Supporting information

for

Template synthesis of ultrathin metallic Ir nanosheets as robust electrocatalyst in acidic water splitting

Yuhua Xie^a, Xue Long^a, Xianwei Li^a, Chaofeng Chang^a, Konggang Qu^b and Zehui Yang^{*a,c}

^aSustainable Energy Laboratory, Faculty of Materials Science and Chemistry, China

University of Geosciences Wuhan, 388 Lumo RD, Wuhan, 430074, P. R. China

^bShandong Provincial Key Laboratory/Collaborative Innovation Center of Chemical

Energy Storage & Novel Cell Technology, Liaocheng University, Liaocheng, 252059,

P. R. China

^cZhejiang Institute, China University of Geosciences, Hangzhou, 311305, P. R. China

Experimental section

Materials: These all reagents have not been purified. Iridium trichloride (IrCl₃) was supplied by Shanghai Bepharm Science & Technology Co., Ltd. Absolute ethanol, ferric nitrate hexahydrate (Fe(NO₃)₃·6H₂O), fumaric acid (C₄H₄O₄), dimethylformamide (DMF) and odium borohydride (NaBH₄) were all purchased from Sinopharm Chemical Reagent Co. Ltd. Nafion solution was acquired from Sigma-Aldrich. Deionized water (resistivity \geq 18.25 MΩ) was obtained from an ultra-pure purification system from ULUPURE.

Synthesis of MIL-88A: Usually, fumaric acid (232 mg) and FeCl₃·6H₂O (234 mg) are ultrasonically dissolved in a flask containing 10mL of dimethylformamide (DMF), and then the flask was placed in an oil bath at 100 °C for 2 hours in air atmosphere. After cooling to room temperature, the whole system was centrifuged (10000 rpm, 6min), washed twice with DMF solution, and finally washed with absolute ethanol for the third time to obtain a yellow precipitate. MIL-88A could be obtained in an oven at 55 °C overnight.

Synthesis of Ir nanosheets and Ir nanoparticle electrocatalyst: The MIL-88A (100 mg) previously obtained and IrCl₃ (30 mg) were weighed and dispersed in 10 mL of deionized water, and sonicated for 5 min for complete dispersion, and then added dropwise to a beaker containing 75 mL of deionized water, stirring for 10 min; During this time, 20 mL of NaBH₄ solution (0.5 M) was prepared, and added dropwise to the mixed solution, the NaBH₄ solution was completely added within 30 min, then the mixed solution was kept stirring for 6 h, suction filtered, washed with deionized water,

and finally dried to obtain the sample. The sample obtained above was mixed with 0.5 $M H_2SO_4$ (50 mL) and stirred at 50 °C for 8 h, the purpose is to remove the residual Fe in the sample. The preparation method of Ir-nanoparticles was the same as that of Ir-nanosheets, except that the template MIL-88A was not added in the precursor (IrCl₃).

Fundamental characterizations: The X-ray photoelectron spectroscopy (XPS) of the Escalab 250XI spectrometer (ThermoFisher, USA) was used to obtain the structural characterization of the sample. The XRD pattern of the sample was obtained by the Bruker D8 Advance, and the nanometer was obtained from the FM-Nanoview 1000AFM by the atomic force microscope (AFM) test. The thickness of the sheet and the micro-topography of the samples are obtained by observation with a field emission electron microscope (SEM, SU8010, Japan). The microstructure of the sample was analyzed by a high-resolution electron projection microscope (TEM, FEI themis 300, USA).

Electrochemical measurements: The electrochemical test of oxygen evolution reaction (OER), hydrogen evolution reaction (HER) and water splitting in acidic environment was carried out in sulfuric acid ($0.5M H_2SO_4$). The related electrochemical performance test was completed by the Gamry Interface 1000E instrument at room temperature with a three-electrode system (glassy carbon electrode-working electrode, carbon rod-counter electrode, Hg/HgO electrode-reference electrode). The catalyst (1 mg) and XC-72 (9 mg) were into 1 mL (780 µL of deionized water, 200 µL of ethylene glycol and 20 µL of Nafion) of solution. After the "ink" was dispersed by ultrasonic for more than 1 h, 10 µL of ink was coated on the surface of glassy carbon electrode

(diameter 3 mm, loading: ~ 0.285 mg cm⁻²), and the tape was completely dried for system test. The electrode coated with electrocatalyst was used in the three-electrode test system, and the electrolyte was kept in oxygen for more than 15 mins (Ar for HER). The OER polarization curve was measured by linear sweep voltammetry (LSV) in the range of 1-1.7 V vs. RHE (HER: 0.241-0.359 V vs. RHE, and the electric double-layer capacitance of the catalyst was provided by different sweep rates (10-100 mV s⁻¹) under cyclic voltammetry (CV). Under the initial voltage of 700 μ A in polarization curve, EIS could be obtained, and the frequency range was from 100 kHz to 0.01 Hz. Finally, the cycle stability and long-term stability of the catalyst were estimated by CV and CA. The test of total electrolyzed water is carried out in a two-electrode system, polarization curve was measured by linear sweep voltammetry (LSV) in the range of 1.0-2.0 V vs. RHE, and long-term stability of the catalyst were estimated and CA.

