S12. HzOR polarization curves of the Mn-CoS_2 in comparison with CoS_2 and commercial Pt/C (20 wt%) in 1 M H_2SO_4 + 0.5 M N_2H_4 aqueous solutions.

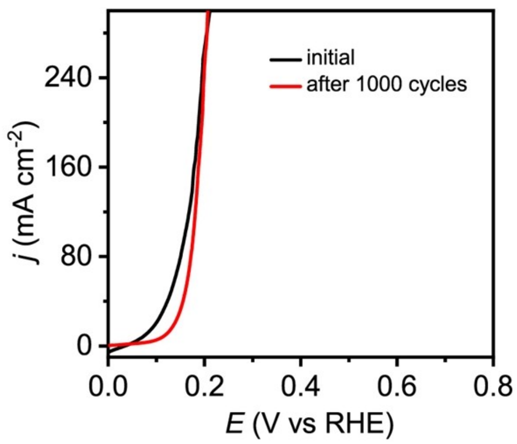

Figure S13. HzOR polarization curves of the Mn-CoS_2 catalyst before and after 1000 CV cycles.

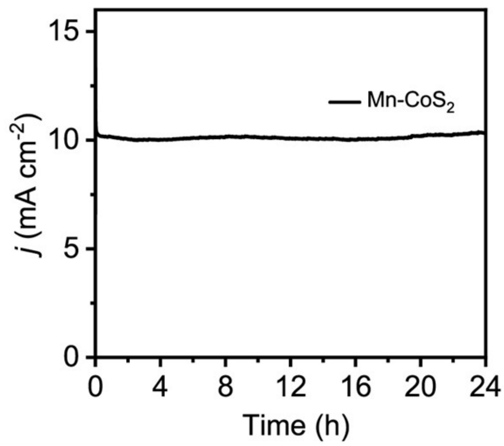

Figure S14. The *i*-*t* curve of the $Mn\text{-}CoS_2$ electrode in the OHzS system for 24 h.

Table S1. Comparison of HER performances in alkaline media for Mn-CoS_2 with previously reported HER electrocatalysts.

Catalysts	*Electrolyte*	η_{-10} (mV)	*Tafel slope* (mV dec^{-1})	*Mass loading* (mg cm^{-2})	*substrate*	*Ref.*
Mn-CoS_2	0.1 KOH	46	63.1	2.9	Ni foam	*This work*
RhIr MNs	1 M KOH	20	30.7	0.14	glassy carbon electrode	*J. Mater. Chem. A 2021, 9, 18323*
P-NiFeP/Ni	1 M KOH	17.9	63	-	Ni foam	*Nanoscale Adv. 2021, 3, 2280*
NiCo-$MoNi_4$ HMNAs/NF	1 M KOH	68	67.5	-	Ni foam	*Chem. Eng. J. 2021, 414, 128818*
P–$CoCO_3$/CF	1 M KOH	46.1	71.16	-	Co foam	*Sustain. Energy Fuels 2021, 5, 2257*
Ni(Cu) CNPs	1 M KOH	41	51.1	-	Ni foam	*J. Mater. Chem. A 2020, 8, 21084*
CoP/Ni_2P@NC	1 M KOH	143	76	-	glassy carbon electrode	*Mater. Chem. Front. 2019, 3, 2428*
CoP/TF	1 M KOH	118	62	-	Ti foil	*Adv. Energy Mater. 2019, 9, 1803970*
Ni_2P-CoP HNSAs/CC	1 M KOH	73(30 mA cm^{-2})	120	-	carbon cloth	*J. Mater. Chem. A 2016, 4, 16992*

Ni_2P NSs/CC		＞200	142	-		
CoP NSs/CC		＞200	177	-		
Ni_2P/Co_2P@NC	1 M KOH	251	81.64	0.199	glassy carbon electrode	*Int. J. Hydrogen Energy 2019, 44, 14908*
	0.5 M H_2SO_4	226	64.9			
Ni_2P@C	0.5 M H_2SO_4	186	64	0.566	glassy carbon electrode	*Appl. Surf. Sci. 2018, 457, 933*
CoP@NPMG	1 M KOH	151	75	0.204	glassy carbon electrode	*Nanoscale 2018, 10, 2603*
CoP/NiCoP	1 M KOH	133	88	2	Ti foil	*Adv. Energy Mater. 2019, 9, 1901213*
$Zn_{0.64}$-CoP/Co_2P@CC	1 M KOH	95	82	5.74	carbon cloth	*J. Solid State Chem. 2020, 285, 121231*
Co_2P/CNT-900	1 M KOH	132	103	~0.75	glassy carbon electrode	*Nano Energy 2016, 30, 303*
SF-Co_xP	1 M KOH	167	75	0.5	glassy carbon electrode	*Small 2018, 14, 1801284*
CF-Co_xP		148	73			
C-Co_xP		121	62			

