

Supporting information

Ru, B Co-doped Hollow Structured Iron Phosphide as Highly Efficient Electrocatalyst toward Hydrogen Generation in Wide pH Range

Zixuan Wang^{1,#}, Yonglong Wang^{1,#}, Weiping Xiao², Xinping Wang¹, Yunlei Fu³, Guangrui Xu⁴, Zhenjiang Li⁴, Zexing Wu^{1,*}, Lei Wang^{1,3,*}

1. Key Laboratory of Eco-chemical Engineering, Ministry of Education, International Science and Technology Cooperation Base of Eco-chemical Engineering and Green Manufacturing, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: splswzx@qust.edu.cn; inorchemwl@126.com

2. College of Science, Nanjing Forestry University, Nanjing, 210037, PR China

3. Shandong Engineering Research Center for Marine Environment Corrosion and Safety Protection, College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao, 266042, PR China.

4. College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao, Shandong province, 266061, PR China

The authors contributed equally to this work.

Physical Characterization

The morphology and lattice striations of the catalysts were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM), the crystal structure of the catalysts was determined by X-ray diffraction (XRD) and the elemental composition of the catalysts was studied by X-ray photoelectron spectroscopy (XPS), the elemental distribution of the catalyst was characterized using an energy dispersive X-ray spectrometer (EDX).

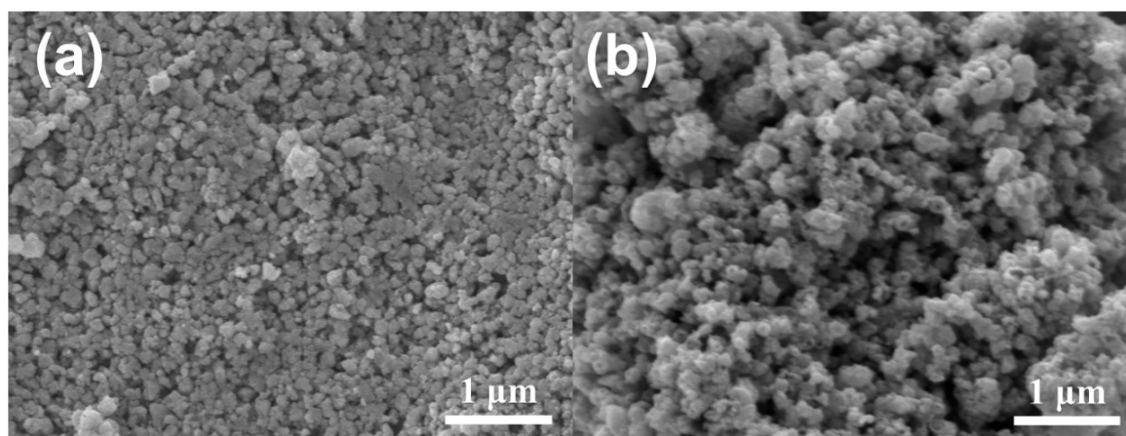


Fig. S1. SEM images of a) B/Ru-FeP. b) H-B/Ru-FeP.

