Cactus-like NC/Co_xP electrode enables efficient and stable hydrogen evolution

for saline water splitting

Xu Chen, Jin-yu Zhao, Wen-sheng Zhang, Xiao-min Wang*

College of Materials Science and Engineering, Taiyuan University of Technology,

Taiyuan 030024, China

E-mail address: wangxiaomin@tyut.edu.cn (X. Wang)

Electrochemical Characterization

The corresponding Tafel plots were obtained by fitting the polarization curves between the overpotential and log current densityby the equation:

$$\eta = blog(j) + a(1)$$

where η is the overpotential, b is the Tafel slope, j is the current density.

Electrochemical active surface area (ECSA) were tested in the non-Faraday region,

which could be calculated via the following equation:

$$ECSA = C_{dl}/C_s$$
 (2)

in which C_s is the specific capacitance for a flat surface and taken as 0.040 mF cm⁻² in

1 M KOH.



Figure S1. SEM and the corresponding EDS elemental mapping images of the NC@CoxP@NF-

10 catalyst.

Table S1. The element content of the NC@Co_xP@NF-10 sample.

Elements	wt%
С	8.90
Ν	1.42
Р	6.08
Со	83.60



Figure S2. Images of NC@Co_xP@NF-10 and Co_xP@NF



Figure S3. N₂ adsorption/desorption isotherm of NC@Co_xP@NF-10.



Figure S4. XPS survey spectra of CoxP@NF, NC@CoxP@NF-5, NC@CoxP@NF-10 and

NC@Co_xP@NF-15 catalysts.

Catalysts	Overpotential@10	Electrolyte	References
	mA cm ⁻²		
NC@CoxP@NF-10	107	1 M KOH	
	133	1 M KOH +0.5	This work
		M NaCl	
0.5CDs-NiCoP/NF	115	1 M KOH	[1]
IrCo ₃ O ₄ @NC	188	1 М КОН	[2]
Co(OH) ₂ /Fe ₇ Se ₈	183	1 M KOH	[3]
CoNC-SA/N*-C	194	1 М КОН	[4]
V ₂ CT _x	134	1 М КОН	[5]
SnS ₂ /SnO ₂	108	1 М КОН	[6]
MnFeCrLDH	154	1 M KOH	[7]
Ni ₂ P-Fe ₂ P/NF	128	1 M KOH	
	155	1 M KOH +0.5	[8]
		M NaCl	
CdFe-BDC	148	1 M KOH	[9]
Ni-Co@Fe-Co PBA	192	1.0 M KOH +	[10]
	185	0.5 M NaCl	
NiFeP/SG	115	1 M KOH	[11]
NiFe(dobpdc)	113	1 M KOH	[12]
2S-MnCo ₂ O ₄ /NC	180	1 M KOH	[13]
CoP _x @FeOOH/NF	117	1 M KOH	[14]
CoP/CoS ₂ /CC	111.2	1 M KOH	[15]
P-Fe ₂ O ₃ -CoP	126	1 M KOH	
	152	1 M KOH+0.5	[16]
		M NaCl	

Table S2. Comparison of HER performance of NC@Co_xP@NF-10 with other reported

electrocatalysts at room temperature.



Figure S5. CV curves at different scan rate for (a) Co_xP@NF, (b) NC@Co_xP@NF-5, (c)



NC@Co_xP@NF-10, (d) NC@Co_xP@NF-15, (e) NF and (f) Pt/C in 1 M KOH.

Figure S6. CV curves at different scan rate for (a) Co_xP@NF, (b) NC@Co_xP@NF-5, (c) NC@Co_xP@NF-10, (d) NC@Co_xP@NF-15, (e) NF and (f) Pt/C in 1 M KOH + 0.5 M NaCl.



Figure S7. (a) Co 2p and (b) P 2p XPS spectra comparison of NC@Co_xP@NF-10 before and after



Figure S8. Zeta potential of all catalysts.

