Supplementary Materials

Three-dimensional macroporous W_2C inverse opals arrays for efficient hydrogen evolution reaction

Haifeng Zhang[†,‡],Qin Pan[§], Zhipeng Sun*[,†,‡] and Chuanwei Cheng*[,§ ‖]

[†]Materials and Energy School, Guangdong University of Technology, No. 100 Waihuan Xi Road, Guang Zhou Higher Education Mega Center, Panyu District, Guangzhou 510006, P.R China
[‡] Dongguan South China Design Innovation Institute, Dongguan 523808, P.R China
[§]Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, School of Physics Science and Engineering, Tongji University, Shanghai 200092, P.R. China
[‖]Institute of Dongguan-Tongji University, Dongguan, Guangdong, 523808, P.R. China
*Corresponding authors: zpsunxj@163.com； cwcheng@tongji.edu.cn

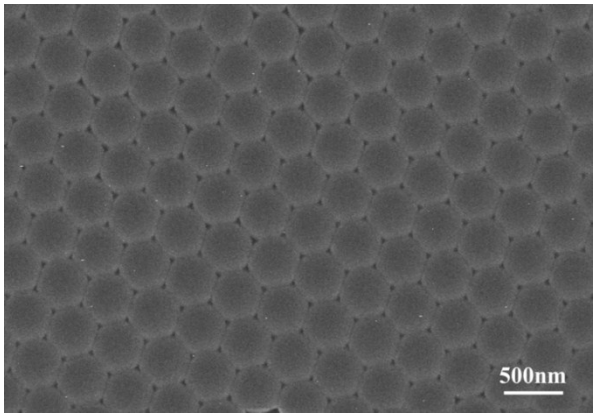

Fig S1 SEM images of PS opal sacrificial templates.

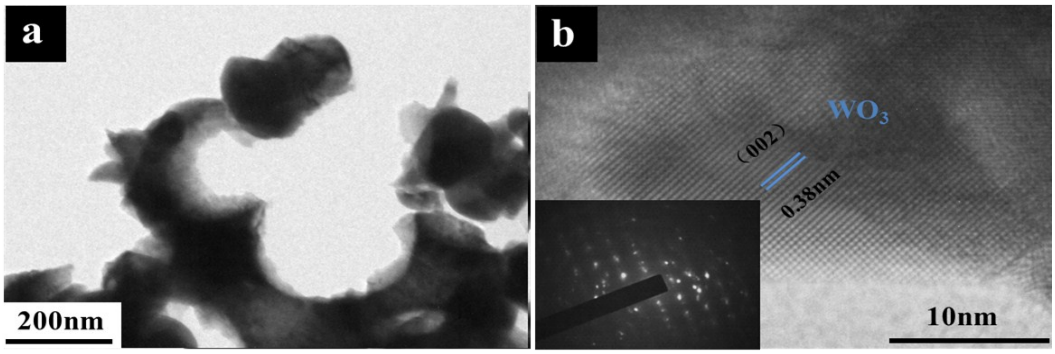

Fig S2 (a) TEM and (b) HRTEM image of WO_3 IO, inset in Fig S2 (b) is the SAED patterns

