

Electronic Supplementary Information

Nanofibrillar hydrogels outperform Pt/C for hydrogen evolution reactions under high-current conditions

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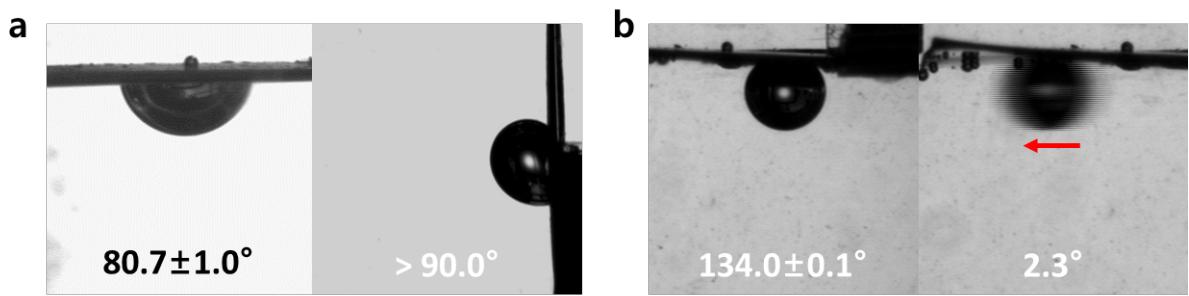


Fig. S1. Air contact and sliding angles of a) fNi and b) hydrogel-coated fNi (HG-fNi).

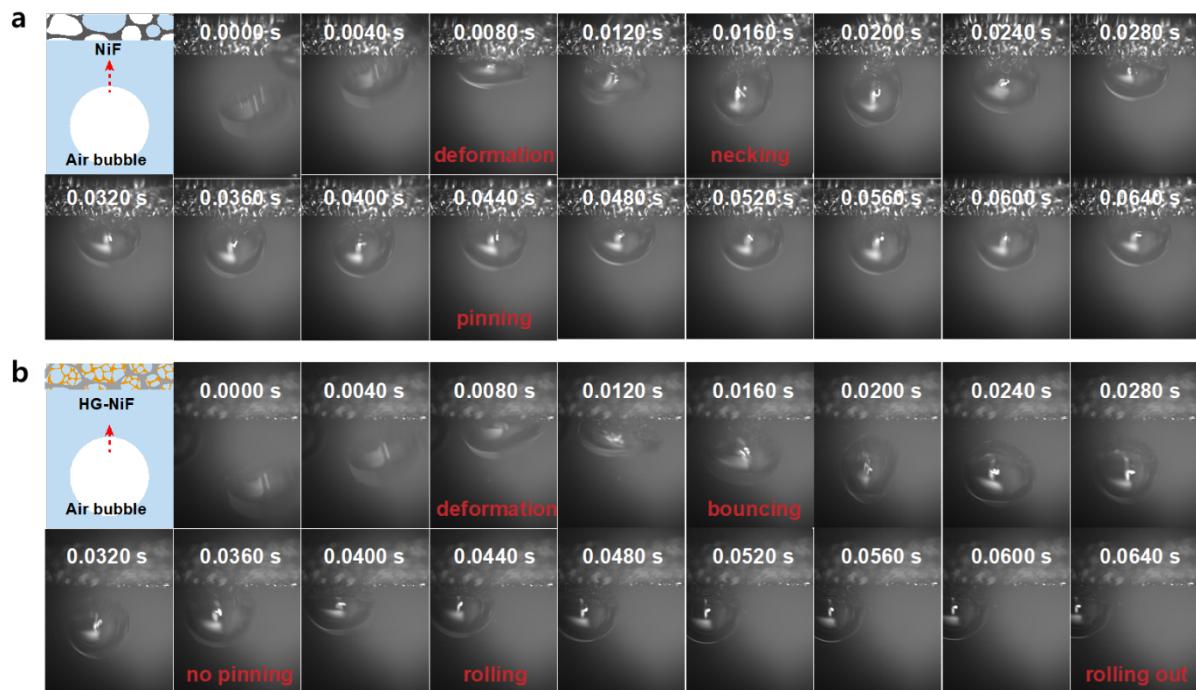


Fig. S2. High-speed camera images of air bubbles (volume = 25 μL) colliding with a) NiF and b) HG-NiF.