References

- Haixing Zhao, Xu Jiang, Mengjing Jin, Jianqiao Song, Muxuan Li, Jinyuan Zhou, Xiaojun Pan, Construction of urchin-like bimetallic phosphides induced by carbon dots for efficient wide pH hydrogen production [J], Journal of Colloid and Interface Science, 2023, 652, 1208-1216.
- [2] Jung S, Senthil R A, Moon C J, et al. Mechanistic insights into ZIF-67-derived Irdoped Co₃O₄@N-doped carbon hybrids as efficient electrocatalysts for overall water splitting using in situ Raman spectroscopy [J]. Chemical Engineering Journal, 2023, 468.
- [3] Gong C, Zhao L, Li D, et al. In-situ interfacial engineering of Co(OH)₂/Fe₇Se₈ nanosheets to boost electrocatalytic water splitting [J]. Chemical Engineering Journal, 2023.
- [4] Wang M, Sun K, Mi W, et al. Interfacial Water Activation by Single-Atom Co-N₃ Sites Coupled with Encapsulated Co Nanocrystals for Accelerating Electrocatalytic Hydrogen Evolution [J]. ACS Catalysis, 2022: 10771-10780.
- [5] Wan J, Wang Y, Zhang H, et al. Local electrons perturbation of V₂CT_x via defect and strain for efficient hydrogen production [J]. Chemical Engineering Journal, 2023, 470.
- [6] Wu J, Zhao R, Xiang H, et al. Exposing highly active (100) facet on a SnS₂/SnO₂ electrocatalyst to boost efficient hydrogen evolution [J]. Applied Catalysis B: Environmental, 2021, 292.
- [7] Pal S, Shimizu K, Khatun S, et al. Electrolyte Engineering for Effective Seawater Splitting Based on Manganese Iron Chromium Layered Triple Hydroxides as Novel Bifunctional Electrocatalysts [J]. Journal of Materials Chemistry A, 2023, 11(23): 12151.
- [8] Wu L, Yu L, Zhang F, et al. Heterogeneous Bimetallic Phosphide Ni₂P Fe₂P as an Efficient Bifunctional Catalyst for Water/Seawater Splitting [J]. Advanced Functional Materials, 2020, 31(1).
- [9] Luo Y, Yang X, He L, et al. Structural and Electronic Modulation of Iron-Based

Bimetallic Metal-Organic Framework Bifunctional Electrocatalysts for Efficient Overall Water Splitting in Alkaline and Seawater Environment [J]. ACS Appl Mater Interfaces, 2022, 14(41): 46374-46385

- [10]Zhang H, Diao J, Ouyang M, et al. Heterostructured Core-Shell Ni-Co@Fe-Co Nanoboxes of Prussian Blue Analogues for Efficient Electrocatalytic Hydrogen Evolution from Alkaline Seawater [J]. ACS Catalysis, 2023, 13(2): 1349-1358.
- [11]Li R-Q, Wang B-L, Gao T, et al. Monolithic electrode integrated of ultrathin NiFeP on 3D strutted graphene for bifunctionally efficient overall water splitting [J]. Nano Energy, 2019, 58: 870-876.
- [12]Qi L, Su Y-Q, Xu Z, et al. Hierarchical 2D yarn-ball like metal-organic framework NiFe(dobpdc) as bifunctional electrocatalyst for efficient overall electrocatalytic water splitting [J]. Journal of Materials Chemistry A, 2020, 8(43): 22974-22982.
- [13]Liucheng Xia, Jinping Wang, Lili Bo, Wenping Shi, Yuning Zhang, Yuxing Shen, Xiaochao Ji, Xiaolin Guan, Yunxia Wang, Jinhui Tong. Electronic structure modulation coupling with interface effect for great improving water electrolysis by multiple dimensional S doped MnCo₂O₄ nanorods/N doped C nanosheets hybrids [J]. Chemical Engineering Journal, 2023, 467, 143464.
- [14]Libo Wu, Luo Yu, Brian McElhenny, Xinxin Xing, Dan Luo, Fanghao Zhang, Jiming Bao, Shuo Chen, Zhifeng Ren, Rational design of core-shell-structured CoP_x@FeOOH for efficient seawater electrolysis [J]. Applied Catalysis B: Environmental, 20212, 94, 120256.
- [15]Xian-Jun Niu, Ya-Jun Wang, Guo-Hong Gao, Teng-Da Yang, Jia-Wei Mei, Yong-Cheng Qi, Run-Ze Tian, Ji-Sen Li, Interfacial engineering of CoP/CoS₂ heterostructure for efficiently electrocatalytic pH-universal hydrogen production [J]. Journal of Colloid and Interface Science, 2023, 652, 989-996.
- [16]Zhijie Cui, Zhibo Yan, Jie Yin, Wenpin Wang, Mei-E Yue, Zhongcheng Li, Engineering P-Fe₂O₃-CoP nanosheets for overall freshwater and seawater splitting
 [J]. Journal of Colloid and Interface Science, 2023, 652, 1117-1125.