Ni_2P/NF	1 M KOH	116	68	-	Ni foam	*Nano Res. 2020, 13, 2098*
Ni_2P/Ni/NF	1 M KOH	98	-	-	Ni foam	*ACS Catal. 2016, 6, 2, 714*
NiFeLDH NiCoP/NF	1 M KOH	120	48.6	2	Ni foam	*Adv. Funct. Mater. 2018, 28, 1706847*
Ni_2P	1 M KOH	148	61	-	Ni foam	*Int. J. Hydrogen Energy 2020, 45, 2546*
Ni_5P_4	1 M KOH	150	53	3.475	Ni foil	*Angew. Chem. Int. Ed. 2015, 54, 12361*
Ni_2P-$NiSe_2$/CC	1 M KOH	66	72.6	9.2	carbon cloth	*Appl. Catal. B 2020, 262, 118245*
V-Ni_2P NSAs/CC	1 M KOH	85	95	-	carbon cloth	*Nanoscale 2019, 11, 4198*
Ni_2P@NPCNFs	1 M KOH	104	79.7	-	carbon cloth	*Angew. Chem. Int. Ed. 2018, 57, 1963*
Co-P/NC	1 M KOH	154	51	0.283	glassy carbon electrode	*Chem. Mater. 2015, 27, 7636*
$Ni(OH)_2$/$NiSe_2$/CC	1 M KOH	82	60	3.45	carbon cloth	*Int. J. Hydrogen Energy 2019, 44, 4832*
CoP/rGO	1 M KOH	150	38	0.28	glassy carbon electrode	*Chem. Sci. 2016, 7, 1690*

p-$CoSe_2$/CC	1 M KOH	138	83	2.3	carbon cloth	*ACS Sustainable Chem. Eng. 2018, 6, 15374*
NiSe-$Ni_{0.85}Se$/CP	1 M KOH	101	102	1.68	carbon fiber paper	*Small 2018, 14, 1800763*
Ni_3S_2/NF	1 M KOH	131	96	1.4	Ni foam	*Nanoscale 2018, 10, 17347*
$NiCo_2O_4$/NF	1 M KOH	164	88	-	Ni foam	*Adv. Funct. Mater. 2016, 26, 3515*

Table S2. Comparison of HzOR performances for Mn-CoS_2 with previously reported HzOR electrocatalysts.

Catalysts	***Electrolyte***	***Potential*** **(mV vs RHE)**	***Mass loading*** **(mg cm^{-2})**	***substrate***	***Ref.***
Mn-CoS_2	0.5 M N_2H_4 + 1 M KOH	E_{10} = 77	2.9	Ni foam	*This work*
3D $NiCoSe_2$/NF	0.1 M N_2H_4 + 0.5 M KOH	E_{onset} = -0.7 V vs SCE	-	Ni foam	*ACS Sustainable Chem. Eng. 2018, 6, 7735*
NSC	0.05 M N_2H_4 + 0.1 M PBS	E_{onset} = 380	-	glassy carbon electrode	*Appl. Catal. B: Environ. 2018, 225, 30*
Co/LaCoOx@N-C-1	0.1 M N_2H_4 + 1 M KOH	E_{onset} = -170	0.285	glassy carbon electrode	*ACS Appl. Mater. Interfaces 2020, 12, 24701*
Co_3O_4/Co	0.3 M N_2H_4 +1 M KOH	E_{50} = -110 E_{200} = -32 E_{300} = -14	6.5	glassy carbon electrode	*ACS Sustainable Chem. Eng. 2020, 8, 7973*
$FeWO_4$-WO_3/NF	0.5 M N_2H_4 +1 M KOH	E_{10} = -34 E_{1000} = 164	-	Ni foam	*Nano Res. 2021, 14, 4356*
MWCNT-NH_2@PQQ	0.01 M N_2H_4 + 0.1 M Tris-HCl	$E_{0.154}$ = 0.36 V vs Ag/AgCl	-	glassy carbon electrode	*ACS Appl. Nano Mater. 2018, 1, 2069*
FeN_4/HPCM	0.1 M N_2H_4 + 1 M KOH	E_{onset} = 200	0.6	filter paper	*Small 2020, 16, 2002203*
NC@Co/NC	0.01 M N_2H_4 + 1 M KOH	E_{onset} = 470	0.25	glassy carbon electrode	*ACS Nano 2021, 15, 10286*

