

Support Information

Synergistic Effect from Ru Nanoclusters on WC_{1-x} Anchored on N-doped Carbon Nanosheet Boosting High-efficient Alkaline Hydrogen Evolution

Hong Li^{a,b}, Lanxin Dai^a, Yinan Zheng^a, Hu Yao^a, Jiayu Bai^a, Xiaohui Guo^{a*}

^a Key Lab of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, and College of Chemistry and Materials Science, Northwest University, Xi'an, 710069, P. R. China.

^b College of Chemistry and Chemical Engineering, Yan'an University, Yan'an, 716000, P. R. China.

*Corresponding author E-mail: guoxh2009@nwu.edu.cn, Tel: 86-2981535031

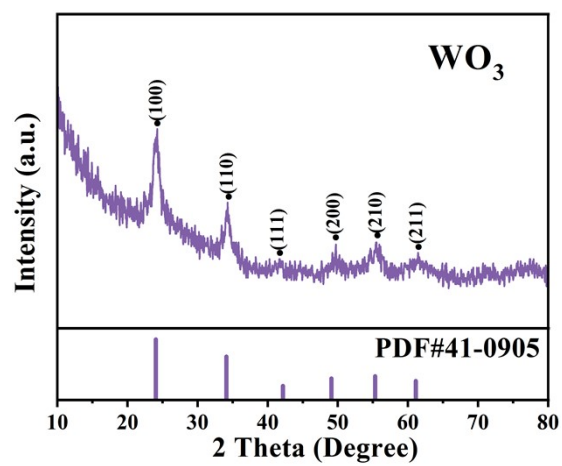


Figure S1 XRD pattern of the as-synthesized WO₃ nanosheets.

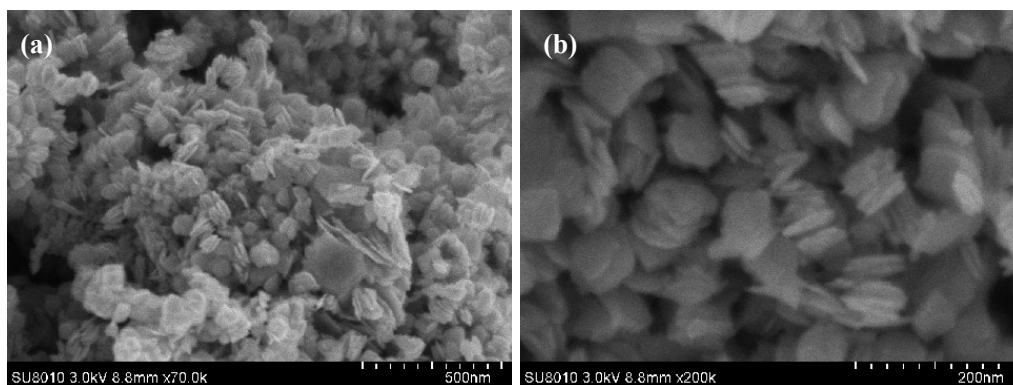


Figure S2 SEM images of the as-synthesized WO₃ nanosheets.

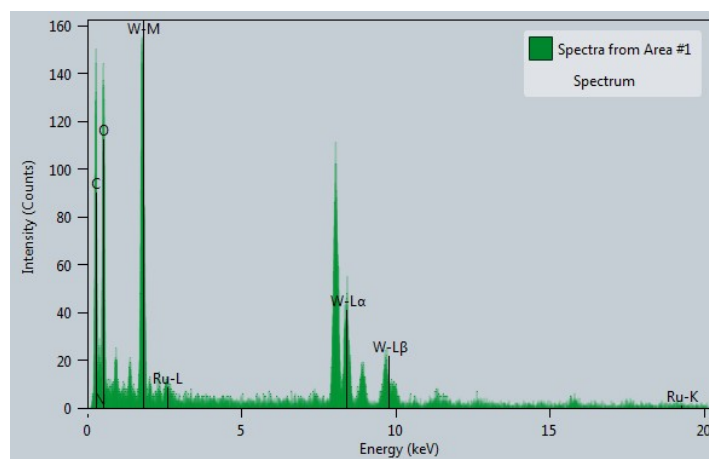


Figure S3 EDX patterns of the Ru/WC_{1-x}@NC hybrid.

