

Electronic Supplementary Information

Hetero-structured Ru-Mo₂C nanoparticles loaded on N, P co-doped carbon for pH universal hydrogen evolution reaction

Yanqiang Li,^{a, b} Zhuo Zhang,^a Yingying Yao,^c Zi'an Wang,^a Zhongzheng Yang,^{a, b}
Yuping Tong,^{*, a, b} Siru Chen^{*, c}

^a School of Materials Science and Engineering, North China University of Water Resources and Electric Power, Zhengzhou, 450045, China E-mail: lyqncwu@126.com; yptong_zz@163.com

^b Henan Engineering Research Center on Special Materials and Applications of Water Conservancy and Hydropower Engineering, Zhengzhou, 450045, China

^c School of Material and Chemical Engineering, Center for Advanced Materials Research, Zhongyuan University of Technology, Zhengzhou, 450007, China E-mail: siruchen@zut.edu.cn

1. Materials characterization

The microstructure of the catalysts was observed by scanning electron microscope (SEM, Nova Nano SEM 450) and transmission electron microscopy (TEM, JEM-2100F). The catalyst's phase and composition were measured by X-ray diffraction (XRD, Lab XRD-7000s) and X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi). The gas adsorption-desorption curves were measured on a surface area analyzer (Micromeritics 3020 instrument).

2. Electrochemical Measurements

Electrochemical measurements were performed in 1.0 M KOH using the standard three-electrode system. Graphite rod, Ag/AgCl (KCl saturated) electrode, and electrocatalyst modified glassy carbon electrode (polished using α -Al₂O₃) are used as the counter electrode, reference electrode, and working electrode, respectively. The catalyst ink is prepared by dispersing 5 mg catalyst into a mixture of 480 μ L H₂O, 480 μ L ethanol and 40 μ L Nafion. The 16 μ L catalyst ink was dipped onto the glass carbon and dried naturally under room temperature. The loading of catalysts is 0.4 mg m⁻², and the Ru content for Ru-Mo₂C@NPC is 0.023 mg cm⁻². The linear sweep voltammetry (LSV) test is performed at a scan rate of 5 mVs⁻¹ with 85% IR compensation. Electrochemical impedance spectroscopy (EIS) was measured at a frequency of 0.01-10⁵ Hz at 0.5 V.

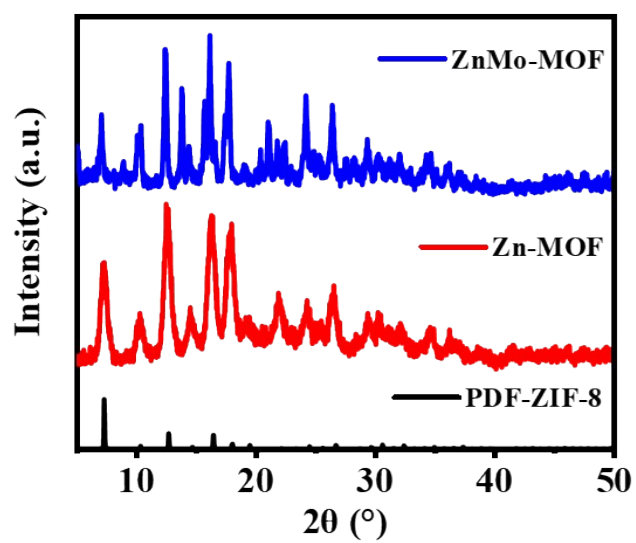


Figure S1. XRD patterns of Zn-MOF and ZnMo-MOF.

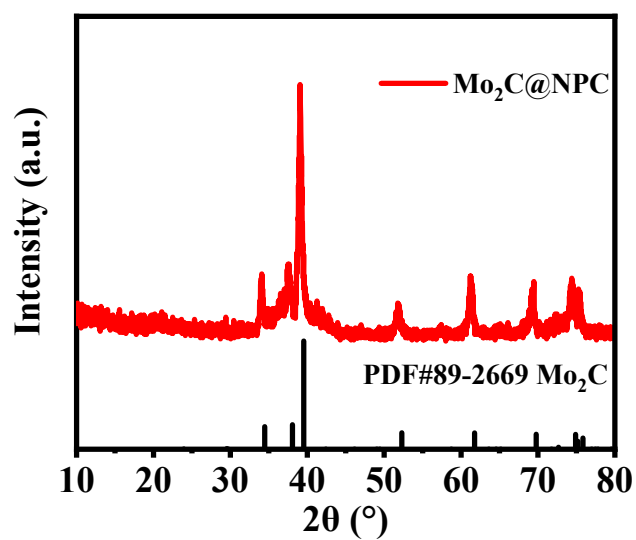


Figure S2. XRD pattern of Mo₂C@NPC.

