

Electronic Supplementary Information for

Phosphorus-induced activation of Ir metallene for efficient acidic water electrolysis

Ziqiang Wang, Xinmiao Li, Hugang Zhang, Kai Deng, Hongjie Yu, You Xu, Xiaonian Li,

Hongjing Wang* and Liang Wang*

State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

*** Corresponding authors**

*E-mails: hjw@zjut.edu.cn; wangliang@zjut.edu.cn

Experimental

Materials and chemicals

Sodium hypophosphite (NaH_2PO_2), iridium chloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, 99.9%), formic acid (HCOOH , 88%) and Sulfuric acid (H_2SO_4 , 95%~98%) were purchased from Aladdin. Trimethylstearylammmonium chloride (OTAC, 98.0%) was obtained from Tokyo Chemical Industry Co. Ltd. Nafion (5wt%) were obtained from Sigma-Aldrich. Commercial Pt/C (20wt%) was purchased from Alfa Aesar.

Synthesis of P-Ir metallene

Ir metallene was first synthesized through a wet chemical reduction method. Typically, 8.0 mg of OTAC was dissolved in 1.0 mL of IrCl_3 (40 mM) and 2.0 mL of deionized water under continuous sonication for 10 min, followed by adding 1.0 mL of HCOOH . Then, the mixture solution was reacted at 95 °C for 4 h. After that, dark grey products were collected by centrifugation and washing for six cycles. For phosphorus doping, 10 mg Ir metallene and 100 mg NaH_2PO_2 was placed in a quartz boat, heating to 300 °C under N_2 atmosphere with heating rate of 2 °C min^{-1} and reacting for 2 h. Finally, the dark grey products were collected after washing. For comparison, we synthesized P-Ir-L metallene and P-Ir-H metallene from different amounts of NaH_2PO_2 under similar conditions (50 and 200 mg), respectively.

Characterizations

Transmission electron microscopy (TEM, TalosS-FEG) equipped with energy dispersive X-ray spectroscopy (EDX) was used to characterize morphology and microstructure of samples. The crystalline of catalysts was analyzed by X-ray powder diffraction (XRD, Ultima IV, Rigaku, Japan).

X-ray photoelectron spectroscopy (XPS, K-Alpha) was used to analyze surface elemental composition and electronic structure of catalysts.

Electrochemical measurements

HER and OER Measurements were performed by CHI660E instrument using conventional three-electrode system in 0.5 M H₂SO₄, in which catalyst-coated glassy carbon electrode (GCE, 0.071 cm²) as working electrode, Ag/AgCl (3M KCl) electrode as reference electrode and carbon rod as counter electrode. The obtained P-Ir metallene was ultrasonically dispersed in water to form homogeneous catalyst ink (2 mg mL⁻¹). Prior to each measurement, catalyst ink (5 μL) was coated on polished GCE, followed by adding 3.0 μL of Nafion (0.05 wt%) to the surface to prepare the working electrode. Linear sweep voltammetry (LSV) was performed at 1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were carried out in 0.5 M H₂SO₄ at -0.28 V in frequency range of 0.1 Hz and 100 kHz with an amplitude of 5 mV. All potentials were converted to reversible hydrogen electrode (RHE) according to the equation $E \text{ (RHE)} = E \text{ (Ag/AgCl)} + 0.2224 \text{ V} + 0.05916 \times \text{pH}$. Overall water splitting was carried out in two-electrode cell under 0.5 M H₂SO₄ using catalyst-dispersed carbon paper as both anode and cathode (1 mg cm⁻²).