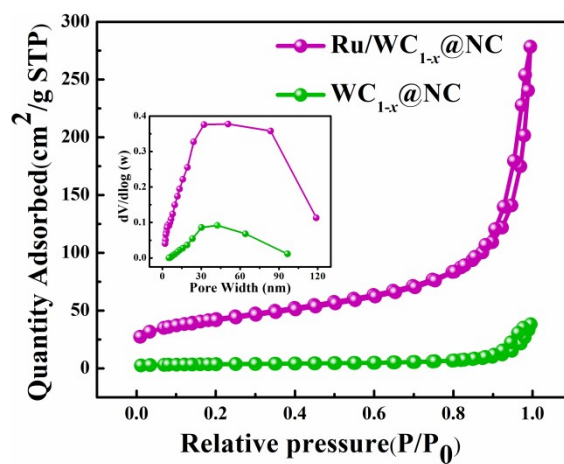


Figure S4 N₂ adsorption/desorption isotherms of Ru/WC_{1-x}@NC (the inset presents the corresponding pore size distribution).

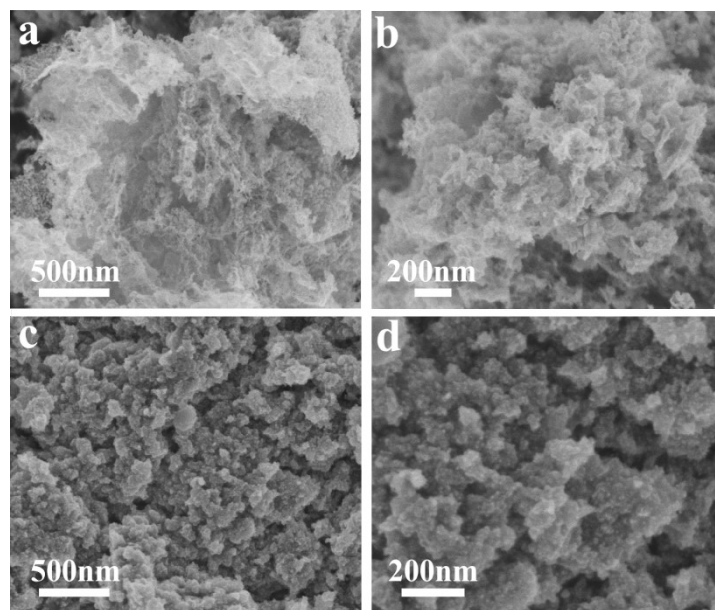


Figure S5 SEM images of the WC_{1-x}@NC (a-b) and Ru@NC (c-d) hybrids.

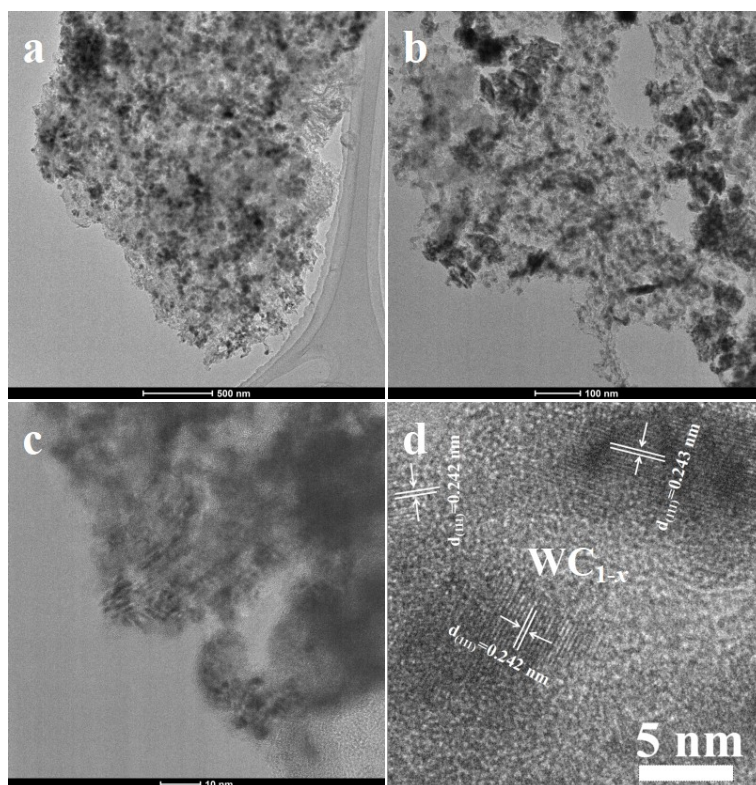


Figure S6 (a-c) TEM and (d) HRTEM images of the as-prepared $WC_{1-x}@NC$ hybrid.

