Electronic Supplementary Information

Nano-interfacial interactions in 2-D Ni_3S_2 - Ni_3N nanosheets for hydrogen evolution reaction in alkaline medium

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Table of contents

S1 PXRD spectrum of Ni₃S₂ and Ni₃N

S2.1 Wide scan XPS spectra of Ni₃S₂-Ni₃N

S2.2 XPS analysis of Ni₃S₂

S2.3 XPS analysis of Ni₃N

S2.4Shifting in the XPS spectra of Ni₂p

S3.1 Table containing the HER activity of recently reported catalyst

S3.2 Table containing the value of R_s and R_{ct} for all the catalysts obtained from EIS analysis

S3.3 XPS analysis of Ni₃S₂-Ni₃N after stability

S3.4 PXRD pattern of the catalyst after stability

S3.5 CV curve used for the calculation of double layer capacitance





Figure S1. (a) and (b) PXRD pattern of Ni_3S_2 and Ni_3N



Figure S2.Wide scan XPS spectra of Ni₃S₂-Ni₃N

S2.2 XPS analysis of Ni₃S₂



Figure S3. (a) Wide scan XPS spectra of Ni_3S_2 (b) high resolution XPS spectra of Ni_2p present in Ni_3S_2 (c) high resolution XPS spectra of S2p present in Ni_3S_2

S2.3 XPS analysis of Ni₃N



Figure S4. (a) Wide scan XPS spectra of Ni₃N (b) high resolution XPS spectra of Ni₂p present in Ni₃N (c) high resolution XPS spectra of N1s present in Ni₃N

S2.4 Shifting in the XPS spectra of Ni₂p



Figure S5. (a) negative shift in the binding energy of Ni2p XPS spectra after the formation of heterointerface with Ni₃S₂ (b) positive shift in the XPS spectra of Ni2p after the formation of heterointerface with Ni₃N

S3.1 Table containing the HER activity of recently reported catalyst

Material	Electrolyte	Substrate	Overpotential (mV cm ⁻²)	Tafel slope (mV/dec)	Reference
PdSe2	1М КОН	GC	138	100	1
Ni-SA/NC	1М КОН	NC	102	120	2
Ni foam/CMP-350	1М КОН	NF	94	94	3
Cu-Ni3S2	1М КОН	NF	121	86.2	4
Ni3S2/NF	1М КОН	NF	161	82	5
NiWO4/Ni3S2-16	1М КОН	NF	136	112.6	6
Ni-MOF/Ni2P@EG	1М КОН	EG foil	132	59	7
Cu3N	1М КОН	GC	149.18	63.28	8
Ni3In0.6Cu0.4N1	1М КОН	GC	143	73.4	9
P-MoP/Mo2N	1М КОН	NF	89	78	10
Shig-NS-rod/NF	1M KOH	NF	137	55	11
CoP/Ni2P@HPNCP	1М КОН	GC	121	61.8	12
f Fe(OH)x@Cu-MOF	1М КОН	Carbon paper	112	76	13
Co2Ni1N	1М КОН	СС	102.6	60.17	14
Ni3Cu1@NG-NC-700	1М КОН	NC	95	84.2	15
Ni–Fe NPs	1М КОН	CFP	100	58	16
MoC-Mo2C/PNCDs	1М КОН	CFP	121	60	17
3% Bi/CoP	1М КОН	GC	122	60.2	18
Ni-SA/NC	1М КОН	NC	102	120	19
CoNiP-41	1М КОН	GC	138	65	20
Ni ₃ S ₂ -Ni ₃ N	1М КОН	NF	96	135	This work

Table S1. Table containing the HER activity of recently reported catalyst

S3.2 Table containing the value of R_{s} and R_{ct} for all the catalysts obtained from EIS analysis

Catalyst	R _s (Ω)	R _{ct} (Ω)
Ni ₃ S ₂ -Ni ₃ N	0.4	0.9
Ni ₃ N	0.38	1.16
Ni ₃ S ₂	0.4	3.2

Table S2. Table containing the value of R_{s} and R_{ct} for all the catalysts obtained from EIS analysis



S3.3 XPS analysis of Ni₃S₂-Ni₃N after stability

Figure S6. XPS analysis of the catalyst after stability

S3.4 PXRD pattern of Ni₃S₂-Ni₃N after stability test.



