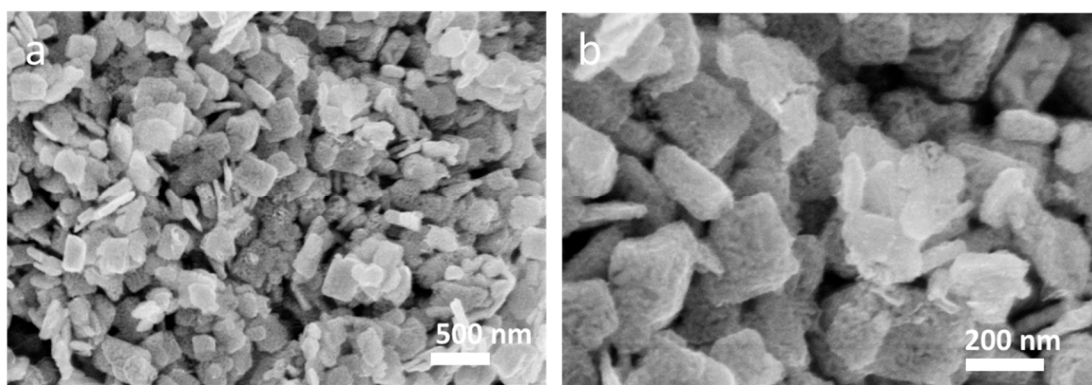


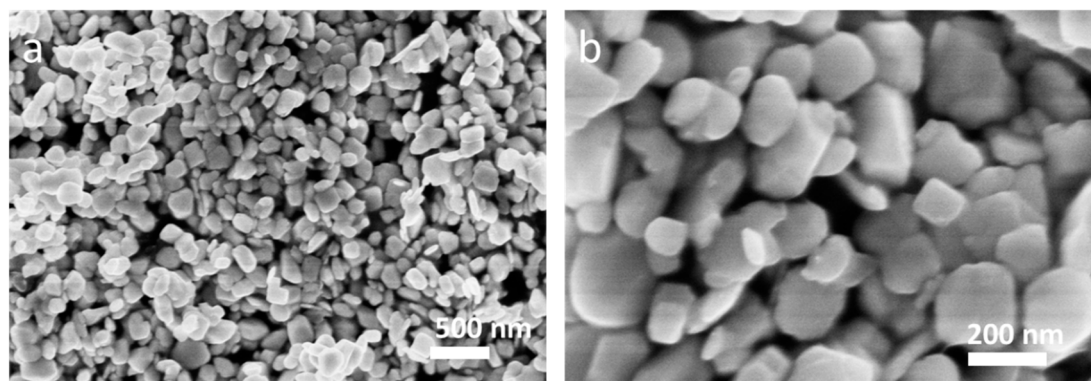
# **Tungsten Carbide/Tungsten Oxide Catalysts for Efficient Electrocatalytic Hydrogen evolution**

**Jian Ouyang <sup>1</sup>, Yu Sun <sup>2,\*</sup>, Yiqiong Zhang <sup>3</sup>, Juzhe Liu <sup>4</sup>, Xin Bo <sup>2,\*</sup> and  
Zenglin Wang <sup>2</sup>**

