Supporting information

NH_4F-induced the morphology control of CoP nanostructures to enhance hydrogen evolution reaction

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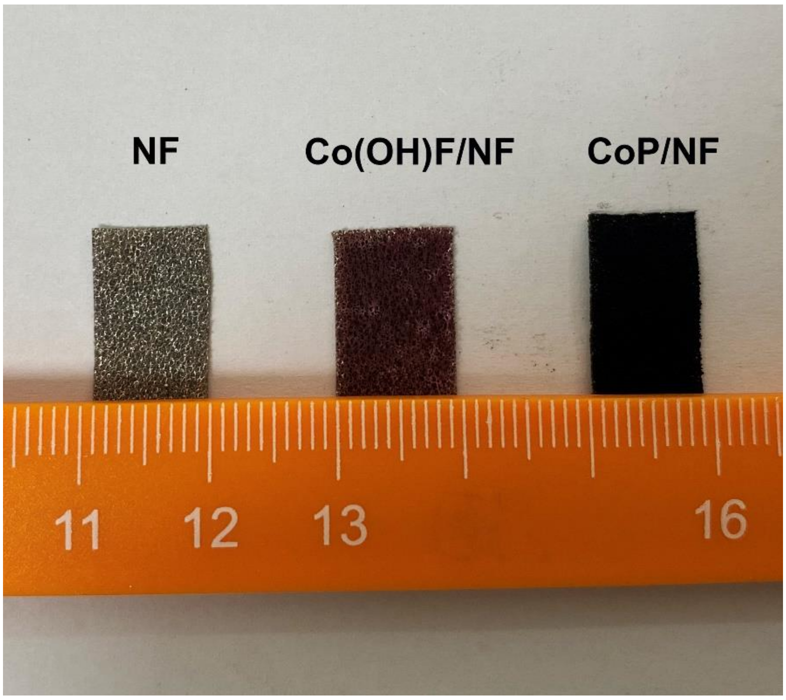

Figure S1 Optical photograph of Ni foam, Co(OH)F/NF and CoP-0.15M/NF.

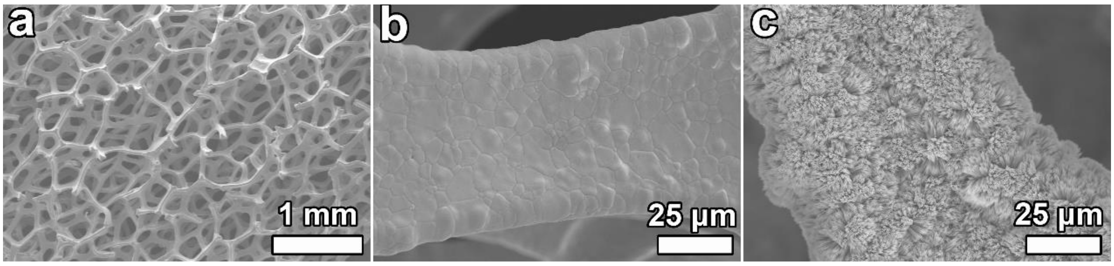

Figure S2 SEM images of (a-b) bare NF and (c) CoP-0.15M at the low magnification.

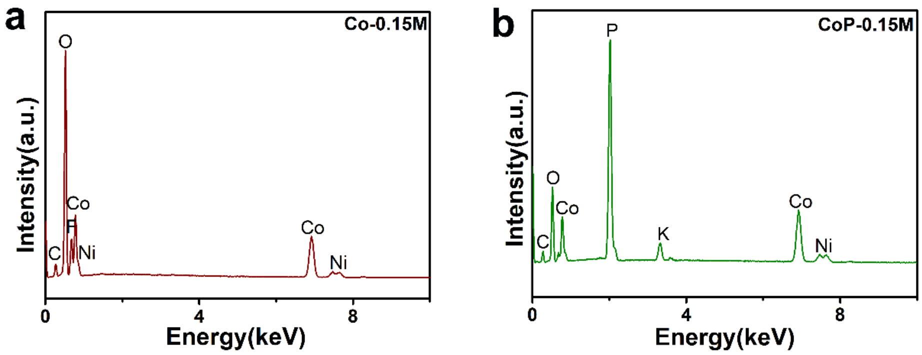

Figure S3 EDS spectra of (a) Co-0.15M precursor and (b) CoP-0.15M.