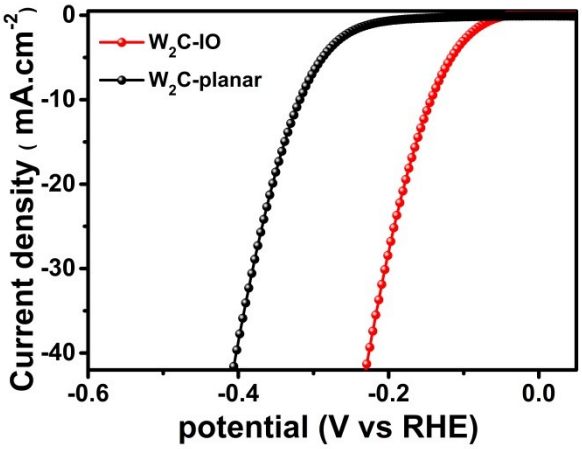

Fig S3. Polarization curves of W_2C IO and planar W_2C films in 0.5 M H_2SO_4

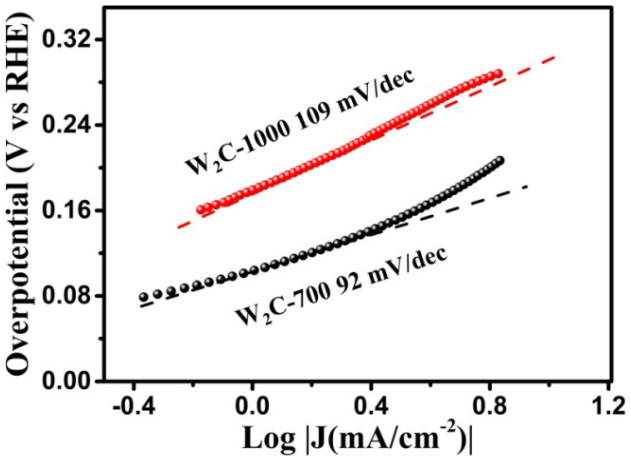

Fig S4. Tafel plots of W_2C-700 and W_2C-1000.

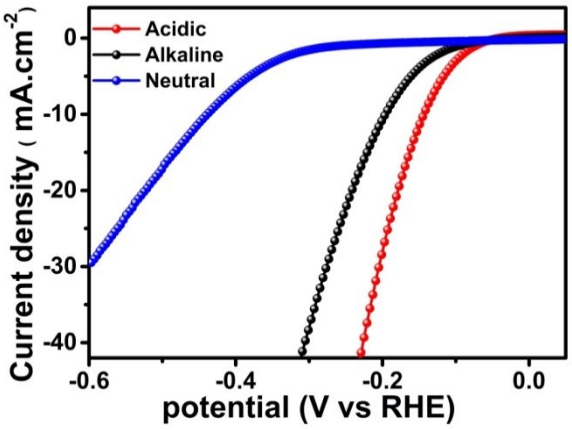

Fig S5. HER performance of W_2C-850 IO in different electroytes (Neutral, Alkaline and Acidic).

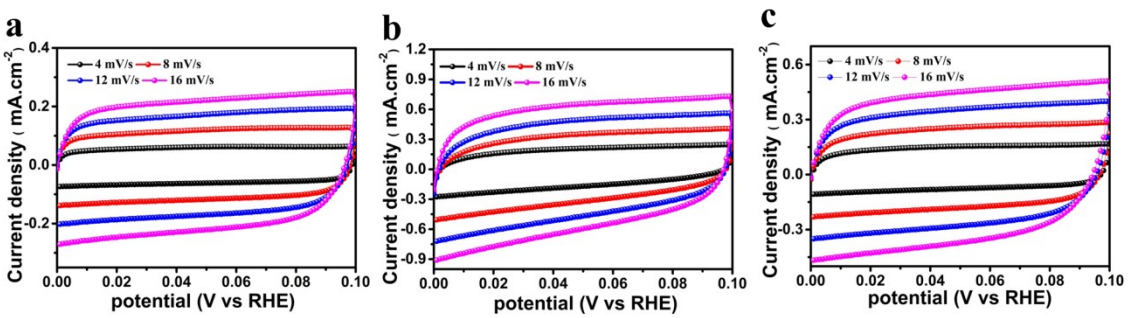

Fig S6. the CVs for (a) WO_3 IO, (b) W_2C IO-700 and (c) W_2C IO-1000 with different rates from 4 to 16 mV/s in the potential range from 0 to 1 V (vs RHE).

Table S1. A comparison of the HER performances of non-precious metal based electrocatalysts from recent literatures.

electrocatalyst	Electrolyte	-10mAcm^{-2} (mV)	Reference
W_2C IO	0.5 M H_2SO_4	-146	Our study
Mo_2C NPs	1 M H_2SO_4	-220	Ref.1
WS_2 Clusters	0.5 M H_2SO_4	-160	Ref.2
Fe-WCN Nanoflake	0.5 M H_2SO_4	-250	Ref.3
MoS Clusters	0.5 M H_2SO_4	-183	Ref.4
MoS_2 NPs	0.5 M H_2SO_4	-219	Ref.5
W_2C NPs	0.5 M H_2SO_4	-120	Ref.6
MoC-Mo_2C HNWS	0.5 M H_2SO_4	-126	Ref.7
Mo_2C NPs/G	0.5 M H_2SO_4	-150	Ref.8

