Supporting Information

Br, N-codoped tungsten nanoarrays for hydrogen evolution at all pH values

Qun Li,[a,b] Ce Han,[a] Xiao Ma,[a,c] Dewen Wang[a,b] Zhicai Xing,[a,*] and Xiurong Yang[a,*]

[a]State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China

[b]University of Science and Technology of China, Hefei 230026, China

[c]University of the Chinese Academy of Sciences, Beijing 100049, China

*Corresponding Author: Tel: +86-431-85262056;

E-mail: xingzc@ciac.ac.cn; xryang@ciac.ac.cn.

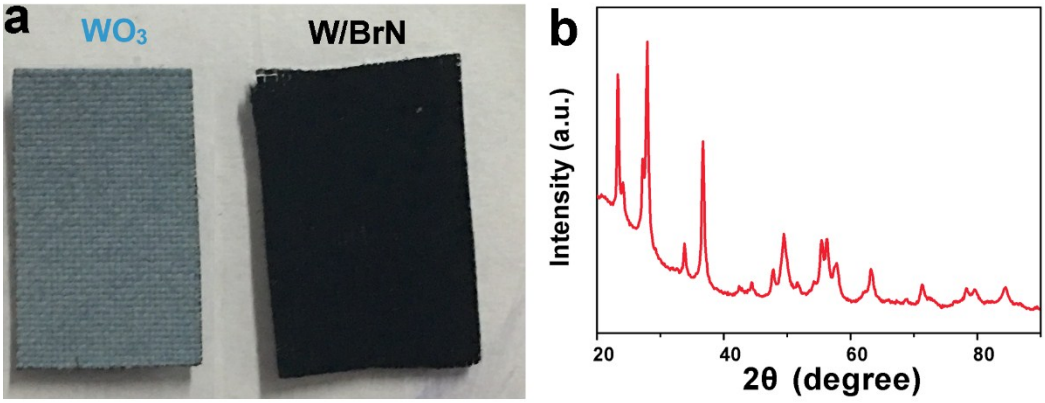


Figure S1. (a) optical photographs of WO3 and W/BrN, (b) XRD pattern for WO3.

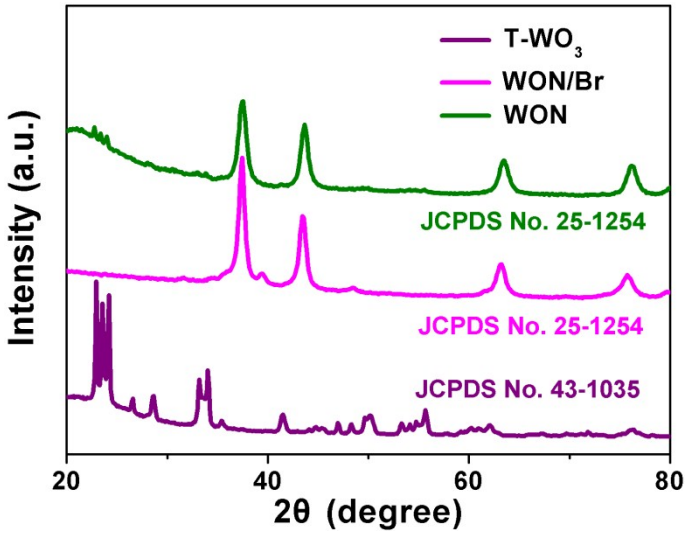


Figure S2. XRD patterns for different materials.

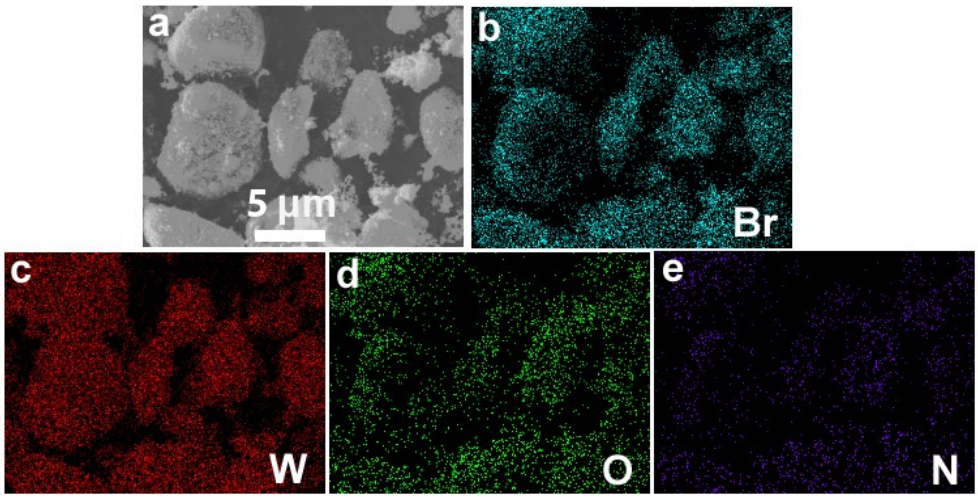


Figure S3. (a) SEM and (b-e) corresponding EDX elemental mapping images for WON/Br.

