Supplementary Information

Insight into the Intrinsic Activity of Transition Metal Sulfides for Hydrogen Evolution Reaction

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Calculation of TOF. The TOF is defined as follows:

$$TOF = \frac{JA}{2Fn} \qquad \text{(S1)}$$

Where J is the current density (A cm^{-2}) at a certain overpotential, A is the surface area (cm^2) of the electrode, 2 is the mole of electrons transferred to generate one mole of H_2, F is the Faraday constant (96485 C mol^{-1}), and n is the number of moles of active sites. TOFs were calculated based on the assumption that all transition metal atoms in the samples are catalytically active.[1,2]

Calculation of ECSA. ECSA is calculated from the C_{dl} according to the equation:

$$ECSA = \frac{C_{dl}}{C_s} \qquad \text{(S2)}$$

where 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. While ideally, one would synthesize smooth, planar surfaces of each catalyst to measure C_s and estimate ECSA, this is not practical for most electrodeposited systems. However, specific capacitances have been measured for a variety of metal electrodes in acidic and alkaline solutions and typical values reported range between C_s = 0.015-0.110 mF cm^{-2} in H_2SO_4 and C_s = 0.022-0.130 mF cm^{-2} in NaOH and KOH solutions.[3,4] For our estimates of surface area, we use general specific capacitances of C_s = 0.035 mF cm^{-2} in 0.5 M H_2SO_4 and C_s = 0.040 mF cm^{-2} in 1 M NaOH based on typical reported values.[5]

Calculation of j_o. A small current density (j=5 mA cm^{-2}) is taken in the micro-polarization region, and the corresponding voltage is equal to the measured voltage (η V vs. RHE). The j_0 is calculated according to the equation:

$$j = j_o \frac{\eta F}{RT} \qquad \text{(S3)}$$

Where η is the overpotential (mV), F is the Faradaic constant, R is the ideal gas constant (8.314 J mol^{-1}K^{-1}), and T is the experimental temperature (298 K).[6]