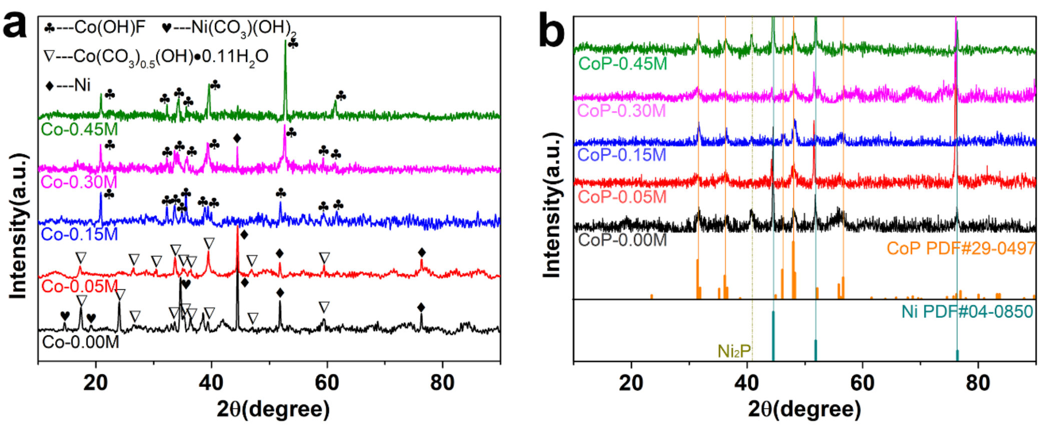

Figure S4 XRD patterns of (a) the obtained precursors and (b) corresponding CoP nanostructures with different morphologies.

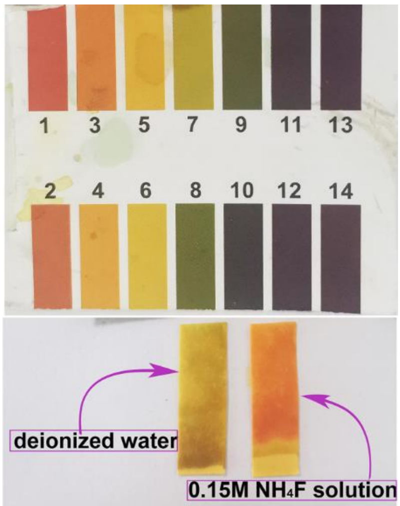

Figure S5 The pH values of deionized water and 0.15M NH_4F solution.

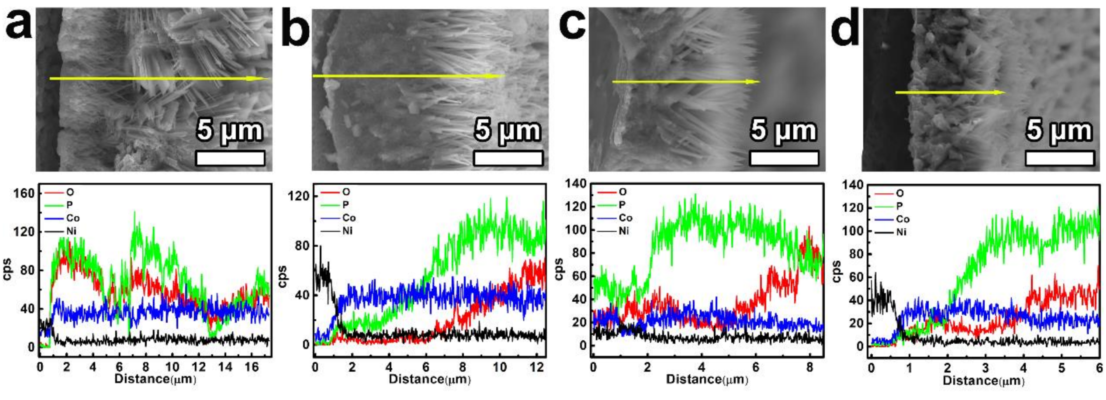

Figure S6 Sectional linear element distribution curves of (a) CoP-0.00M, (b) CoP-0.05M, (c) CoP-0.15M, and (d) CoP-0.30M.