Figure S7 PXRD pattern of the catalyst after stability test

S3.5 CV curve used for the calculation of double layer capacitance



Figure S8. Cyclic voltammetry curve of (a) Ni₃S₂-Ni₃N, (b) Ni₃N and (c) Ni₃S₂ used for the calculation of double layer capacitance

Rreferences:

- Lin, Z., Xiao, B., Wang, Z., Tao, W., Shen, S., Huang, L., Zhang, J., Meng, F., Zhang, Q., Gu, L. and Zhong, W., 2021. Planar-Coordination PdSe2 Nanosheets as Highly Active Electrocatalyst for Hydrogen Evolution Reaction. *Advanced Functional Materials*, *31*(32), p.2102321.
- Zang, W., Sun, T., Yang, T., Xi, S., Waqar, M., Kou, Z., Lyu, Z., Feng, Y.P., Wang, J. and Pennycook, S.J., 2021. Efficient hydrogen evolution of oxidized Ni-N3 defective sites for alkaline freshwater and seawater electrolysis. *Advanced Materials*, 33(8), p.2003846.
- 3. Zhao, S., Berry-Gair, J., Li, W., Guan, G., Yang, M., Li, J., Lai, F., Corà, F., Holt, K., Brett, D.J. and He, G., 2020. The role of phosphate group in doped cobalt molybdate: improved electrocatalytic hydrogen evolution performance. *Advanced Science*, *7*(12), p.1903674.
- Zhang, L., Gao, X., Zhu, Y., Liu, A., Dong, H., Wu, D., Han, Z., Wang, W., Fang, Y., Zhang, J. and Kou, Z., 2021. Electrocatalytically inactive copper improves the water adsorption/dissociation on Ni 3 S 2 for accelerated alkaline and neutral hydrogen evolution. *Nanoscale*, *13*(4), pp.2456-2464.
- Liu, H.J., Yu, W.L., Li, M.X., Dou, S.Y., Wang, F.L., Fan, R.Y., Ma, Y., Zhou, Y.L., Chai, Y.M. and Dong, B., 2021. The rational design of Ni 3 S 2 nanosheets–Ag nanorods on Ni foam with improved hydrogen adsorption sites for the hydrogen evolution reaction. *Sustainable Energy & Fuels*, *5*(13), pp.3428-3435.
- Huang, S., Meng, Y., Cao, Y., Yao, F., He, Z., Wang, X., Pan, H. and Wu, M., 2020. Amorphous NiWO4 nanoparticles boosting the alkaline hydrogen evolution performance of Ni3S2 electrocatalysts. *Applied Catalysis B: Environmental*, 274, p.119120.
- Cheng, F., Wang, L., Wang, H., Lei, C., Yang, B., Li, Z., Zhang, Q., Lei, L., Wang, S. and Hou, Y., 2020. Boosting alkaline hydrogen evolution and Zn–H2O cell induced by interfacial electron transfer. *Nano Energy*, *71*, p.104621.
- Sajeev, A., Paul, A.M., Nivetha, R., Gothandapani, K., Gopal, T.S., Jacob, G., Muthuramamoorty, M., Pandiaraj, S., Alodhayb, A., Kim, S.Y. and Van Le, Q., 2022. Development of Cu3N electrocatalyst for hydrogen evolution reaction in alkaline medium. *Scientific Reports*, *12*(1), pp.1-13.
- Su, H., Tang, Y., Shen, H., Zhang, H., Guo, P., Gao, L., Zhao, X., Xu, X., Li, S. and Zou, R., 2022. Insights into Antiperovskite Ni3In1-xCuxN Multi-Crystalline Nanoplates and Bulk Cubic Particles as Efficient Electrocatalysts on Hydrogen Evolution Reaction. *Small*, *18*(12), p.2105906.
- Fu, Q., Wang, X., Han, J., Zhong, J., Zhang, T., Yao, T., Xu, C., Gao, T., Xi, S., Liang, C. and Xu, L., 2021. Phase-Junction Electrocatalysts towards Enhanced Hydrogen Evolution Reaction in Alkaline Media. *AngewandteChemie*, *133*(1), pp.263-271.
- Yang, D., Cao, L., Huang, J., Kajiyoshi, K., Feng, L., Kou, L., Liu, Q. and Feng, L., 2020. Generation of Ni 3 S 2 nanorod arrays with high-density bridging S 2 2- by introducing a small amount of Na 3 VO 4. 12H 2 O for superior hydrogen evolution reaction. *Nanoscale*, *12*(3), pp.2063-2070.
- Zhang, R., Zhu, R., Li, Y., Hui, Z., Song, Y., Cheng, Y. and Lu, J., 2020. CoP and Ni 2 P implanted in a hollow porous N-doped carbon polyhedron for pH universal hydrogen evolution reaction and alkaline overall water splitting. *Nanoscale*, *12*(46), pp.23851-23858.
- Cheng, W., Zhang, H., Luan, D. and Lou, X.W., 2021. Exposing unsaturated Cu1-O2 sites in nanoscale Cu-MOF for efficient electrocatalytic hydrogen evolution. *Science Advances*, 7(18), p.eabg2580.
- 14. Feng, X., Wang, H., Bo, X. and Guo, L., 2019. Bimetal–organic framework-derived porous rodlike Cobalt/Nickel nitride for All-pH value electrochemical hydrogen evolution. *ACS applied materials & interfaces*, *11*(8), pp.8018-8024.
- Liu, B., Peng, H.Q., Cheng, J., Zhang, K., Chen, D., Shen, D., Wu, S., Jiao, T., Kong, X., Gao, Q. and Bu, S., 2019. Nitrogen-Doped Graphene-Encapsulated Nickel–Copper Alloy Nanoflower for Highly Efficient Electrochemical Hydrogen Evolution Reaction. *Small*, *15*(48), p.1901545.