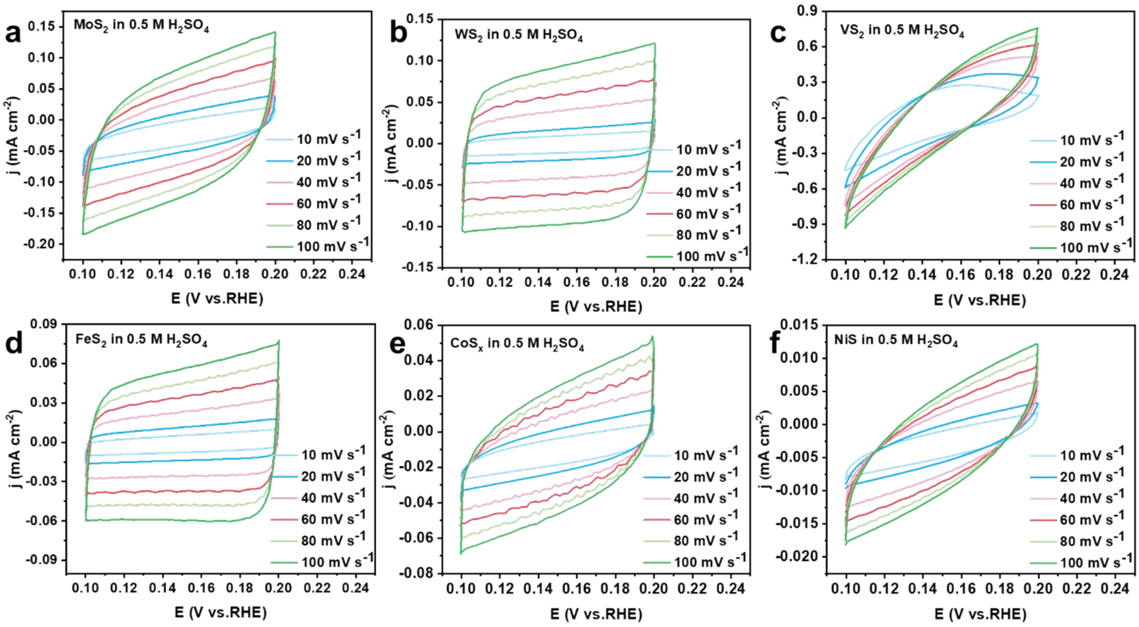

Fig. S1 CV curves of (a) MoS_2, (b) WS_2, (c) VS_2, (d) FeS_2, (e) CoS_x, and (f) NiS at different scan rates of 10, 20, 40, 60, 80, and 100 mV s^{-1} in 0.5 M H_2SO_4.

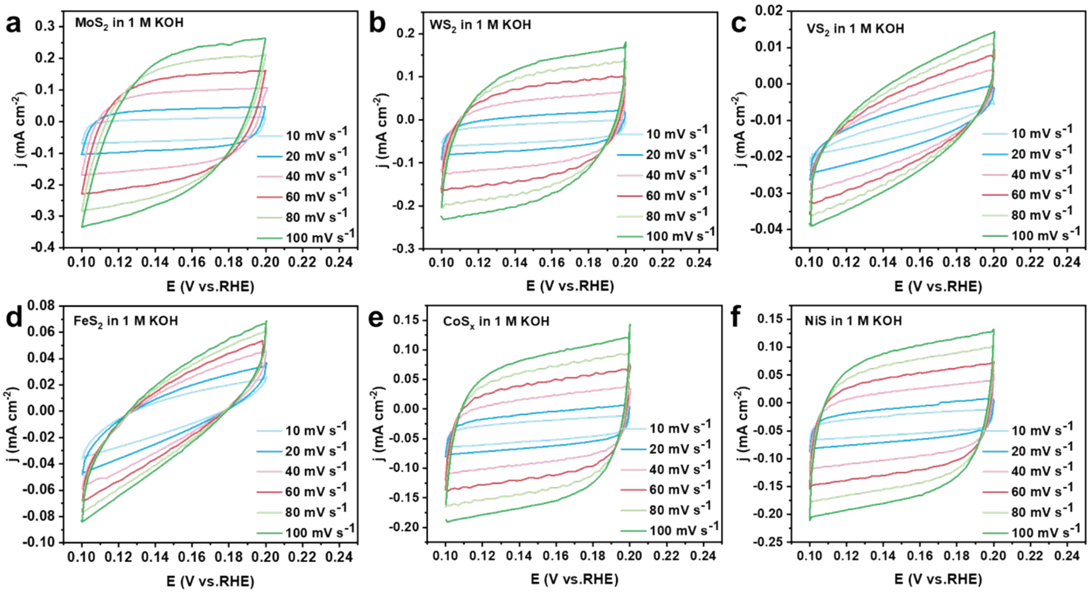

Fig. S2 CV curves of (a) MoS_2, (b) WS_2, (c) VS_2, (d) FeS_2, (e) CoS_x, and (f) NiS at different scan rates of 10, 20, 40, 60, 80, and 100 mV s^{-1} in 1 M KOH.