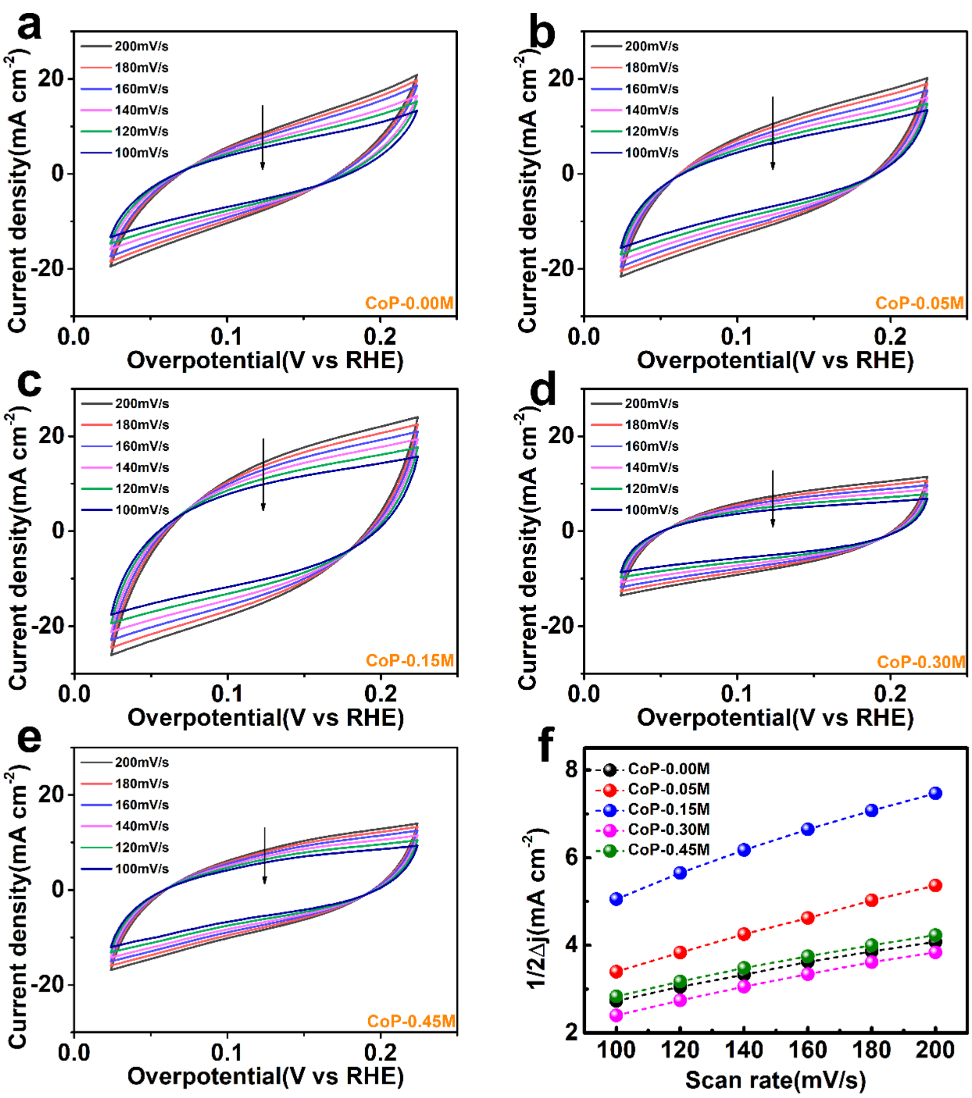

Figure S7 CVs of (a) CoP-0.00M, (b) CoP-0.05M, (c) CoP-0.15M, (d) CoP-0.30M, and (e) CoP-0.45M at scan rates of 100, 120, 140, 160, 180, and 200 mV s^{-1}, respectively. (f) Corresponding fitted curves.