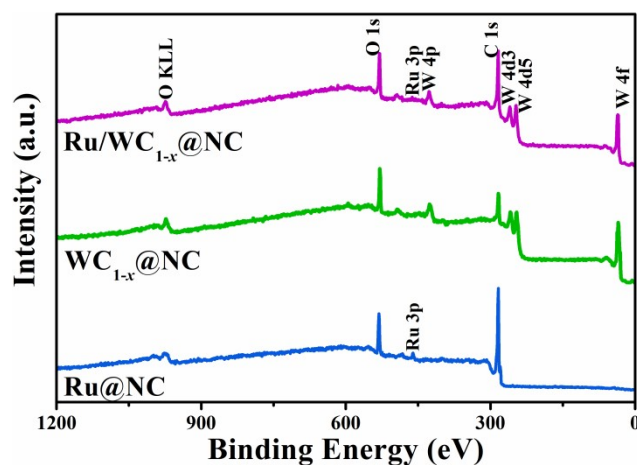


Figure S7 XPS surveys of the as-prepared $Ru/WC_{1-x}@NC$, $WC_{1-x}@NC$ and $Ru@NC$ hybrids.

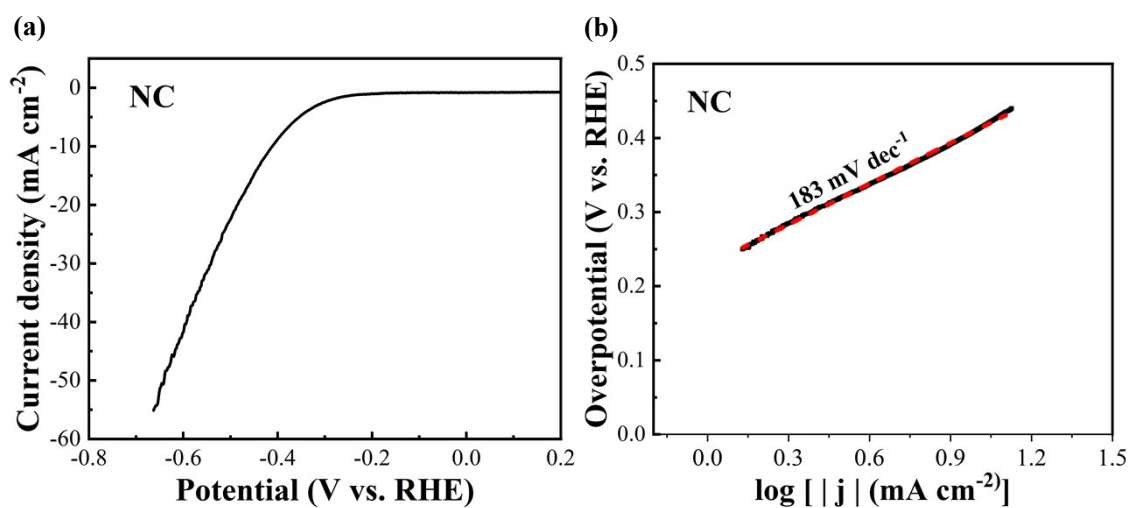


Figure S8 (a) LSV curve and (b) Tafel slope of nitrogen-doped carbon (NC) in 1 M KOH solution.