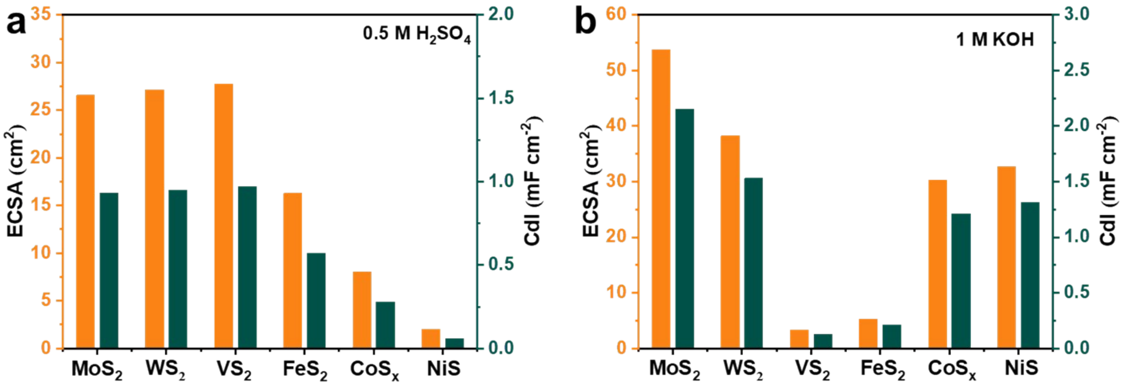

Fig. S3 ECSA (left) and C_{dl} (right) values of MoS_2, WS_2, VS_2, FeS_2, CoS_x, and NiS in (a) 0.5 M H_2SO_4 and (b) 1 M KOH.

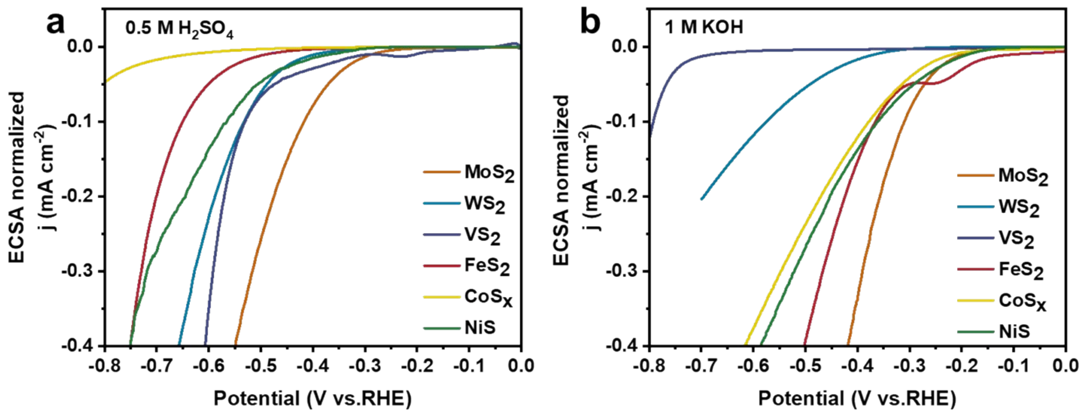

Fig. S4 ECSA-normalized HER polarization curves of MoS_2, WS_2, VS_2, FeS_2, CoS_x and NiS in (a) 0.5 M H_2SO_4 and (b) 1 M KOH.