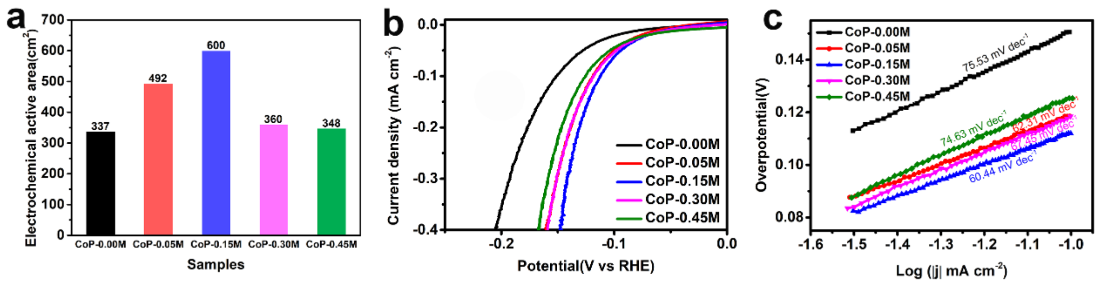

Figure S8 (a) The ECSA of the obtained CoP catalysts. (b) The LSV curves and (c) the Tafel slope plots of the obtained CoP catalysts normalized to their ECSA. The ECSA calculated by the equation of ECSA= C_{dl}/C_s, where the specific capacitance (C_s) value is estimated to be 0.04 mF cm^{-2}.

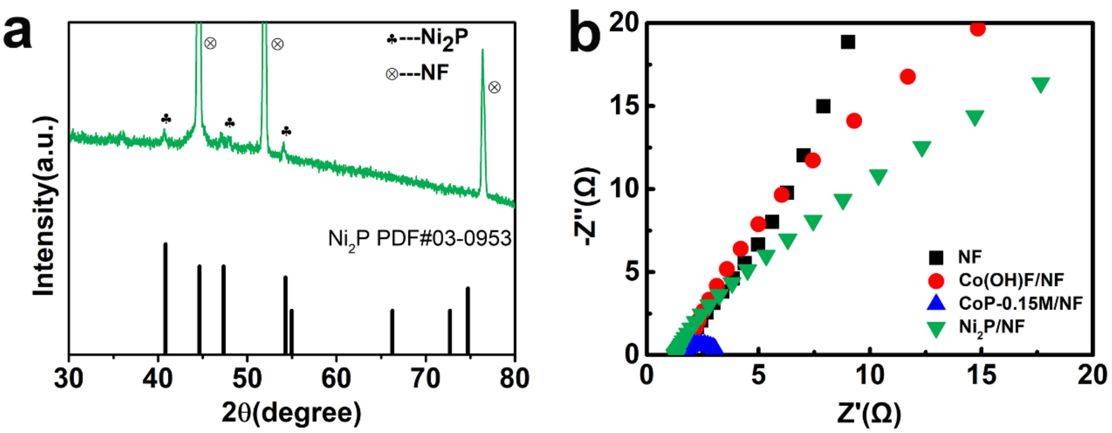

Figure S9 (a) XRD pattern of Ni_2P/NF obtained by the direct phosphorization of NF. (b) Nyquist plots of NF, Co(OH)F, Ni_2P/NF, and CoP-0.15M/NF electrodes at the overpotential of 76 mV.