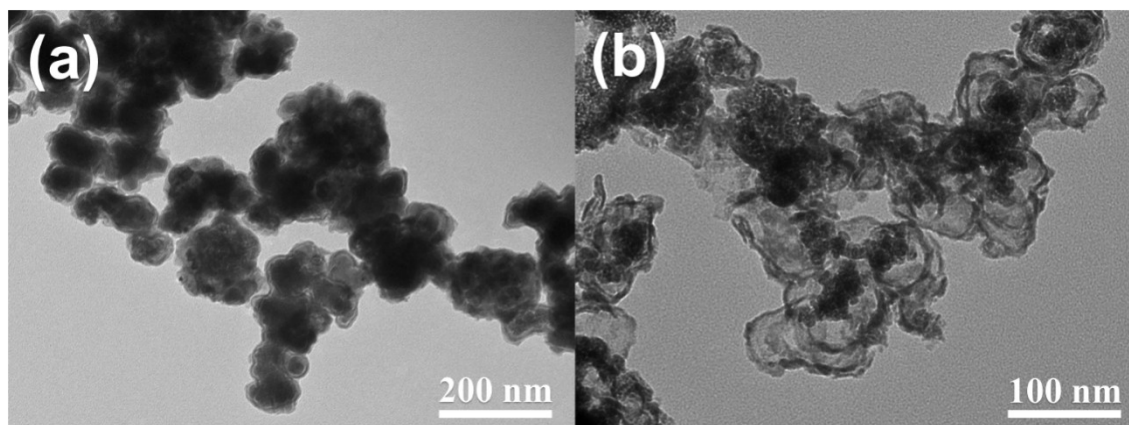


Fig. S2. TEM images of a) B/Ru-FeP. b) H-B/Ru-FeP.

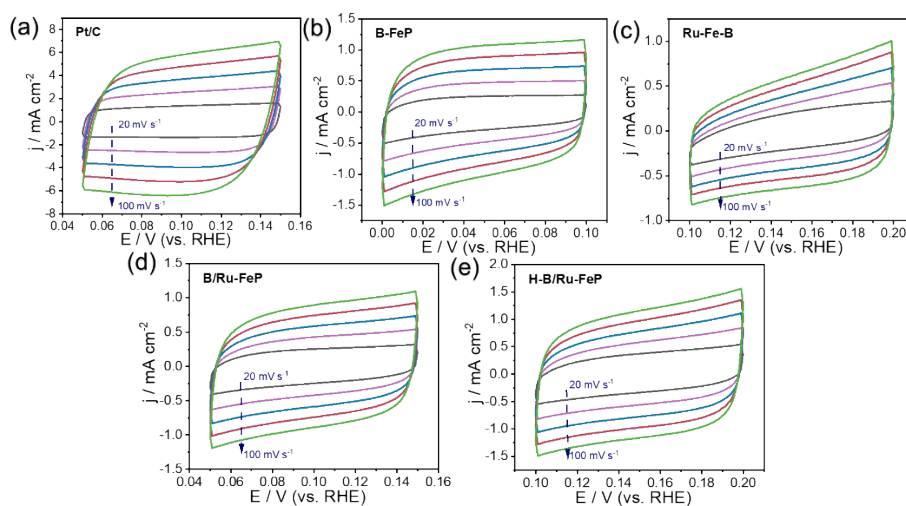


Fig. S3 Cyclic voltammety profiles for (a) Pt/C (b) B-FeP (c) Ru-Fe-B (d) B/Ru-FeP and (e) H-B/Ru-FeP at different scan rates (20, 40, 60, 80 and 100 mV s^{-1}) in a 0.5 M H_2SO_4 solution.