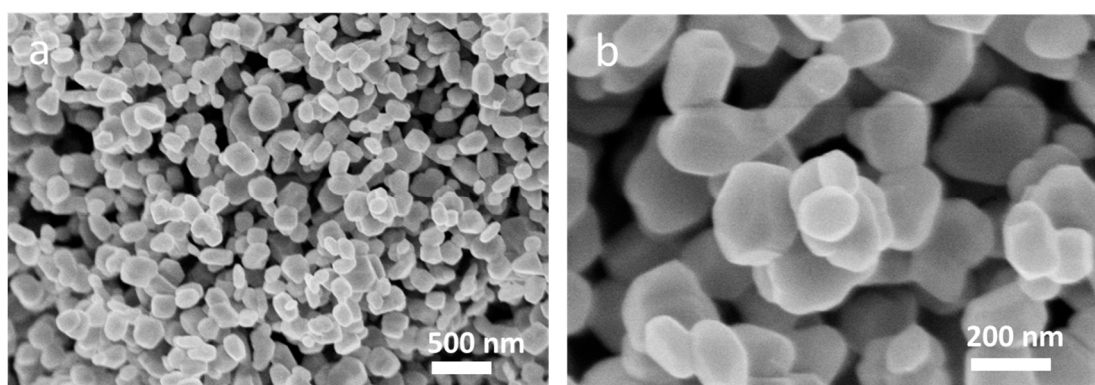
- 1 Shenzhen Kohodo Hydrogen Energy Co., Ltd., Shenzhen 518109, China;  
ouyangjian@kohodo.cn
  - 2 Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of  
Education, School of Chemistry and Chemical Engineering, Shaanxi Normal  
University, Xi'an 710119, China; sy15536162071@snnu.edu.cn (Y.S.)
  - 3 College of Materials Science and Engineering, Changsha University of Science &  
Technology, Changsha, Hunan, 410114, China
  - 4 Key Laboratory of Resources and Environmental Systems Optimization,  
Ministry of Education, College of Environmental Science and Engineering,  
North China Electric Power University, Beijing 102206, China
- \* Correspondence: sy15536162071@snnu.edu.cn (Y.S.); box@snnu.edu.cn (X.B.)



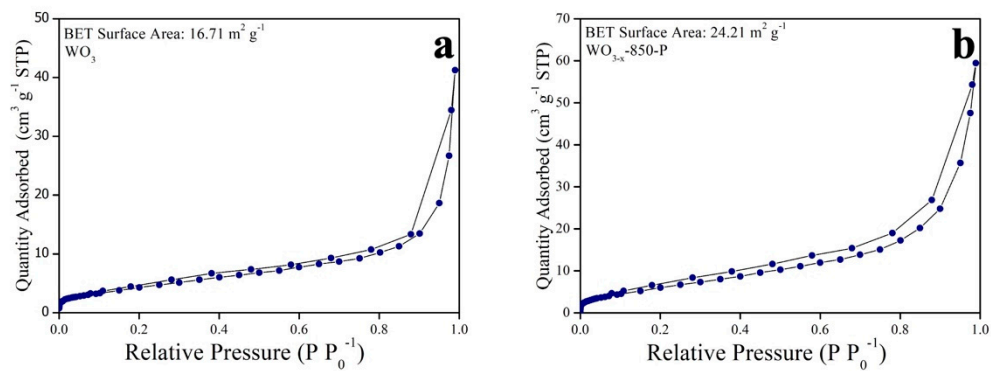
**Figure S1.** SEM images of the  $\text{WO}_{3-x}$ -750.



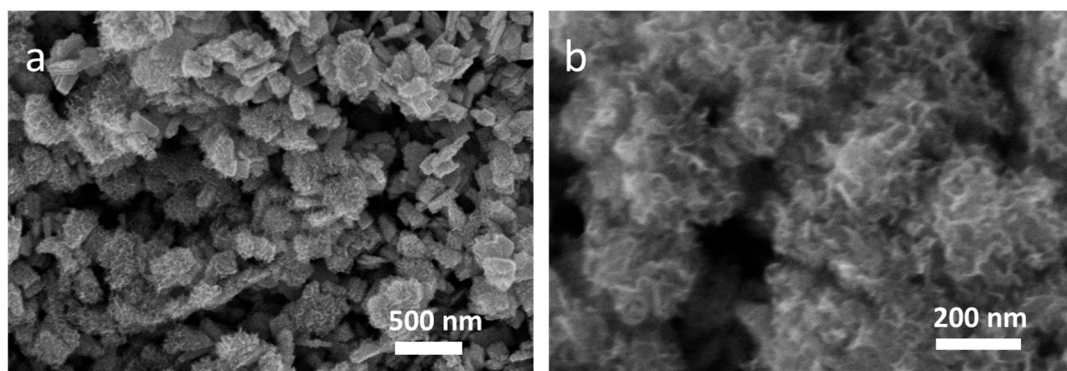
**Figure S2.** SEM images of the  $\text{WO}_{3-x}$ -800.