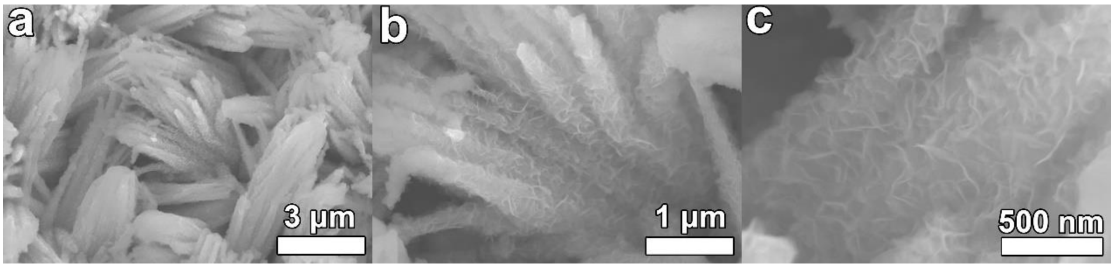

Figure S10 (a-c) SEM images of CoP-0.15M/NF after the 24 h HER test in 1.0 M KOH.

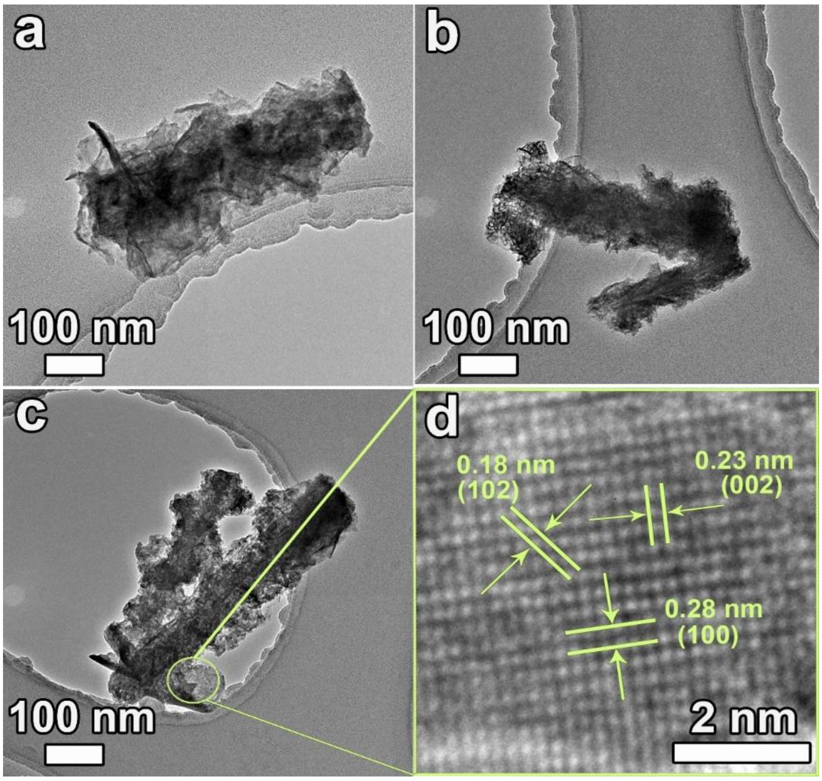

Figure S11 (a-c) TEM images and (d) HRTEM image of CoP-0.15M after the 24 h HER test.