Table S1 Comparison of OER performance with reported Ir based electrocatalysts.

Electrocatalyst	Catalyst	Current density	Mass activities	Reference
	loading	@1.55 V vs.	@ 1.55 V vs.	
	$(\mu g_{Ir} \ cm^{-2})$	RHE / mA cm ⁻²	RHE/ mA µg Ir ⁻¹	
IrNi NCs	12.5	10	0.80	1
np-IrAl	120	12	0.10	2
IrNiFe NPs	92	6	0.07	3
Ir WNWs	31	49	1.58	4
IrCoNi/C	10	18	1.80	5
Ir-Ni TL/C	2	3	1.50	6
Li-IrOx	50	24	0.48	7
Sr ₂ IrO ₄	80	30	0.38	8
Ir/g-C ₃ N ₄ /NG	6.7	32	4.78	9
IrCo _{0.65} NDs	90	35	0.39	10
Ir-NS	~71	91	1.28	This work



Figure S1 XRD pattern of MIL-88A.



Figure S2 SEM image of MIL-88A.



Figure S3 XRD patterns of Ir-NS electrocatalyst with and without acidic etching.





Figure S4 SEM image of Ir-NS electrocatalyst without acidic etching.

Figure S5 CV curves of IrO2, Ir-NP, and Ir-NS electrocatalysts recorded at various



can rate and related double layer capacitances.

Figure S6 OER performance of single active site of IrO₂, Ir-NP and Ir-NS.



Figure S7 Mass activities of IrO_2 , Ir-NP and Ir-NS.



Figure S8 Electrochemical impedance spectroscopies of IrO₂, Ir-NP and Ir-NS.



Figure S9 CV curves of Ir-NS after 1000 cycles. (b) Calculated ECSA values of Ir-

NS before and after 1000 cycles. (c) Electrochemical impedance spectroscopies of Ir-



NS before and after 1000 cycles.

Figure S10 OER performance (a), CV curve (b), ECSA (c) and electrochemical impedance spectroscopy (d) of Ir-NP electrocatalyst before and after 1000 cycles.



Figure S11 OER performance (a), double-layer capacitance (b), cyclic voltammetry curves (c) and electrochemical impedance spectroscopies (EIS) of commercial IrO₂

before and after 1000 potential cycles.



Figure S12 OER performance of Ir-NS electrocatalyst before and after CA test.



Figure S13 Mass activities of Pt/C, Ir-NP and Ir-NS electrocatalysts.



Figure S14 CV curves and related double layer capacitances of Ir-NS, Ir-NP and Pt/C

electrocatalysts.



Figure S15 HER performance of single active center of Ir-NS, Ir-NP and Pt/C

electrocatalysts.



Figure S16 Electrochemical impedance spectroscopies of Ir-NS and Ir-NP.



Figure S17 CV curves, double layer capacitance and electrochemical impedance



spectroscopies of Ir-NS before and after potential cycles.

Figure S18 LSV, CV curves, double layer capacitances and electrochemical impedance spectroscopies of Ir-NP before and after 1000 potential cycles.



Figure S19 LSV, CV curves and double layer capacitances of Pt/C before and after

1000 potential cycles.



Figure S20 HER performance of Ir-NS electrocatalyst before and after CA test.

References

- 1. Y. Pi, Q. Shao, P. Wang, J. Guo and X. Huang, *Adv. Funct. Mater.*, 2017, 27, 1700886.
- 2. Q. Li, J. Li, J. Xu, N. Zhang, Y. Li, L. Liu, D. Pan, Z. Wang and F. L. Deepak, *ACS Appl. Energy Mater.*, 2020, 3, 3736-3744.
- 3. L. Fu, G. Cheng and W. Luo, J. Mater. Chem. A, 2017, 5, 24836-24841.
- 4. L. Fu, F. Yang, G. Cheng and W. Luo, *Nanoscale*, 2018, 10, 1892-1897.
- 5. J. Feng, F. Lv, W. Zhang, P. Li, K. Wang, C. Yang, B. Wang, Y. Yang, J. Zhou, F. Lin, G.-C. Wang and S. Guo, *Adv. Mater.*, 2017, 29, 1703798.
- 6. J. Lim, S. Yang, C. Kim, C.-W. Roh, Y. Kwon, Y.-T. Kim and H. Lee, *Chem. Commun.*, 2016, 52, 5641-5644.
- J. Gao, C.-Q. Xu, S.-F. Hung, W. Liu, W. Cai, Z. Zeng, C. Jia, H. M. Chen, H. Xiao, J. Li, Y. Huang and B. Liu, J. Am. Chem. Soc., 2019, 141, 3014-3023.

- 8. A. L. Strickler, D. Higgins and T. F. Jaramillo, *ACS Appl. Energy Mater.*, 2019, 2, 5490-5498.
- 9. B. Jiang, T. Wang, Y. Cheng, F. Liao, K. Wu and M. Shao, *ACS Appl. Mater. Interfaces*, 2018, 10, 39161-39167.
- 10. L. Fu, X. Zeng, G. Cheng and W. Luo, ACS Appl. Mater. Interfaces, 2018, 10, 24993-24998.