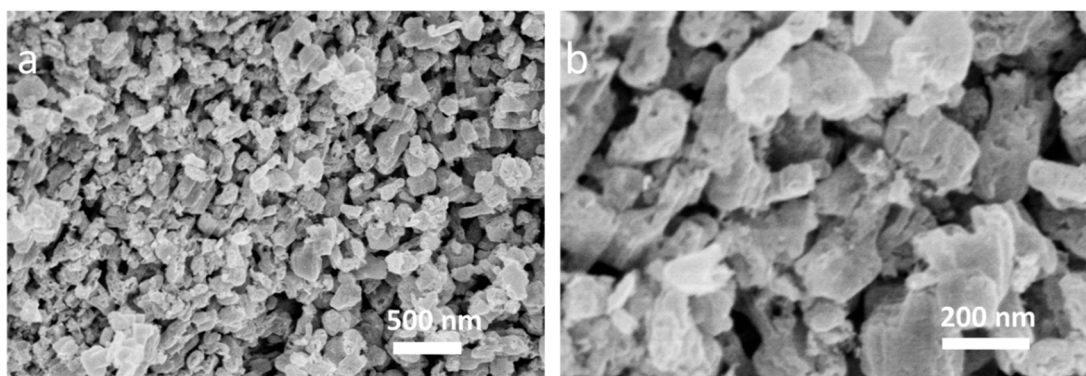
**Figure S3.** SEM images of the  $\text{WO}_{3-x}$ -850.



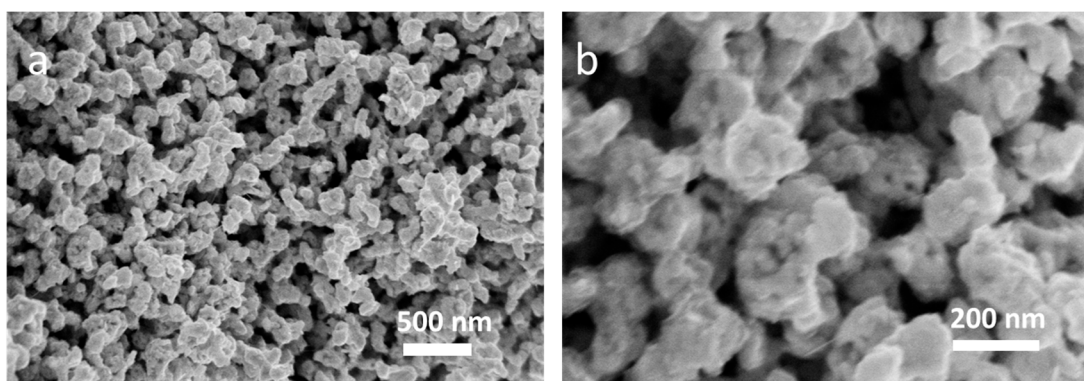
**Figure S4.** BET measurements of  $\text{WO}_3$  (a) and  $\text{WO}_{3-x}\text{-850-P}$  (b)



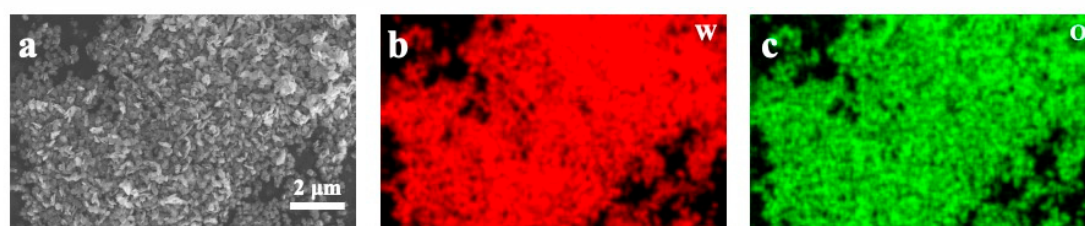
**Figure S5.** SEM images of the  $\text{WO}_{3-x}\text{-750-P}$ .