- Suryanto, B.H., Wang, Y., Hocking, R.K., Adamson, W. and Zhao, C., 2019. Overall electrochemical splitting of water at the heterogeneous interface of nickel and iron oxide. *Nature communications*, 10(1), pp.1-10.
- 17. Lu, X.F., Yu, L., Zhang, J. and Lou, X.W., 2019. Ultrafine dual-phased carbide nanocrystals confined in porous nitrogen-doped carbon dodecahedrons for efficient hydrogen evolution reaction. *Advanced Materials*, *31*(30), p.1900699.
- Guo, L., Bai, X., Xue, H., Sun, J., Song, T., Zhang, S., Qin, L., Huang, K., He, F. and Wang, Q., 2020. MOF-derived hierarchical 3D bi-doped CoP nanoflower eletrocatalyst for hydrogen evolution reaction in both acidic and alkaline media. *Chemical Communications*, *56*(56), pp.7702-7705.
- 19. Zang, W., Sun, T., Yang, T., Xi, S., Waqar, M., Kou, Z., Lyu, Z., Feng, Y.P., Wang, J. and Pennycook, S.J., 2021. Efficient hydrogen evolution of oxidized Ni-N3 defective sites for alkaline freshwater and seawater electrolysis. *Advanced Materials*, *33*(8), p.2003846.
- Lu, Y., Deng, Y., Lu, S., Liu, Y., Lang, J., Cao, X. and Gu, H., 2019. MOF-derived cobalt– nickel phosphide nanoboxes as electrocatalysts for the hydrogen evolution reaction. *Nanoscale*, *11*(44), pp.21259-21265.