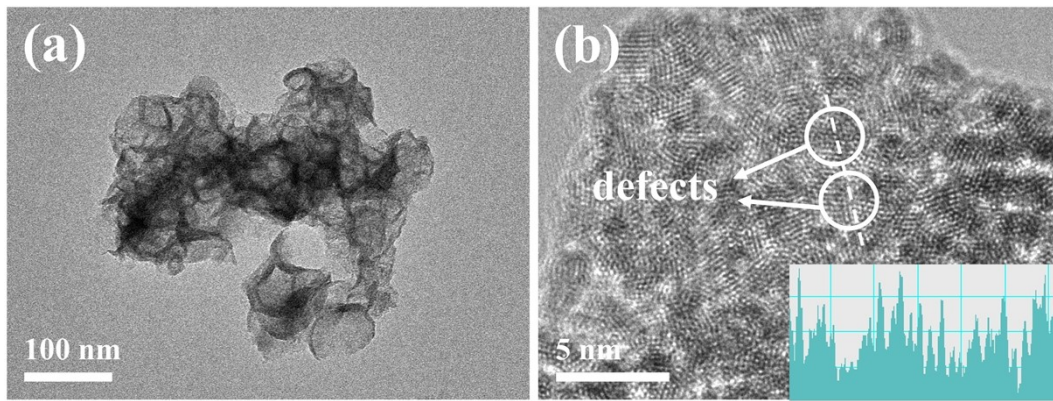


Fig. S1 (a) TEM (b) HRTEM images of Ir metallene, and the insets in (b) illustrate the intensity profile along the line.

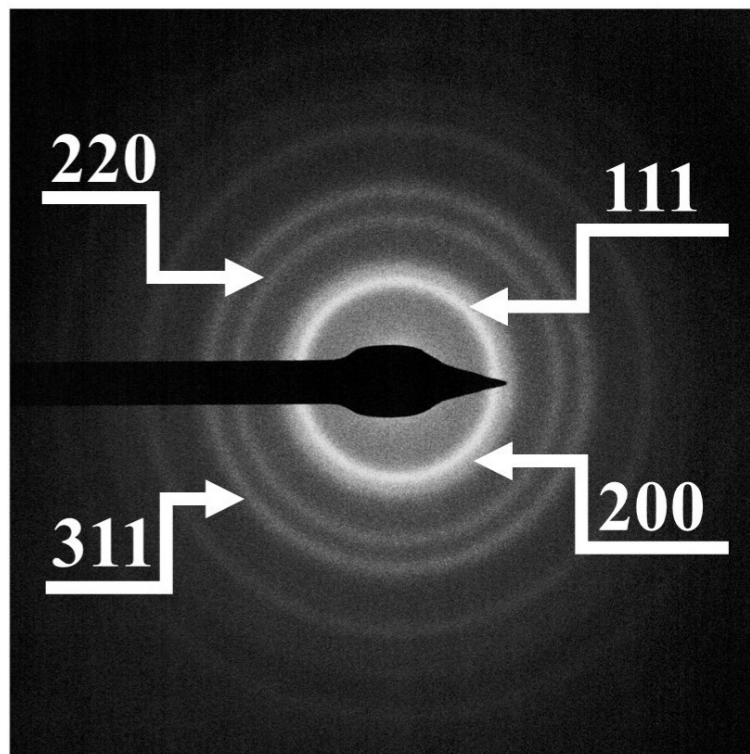


Fig. S2 SAED pattern of P-Ir metallene.

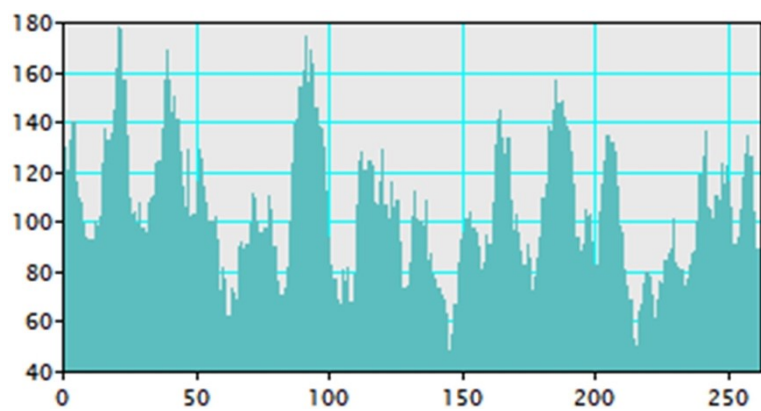


Fig. S3 The atomic intensity map along the linear direction of P-Ir metallene.