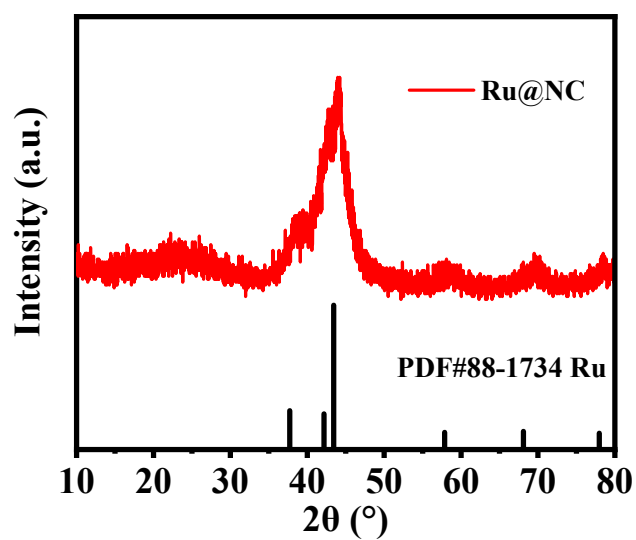


Figure S3. XRD pattern of Ru@NC.

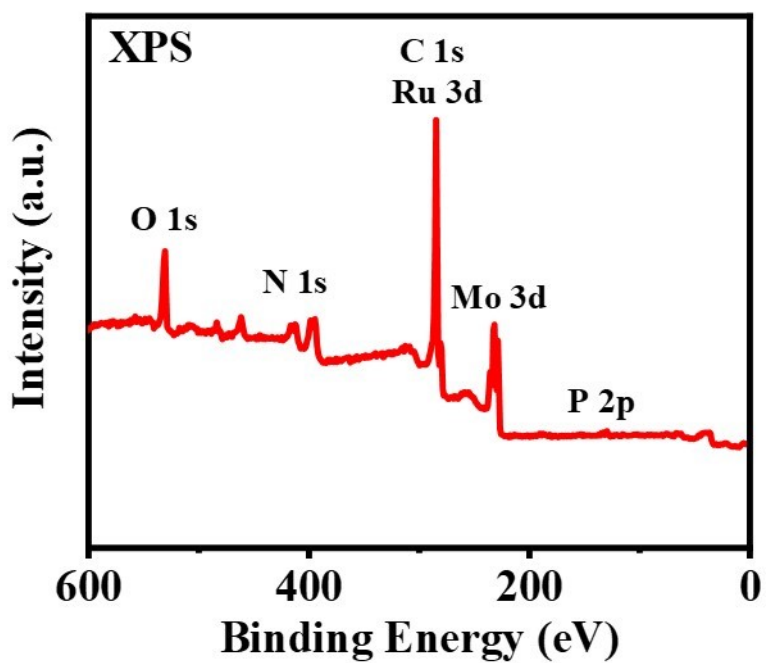


Figure S4. XPS survey spectra of Ru-Mo₂C@NPC.

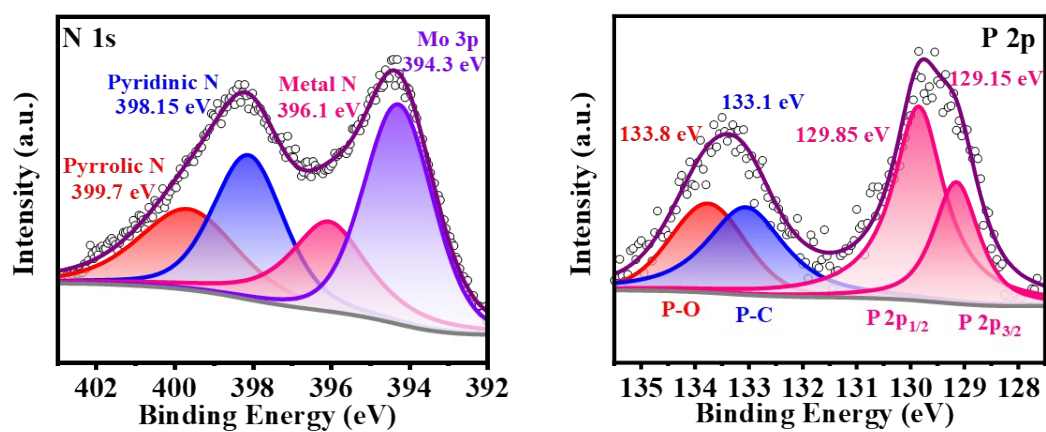


Figure S5. N 1s and P 2p spectra of Ru-Mo₂C@NPC.