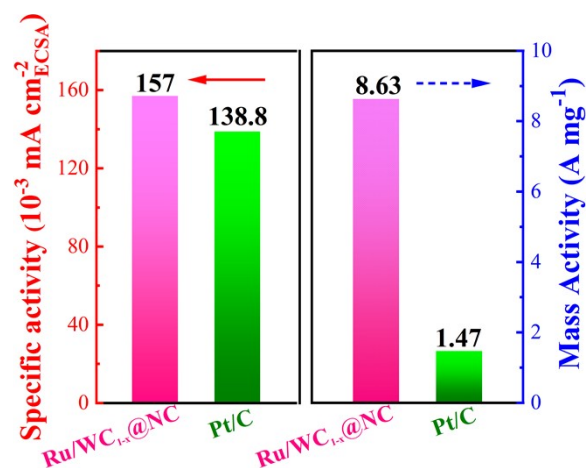


Figure S9. Specific activity and Mass activity of Ru/WC_{1-x}@NC hybrids at the overpotential of 100 mV, in comparison with the commercial Pt/C (20 wt.%).

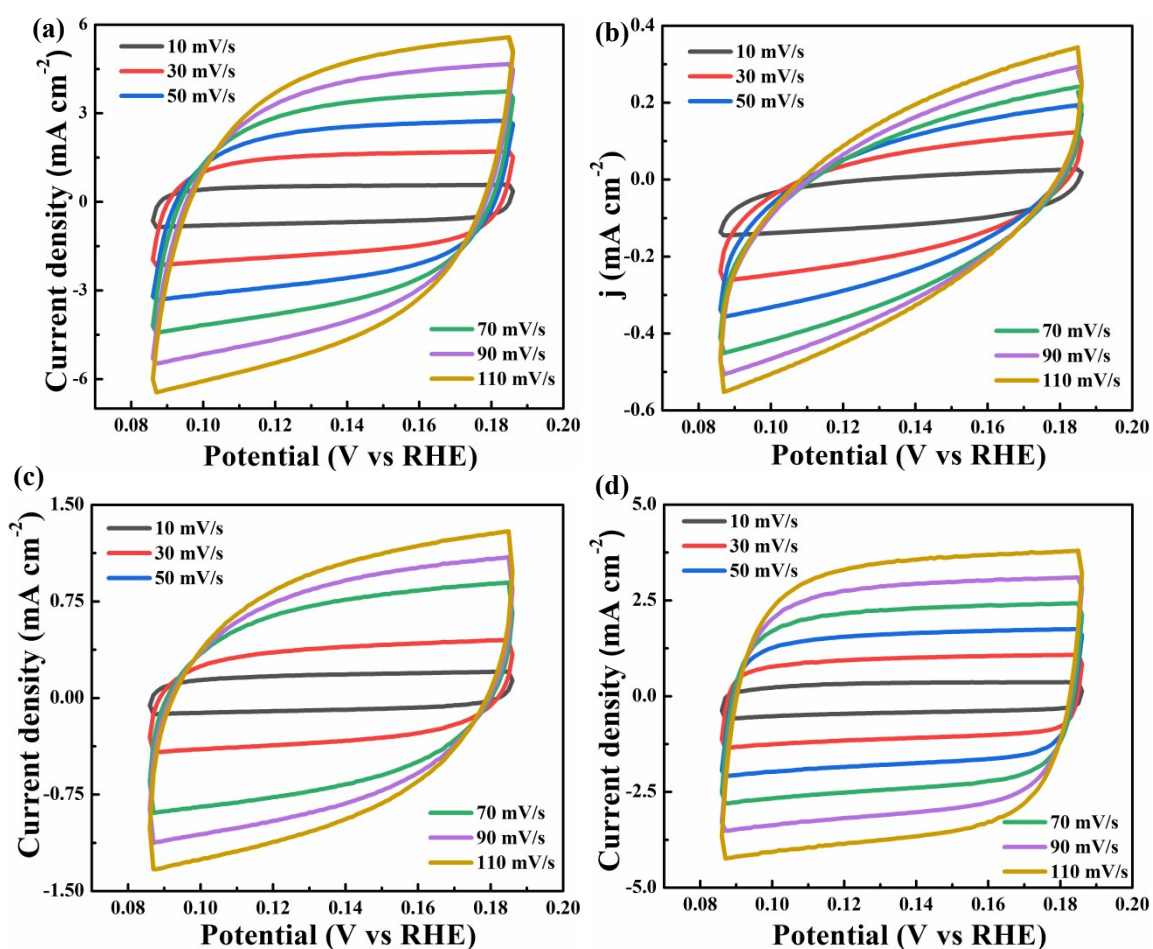


Figure S10 The CV curves measured at different scan rates in the nonfaradaic potential region (0.085-0.185 V vs. RHE) for (a) Ru/WC_{1-x}@NC, (b) WC_{1-x}@NC, (c) Ru@NC and (d) commercial Pt/C catalysts in 1 M KOH, respectively.