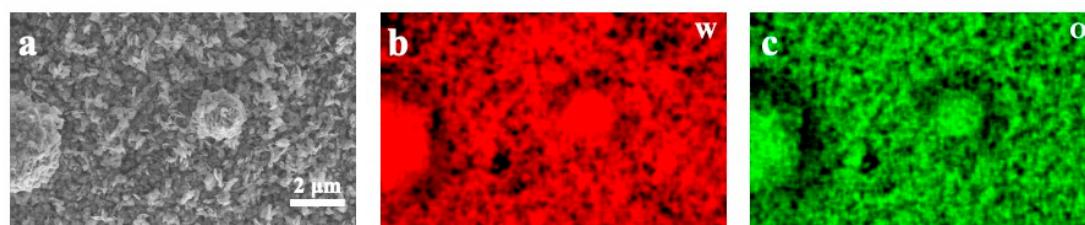
**Figure S6.** SEM images of the  $\text{WO}_{3-x}\text{-800-P}$ .



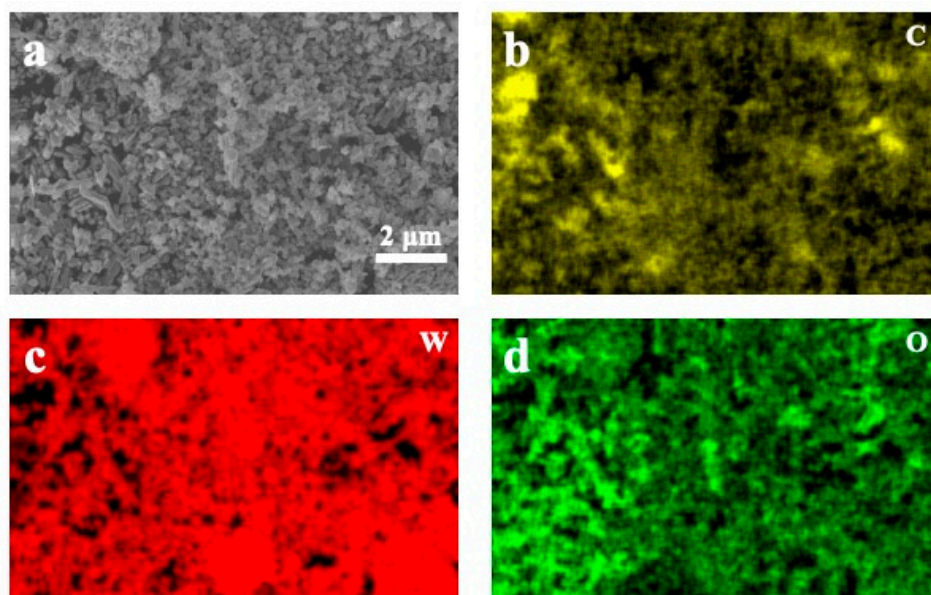
**Figure S7.** SEM images of the  $\text{WO}_{3-x}$ -850-P.