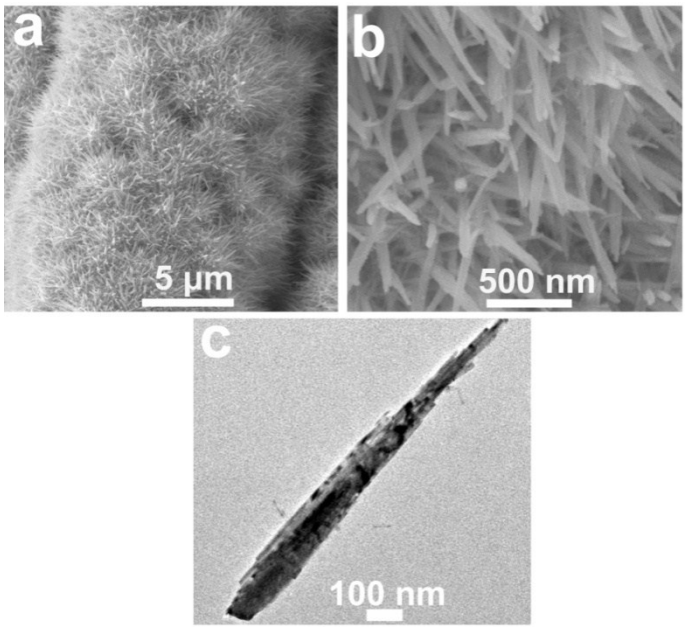


Figure S4. (a,b) SEM and (c) TEM images for WO_3.

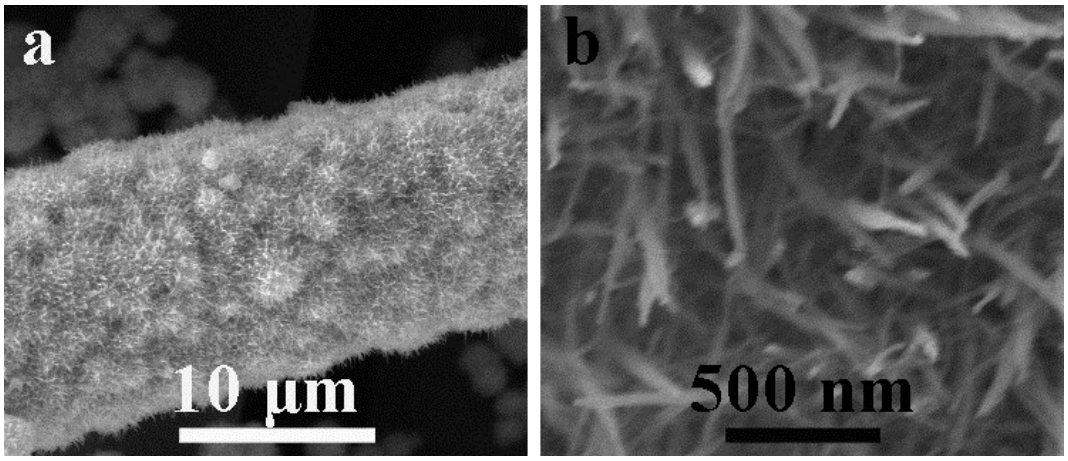


Figure S5. (a,b) SEM images for W nanowires.

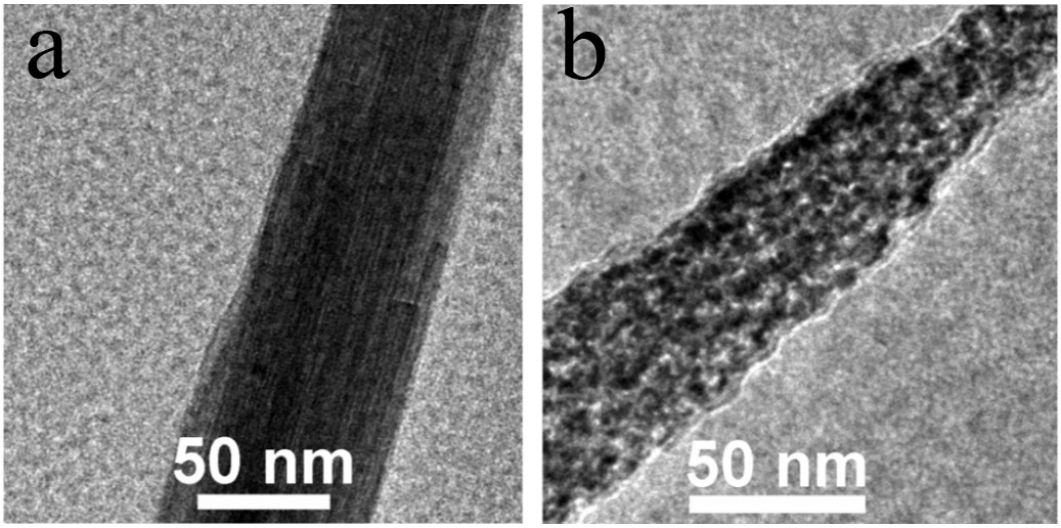


Figure S6. High magnification TEM images of (a) WO_3 and (b) W/BrN.