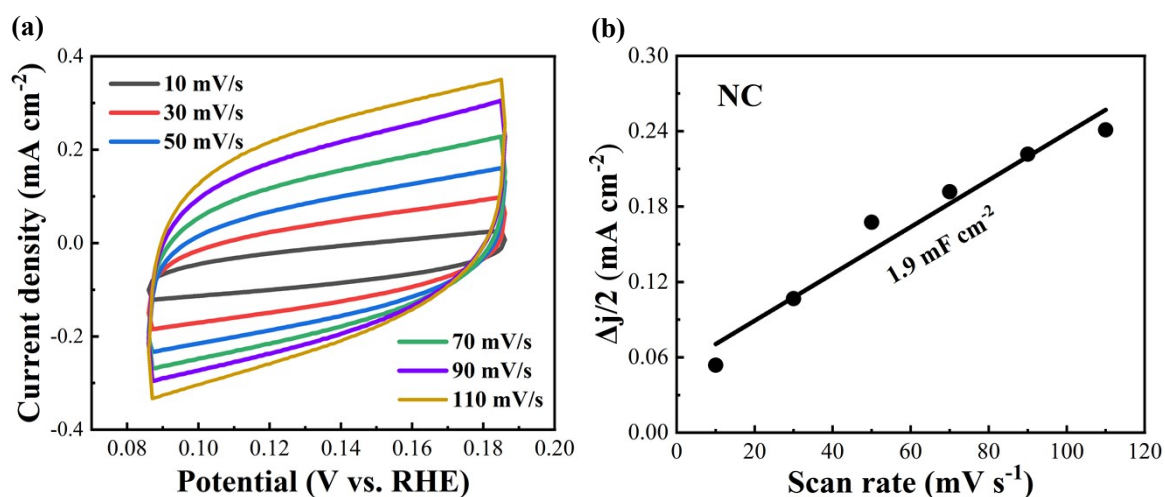


Figure S11 (a) The CV curves measured at different scan rates in the nonfaradaic potential region (0.085-0.185 V vs. RHE) and (b) the corresponding C_{dl} curve for NC support in 1 M KOH.

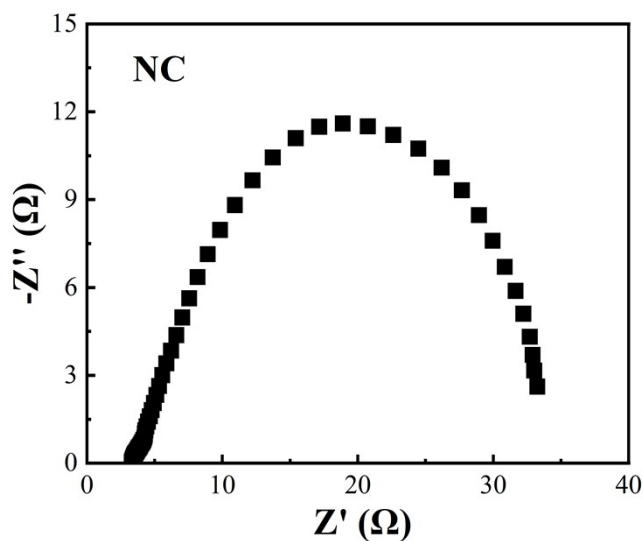


Figure S12. Nyquist plots of NC support in 1 M KOH solution.