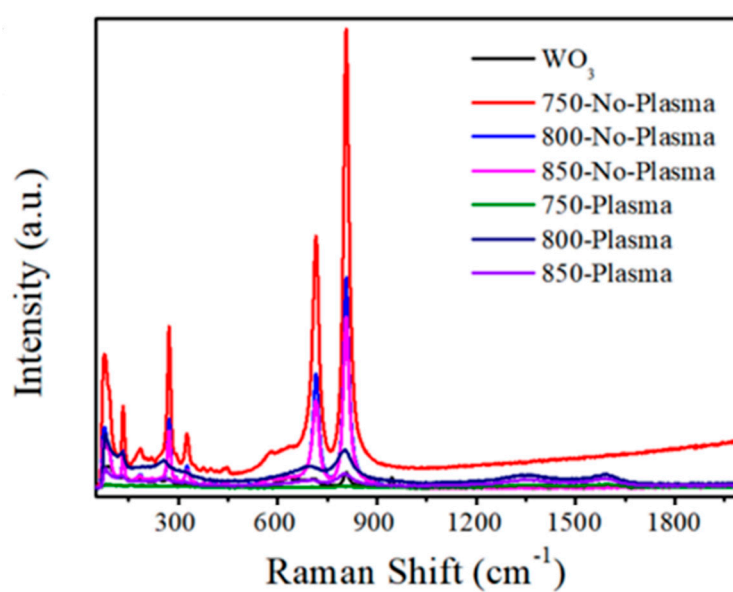
**Figure S8.** SEM (a) and the relevant EDS mapping of W (b) and O (c) elements on  $\text{WO}_3$  sample.



**Figure S9.** SEM (a) and the relevant EDS mapping of W (b) and O (c) elements on  $\text{WO}_{3-x}$ -850

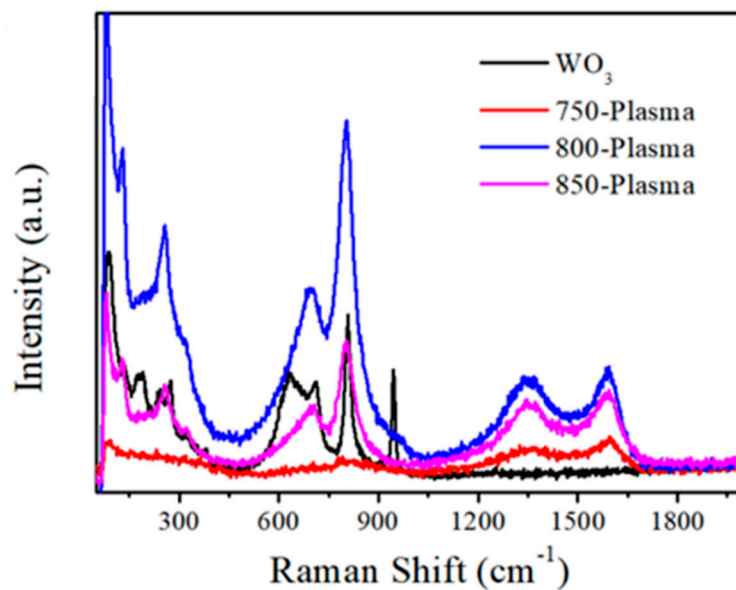


**Figure S10.** SEM (a) and the relevant EDS mapping of C (b), W (c) and O (d) elements on  $\text{WO}_{3-x}$ -850-P.

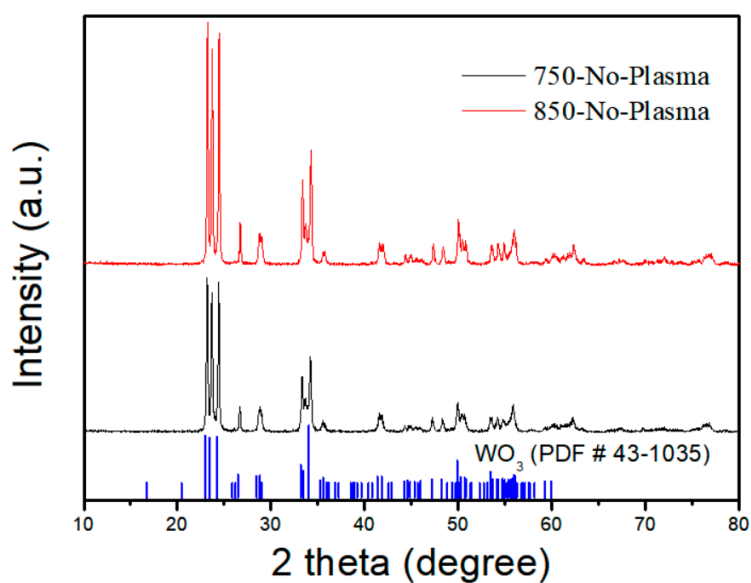


**Figure S11.** Raman spectra of  $\text{WO}_3$  and  $\text{WO}_3$  nanomaterials annealed at different temperatures or carburized at the same temperature and treated with plasma.