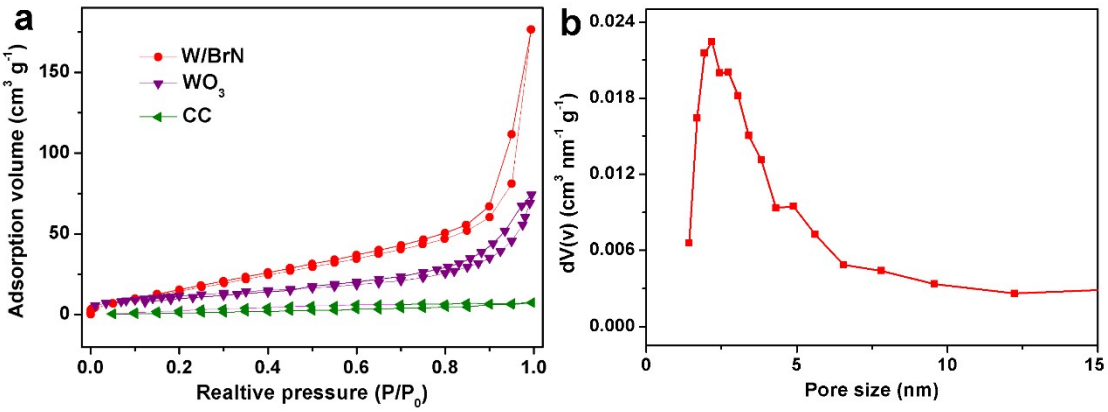


Figure S7. (a) Nitrogen adsorption/desorption isotherm for W/BrN, WO3 and CC, (b) the BJH pore-size distribution curve for W/BrN and WO_3. The WO_3 and W/BrN were scraped from CC for BET tested. Due to a small surface area of 7.3 m^2 g^{-1} for CC, a bit of carbon fiber that derived from scraped samples have little effect on surface area of WO_3 and W/BrN.

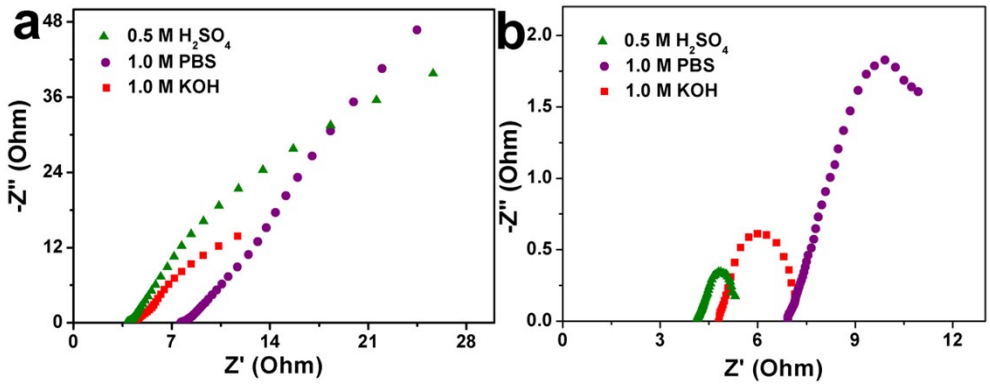


Figure S8. Nyquist plots of (a) W/BrN and (b) Pt/C at overpotential of 60 mV in different electrolytes.

Table S1. Comparison of HER performance in 0.5 M H_2SO_4 for W/BrN with other recently reported W based HER electrocatalysts

Catalyst	Current density (*j*, mA cm^{-2})	Overpotential at the corresponding *j* (mV)	Ref.
$W_xC@WS_2$	10	146	[1]
WS_2/graphene/Ni	10	87	[2]
WC nanowalls	10	88	[3]
WS_2/oCF	10	250	[4]
P-WN/rGO	10	85	[5]
Ultrathin WS_2 nanoflakes	10	~400	[6]
Amorphous WP	10	120	[7]
metallic WO_2–carbon	10	58	[8]
$WS_2@WS_2$ nanorattles	71	300	[9]
W/BrN	10	148	This work
	100	217	