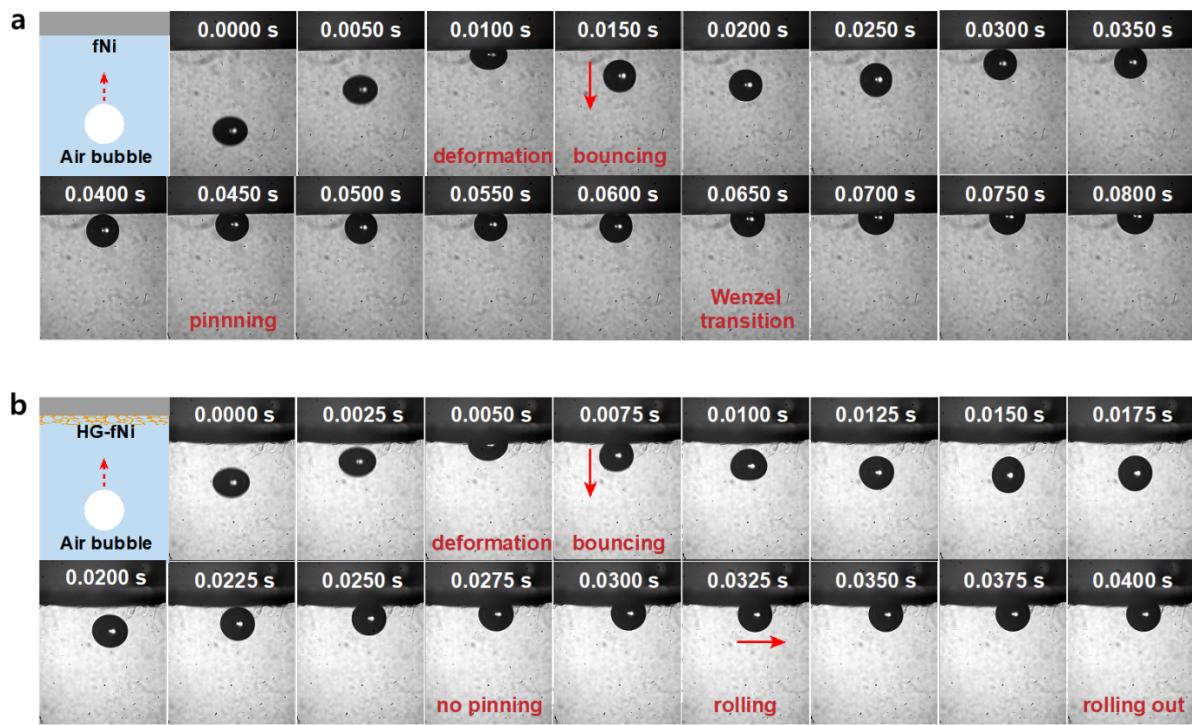


Fig. S3. High-speed camera images of air bubbles (volume = 1 μL) colliding with a) fNi and b) HG-fNi.

Table S1. Fitting results of electrochemical impedance spectra shown in Figure 4d.

	$R_1^{\text{a}} (\Omega)$	$R_2^{\text{b}} (\Omega)$	CPE ^c (mF)
Ni	4.46	29.86	
HG-NiF	3.877	46.98	
		21.85	
		30.78	

^a R_1 is a series resistance of electrical conduction through an external circuit and ionic conduction through an electrolyte.

^b R_2 represents a resistance related to catalytic hydrogen evolution reaction.

^cCPE represent a constant phase element.

Table S2. Overpotentials of various superaerophobic electrodes shown in Figure 4e for alkaline hydrogen evolution reaction.

Catalyst	Electrolyte	Overpotential (mV)	Ref.
HG-NiF	1.0 M KOH	-750 @ -1000 mA cm ⁻²	This work
Pt/C	1.0 M KOH	-750 @ -693 mA cm ⁻²	This work
CoMoS _x	1.0 M KOH	-280 @ -600 mA cm ⁻²	[1]
P-Ni(OH) ₂ /NiMoO ₄	1.0 M KOH	-500 @ -300 mA cm ⁻²	[2]
NSF/CNT	1.0 M KOH	-320 @ -300 mA cm ⁻²	[3]
CoSF/CNT	1.0 M KOH	-700 @ -350 mA cm ⁻²	[3]
FeSF/CNT	1.0 M KOH	-500 @ -300 mA cm ⁻²	[3]
FeCoNi-HNTAs	1.0 M KOH	-280 @ -150 mA cm ⁻²	[4]
MoS ₂	1.0 M KOH	-600 @ -150 mA cm ⁻²	[4]
Cu ₃ P	1.0 M KOH	-400 @ -120 mA cm ⁻²	[5]
CoMnP/Ni ₂ P	1.0 M KOH	-200 @ -50 mA cm ⁻²	[6]

Table S3. Comparison of HG-NiF to the efficiency and prices of various inorganic catalysts in 1.0 M KOH solution.

