Supplementary Materials

CoP/EEBP/N-FLGS Nanocomposite as an Efficient Electrocatalyst of Hydrogen Evolution Reaction in Alkaline Media

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1. Results

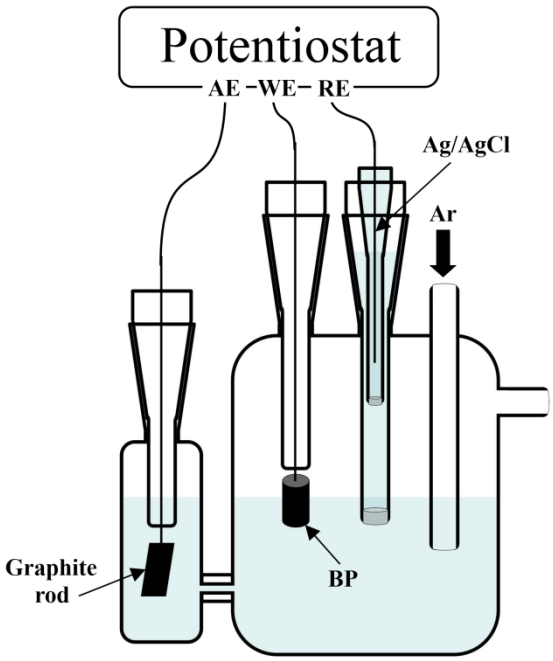

Figure S1. Schematic diagram of the cell for electrochemical expansion of black phosphorus.

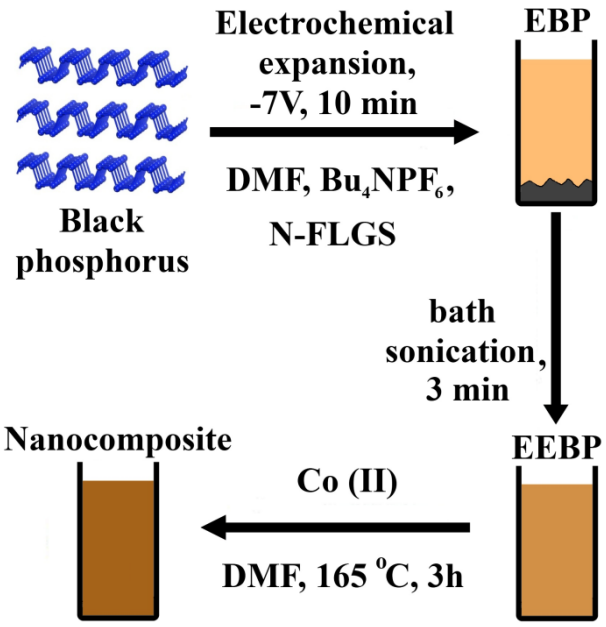

Figure S2. Schematic diagram of the synthesis of CoP/EEBP/N-FLGS nanocomposite.

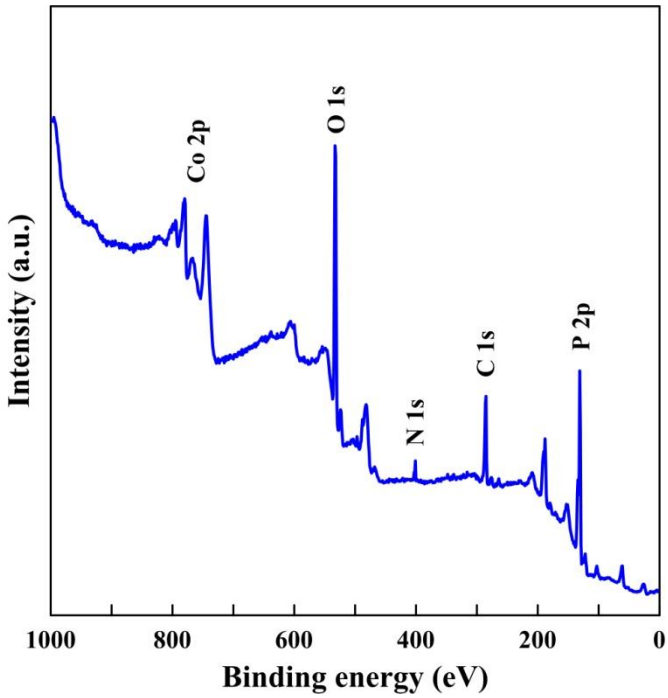

Figure S3. Survey XPS spectrum of CoP/EEBP/N-FLGS nanocomposite.

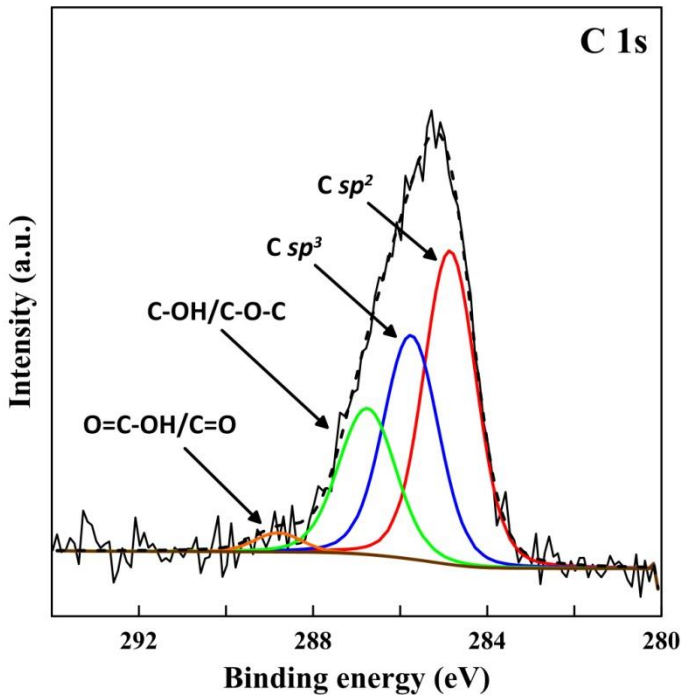

Figure S4. High resolution C 1s XPS spectrum of CoP/EEBP/N-FLGS nanocomposite.