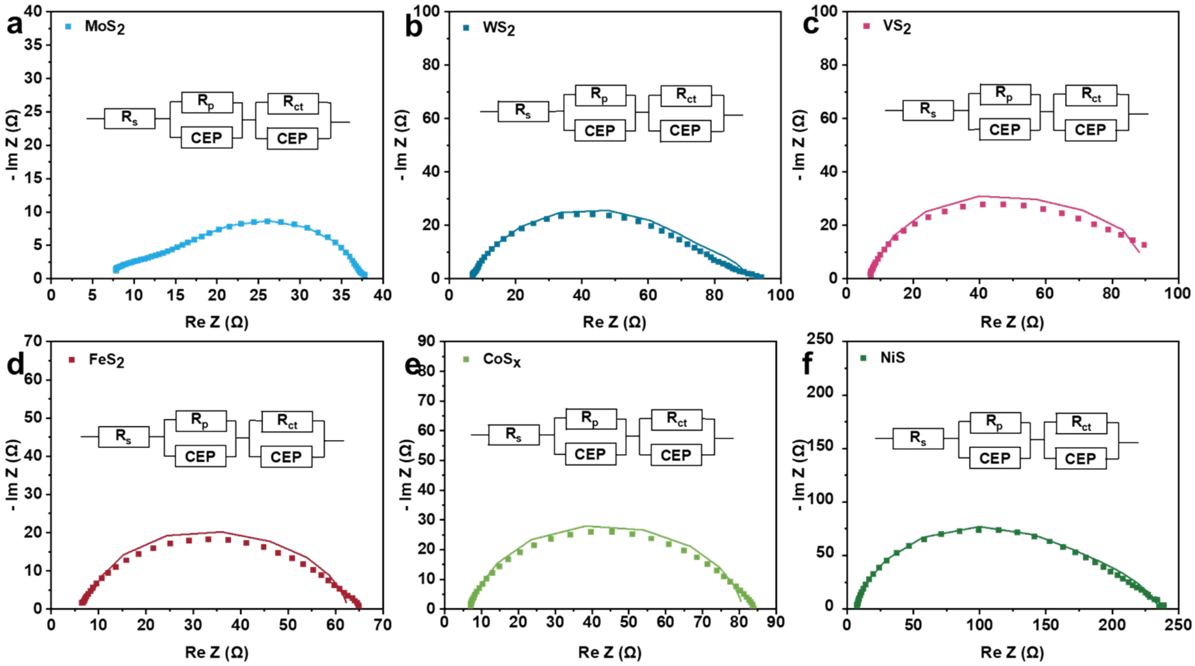

Fig. S5 EIS curves of (a) MoS_2, (b) WS_2, (c) VS_2, (d) FeS_2, (e) CoS_x, and (f) NiS in 0.5 M H_2SO_4.

Table S1 The parameter of R_s, R_p, and R_{ct} for MoS_2, WS_2, VS_2, FeS_2, CoS_x, and NiS in 0.5 M H_2SO_4.

Sample	R_s (Ω)	R_p (Ω)	R_{ct} (Ω)
MoS_2	6.63	9.90	21.24
WS_2	6.98	67.46	16.21
VS_2	7.48	66.76	15.34
FeS_2	7.81	32.00	22.85
CoS_x	7.76	43.91	29.24
NiS	6.76	153.80	75.21

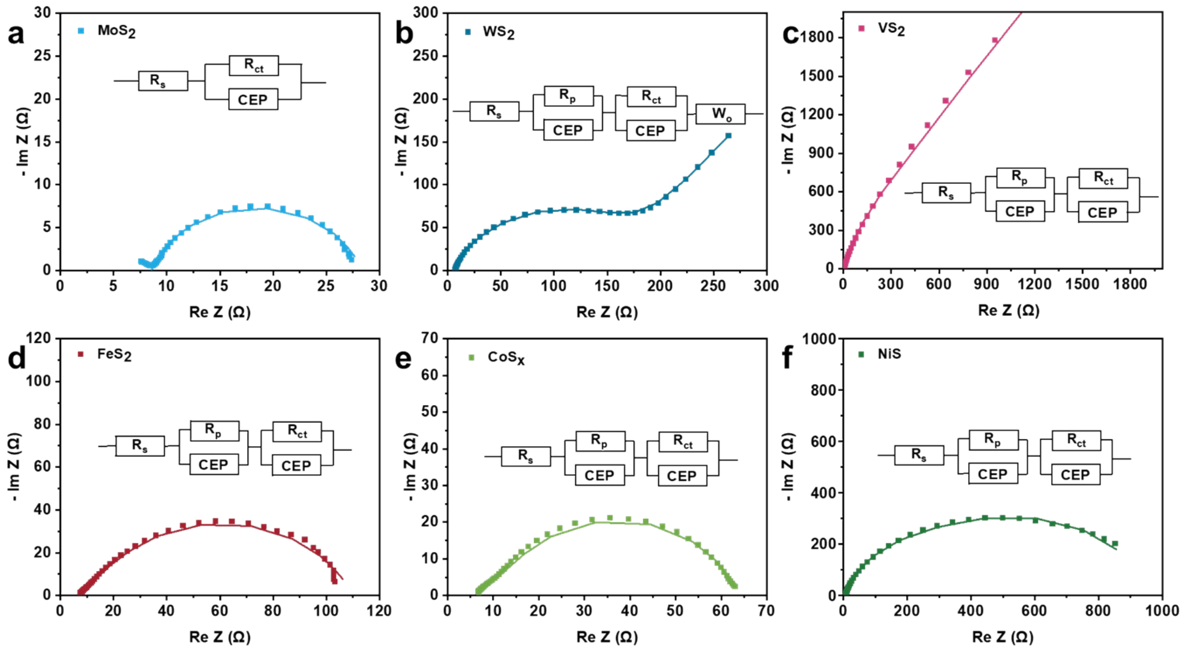

Fig. S6 EIS curves of (a) MoS_2, (b) WS_2, (c) VS_2, (d) FeS_2, (e) CoS_x, and (f) NiS in 1 M KOH.