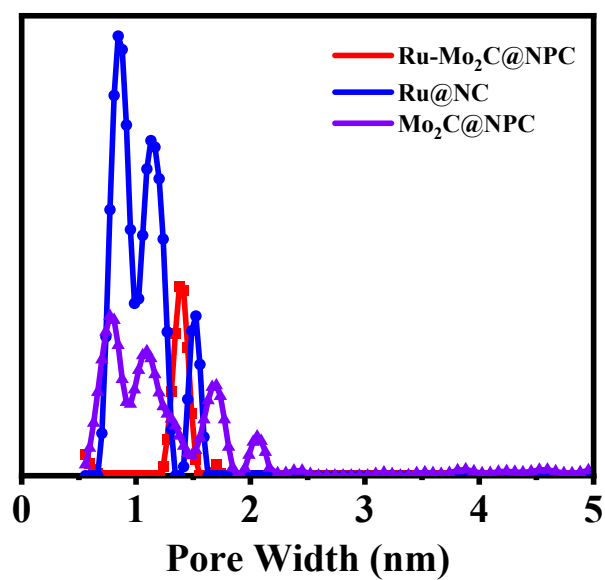


Figure S6. Pore size distribution of the catalysts.

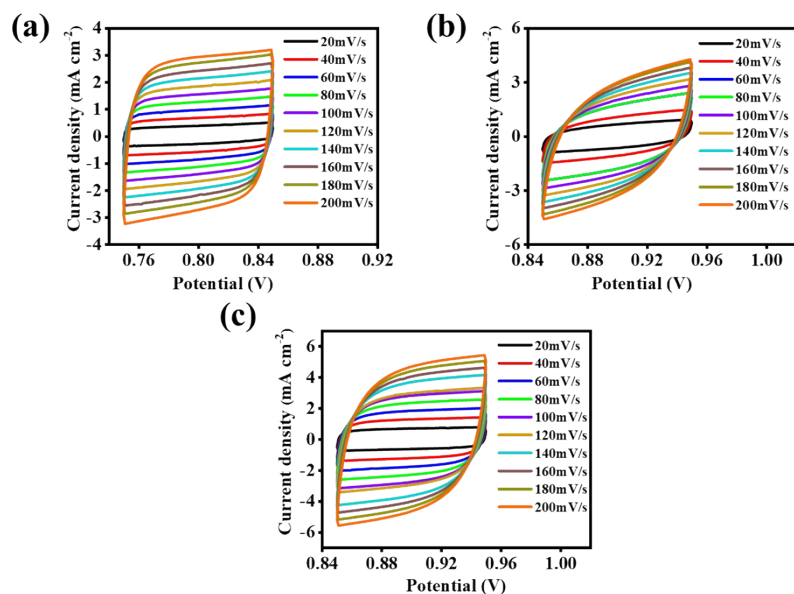


Figure S7. The CV curves of Ru-Mo₂C@NPC (a), Ru@NC (b) and Mo₂C@NPC in 0.5 M H₂SO₄.

Table S1 Comparison of HER properties of Ru-Mo₂C@NPC and other molybdenum carbide-based catalysts

Materials	Electrolyte	η_{10} (HER, mV)	Ref.
Ru-Mo ₂ C@NPC	1 M KOH	64	This work
	0.5 H ₂ SO ₄	62	
	1 M PBS	170	
Ru/Mo ₂ C	1 M KOH	35	[1]
	0.5 H ₂ SO ₄	44	
Ru-Mo ₂ C@CSC	1 M PBS	196	[2]
	1 M KOH	40	
Mo ₂ C/CN	1 M KOH	34	[3]
	1 M KOH	51	
Ru@2H-MoS ₂	0.5 H ₂ SO ₄	168	[4]
	1 M PBS	137	
	1 M KOH	47	
Ru-CoP	0.5 H ₂ SO ₄	80	[5]
	1 M PBS	107	
	1 M KOH	64	
HMCs@Ru	0.5 H ₂ SO ₄	2.8	[6]
	0.5 M PBS	78	

Reference

1. H. Jayawardana, B. Yusuf, S. Meng, Y. Li, H. Ren, Q. Nie, Y. Xu, J. Xie and M. Chen, *J. Alloys Compd.*, 2024, **997**, 174809.
2. Y. Feng, W. A, F. Gao, T. Shen, Y. Du, Z. Ding, T. Yang, C. Wang, G. Huang, T. Cao, Y. Zhang, S. Xu, *Fuel*, 2025, **379**, 133085.
3. J. Chen, C. Chen, Y. Chen, H. Wang, S. Mao, Y. Wang, *J. Catal.*, 2020, **392**, 313-321.
4. J. Wang, W. Fang, Y. Hu, Y. Zhang, J. Dang, Y. Wu, B. Chen, H. Zhao, Z. Li, *Appl. Catal. B-Environ.*, 2021, **298**, 120490.
5. Y. Wang, R. Liu, W. Xiao, X. Wang, B. Li, Z. Li, Z. Wu, L. Wang, *Fuel*, 2023, **334**, 126635.
6. X. Ma, H. Xiao, Y. Jing, Y. Gao, Y. He, M. Zhao, J. Jia, H. Wu, *Rare Met.*, 2023, **42**, 4015-4028.