Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Synergistic tailoring of doping and vacancy in tungsten carbide for efficient hydrogen evolution

Chenfan Yang[*a], Guoling Mao[a], Chuangen Zhu[a], Ning Ding[a], Bowen Pu[a], Lei Zhong[a], and Bo Wu[a]*

[a] China North Engine Research Institute (Tianjin), Tianjin 300400, China.

[*]Corresponding authors.

E-mail addresses: chenfany1018@163.com (C. Yang)

Supporting Figures

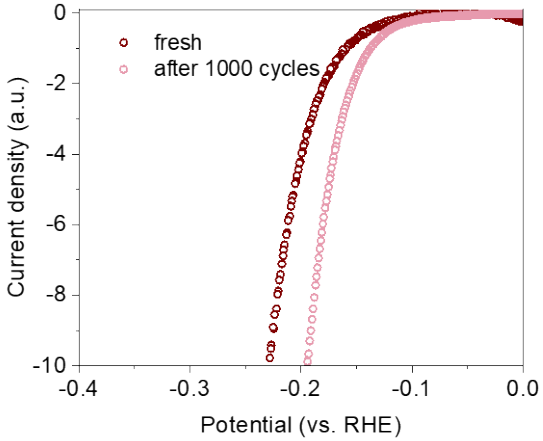

Fig. S1 The LSVs of the V_C-Zn-WC catalyst in the fresh and 1000th cycles.

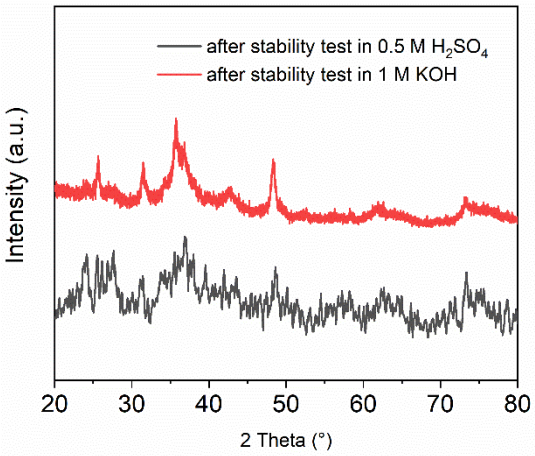

Fig. S2 XRD patterns of the V_C-Zn-WC catalyst after a stability test conducted at –0.187 V (*vs.* RHE) in 1 M KOH and –0.229 V (*vs.* RHE) in 0.5 M H_2SO_4.

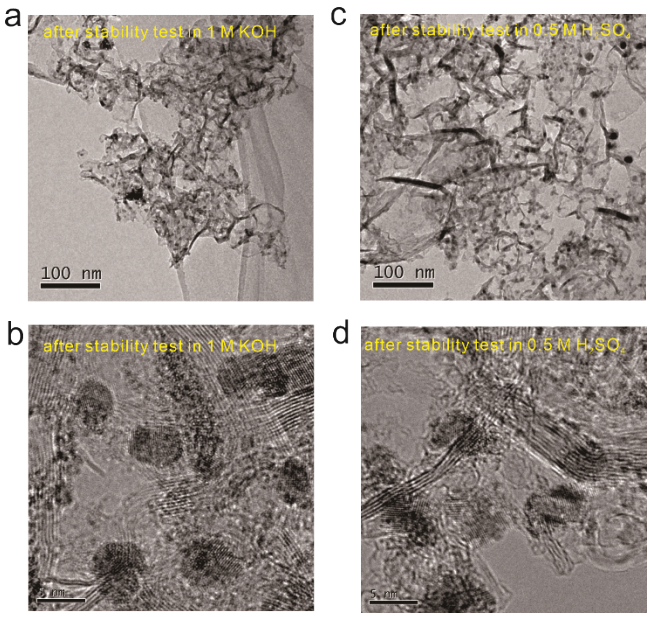

Fig. S3 HRTEM images of the V_C-Zn-WC catalyst after a long-term durability test conducted at –0.187 V (*vs.* RHE) in 1 M KOH and –0.229 V (*vs.* RHE) in 0.5 M H_2SO_4.