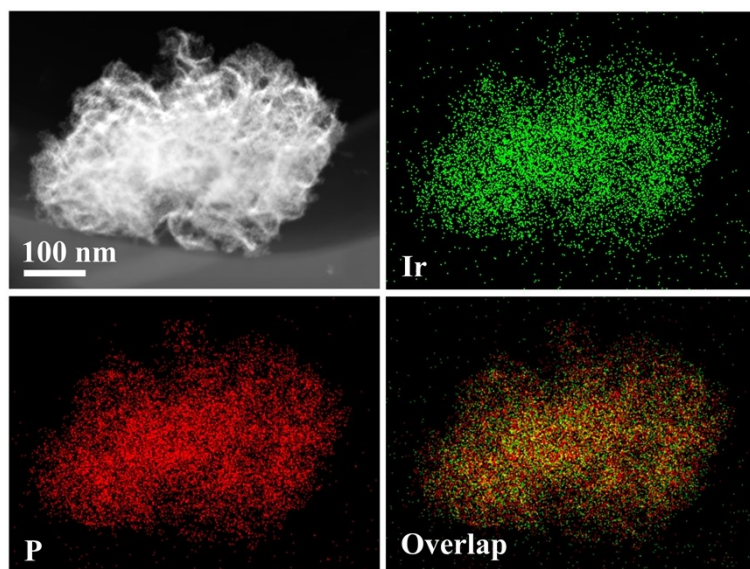


Fig. S4 HAADF-STEM image and the corresponding EDX mapping images of P-Ir metallene.

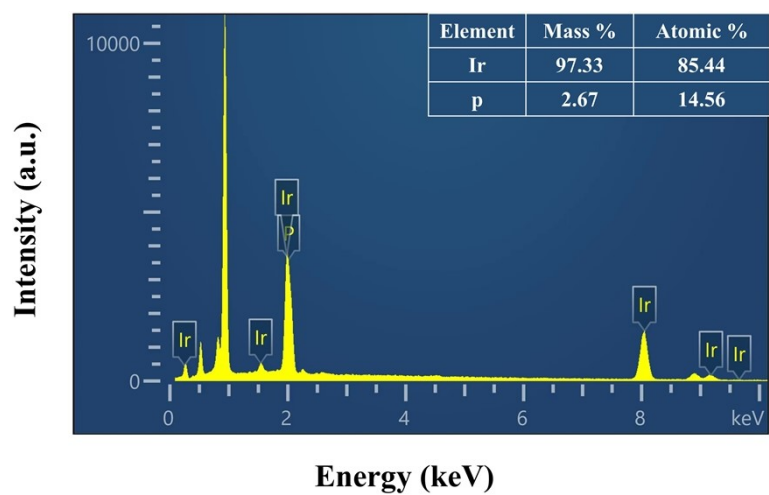


Fig. S5 EDX spectrum of P-Ir metallene.

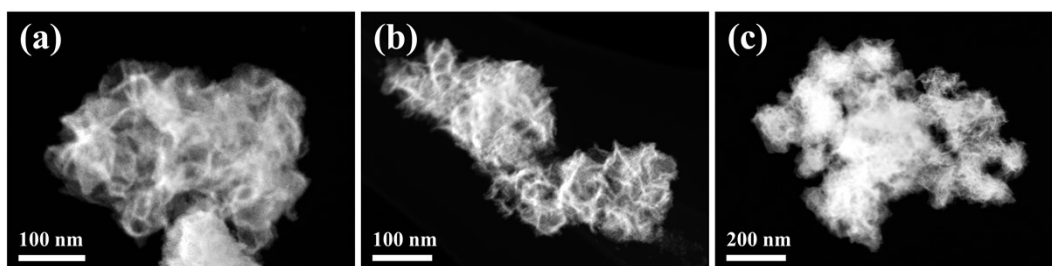


Fig. S6 TEM images of samples prepared with different amounts of NaH_2PO_2 under the typical synthesis: (a) 50 mg, (b) 100 mg and (c) 200 mg.

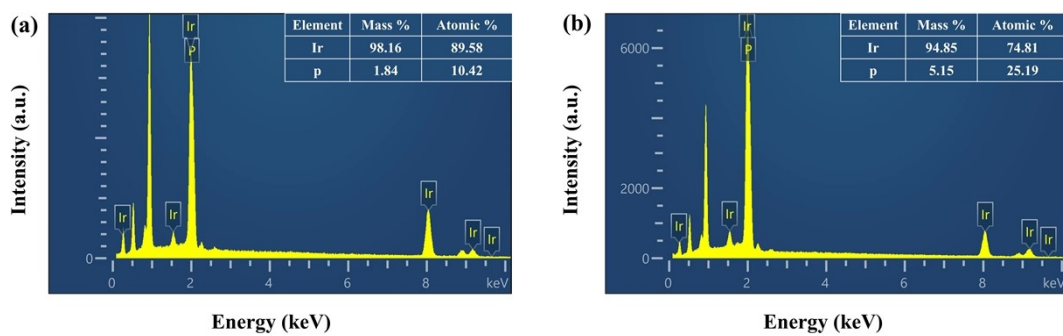


Fig. S7 EDX spectra of P-Ir-L metallene and P-Ir-H metallene.