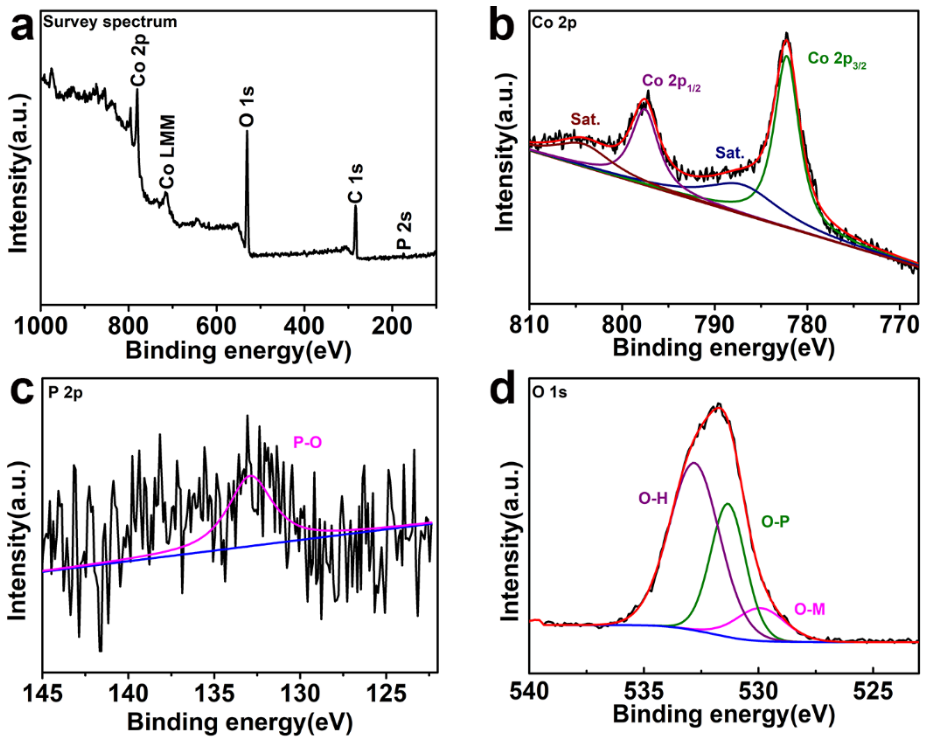

Figure S12 (a) XPS survey spectrum and (b-d) high resolution Co 2p, P 2p, and O1s spectra of CoP-0.15M after the 24 h HER test.

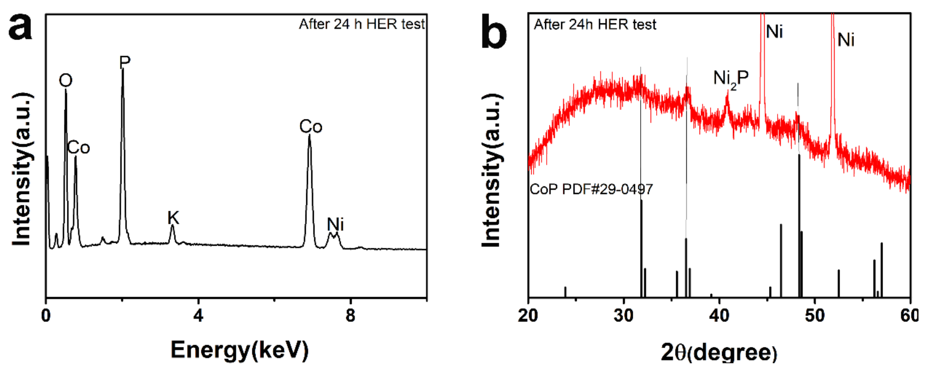

Figure S13 (a) EDS spectrum and (b) XRD pattern of CoP-0.15M after the 24 h HER test.

Table S1 The elemental compositions of the prepared Co-0.00M, Co-0.05M, Co-0.15M, Co-0.30M, and Co-0.45M precursors.

Element (at%)	Co	Ni	O	F	C
Co-0.00M	27.35	3.24	53.07	0	16.34
Co-0.05M	27.81	5.63	48.59	4.17	13.81
Co-0.15M	21.89	3.34	51.47	8.95	14.35
Co-0.30M	15.59	2.71	51.46	14.29	15.43
Co-0.45M	22.55	0	29.99	38.71	8.75

Table S2 The elemental compositions of the prepared CoP-0.00M, CoP-0.05M, CoP-0.15M, CoP-0.30M, and CoP-0.45M samples.

Element (at%)	Co	Ni	O	P
CoP-0.00M	25.17	9.61	45.84	19.4
CoP-0.05M	26.10	3.92	47.90	34.96
CoP-0.15M	32.58	5.25	29.86	32.31
CoP-0.30M	19.42	3.76	48.30	28.52
CoP-0.45M	44.54	3.70	25.16	26.60

Table S3 The R_s and R_{ct} values of the obtained CoP catalysts according to the fitted equivalent circuit.