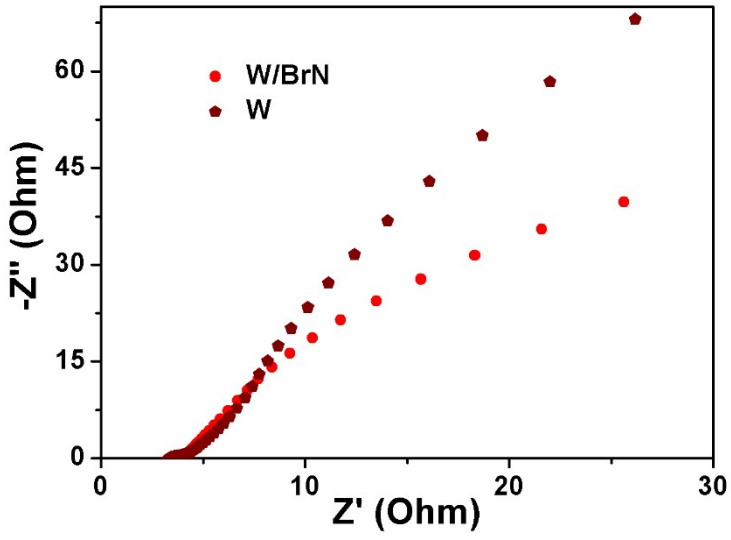


Figure S9. Nyquist plots of W nanowires and W/BrN.

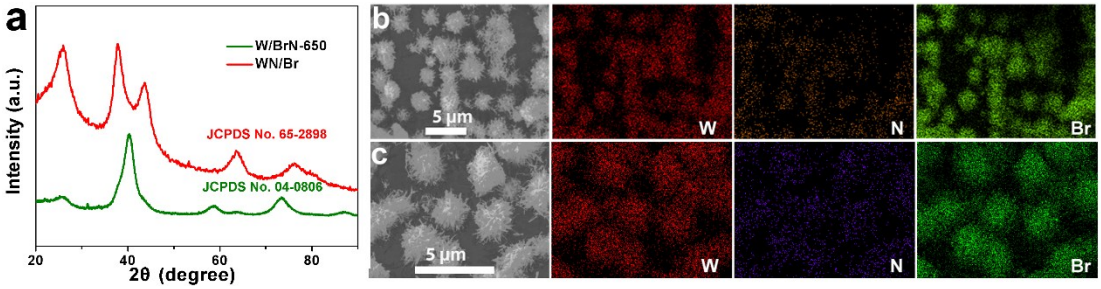


Figure S10. (a) XRD patterns for W/BrN-650 and WN/Br. SEM and corresponding EDX elemental mapping images for (b) W/BrN-650 and (c) WN/Br scratched down from CC.

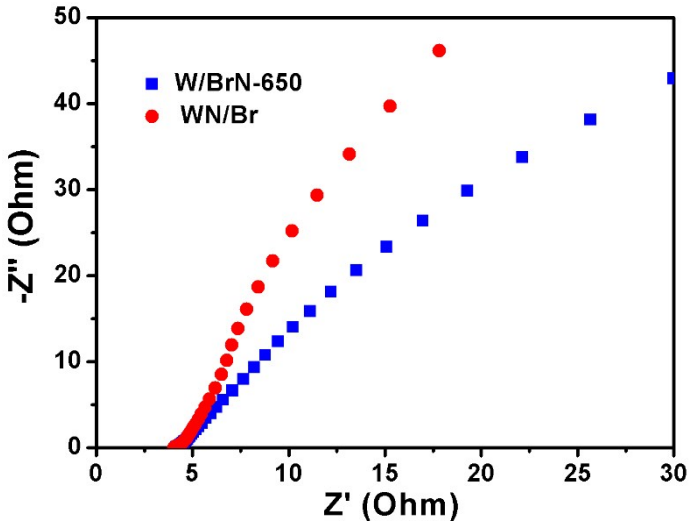


Figure S11. Nyquist plots W/BrN-650 and WN/Br.

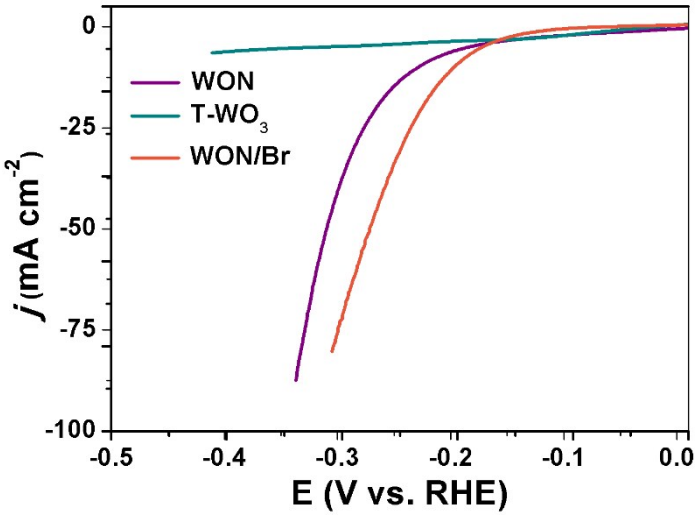


Figure S12. The polarization curves of WON, T-WO_3, WON/Br.