Table S1. Elemental composition of the CoP/EEBP/N-FLGS surface (according to XPS results).

Sample	C, at. %	O, at. %	N, at. %	P, at. %	Co, at. %
CoP/EEBP/N-FLGS	23.3	29.5	1.2	41.9	4.1

Table S2. Comparison of electrocatalytic activity of catalysts based on cobalt phosphides towards HER.

№	Catalyst	η_{10}*, mV	Tafel slope, mV dec–1	Ref.
1	Co_2P/BP	260	72	[36]
2	CoP	209	129	[47]
3	CoP/Co_2P	198	82	[48]
4	CoP	275	101	[48]
5	CoP	265	123	[49]
6	CoP	280	94	[50]
7	Co_2P	215	78	[51]
8	Co_2P	345	128	[52]
9	CoP/Co_2P	226	114	[53]
10	CoP	203	65	[54]
11	CoP	215	52	[55]
12	CoP/EEBP/N-FLGS	190	78	This work

* η_{10} is overpotential at current density of 10 mA cm^{-2}.

References

36. Wang, J.; Liu, D.; Huang, H.; Yang, N.; Yu, B.; Wen, M.; Wang, X.; Chu, P.K.; Yu, X.-F. In-Plane Black Phosphorus/Dicobalt Phosphide Heterostructure for Efficient Electrocatalysis. *Angew. Chem.* **2018**, *130*, 2630–2634, doi:10.1002/ange.201710859.

47. Tian, J.; Liu, Q.; Asiri, A.M.; Sun, X. Self-Supported Nanoporous Cobalt Phosphide Nanowire Arrays: An Efficient 3D Hydrogen-Evolving Cathode over the Wide Range of pH 0–14. *J. Am. Chem. Soc.* **2014**, *136*, 7587–7590, doi:10.1021/ja503372r.

48. Lv, X.; Ren, J.-T.; Wang, Y.; Liu, Y.-P.; Yuan, Z.-Y. Well-Defined Phase-Controlled Cobalt Phosphide Nanoparticles Encapsulated in Nitrogen-Doped Graphitized Carbon Shell with Enhanced Electrocatalytic Activity for Hydrogen Evolution Reaction in all-pH. *ACS Sustain. Chem. Eng.* **2019**, *7*, 8993-9001, doi:10.1021/acssuschemeng.9b01263

49. Song, J.; Zhu, C.; Xu, B.Z.; Fu, S.; Engelhard, M.H.; Ye, R.; Du, D.; Beckman, S.P.; Lin, Y. Bimetallic Cobalt-Based Phosphide Zeolitic Imidazolate Framework: CoP_x Phase-Dependent Electrical Conductivity and Hydrogen Atom Adsorption Energy for Efficient Overall Water Splitting. *Adv. Energy Mater.* **2017**, *7*, 1601555, doi:10.1002/aenm.201601555.
50. Feng, Y.; Yu, X.-Y.; Paik, U. Nickel Cobalt Phosphides Quasi-Hollow Nanocubes as an Efficient Electrocatalyst for Hydrogen Evolution in Alkaline Solution. *Chem. Commun.* **2016**, *52*, 1633–1636, doi:10.1039/C5CC08991C.
51. Yang, M.; Feng, F.; Wang, K.; Li, S.; Huang, X.; Gong, L.; Ma, L.; Li, R. Synthesis of Metal Phosphide Nanoparticles Supported on Porous N-Doped Carbon Derived from Spirulina for Universal-pH Hydrogen Evolution. *ChemSusChem* **2020**, *13*, 351–359, doi:10.1002/cssc.201902920.
52. Zhang, X.-Y.; Guo, B.-Y.; Chen, Q.-W.; Dong, B.; Zhang, J.-Q.; Qin, J.-F.; Xie, J.-Y.; Yang, M.; Wang, L.; Chai, Y.-M.; et al. Ultrafine and Highly-Dispersed Bimetal Ni_2P/Co_2P Encapsulated by Hollow N-Doped Carbon Nanospheres for Efficient Hydrogen Evolution. *Int. J. Hydrogen Energy* **2019**, *44*, 14908–14917, doi:10.1016/j.ijhydene.2019.04.108.
53. Chen, A.; Fu, L.; Xiang, W.; Wei, W.; Liu, D.; Liu, C. Facile Synthesis of Ni_5P_4 Nanosheets/Nanoparticles for Highly Active and Durable Hydrogen Evolution. *Int. J. Hydrogen Energy* **2021**, *46*, 11701–11710, doi:10.1016/j.ijhydene.2021.01.079.
54. Yang, S.; Chen, L.; Wei, W.; Lv, X.; Xie, J. CoP Nanoparticles Encapsulated in Three-Dimensional N-Doped Porous Carbon for Efficient Hydrogen Evolution Reaction in a Broad PH Range. *Appl. Surf. Sci.* **2019**, *476*, 749–756, doi:10.1016/j.apsusc.2019.01.131.
55. 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*, 1601671, doi:10.1002/aenm.201601671.