	Pt	WO_3-W	WO_3-O	W_2C-C	W_2C-W
E_{base}	-117.09	-117.09	-117.09	-117.09	-117.09
E_{ads}	-6.759	-6.759	-6.759	-6.759	-6.759
E_{total}	-120.89	-425.83	-425.42	-408.60	-412.87
ΔE_{ads}	-0.42	0.03	0.38	-0.86	-0.44
$\triangle G_H$	-0.18	0.21	0.62	-0.62	-0.20

Table S2 E_{base}, E_{ads}, E_{total} $\triangle E_{ads}$ and $\triangle G_H$ for HER on Pt (111) surface, WO_3-W (001) surface, WO_3-O (001) surface, W_2C-C (001) surface and W_2C-W (001) surface by DFT calculation.

Theoretical calculations: Our computational simulations were performed by Vienna ab-initio simulation package (VASP) with the projector augmented wave pseudo-potentials (PAW) to describe the interaction between atomic cores and valence electrons with density functional theory (DFT). The Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was used to implement DFT calculations.[9] The W_2C(001) by the W-determined or C-determined, Pt(111) and WO_3(001) 2×2 slab models were employed to simulate the surface properties. The reasonable vacuum layers were set around 15 Å in the z-direction for avoiding interaction between planes. A cutoff energy of 400 eV was provided and a 5×5×1 Monkhorst Pack k-point sampling was chosen for the well converged energy values. Geometry optimizations were pursued until the force on each atom falls below the convergence criterion of 0.02 eV/Å and energies were converged within 10^{-6} eV. Moreover, all calculations were spin polarized.

Hydrogen adsorption and free energy

The hydrogen adsorption energy on various surfaces is defined as

$$\Delta E_{ads} = E_{base-H} - E_{base} - \frac{1}{2}E_{H_2}$$

where E_{base-H} is the total energy of slab model with *H adsorption, E_{base} is the energy of a clean slab surface, and E_{H_2} is that for hydrogen molecules in the gas phase.

The Gibbs free energy for hydrogen adsorption (ΔG_{H*}) can be calculated by taking zero point energy and entropy corrections into account such that $\Delta G_H = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S$. Where ΔE_{ZPE} and $T\Delta S$ are the difference in zero point

energy and entropy between the adsorbed hydrogen and hydrogen in the gas phase, respectively. As the vibrational entropy of H* in the adsorbed state is small, the entropy of adsorption of $1/2^{H_2}$ is $\Delta S_H \approx \Delta E_{ads} + 0.24eV$.[10,11]

References

1. H. Vrubel and X. Hu, *Angew. Chem. Int. Ed*,. 2012, **51**, 12703.
2. L. Cheng, W. J. Huang, Q. F. Gong, C. H. Liu, Z. Liu, Y. G. Li and H. J. Dai, *Angew. Chem. Int. Ed.*, 2014, **53**, 7860.
3. Y. Zhao, K. Kamiya, K. Hashimoto and S. Nakanishi, *Angew Chem Int Ed*, 2013, **52**, 13638.
4. J. Kibsgaard, TF. Jaramillo and F. Besenbacher, *Nat Chem*, 2014, **6**, 248.
5. H. Deng, C. Zhang, Y. C. Xie, T. Tumlin, L. Giri, S. P. Karna and J. Lin, *J Mater Chem A*, 2016, **4**, 6824.
6. Q. F. Gong, Y. Wang, Q. Hu, J. G. Zhou, RF. Feng, P. N. Duchesne, P. Zhang, F. J. Chen. N. Han, Y. F. Li, CH. Jin, Y. G. Li and S. T. Lee, *Nat Commun*, 2016, **7**, 13216.
7. H. L. Lin, Z. P. Shi, S. N. He, X.Yu, S. N. Wang, Q. S. Gao and Y. Tang, *Chem Sci*, 2016, **7**, 3399.
8. C. He and J. Tao, *Chem Commun*, 2015, **51**, 8323.
9. M. Bajdich, M. Garcia-Mota, A. Vojvodic, J. K. Norskov and A. T. Bell, *J. Am. Chem. Soc*. 2013, 1**35**, 13521.
10. Y. Jiao, Y. Zheng, K. Davey and S. Z. Qiao, *Nat Energy* 2016, **1**, 16130.
11. C. Zhang, Y. Huang, Y. Yu, J. Zhang, S. Zhuo, B. Zhang, *Chem Sci*, 2017, **8**, 2769.