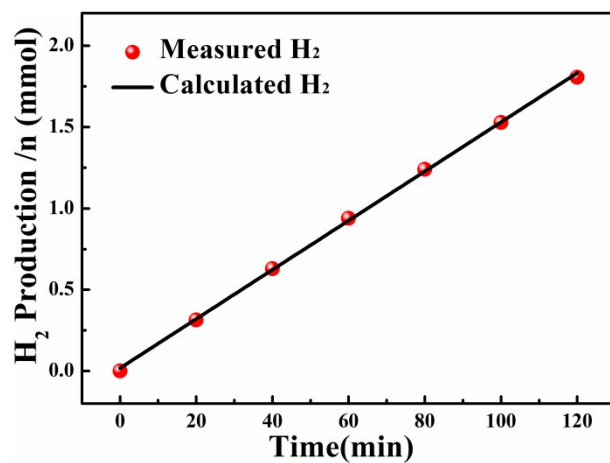


Figure S13. Comparison of the calculated and measured H₂ evolution amount of Ru/WC_{1-x}@NC hybrid at a period time.

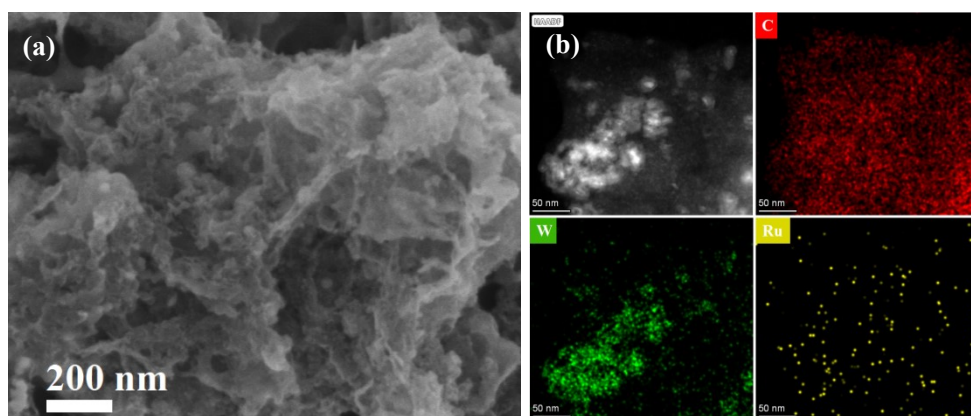


Figure S14. (a) SEM image and (b) EDX mapping spectra of Ru/WC_{1-x}@NC hybrid after 6000 CV cycles.

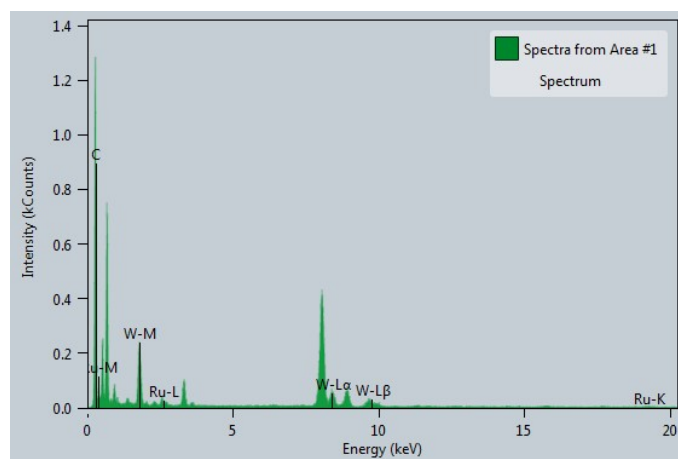


Figure S15. EDX patterns of the Ru/WC_{1-x}@NC hybrid after 6000 CV cycles.

Table S1. Ru content in the as-synthesized Ru/WC_{1-x}@NC hybrids measured through ICP-AES.

Samples	Ru content (wt.%)
Ru/WC _{1-x} @NC	2.5

Table S2 Comparison of Ru content in the resulted Ru/WC_{1-x}@NC hybrid in this work and the reported Ru-based catalysts in recent years.

catalysts	Ru content wt.%	measurement	Ref.
Ru/WC _{1-x} /NC	2.5	ICP-AES	This work
Ru ₂ P/WO ₃ @NP	3.4	ICP-AES	[1]
C			
(Ru-Co)O _x	28.4	ICP-AES	[2]
RuCo@NC	3.58	ICP-AES	[3]
Pyrite-type RuS ₂	14.1	ICP-OES	[4]
Ru/Co ₃ O ₄ NW	5.45	ICP-OES	[5]
Ru/g-C ₃ N ₄	20	TEM-EDS	[6]
Ru NCs/BNG	14.25	TGA	[7]
RuP ₂ @NPC	23.3	ICP-AES	[8]

S-RP/C	21.4	TGA	[9]
--------	------	-----	-----

Table S3 Comparison of HER activity of the resulted Ru/WC_{1-x}@NC hybrid in this work with reported WC_{1-x}-based or Ru-based electrocatalysts.