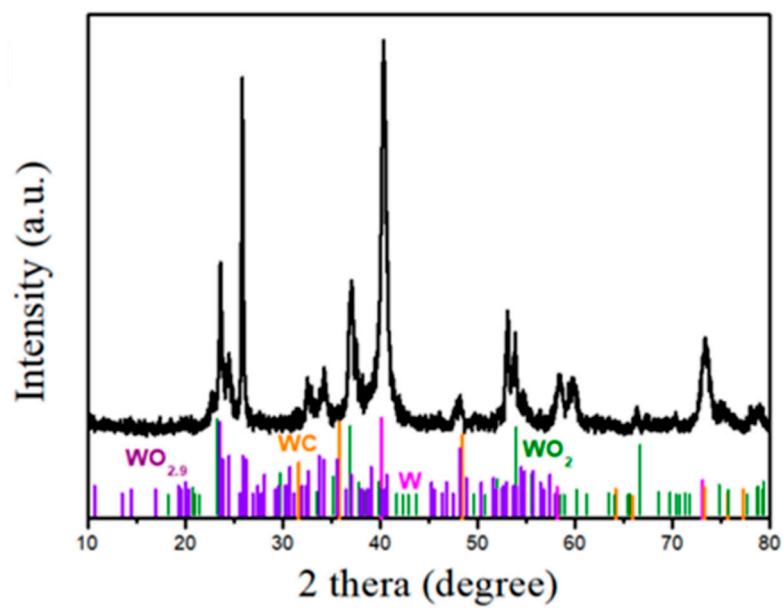




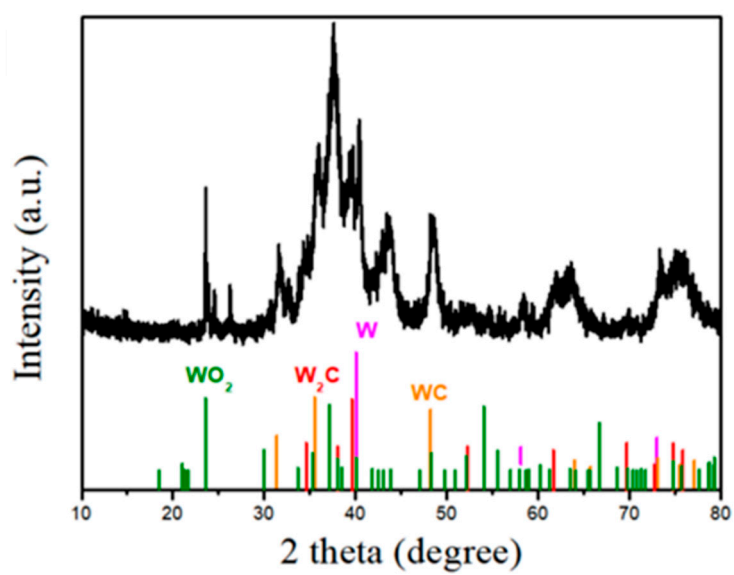
**Figure S12.** Raman spectra of WO<sub>3</sub> and WO<sub>3</sub> nanomaterials annealed at different temperatures and treated with plasma.