Catalyst	Electrolyte	Overpotential (mV)	Current density (mA cm ⁻²)	Mass loading (mg cm ⁻²)	Price (\$ mg ⁻¹)	Ref.
HG-NiF	1.0 M KOH	750	1000	0.002	22.5	This work
Pt/C	1.0 M KOH	750	693	28	0.0070	This work
Ru@Co-SAs	1.0 M KOH	7	10	0.285	0.0032	[7]
RuCo	1.0 M KOH	28	10	0.28	0.0021	[8]
Ni-MOF	1.0 M KOH	40	10	0.5	0.000018	[9]
Ni(OH) ₂ /CuS	1.0 M KOH	95	10	0.29	0.000012	[10]
CoSAs-CoNPs	1.0 M KOH	205	10	14	0.000053	[11]

Supporting References

- [1] X. Shan, J. Liu, H. Mu, Y. Xiao, B. Mei, W. Liu, G. Lin, Z. Jiang, L. Wen, L. Jiang, An engineered superhydrophilic/superaerophobic electrocatalyst composed of the supported CoMoS_x chalcogel for overall water splitting, *Angew. Chem. Int. Ed.* 59 (2020) 1659-1665.
- [2] W. Xi, G. Yan, H. Tan, L. Xiao, S. Cheng, S.U. Khan, Y. Wang, Y. Li, Superaerophobic P-doped Ni(OH)₂/NiMoO₄ hierarchical nanosheet arrays grown on Ni foam for electrocatalytic overall water splitting, *Dalton Trans.* 47 (2018) 8787-8793.
- [3] M. Guo, A. Qayum, S. Dong, X. Jiao, D. Chen, T. Wang, In situ conversion of metal (Ni, Co or Fe) foams into metal sulfide (Ni₃S₂, Co₉S₈ or FeS) foams with surface grown N-doped carbon nanotube arrays as efficient superaerophobic electrocatalysts for overall water splitting, *J. Mater. Chem. A* 8 (2020) 9239-9247.
- [4] H. Li, S. Chen, Y. Zhang, Q. Zhang, X. Jia, Q. Zhang, L. Gu, X. Sun, L. Song, X. Wang, Systematic design of superaerophobic nanotube-array electrode comprised of transition-metal sulfides for overall water splitting, *Nat. Commun.* 9 (2018) 2452.
- [5] J. Hao, W. Yang, Z. Huang, C. Zhang, Superhydrophilic and superaerophobic copper phosphide microsheets for efficient electrocatalytic hydrogen and oxygen evolution, *Adv. Mater. Interfaces*, 3 (2016) 1600236.
- [6] M. Liu, Z. Sun, S. Li, X. Nie, Y. Liu, E. Wang, Z. Zhao, Hierarchical superhydrophilic/superaerophobic CoMnP/Ni₂P nanosheet-based microplate arrays for enhanced overall water splitting, *J. Mater. Chem. A* 9 (2021) 22129-22139.
- [7] S. Yuan, Z. Pu, H. Zhou, J. Yu, I.S. Amiinu, J. Zhu, Q. Liang, J. Yang, D. He, Z. Hu, G. Van Tendeloo, S. Mu, A universal synthesis strategy for single atom dispersed cobalt/metal clusters heterostructure boosting hydrogen evolution catalysis at all pH values, *Nano Energy* 59 (2019) 472-480.
- [8] J. Su, Y. Yang, G. Xia, J. Chen, P. Jiang, Q. Chen, Ruthenium-cobalt nanoalloys encapsulated in nitrogen-doped graphene as active electrocatalysts for producing hydrogen in alkaline media, *Nat. Commun.* 8 (2017) 14969.
- [9] L. Wang, L. Ren, X. Wang, X. Feng, J. Zhou, B. Wang, Multivariate MOF-templated pomegranate-like Ni/C as efficient bifunctional electrocatalyst for hydrogen evolution and urea

oxidation, ACS Appl. Mater. Interfaces 10 (2018) 4750-4756.

[10] S.-Q. Liu, H.-R. Wen, G. Ying, Y.-W. Zhu, X.-Z. Fu, R. Sun, C.-P. Wong, Amorphous Ni(OH)₂ encounter with crystalline CuS in hollow spheres: A mesoporous nano-shelled heterostructure for hydrogen evolution electrocatalysis, Nano Energy 44 (2018) 7-14.

[11] M. Wang, M. Li, Y. Zhao, N. Shi, H. Zhang, Y. Zhao, Y. Zhang, H. Zhang, W. Wang, K. Sun, Y. Pan, S. Liu, H. Zhu, W. Guo, Y. Li, Y. Liu, C. Liu, Construction of N-doped carbon frames anchored with Co single atoms and Co nanoparticles as robust electrocatalyst for hydrogen evolution in the entire pH range, J. Energy Chem. 67 (2022) 147-156.