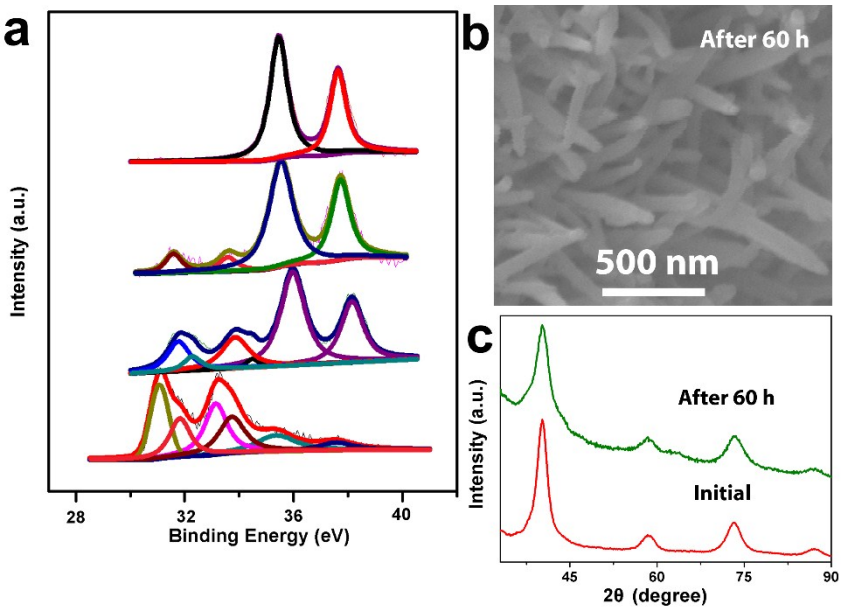


Figure S13. (a) XPS spectra in W 4f region after electrolysis for different time (from bottom to top is initial, 10 h, 24 h, 48h), (b) SEM image after 60 h electrolysis, and (c) XRD patterns for W/BrN before and after 60 h electrolysis in 0.5 M H_2SO_4.

Table S2. The concentration of W ion in 0.5 M H_2SO_4 detected by ICP-OES after electrolysis for different time.

T/h	10	24	48	60
C/ppm	2.34	7.43	8.03	8.29

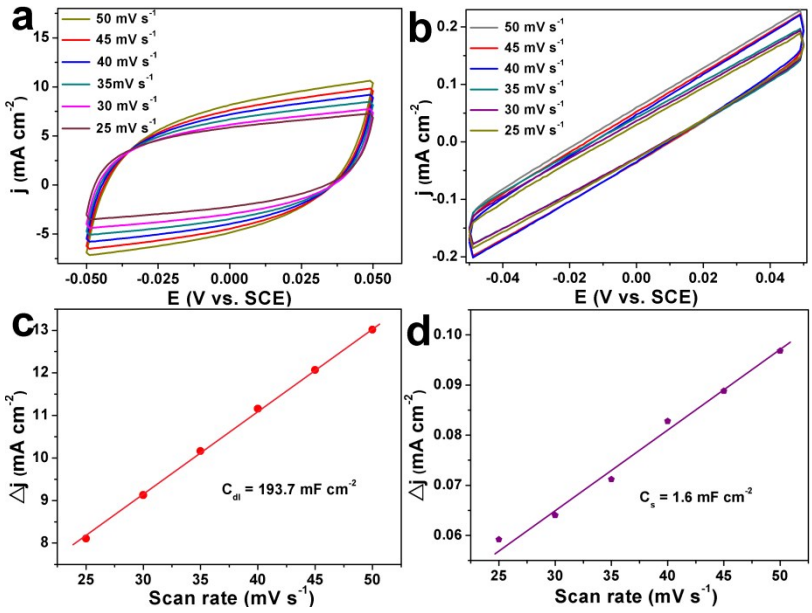


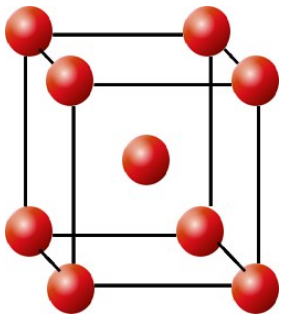
Figure S14. CVs for (a) W/BrN and (b) CC. The capacitive currents at 0 V vs. SCE as a function of scan rate for (c) W/BrN and (d) CC.