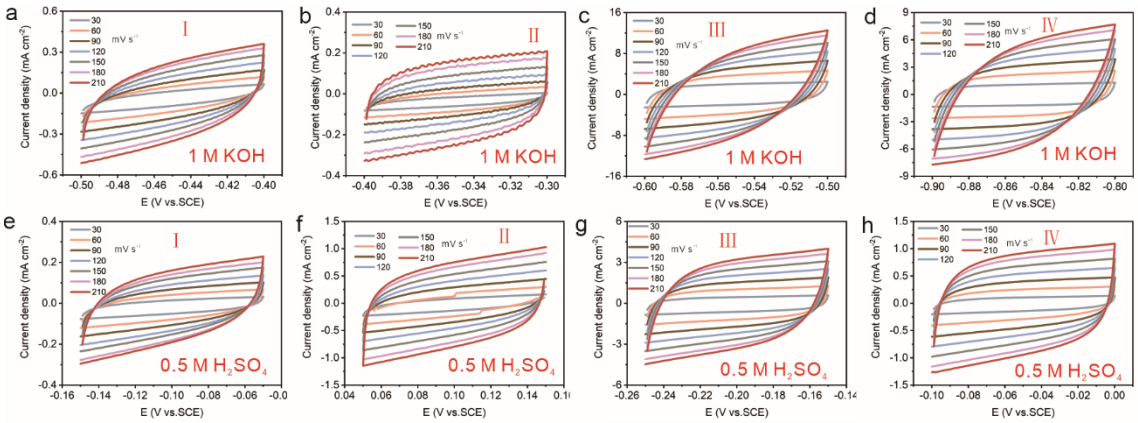

Fig. S4 CVs of the WC (I), Zn-WC-0.05 (II), V_C-Zn-WC (III), and Zn-WC-0.2 (IV) catalysts in a-d)1 M KOH and e-h) 0.5 M H_2SO_4 at different scan rates.

Supporting Tables

Table S1. Performance comparison of the reported WC-based HER catalysts at current density of –10 mA cm^{-2}.

Catalyst	Electrolyte	Overpotential (mV)	Ref.
WC/MWCNT	0.5 M H_2SO_4	250	[S1]
W_2C@WC_{1-x}@C_8	0.5 M H_2SO_4	240	[S2]
W_2C/WC nanoparticles	0.5 M H_2SO_4	310	[S3]
2D i-WC-G	1 M KOH	225	[S4]
Porous WC film	0.5 M H_2SO_4	260	[S5]
α-WC/CB	0.5 M H_2SO_4	256	[S6]
porous WC film	0.5 M H_2SO_4	275	[S7]
β-$Ta_{0.3}W_{0.7}$C/CB	0.5 M H_2SO_4	242	[S8]
WC_x/C	0.5 M H_2SO_4	264	[S9]
WC-1273K	0.5 M H_2SO_4	250	[S10]
WC@NC	0.5 M H_2SO_4	290	[S11]
WC nanocrystal	0.5 M H_2SO_4	248	[S12]
WC-graphene	1 M KOH	225	[S13]
WC@GCFs (~100 nm)	1 M KOH	310	[S14]
Fe-WCN nanoparticle	1 M KOH	250	[S15]
V_C-Zn-WC	0.5 M H_2SO_4	229	This work
V_C-Zn-WC	1 M KOH	187	This work

Supporting References

[S1] Q. Gong, Y. Wang, Q. Hu, J. Zhou, R. Feng, P. N. Duchesne, P. Zhang, F. Chen, N. Han, Y. Li, C. Jin, Y. Li, S. Lee, *Nat. Commun.* **2016**, 7, 13216.