Electrocatalysts	Electrolyte	Overpotential ($\eta=10 \text{ mA cm}^{-2}$)	Tafel slope	Ref.
Carbon-encapsulated W ₂ C@WC _{1-x}	0.5 M H ₂ SO ₄	240 mV	86 mV dec ⁻¹	[10]
Pt(10 wt.%)/WC _{1-x} @C	0.5 M H ₂ SO ₄	127 mV	32 mV dec ⁻¹	[11]
W ₂ C@WC _{1-x} /Mo film	0.5 M H ₂ SO ₄	58 mV	41 mV dec ⁻¹	[12]
WC _{1-x} nanocrystals	1 M KOH	216 mV	122.2 mV dec ⁻¹	[13]
Ru nanoparticles/WSe ₂ nanosheets	1 M KOH	87 mV	118 mV dec ⁻¹	[14]
Ru nanoparticles/CoO nanorods	1 M KOH	55 mV	72 mV dec ⁻¹	[15]
Ru/TiO ₂ -VO@C hybrids	1 M KOH	64 mV	73 mV dec ⁻¹	[16]
Ru nanoparticle/CeO ₂ hybrids	1 M KOH	28.9 mV	53.2 mV dec ⁻¹	[17]
Ru-doped Mo ₂ C nanoparticles/NC	1 M KOH	34 mV	80 mV dec ⁻¹	[18]
Ru nanoparticles/N-doped carbon	1 M KOH	32 mV	53 mV dec ⁻¹	[19]
Ru nanoclusters/WC _{1-x} nanosheets /NC	1 M KOH	24 mV	45 mV dec ⁻¹	This work

References:

- [1] X. L. Jiang, H. Jang, S. G. Liu, Z. J. Li, M. G. Kim, C. Li, Q. Qin, X. E. Liu, J. Cho, The heterostructure of Ru₂P/WO₃/NPC synergistically promotes H₂O dissociation for improved hydrogen evolution. *Angew. Chem. Int. Ed.*, 2021, 60, 4110-4116.
- [2] C. Wang, L. M. Qi. Heterostructured inter-doped ruthenium-cobalt oxide hollow nanosheet arrays for highly efficient overall water splitting. *Angew. Chem. Int. Ed.*, 2020, 59, 17219-17224.
- [3] J. W. Su, Y. Yang, G. L. Xia, J. T. Chen, P. Jiang, Q. W. Chen. Ruthenium-cobalt nanoalloys encapsulated in nitrogen-doped graphene as active electrocatalysts for producing hydrogen in alkaline media. *Nat. Commun.*, 2017, 8, 14969.
- [4] Y. J. Xu, C. C. Du, Q. H. Shen, J. L. Huang, X. H. Zhang, J. H. Chen. Well-dispersed pyrite-type RuS₂ nanocrystals anchored on porous nitrogen and sulfur co-doped hollow carbon spheres for enhanced alkaline hydrogen evolution. *Chem. Eng. J.*, 2021, 417, 129318.
- [5] Z. Liu, L. L. Zeng, J. Y. Yu, L. J. Yang, J. Zhang, X. L. Zhang, F. Han, L. L. Zhao, X. Li, H. Liu, W. J. Zhou. Charge redistribution of Ru nanoclusters on Co₃O₄ porous nanowire via the oxygen regulation for enhanced hydrogen evolution reaction. *Nano Energy*, 2021, 85, 105940.
- [6] D. Z. Li, Y. Liu, J. Yang, C. Q. Hu, L. G. Feng. Electrochemical hydrogen evolution reaction efficiently catalyzed by Ru-N coupling in defect-rich Ru/g-C₃N₄ nanosheets. *J. Mater. Chem. A*, 2021, 9, 15019-15026.
- [7] S. H. Ye, F. Y. Luo, T. T. Xu, P. Y. Zhang, H. D. Shi, S. Q. Qin, J. P. Wu, C. X. He, X. P. Ouyang,

Q. L. Zhang, J. L. Liu, X. L. Sun. Boosting the alkaline hydrogen evolution of Ru nanoclusters anchored on B/N-doped graphene by accelerating water dissociation. *Nano Energy*, 2020, 68,104301.