TOF was calculated using the following formulas

$$TOF = \frac{TON \times |j|}{active\ sites \times A_{ECSA}^{W/BrN}}$$

$$A_{ECSA}^{W/BrN} = \frac{193.7\ mF\ cm^{-2}}{1.6\ mF\ cm^{-2}} = 121$$

$$TON = 3.12 \times 10^{15} \frac{H/s}{cm^2} \text{ per } \frac{mA}{cm^2}$$



W unit cell :
Contains 2 W cell;
Volume: 31.7Å^3;
Cell axis : 3.1648 Å

#active sites = $(\overline{31.7\text{Å}\ cell}_{2atoms/unit\ cell}^{3}\ /unit)^{\frac{2}{3}}$ =1.585×10^{15} atoms cm^{-2}

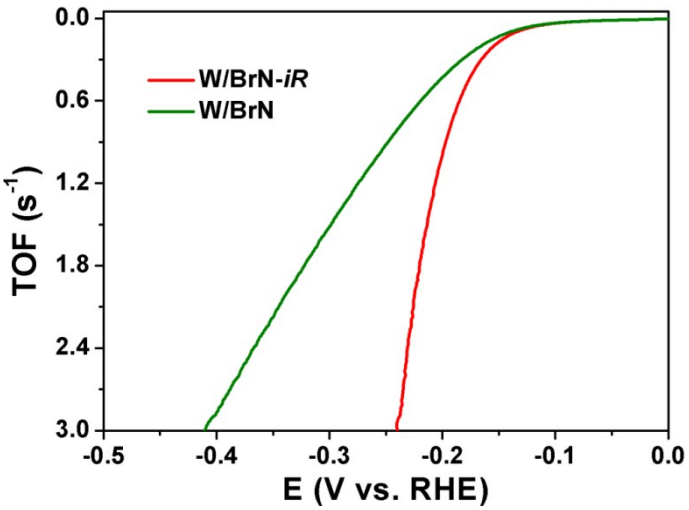


Figure S15. TOFs for W/BrN in 0.5 M H_2SO_4.

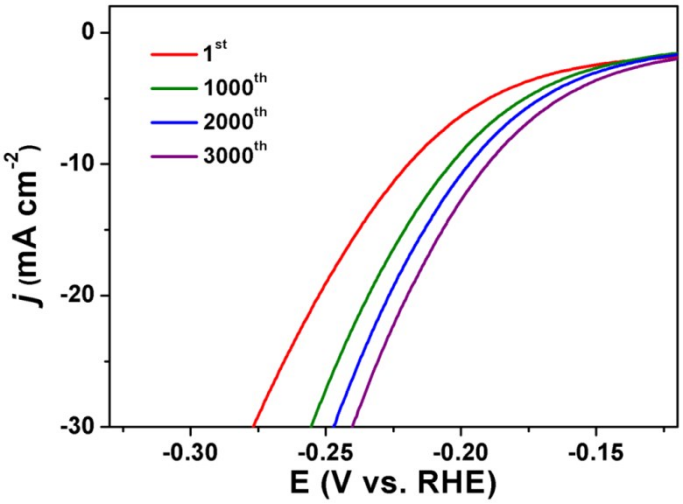


Figure S16. Polarization curves of W/BrN revealing a gradual activation for HER in 1.0 M PBS.

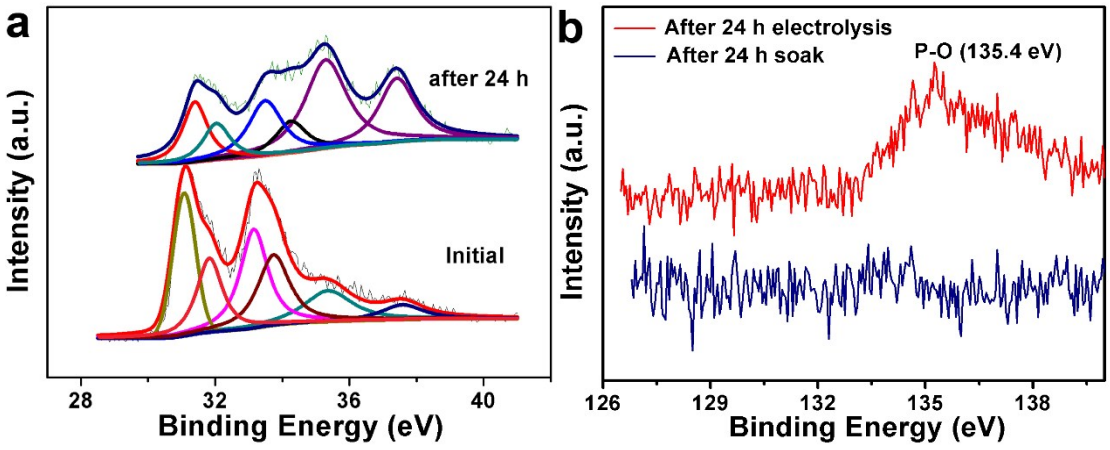


Figure S17. (a) XPS spectra in W 4f regions of W/BrN before and after electrolysis in 1.0 M PBS. (b) XPS spectra in P 2p regions of W/BrN after 24 h soak and 24 h electrolysis in 1.0 M PBS.