	CoP-0.00M	**CoP-0.05M**	**CoP-0.15M**	**CoP-0.30M**	**CoP-0.45M**
R_s (Ω)	1.68	1.65	1.63	1.59	1.67
R_{ct} (Ω)	5.45	2.50	1.98	3.55	5.33

Table S4 Comparisons of the overpotentials and Tafel slopes of CoP-0.15M and reported CoP electrocatalysts for HER in 1.0 M KOH.

Electrocatalysts	**Tafel slope (mV dec^{-1})**	**η_{10} (mV)**	**Reference**
CoP nanorods	**60.75**	**71**	**This work**
CoP NC/CNT	54	122	1
CoP/rGO	50	105	2
CoP HP	59	159	3
CoP@BCN	52	215	4
Ni_2P-CoP	64	105	5
HNDCM-Co/CoP	64	135	6
Co_2P/CNTs	103	132	7
$Ni_{0.69}Co_{0.31}$–P	62	96	8
CoP/NiCoP/NC	64	75	9
Fe–Co_2P/NCNTs	68	104	10
CoP/CoP_2/Al_2O_3	63	138	11
P-Co_3O_4	52	120	12
NC@$CuCo_2N_x$/C	76	105	13
NiCo-nitrides/$NiCo_2O_4$/GF	62	71	14
Co/CoN/Co_2P-NPC	51	99	15

Table S5 The elemental compositions of CoP-0.15M before and after the 24 h HER test.

Element (at%)	Co	Ni	O	P
Before	32.58	5.25	29.86	32.31
After	40.41	6.42	37.01 ↑	16.16 ↓

Reference

1. Liu, Q.; Tian, J.; Cui, W.; Jiang, P.; Cheng, N.; Asiri, A. M.; Sun, X. Carbon nanotubes decorated with CoP nanocrystals: a highly active non-noble-metal nanohybrid electrocatalyst for hydrogen evolution. *Angew. Chem. Int. Ed.* **2014,** 53 (26), 6710-6714 DOI: 10.1002/anie.201404161.

2. Jiao, L.; Zhou, Y. X.; Jiang, H. L. Metal-organic framework-based CoP/reduced graphene oxide: high-performance bifunctional electrocatalyst for overall water splitting. *Chem. Sci.* **2016,** 7 (3), 1690-1695 DOI: 10.1039/c5sc04425a.

3. Liu, M.; Li, J. Cobalt Phosphide Hollow Polyhedron as Efficient Bifunctional Electrocatalysts for the Evolution Reaction of Hydrogen and Oxygen. *ACS Appl. Mater. Interfaces* **2016,** 8 (3), 2158-2165 DOI: 10.1021/acsami.5b10727.

4. Tabassum, H.; Guo, W.; Meng, W.; Mahmood, A.; Zhao, R.; Wang, Q.; Zou, R. Metal-Organic Frameworks Derived Cobalt Phosphide Architecture Encapsulated into B/N Co-Doped Graphene Nanotubes for All pH Value Electrochemical Hydrogen Evolution. *Adv. Energy Mater.* **2017,** 7 (9), 1601671-1601677 DOI: 10.1002/aenm.201601671.

5. Liang, X.; Zheng, B.; Chen, L.; Zhang, J.; Zhuang, Z.; Chen, B. MOF-Derived Formation of Ni_2P-CoP Bimetallic Phosphides with Strong Interfacial Effect toward Electrocatalytic Water Splitting. *ACS Appl. Mater. Interfaces* **2017,** 9 (27), 23222-23229 DOI: 10.1021/acsami.7b06152.

6. Wang, H.; Min, S.; Wang, Q.; Li, D.; Casillas, G.; Ma, C.; Li, Y.; Liu, Z.; Li, L. J.; Yuan, J.; Antonietti, M.; Wu, T. Nitrogen-Doped Nanoporous Carbon Membranes with Co/CoP Janus-Type Nanocrystals as Hydrogen Evolution Electrode in Both Acidic and Alkaline Environments. *ACS Nano.* **2017,** 11 (4), 4358-4364 DOI: 10.1021/acsnano.7b01946.