	0.05 M N_2H_4 + 1 M KOH	E_{onset} = 410			
	0.1 M N_2H_4 + 1 M KOH	E_{onset} = 370			
β-Ni(OH)2/SSM	0.5 M N_2H_4 + 1 M KOH	E_{50} = 1340	0.8	Stainless steel mesh	*ChemCatChem 2021, 13, 1165*
RhIr MNs	0.5 M N_2H_4 + 1 M KOH	E_{10} = -12 E_{100} = 117	0.14	glassy carbon electrode	*J. Mater. Chem. A 2021, 9, 18323*
Pt/C		E_{10} = 123 E_{100} = 300			
CoP/Co-20	0.5 M N_2H_4 + 1 M KOH	E_{10} = -69 E_{100} = 177	0.275	glassy carbon electrode	*J. Phys. Chem. Lett. 2021, 12, 4849*
P-NiFeP/Ni	0.1 M N_2H_4 + 1 M KOH	E_{10} = 77	-	Ni foam	*Nanoscale Adv. 2021, 3, 2280*
NiCo-MoNi$_4$ HMNAs/NF	0.1 M N_2H_4 + 1 M KOH	E_{10} = -30	-	Ni foam	*Chem. Eng. J. 2021, 414, 128818*
NiCoP/NF	0.5 M N_2H_4 + 1 M NaOH	E_{1511} = 300	-	Ni foam	*Electrochim. Acta 2021, 387, 138492*
Ni−Co/NF	0.5 M N_2H_4 + 1 M NaOH	E_{onset} = -160 E_{1213} = 300	-	Ni foam	*ACS Sustainable Chem. Eng. 2020, 8, 16583*
A-Ru-KB	0.1 M N_2H_4 + 1 M KOH	E_{onset} = -83	3	glassy carbon electrode	*ACS Appl. Mater. Interfaces 2021, 13, 8488*
Pt/C		E_{onset} = 61			

Ni@Pd-Ni	0.02 M N_2H_4 + 1 M KOH	E_{onset} = -990 vs Ag/AgCl	-	Ni nanowire arrays	*ChemElectroChem, 2019, 6, 5581*
MoC_x– NC-900	0.02 M N_2H_4 + 0.1 M KOH	E_{onset} = 650	1	glassy carbon electrode	*Electrochim. Acta 2021, 384, 138417*
Cas–Cu–R	0.05 M N_2H_4 + 0.1 M PBS	E_{onset} = 350	0.1	glassy carbon electrode	*J. Electroanal. Chem. 2021, 882, 114997*
PNC_3	0.1 M N_2H_4 + 0.01 M PBS	E_{onset} = 420	-	glassy carbon electrode	*ACS Appl. Energy Mater. 2019, 2, 2313*
$Ni_{0.85}Se$/rGO	0.1 M N_2H_4 + 1 M KOH	E_{onset} = 40	-	Ni foam	*J. Electrochem. Soc. 2021 168 104510*
P–$CoCO_3$/CF	0.3 M N_2H_4 + 1 M KOH	E_{100} = -42.3	-	Co foam	*Sustain. Energy Fuels, 2021, 5, 2257*
Ni(Cu) CNPs	0.5 M N_2H_4 + 1 M KOH	E_{10} = -18	-	Ni foam	*J. Mater. Chem. A 2020, 8, 21084*
CoP/TiM	0.1 M N_2H_4 + 1 M KOH	E_{100} = -6	0.7	Ti mesh	*ChemElectroChem 2017, 4, 481*
S-LDH-3	0.02 M N_2H_4 + 0.1 M KOH	E_{onset} = 210	-	Ni foam	*J. Mater. Chem. A 2019, 7, 24437*
NiS_2/TiM	0.5 M N_2H_4 + 1 M KOH	E_{300} = 218	1.2	Ti mesh	*Mater. Today Energy 2017, 3, 9*
Ni@Ni_2P NTA/NF	0.5 M N_2H_4 + 1 M KOH	E_{onset} = -90 E_{1120} = 300	-	Ni foam	*ACS Sustainable Chem. Eng. 2021, 9, 4564*

Table S3. Comparison of OHzS performances in alkaline media for Mn-CoS_2 with previously reported OHzS electrocatalysts.

Catalysts	*Electrolyte*	*Potential* (mV vs RHE)	*Mass loading* (mg cm^{-2})	*substrate*	*Ref.*
Mn-CoS_2	0.5 M N_2H_4 + 1 M KOH	E_{200} = 447	2.9	Ni foam	*This work*
Ni NCNA	0.3 M N_2H_4 + 1 M KOH	E_{10} = 23	2.8	Ni foam	*Small 2021, 17, 2008148*
N-$Ni_1Co_3Mn_{0.4}O$/NF	0.5 M N_2H_4 + 1 M KOH	E_{100} = 272	5.92	Ni foam	*Int. J. Hydrog. Energy 2022, 47, 5766-5778*
Ni_3N-Co_3N	0.1 M N_2H_4 + 1 M KOH	E_{10} = 71	-	Ni foam	*Angew. Chem. Int. Ed. 2021, 60, 5984*
CoP/Co	0.5 M N_2H_4 + 1 M KOH	E_{10} = 260	-	glassy carbon electrode	*J. Phys. Chem. Lett. 2021, 12, 4849*
Mn-SA/BNC	0.5 M N_2H_4 + 1 M KOH	E_{10} = 410	1	glassy carbon electrode	*Nanoscale, 2021, 13, 4767*
Rh-NS-HCS	0.5 M N_2H_4 + 1 M KOH	E_{10} = 110	0.5	carbon paper	*Mater. Chem. Front., 2021, 5, 3125*
NiCo/$MoNi_4$	0.1 M N_2H_4 + 1 M KOH	E_{250} = 630	-	Ni foam	*Chem. Eng. J. 2021, 414, 128818*