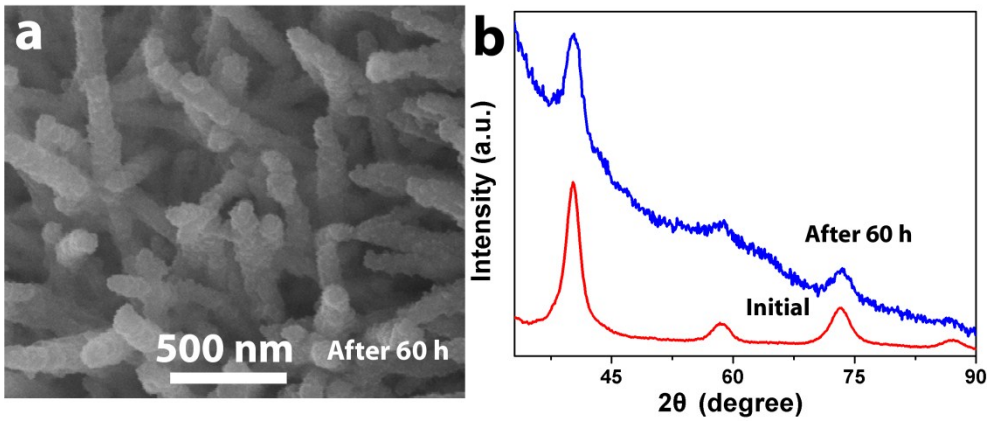


Figure S18. (a) SEM image after electrolysis for W/BrN. (b) XRD patterns of W/BrN before and after electrolysis in 1.0 M PBS.

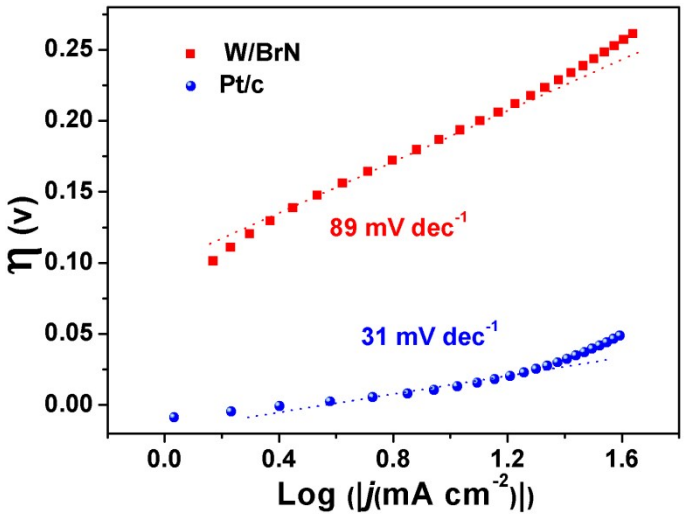


Figure S19. Tafel plots of W/BrN and Pt/C in 1.0 M PBS.

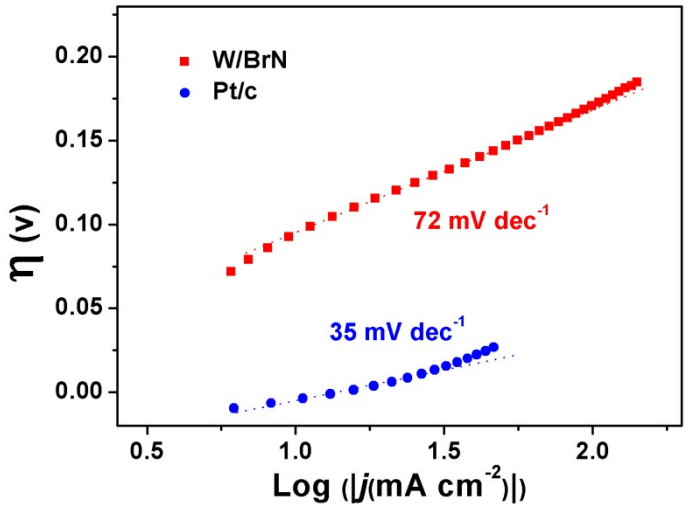


Figure S20. Tafel plots of W/BrN and Pt/C in 1.0 M KOH.