7. Das, D.; Nanda, K. K. One-step, integrated fabrication of Co_2P nanoparticles encapsulated N, P dual-doped CNTs for highly advanced total water splitting. *Nano Energy* **2016,** 30, 303-311 DOI: 10.1016/j.nanoen.2016.10.024.

8. Yin, Z.; Zhu, C.; Li, C.; Zhang, S.; Zhang, X.; Chen, Y. Hierarchical nickel-cobalt

phosphide yolk-shell spheres as highly active and stable bifunctional electrocatalysts for overall water splitting. *Nanoscale* **2016,** 8 (45), 19129-19138 DOI: 10.1039/c6nr07009d.

9. Boppella, R.; Tan, J.; Yang, W.; Moon, J. Homologous CoP/NiCoP Heterostructure on N-Doped Carbon for Highly Efficient and pH-Universal Hydrogen Evolution Electrocatalysis. *Adv. Funct. Mater.* **2018,** 29 (6), 1807976-1807984 DOI: 10.1002/adfm.201807976.

10. Pan, Y.; Liu, Y.; Lin, Y.; Liu, C. Metal Doping Effect of the M-Co_2P/Nitrogen-Doped Carbon Nanotubes (M = Fe, Ni, Cu) Hydrogen Evolution Hybrid Catalysts. *ACS Appl. Mater. Interfaces* **2016,** 8 (22), 13890-901 DOI: 10.1021/acsami.6b02023.

11. Li, W.; Zhang, S.; Fan, Q.; Zhang, F.; Xu, S. Hierarchically scaffolded CoP/CoP_2 nanoparticles: controllable synthesis and their application as a well-matched bifunctional electrocatalyst for overall water splitting. *Nanoscale* **2017,** 9 (17), 5677-5685 DOI: 10.1039/c7nr01017f.

12. Xiao, Z.; Wang, Y.; Huang, Y.-C.; Wei, Z.; Dong, C.-L.; Ma, J.; Shen, S.; Li, Y.; Wang, S. Filling the oxygen vacancies in $Co_3O_4$with phosphorus: an ultra-efficient electrocatalyst for overall water splitting. *Energy Environ.Sci.* **2017,** 10 (12), 2563-2569 DOI: 10.1039/c7ee01917c.

13. Zheng, J.; Chen, X.; Zhong, X.; Li, S.; Liu, T.; Zhuang, G.; Li, X.; Deng, S.; Mei, D.; Wang, J.-G. Hierarchical Porous NC@CuCo Nitride Nanosheet Networks: Highly Efficient Bifunctional Electrocatalyst for Overall Water Splitting and Selective Electrooxidation of Benzyl Alcohol. *Adv. Funct. Mater.* **2017,** 27 (46), 1704169-1704179 DOI: 10.1002/adfm.201704169.

14. Liu, Z.; Tan, H.; Liu, D.; Liu, X.; Xin, J.; Xie, J.; Zhao, M.; Song, L.; Dai, L.; Liu, H. Promotion of Overall Water Splitting Activity Over a Wide pH Range by Interfacial Electrical Effects of Metallic NiCo-nitrides Nanoparticle/$NiCo_2O_4$ Nanoflake/graphite Fibers. *Adv. Sci.* **2019,** 6 (5), 1801829-1801838 DOI: 10.1002/advs.201801829.

15. Hu, L.; Hu, Y.; Liu, R.; Mao, Y.; Balogun, M. S.; Tong, Y. Co-based MOF-derived Co/CoN/Co_2P ternary composite embedded in N- and P-doped carbon as bifunctional nanocatalysts for efficient overall water splitting. *Int. J. Hydrogen Energy* **2019,** 44 (23),

11402-11410 DOI: 10.1016/j.ijhydene.2019.03.157.