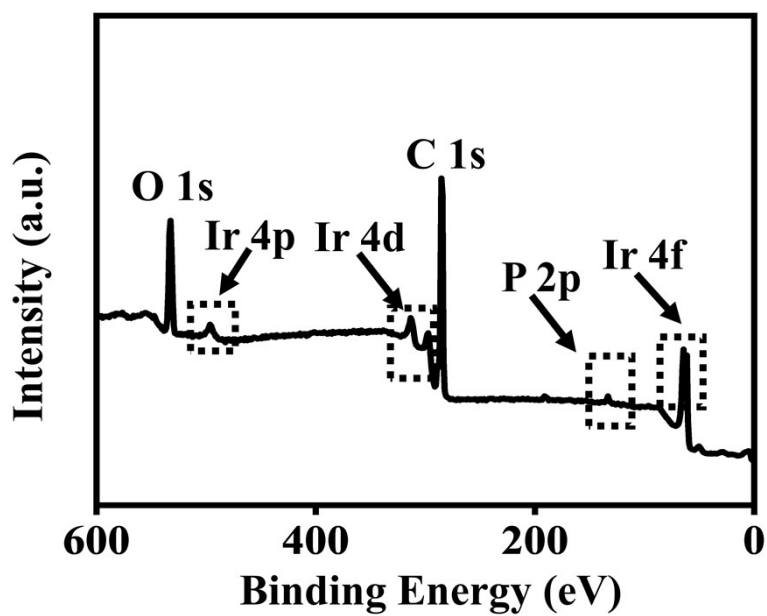


Fig. S8 XPS survey spectrum of the P-Ir metallene.

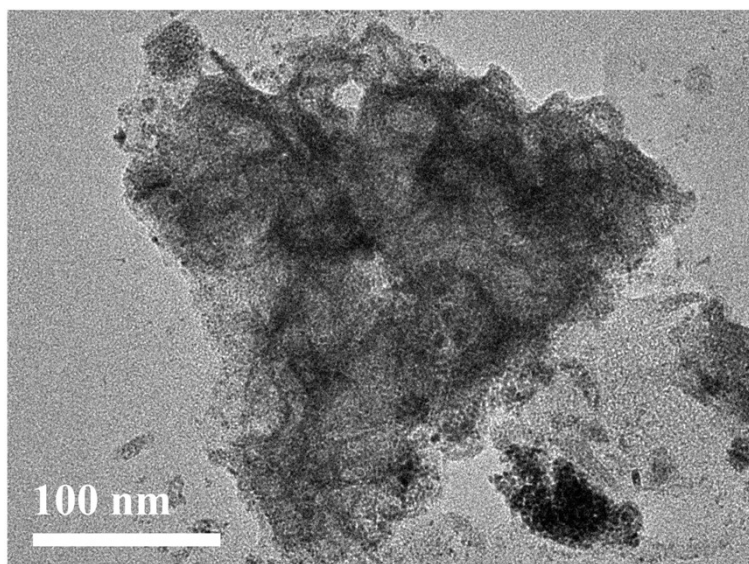


Fig. S9 TEM image of P-Ir metallene after a long OER test.