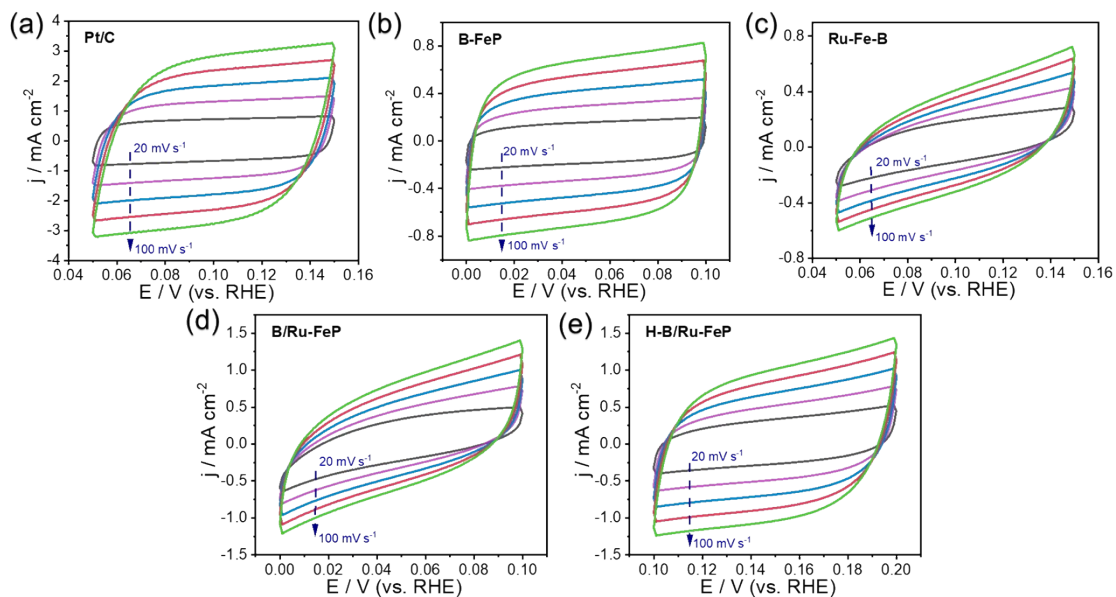


Fig. S4 Cyclic voltammetry profiles for (a) Pt/C (b) B-FeP (c) Ru-Fe-B (d) B/Ru-FeP and (e) H-B/Ru-FeP at different scan rates (20, 40, 60, 80 and 100 mVs⁻¹) in a 1 M PBS solution.

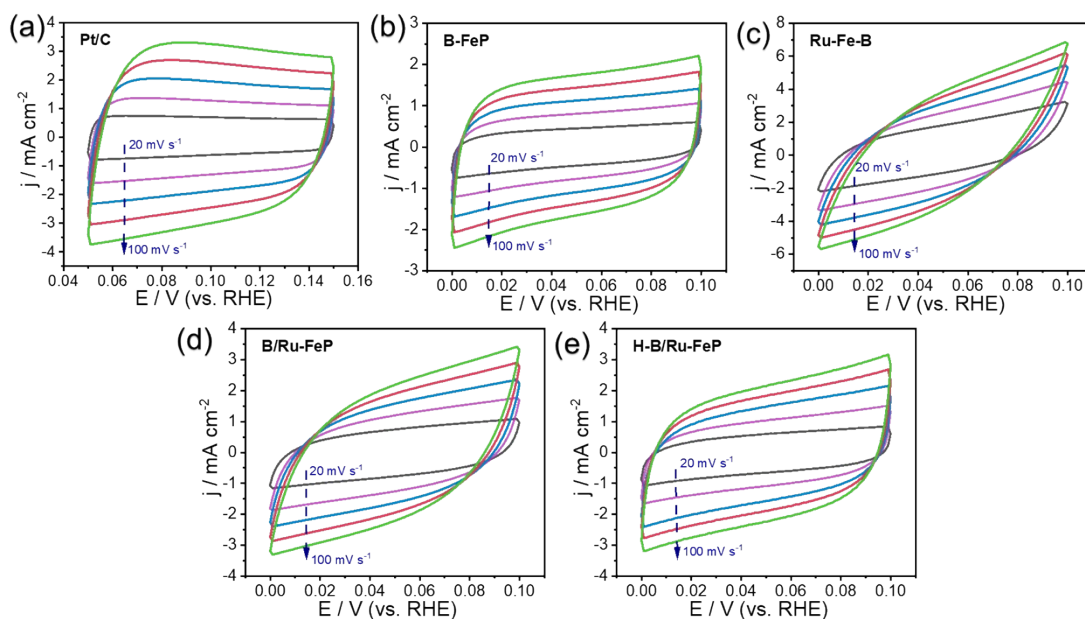


Fig. S5 Cyclic voltammetry profiles for (a) Pt/C (b) B-FeP (c) Ru-Fe-B (d) B/Ru-FeP and (e) H-B/Ru-FeP at different scan rates (20, 40, 60, 80 and 100 mVs⁻¹) in a 1 M KOH solution.