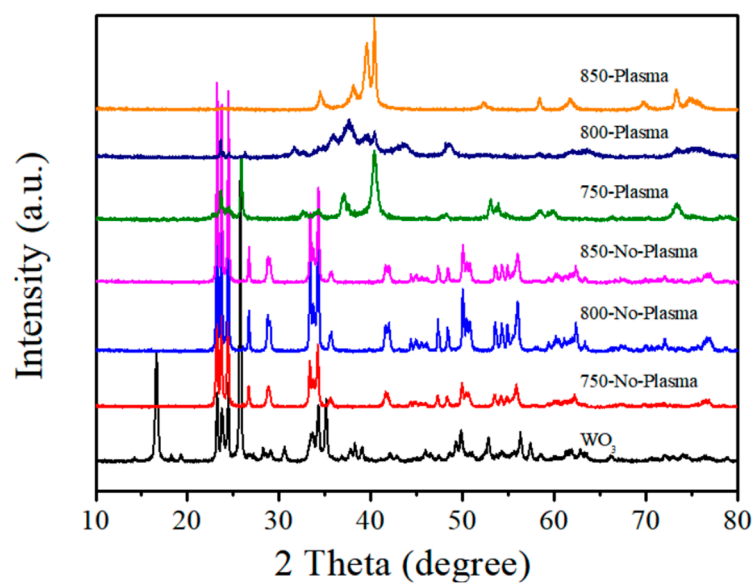
**Figure S13.** XRD patterns for the WO<sub>3-x</sub>-750 and the WO<sub>3-x</sub>-850.



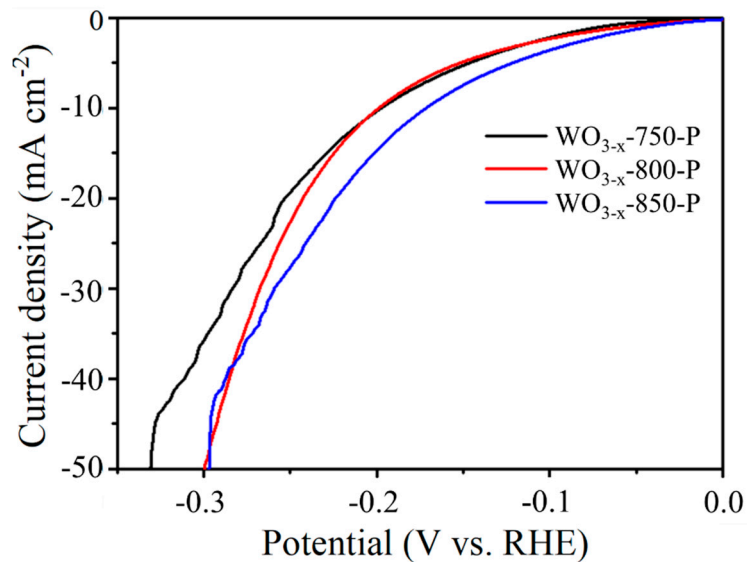
**Figure S14.** XRD patterns for the WO<sub>3-x</sub>-750-P.



**Figure S15.** XRD patterns for the WO<sub>3-x</sub>-800-P.



**Figure S16.** Comparative analysis of the XRD pattern for  $\text{WO}_3$ , heat treated with and without plasma under different temperature (750°C, 800°C, and 850°C).



**Figure S17.** The LSV profiles of the  $\text{WO}_{3-x}$ -750-P,  $\text{WO}_{3-x}$ -800-P, and  $\text{WO}_{3-x}$ -850-P in 0.5 M  $\text{H}_2\text{SO}_4$ .



**Table S1.** HER activity comparison

electrolyte	Catalysts	Overpotential (mV)	Ref.
		@10 mA cm <sup>-2</sup>	
0.5 M H <sub>2</sub> SO <sub>4</sub>	This work	170	This work
0.5 M H <sub>2</sub> SO <sub>4</sub>	Mo <sub>2</sub> C/C hollow microspheres	175	[1]
0.5 M H <sub>2</sub> SO <sub>4</sub>	Mo <sub>2</sub> CT <sub>x</sub>	189	[2]
0.5 M H <sub>2</sub> SO <sub>4</sub>	Ta <sub>0.3</sub> W <sub>0.7</sub> C/CB	~245	[3]
0.5 M H <sub>2</sub> SO <sub>4</sub>	Re@Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	298	[4]
0.5 M H <sub>2</sub> SO <sub>4</sub>	WC <sub>x</sub> /C	264	[5]
0.5 M H <sub>2</sub> SO <sub>4</sub>	N-doped WC	290	[6]
0.5 M H <sub>2</sub> SO <sub>4</sub>	W <sub>2</sub> C-thinfiln	263	[7]
0.5 M H <sub>2</sub> SO <sub>4</sub>	WC/CNT	435	[8]