[S2] I. Kim, S. Park, D. Kim, *Nanoscale*, **2018**, 10, 21123.

[S3] S. Emin, C. Altinkaya, A. Semerci, H. Okuyucu, A. Yildiz, P. Stefanov, *Appl. Catal., B: Environ*. **2018**, 236, 147.

[S4] M. Zenga, Y. Chena, J. Lia, H. Xuea, R. Mendesb, J. Liua, T. Zhanga, M. Rümmeli, L. Fu, *Nano Energy*, **2017**, 33, 356-362.

[S5] Fei, H.; Yang, Y.; Fan, X.; Wang, G.; Ruan, G.; Tour, J. M. Tungsten-Based Porous Thin-Films for Electrocatalytic Hydrogen Generation. *J. Mater. Chem. A*, **2015**, 3, 5798- 5804.

[S6] Hunt, S. T.; Nimmanwudipong, T.; Román-Leshkov, Y. Engineering Non-sintered, Metal-Terminated Tungsten Carbide Nanoparticles for Catalysis. Angew. Chem., Int. Ed. 2014, 53 (20), 5131-5136.

[S7] H. Fei, Y. Yang, X. Fan, G. Wang, G. Ruan, M. Tour, Tungsten-based porous thin-films for electrocatalytic hydrogen generation, *J. Mater. Chem. A*, **2015**, 3, 5798.

[S8] T. Hunt, T. Kokumai, D. Zanchet, Y. Leshkov, Alloying Tungsten Carbide Nanoparticles with Tantalum: Impact on Electrochemical Oxidation Resistance and Hydrogen Evolution Activity, *J. Phys. Chem. C*, **2015**, 119, 13691.

[S9] Z. Chen, L. Duan, T. Sheng, X. Lin, Y. Chen, Y. Chu, S. Sun, W. Lin, Dodecahedral W@WC Composite as Efficient Catalyst for Hydrogen Evolution and Nitrobenzene Reduction Reactions, *ACS Appl. Mater. Interfaces*, **2017**, 9, 20594-20602.

[S10] C. Tang, D. Wang, Z. Wu, B. Duan, Tungsten carbide hollow microspheres as electrocatalyst and platinum support for hydrogen evolution reaction, *Int. J. Hydrogen Energy*, **2015**, 40, 3229-3237.

[S11] L. Han, M. Xu, Y. Han, Y. Yu, S. Dong, Core-shell-structured tungsten carbide encapsulated within nitrogen-doped carbon spheres for enhanced hydrogen evolution, *ChemSusChem*, **2016**, 9, 2784-2787.

[S12] Y. Ko, J. Choi, I. Kim, D. Jeong, K. Lee, J. Park, Y. Baik, H. Choi, W. Lee, Tungsten carbide nanowalls as electrocatalyst for hydrogen evolutionreaction: New approach to durability issue, *Appl. Catal. B. Environ*. **2017**, 203, 684-691.

[S13] M. Zeng, Y. Chen, J. Li, H. Xue, R. Mendes, J. Liu, T. Zhang, M. Rümmeli, L. Fu, 2D WC single crystal embedded in graphene for enhancing hydrogen evolution reaction, *Nano Energy*, **2017**, 33, 356-362.

[S14] Y. Yin, M. Wen, Z. Tong, Q. Zhan, J. Chen, X. Liu, Y. Li, Z. Wu, D. Dionysiou, In-situ mediation of graphitic carbon film-encapsulated tungsten carbide for enhancing hydrogen evolution performance and stability, *Electrochimica Acta*, 2021, 388, 138566.

[S15] Y. Zhao, K. Kamiya, K. Hashimoto, S. Nakanishi, Hydrogen evolution by tungsten carbonitride nano electrocatalysts synthesized by the formation of a tungsten acid/polymer hybrid in situ, *Angew. Chem. Int. Ed*. 2013, 52,13638-13641.