Table S1. Comparison of HER activity in 0.5 M H₂SO₄ for various electrocatalysts.

Electrocatalysts	Overpotential at 10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	Reference
H-B/Ru-FeP	29 mV	35.2	This work
RuP ₂ @NPC	38 mV	38	1
FeP nanorod array	58 mV	45	2
FeP/CF	88 mV	35.5	3
Fe-P/WO ₂	98 mV	47	4
Ru-MC	40 mV	42	5
RuFeP-NCs/CNF	65.8 mV	43.4	6
P-Ru/C	74 mV	51	7
Ni@Ni ₂ P-Ru	51 mV	35	8

Table S2. Comparison of HER activity in 1 M PBS for various electrocatalysts.

Electrocatalysts	Overpotential at 10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	Reference
H-B/Ru-FeP	86	72.5	This work
FeP/NCNSs	205	70	9
Ni-FeP/C	117	70	10
0.02-Ru@CN-6	82	103	11
RuP@NPC	110	57	12
Ru-NiFeP/NF	105.1	82.7	13
FePSe ₃ /NC	140.1	167	14
Co-Fe-P	138	138	15
RuP ₂ @NPC	57	87	1

Table S3. Comparison of HER activity in 1 M KOH for various electrocatalysts.

Electrocatalysts	Overpotential at 10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	Reference
H-B/Ru-FeP	110	76.7	This work
FeB ₂ NPs	61	87.5	16
NiFeP@C	160	78.5	17
Ni ₃ FeN	185	112.7	18
Ni-Fe-P-350	182	85	19
Fe-Co ₂ P BNRs	156	90	20
P-Ru/C	31	105	7
FeP Nanocubes-CP	140	61.9	18
FeCoP ₂ @NPPC	150	79	21

Table S4. Comparison of overall water splitting activity in 1 M KOH for various electrocatalysts.

Electrocatalysts	Overpotential at 10 mA cm ⁻²	Reference
H-B/Ru-FeP	1.54	This Work
Ni-Fe-P/NF ₃₀	1.58	22
Co-Mo-B-P/CF	1.59	23
Fe-Ni ₂ P/MoS _x /NF	1.61	24
FCP@NG	1.63	25
δ-FeOOH NSs	1.62	26
Ni _{0.7} Fe _{0.3} S ₂	1.63	27
NiFe-Se/C	1.68	28
Ni-Fe-P-350	1.67	19

References

1. Z. Pu, I. S. Amiin, Z. Kou, W. Li and S. Mu, *Angew. Chem. Int. Ed.*, 2017, **56**, 11559-11564.
2. Y. Liang, Q. Liu, A. M. Asiri, X. Sun and Y. Luo, *ACS Catal.*, 2014, **4**, 4065-4069.
3. Y. Yan, B. Y. Xia, X. Ge, Z. Liu, A. Fisher and X. Wang, *Chem. Eur. J.*, 2015, **21**, 18062-18067.
4. X. Sun, F. Yang, Z. Liu, L. Zeng and X. Cui, *Chem. Lett.*, 2019, **48**, 1232-1235.
5. Y. Jiang, Y. Qin, W. Luo, H. Liu, W. Shen, Y. Jiang, M. Li and R. He, *ChemElectroChem*, 2022, **9**, e202101580.
6. B. Yang, J. Xu, D. Bin, J. Wang, J. Zhao, Y. Liu, B. Li, X. Fang, Y. Liu, L. Qiao, L. Liu and B. Liu, *Appl. Catal. B-Environ.*, 2021, **283**, 119583.
7. Y. Zhao, X. Wang, G. Cheng and W. Luo, *ACS Catal.*, 2020, **10**, 11751-11757.
8. Y. Liu, S. Liu, Y. Wang, Q. Zhang, L. Gu, S. Zhao, D. Xu, Y. Li, J. Bao and Z. Dai, *J. Am. Chem. Soc.*, 2018, **140**, 2731-2734.
9. Y. Yu, Z. Peng, M. Asif, H. Wang, W. Wang, Z. Wu, Z. Wang, X. Qiu, H. Tan and H. Liu, *ACS Sustain. Chem. Eng.*, 2018, **6**, 11587-11594.