**Table S2** Simulated parameters of EIS plots

Catalysts	R <sub>s</sub> /Ohm	R <sub>ct</sub> /Ohm	CPE/F	n
WO <sub>3</sub>	11.74	50.3	0.002593	0.8262
WO <sub>3-x</sub> -850	12.63	38.71	0.002543	0.88942
WO <sub>3-x</sub> -850-P	12.62	33.32	0.002998	0.89999

## References

1. Wang, C.; Sun, L.; Zhang, F.; Wang, X.; Sun, Q.; Cheng, Y.; Wang, L., Formation of Mo-Polydopamine Hollow Spheres and Their Conversions to MoO<sub>2</sub>/C and Mo<sub>2</sub>C/C for Efficient Electrochemical Energy Storage and Catalyst. *Small* **2017**, 13, (32), 1701246.
2. Seh, Z. W.; Fredrickson, K. D.; Anasori, B.; Kibsgaard, J.; Strickler, A. L.; Lukatskaya, M. R.; Gogotsi, Y.; Jaramillo, T. F.; Vojvodic, A., Two-Dimensional Molybdenum Carbide (MXene) as an Efficient Electrocatalyst for Hydrogen Evolution. *ACS Energy Letters* **2016**, 1, (3), 589-594.
3. Hunt, S. T.; Kokumai, T. M.; Zanchet, D.; Román-Leshkov, Y., Alloying Tungsten Carbide Nanoparticles with Tantalum: Impact on Electrochemical Oxidation Resistance and Hydrogen Evolution Activity. *The Journal of Physical Chemistry C* **2015**, 119, (24), 13691-13699.
4. Suragtkhuu, S.; Sunderiya, S.; Purevdorj, S.; Bat-Erdene, M.; Sainbileg, B.; Hayashi, M.; Bati, A. S. R.; Shapter, J. G.; Davaasambu, S.; Batmunkh, M., Rhenium Anchored Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (Mxene) Nanosheets for Electrocatalytic Hydrogen Production. *Nanoscale Adv* **2023**, 5, (2), 349-355.
5. Chen, Z.; Qin, M.; Chen, P.; Jia, B.; He, Q.; Qu, X., Tungsten

Carbide/Carbon Composite Synthesized by  
Combustion-Carbothermal Reduction Method as Electrocatalyst  
for Hydrogen Evolution Reaction. *International Journal of  
Hydrogen Energy* **2016**, 41, (30), 13005-13013.

6. Han, L.; Xu, M.; Han, Y.; Yu, Y.; Dong, S., Core-Shell-Structured Tungsten Carbide Encapsulated within Nitrogen-Doped Carbon Spheres for Enhanced Hydrogen Evolution. *ChemSusChem* **2016**, 9, (19), 2784-2787.
7. Zheng, H.; Huang, J.; Wang, W.; Ma, C., Preparation of Nano-Crystalline Tungsten Carbide Thin Film Electrode And Its Electrocatalytic Activity for Hydrogen Evolution. *Electrochemistry Communications* **2005**, 7, (10), 1045-1049.
8. Lin, J.-F.; Pitkänen, O.; Mäklin, J.; Puskas, R.; Kukovecz, A.; Dombovari, A.; Toth, G.; Kordas, K., Synthesis of Tungsten Carbide and Tungsten Disulfide on Vertically Aligned Multi-Walled Carbon Nanotube Forests and Their Application as Non-Pt Electrocatalysts for the Hydrogen Evolution Reaction. *Journal of Materials Chemistry A* **2015**, 3, (28), 14609-14616.