Table S2 The parameter of R_s, R_p, and R_{ct} for MoS_2, WS_2, VS_2, FeS_2, CoS_x, and NiS in 1 M KOH.

Sample	R_s (Ω)	R_p (Ω)	R_{ct} (Ω)
MoS_2	8.565	/	19.74
WS_2	6.899	23.59	126.30
VS_2	6.914	567.50	12302
FeS_2	6.058	14.52	89.85
CoS_x	4.421	18.99	42.11
NiS	7.374	281.30	673.20

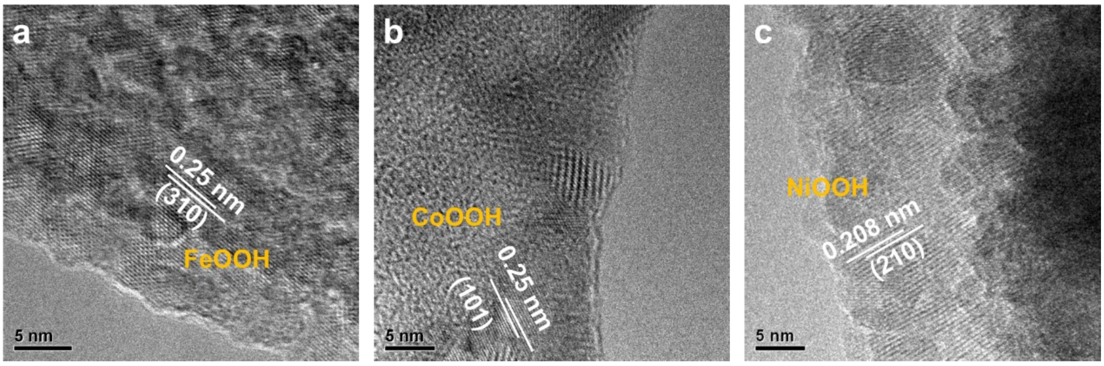

Fig. S7 TEM characterization of (a) FeS_2, (b) CoS_x and (c) NiS after the reaction.

Table S3 Performances of TMS-based electrocatalysts for HER.

Catalyst	Electrolyte	Overpotential η_{10} (mV)	Tafel slope (mV dec^{-1})	Ref.
MoS_2	0.5 M H_2SO_4	390	124	This work
Strained vacancy MoS_2	0.5 M H_2SO_4	170	60	[7]
1T′-MoS_2	0.5 M H_2SO_4	175	100	[8]
MoS_2/CNS	0.5 M H_2SO_4	200	53	[9]
MoS_2 Particles	0.5 M H_2SO_4	160	82	[10]
double-gyroid MoS_2	0.5 M H_2SO_4	200	50	[11]
2H Planar MoS_2	0.5 M H_2SO_4	364	108	[12]
Vertically aligned 2H MoS_2	0.5 M H_2SO_4	400	105	[13]
MoS_2	1 M KOH	256	115	This work
2H MoS_2 bulk	1 M KOH	600	131	[14]
2H MoS_2 nanosheets	1 M KOH	500	108	[14]
2D-MoS_2/$Co(OH)_2$	1 M KOH	128	76	[15]
MoS_2	1 M KOH	300 (η_5)	144	[16]
Co_3O_4/MoS_2	1 M KOH	205	98	[17]
H-MoS_2	1 M KOH	326	134	[18]
MoS_2/NC	1 M KOH	185	90	[19]

η_{10}: Overpotential at the current density of 10 mA cm^{-2}

References

1 K. Huang, J. Xia, Y. Lu, B. Zhang, W. Shi, X. Cao, X. Zhang, L.M. Woods, C. Han, C. Chen, T. Wang, J. Wu and Y. Huang, *Adv. Sci.*, 2023, **10**, 2300094.