10. X. F. Lu, L. Yu and X. W. Lou, *Sci. Adv.*, 2019, **5**, eaav6009.
11. N. Wang, X. Bo and M. Zhou, *J. Colloid Interface Sci.*, 2021, **604**, 885-893.
12. J. Chi, W. Gao, J. Lin, B. Dong, K. Yan, J. Qin, B. Liu, Y. Chai and C. Liu, *ChemSusChem*, 2018, **11**, 743-752.
13. Y. Lin, M. Zhang, L. Zhao, L. Wang, D. Cao and Y. Gong, *Appl. Surf. Sci.*, 2021, **536**, 147952.
14. J. Yu, W. Li, H. Zhang, F. Zhou, R. Li, C. Xu, L. Zhou, H. Zhong and J. Wang, *Nano Energy*, 2019, **57**, 222-229.
15. J. Chen, J. Liu, J. Xie, H. Ye, X. Fu, R. Sun and C. Wong, *Nano Energy*, 2019, **56**, 225-233.
16. H. Li, P. Wen, Q. Li, C. Dun, J. Xing, C. Lu, S. Adhikari, L. Jiang, D. L. Carroll and S. M. Geyer, *Adv. Energy Mater.*, 2017, **7**, 1700513.
17. Q. Kang, M. Li, J. Shi, Q. Lu and F. Gao, *ACS Appl. Mater. Interfaces*, 2020, **12**, 19447-19456.
18. X. Liu, X. Lv, P. Wang, Q. Zhang, B. Huang, Z. Wang, Y. Liu, Z. Zheng and Y. Dai, *Electrochim. Acta.*, 2020, **333**, 135488.
19. C. Xuan, J. Wang, W. Xia, Z. Peng, Z. Wu, W. Lei, K. Xia, H. L. Xin and D. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 26134-26142.
20. Y. Lin, K. Sun, X. Chen, C. Chen, Y. Pan, X. Li and J. Zhang, *J. Energy Chem.*, 2021, **55**, 92-101.
21. Y. Wang, Z. Yang, D. Yang, L. Zhao, X. Shi, G. Yang and B. Han, *ACS Appl. Mater. Interfaces*, 2021, **13**, 8832-8843.
22. K. Wang, K. Sun, T. Yu, X. Liu, G. Wang, L. Jiang and G. Xie, *J. Mater. Chem. A.*, 2019, **7**, 2518-2523.
23. Y. Wei, P. Zou, Y. Yue, M. Wang, W. Fu, S. Si, L. Wei, X. Zhao, G. Hu and H. L. Xin, *ACS Appl. Mater. Interfaces*, 2021, **13**, 20024-20033.
24. X. Zhang, C. Liang, X. Qu, Y. Ren, J. Yin, W. Wang, M. Yang, W. Huang and X. Dong, *Adv. Mater. Interfaces*, 2020, **7**, 1901926.
25. Y. Lu, Y. Chen, K. Srinivas, Z. Su, X. Wang, B. Wang and D. Yang, *Electrochim. Acta*, 2020, **350**, 136338.
26. B. Liu, Y. Wang, H.-Q. Peng, R. Yang, Z. Jiang, X. Zhou, C.-S. Lee, H. Zhao and W. Zhang, *Adv. Mater.*, 2018, **30**, 1803144.
27. J. Yu, G. Cheng and W. Luo, *J. Mater. Chem. A.*, 2017, **5**, 15838-15844.
28. B. Xu, H. Yang, L. Yuan, Y. Sun, Z. Chen and C. Li, *J. Power Sources*, 2017, **366**, 193-199.