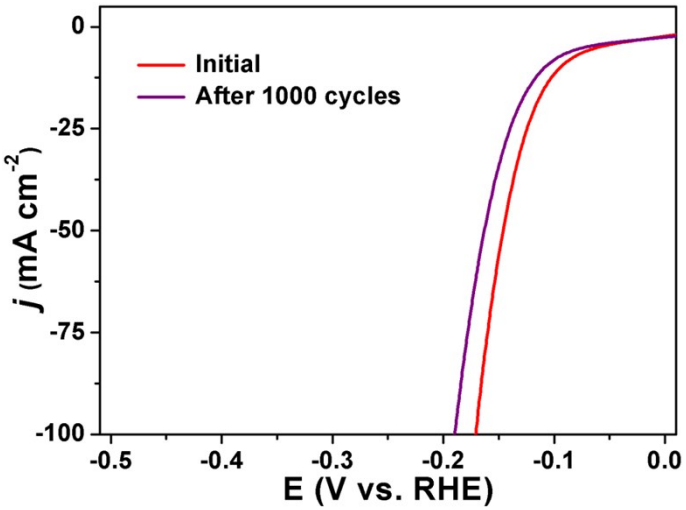


Figure S21. Polarization curves for W/BrN initially and after 1000 CV cycles in 1.0 M KOH.

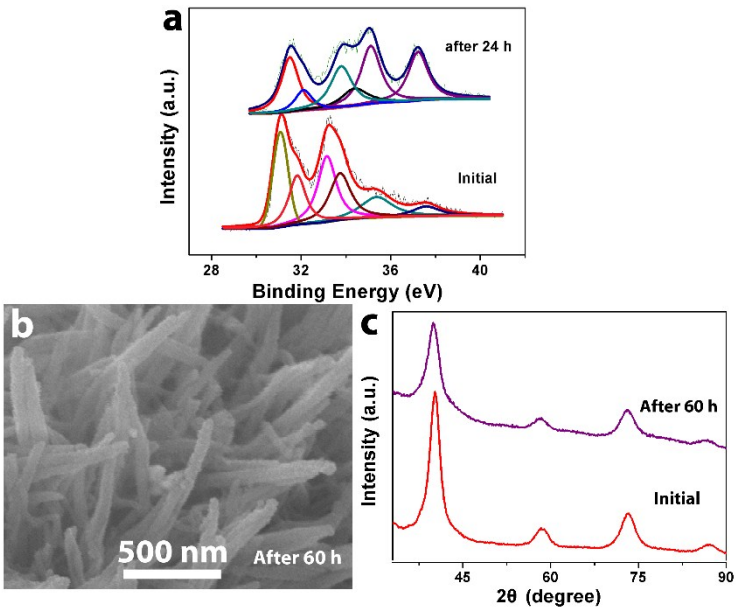


Figure S22. (a) XPS spectra in W 4f region, (b) SEM image after electrolysis, and (c) XRD patterns for W/BrN before and after electrolysis in 1.0 M KOH.

Table S3. The concentration of W ion in different electrolytes detected by ICP-OES after 24 h electrolysis.

Electrolyte	0.5 M H_2SO_4	1.0 M PBS	1.0 M KOH
C/ppm	7.43	12.88	30.55

References

1. F. Wang, P. He, Y. Li, T. A. Shifa, Y. Deng, K. Liu, Q. Wang, F. Wang, Y. Wen, Z. Wang, X. Zhan, L. Sun, J. He, *Adv. Funct. Mater.* 2017, **27***,* 1605802.

2. F. Qi, P. Li, Y. Chen, B. Zheng, J. Liu, J. Zhou, J. He, X. Hao, W. Zhang, *Int. J. Hydrogen Energy* 2017, **42**, 7811.

3. Y. Ko, J. Cho, I. Kim, D. Jeong, K. Lee, J. Park, Y. Baik, H. Choi, W. Lee, *Appl. Catal. B: Environ.* 2017, **203**, 684.

4. X. Shang, K. Yan, Z. Liu, S. Lu, B. Dong, J. Chi, X. Li, Y. Liu, Y. Chai, C. Liu, *Appl. Surf. Sci*. 2017, **402**, 120.

5. H. Yan, C. Tian, L. Wang, A. Wu, M. Meng, L. Zhao, H. Fu *Angew. Chem*. *2015*, **54**, 6325.

6. L. Cheng, W. Huang, Q. Gong, C. Liu, Z. Liu, Y. Li, H. Dai, *Angew. Chem.* 2014, **53***,* 7860.

7. J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, C. G. Read, N. S. Lewis, R. E. Schaak, *Chem. Commun.* 2014, **50**, 11026.

8. R. Wu, J. Zhang, Y. Shi, D. Liu, B. Zhang, *J. Am. Chem. Soc.* 2015, **137**, 6983.

9. Y. Wen, Y. Xia, S. Zhang, *J. Power Sources* 2016, **307**, 593.