2 J. Wang, X. Yue, Y. Yang, S. Sirisomboonchai, P. Wang, X. Ma, A. Abudula and G. Guan, *J. Alloy. Compd.*, 2020, **819**, 153346.

3 Y. Lu, H. Xu, J. Wang and X. Kong, *Electrochim. Acta.,* 2009, **54**, 3972-3978.

4 T.A. Centeno, and F. Stoeckli, *J. Power Sources.*, 2006, **154**, 314-320.

5 C.C. McCrory, S. Jung, J.C. Peters and T.F. Jaramillo, *J. Am. Chem. Soc.*, 2013, **135**, 16977-16987.

6 F. Song, W. Li, J. Yang, G. Han, P. Liao and Y. Sun, *Nat. Commun.*, 2018, **9**, 4531.

7 H. Li, C. Tsai, A. L. Koh, L. Cai, A. W. Contryman, A. H. Fragapane, J.K. Nørskov and X. Zheng, *Nat. Mater.*, 2016, **15**, 48-53.

8 Y. Yu, G.-H. Nam, Q. He, X.-J. Wu, K. Zhang, Z. Yang, J. Chen, Q. Ma, M. Zhao, Z. Liu, F. Ran, X. Wang, H. Li, X. Huang, B. Li, Q. Xiong, Q. Zhang, Z. Liu, L. Gu, Y. Du, W. Huang, and Zhang, H. *Nat. Chem.*, 2018, **10**, 638-643.

9 W. Hu, G. Han, Y. Liu, B. Dong, Y. Chai, Y. Liu and C. Liu, *Int. J. Hydrog. Energy.*, 2015, **40**, 6552.

10 T. Wang, D. Guo, J. Zhou, Z. Zhu, P. Papakonstantinou, Y. li and M. li, *Chem. Eur. J.* 2013, **19**, 11939-11948.

11 J. Kibsgaard, Z. Chen, B.N. Reinecke and T.F. Jaramillo, *Nat. Mater.* 2012, **11**, 963-969.

12 Y. Chen, A. Lu, P. Lu, X. Yang, C. Jiang, M. Mariano, B. Kaehr, O. Lin, A. Taylor,

I.D. Sharp, L.J. Li, S.S. Chou and V. Tung, *Adv. Mater.*, 2017, **29**, 1703863.

13 D. Kong, H. Wang, J.J. Cha, M. Pasta, K.J. Koski, J. Yao and Y. Cui, *Nano Lett.*, 2013, **13**, 1341-1347.

14 S. Wang, D. Zhang, B. Li, C. Zhang, Z. Du, H. Yin, X. Bi and S. Yang, *Adv. Energy Mater.*, 2018, **8**, 1801345.

15 Z. Zhu, H. Yin, C.T. He, M. Al-Mamun, P. Liu, L. Jiang, Y. Zhao, Y. Wang, H.G. Yang, Z. Tang, D. Wang, X.M. Chen and H. Zhao, *Adv. Mater.*, 2018, **30**, 1801171.

16 S. Saleem, M. Salman, S. Alia, Y. Ling and M. Khan, Int. *J. Hydrog. Energy.*, 2022, **47**, 7713-7723.

17 A. Muthurasua, V. Maruthapandianc and H.Y. Kim, *Appl. Catal. B*., 2019, **248**, 202–210.

18 Q. Liu, Z. Xue, B. Jia, Q. Liu, K. Liu, Y. Lin, M. Liu, Y. Li and G. Li, *Small*, 2020, **16**, 2002482.

19 X. Huang, H. Xu, D. Cao and D. Cheng, *Nano Energy.*, 2020, 78, 105253.