[8] Z. H. Pu, I. S. Amiin, Z. K. Kou, W. Q. Li, S. S. Mu. RuP₂-based catalysts with platinum-like activity and higher durability for the hydrogen evolution reaction at all pH values. *Angew. Chem.* 2017, 129, 11717-11722.

[9] J. Yu, Y. A. Guo, S. X. She, S. S. Miao, M. Ni, W. Zhou, M. L. Liu, Z. P. Shao. Bigger is surprisingly better: agglomerates of larger RuP nanoparticles outperform benchmark Pt nanocatalysts for the hydrogen evolution reaction. *Adv. Mater.*, 2018, 30, 1800047.

[10] I. Kim, S. -W. Park, D. -W. Kim. Carbon-encapsulated multi-phase nanocomposite of W₂C@WC_{1-x} as a highly active and stable electrocatalyst for hydrogen generation. *Nanoscale*, 2018, 10, 21123-21131.

[11] I. Shanenkov, A. Ivashutenko, Y. Shanenkova, D. Nikitin, Y. K. Zhu, J. Z. Li, W. Han, A. Sivkov. Composite material WC_{1-x}@C as a noble-metal-economic material for hydrogen evolution reaction. *J. Alloy. Compd.*, 2020, 834, 155116.

[12] S. S. Xu, L. Q. Yang, Y. -Z. Liu, Y. Hua, X. M. Gao, A. Neville. Boosting hydrogen evolution performance by using a plasma-sputtered porous monolithic W₂C@WC_{1-x}/Mo film electrocatalyst. *J. Mater. Chem. A*, 2020, 8, 19473-19483.

[13] R. Tong, Y. J. Qu, Q. Zhu, X. N. Wang, Y. H. Lu, S. P. Wang, H. Pan. Combined experimental and theoretical assessment of WX_y (X = C, N, S, P) for Hydrogen evolution reaction. *ACS Appl. Energy Mater.* 2020, 3, 1082-1088.

- [14] Y. M. Zhao, G. X. Mao, C. Z. Huang, P. Cai, G. Z. Cheng, W. Luo. Decorating WSe₂ nanosheets with ultrafine Ru nanoparticles for boosting electrocatalytic hydrogen evolution in alkaline electrolytes. *Inorg. Chem. Front.*, 2019, 6, 1382-1387.
- [15] J. -X. Guo, D. -Y. Yan, K. -W. Qiu, C. Mu, D. Jiao, J. Mao, H. Wang, T. Ling. High electrocatalytic hydrogen evolution activity on a coupled Ru and CoO hybrid electrocatalyst. *J. Energy. Chem.*, 2019, 37, 143-147.
- [16] Z. Z. Wei, Z. J. Zhao, J. Wang, Q. Zhou, C. X. Zhao, Z. H. Yao, J. G. Wang. Oxygen-deficient TiO₂ and carbon coupling synergistically boost the activity of Ru nanoparticles for the alkaline hydrogen evolution reaction. *J. Mater. Chem. A*, 2021, 9, 10160-10168.
- [17] W. Wang, Y. R. Tao, X. C. Wu, L. J. Yang. Flower-like CeO₂-supported small-sized Ru nanoparticle hybrids for highly efficient alkaline hydrogen evolution: Roles of interfacial effects. *Appl. Surf. Sci.*, 2022, 581, 152256.
- [18] J. D. Chen, C. H. Chen, Y. Z. Chen, H. Y. Wang, S. J. Mao, Y. Wang. Improving alkaline hydrogen evolution reaction kinetics on molybdenum carbide: Introducing Ru dopant. *J. Catal.*, 2020, 392, 313-321.
- [19] J. Wang, Z. Z. Wei, S. J. Mao, H. R. Li, Y. Wang. Highly uniform Ru nanoparticles over N-doped carbon: pH and temperature-universal hydrogen release from water reduction. *Energy Environ. Sci.*, 2018, 11, 800-806.