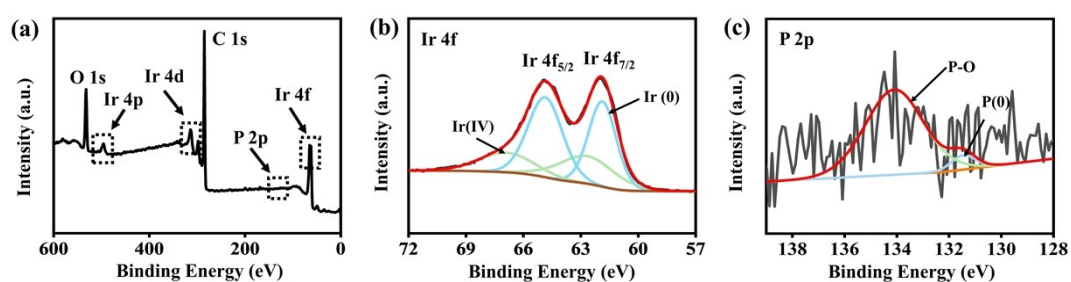


Fig. S10 (a) XPS survey spectrum of P-Ir metallene after a long OER test. (b) XPS spectra of Ir 4f and (c) P 2p for P-Ir metallene after a long OER test.

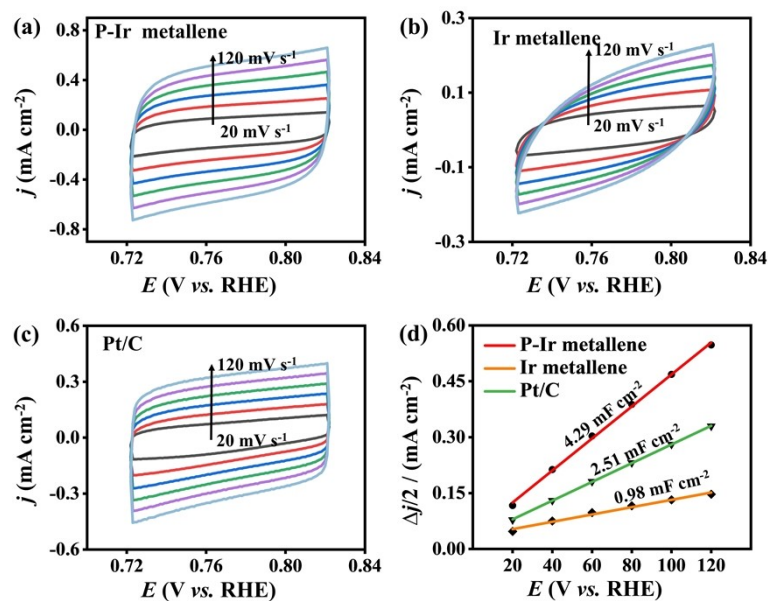


Fig. S11 Cyclic voltammograms for (a) P-Ir metallene, (b) Ir metallene and (c) Pt/C recorded in the same potential range with increasing scan rates, and (d) corresponding capacitive current densities at 0.55 V derived.

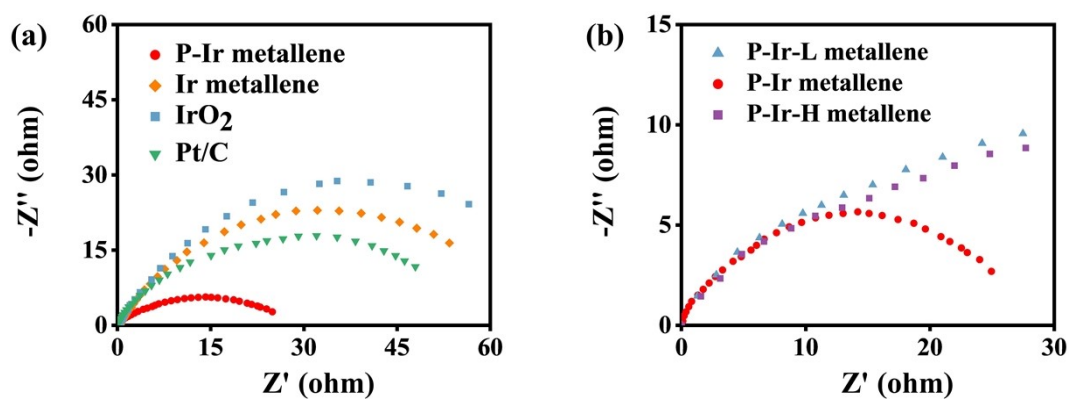


Fig. S12 Nyquist plots for (a) P-Ir metallene, Ir metallene, IrO₂ and Pt/C and (b) P-Ir-L metallene, P-Ir metallene and P-Ir-H metallene recorded at -0.28 V in the frequency ranges from 100 kHz to 0.1 Hz.

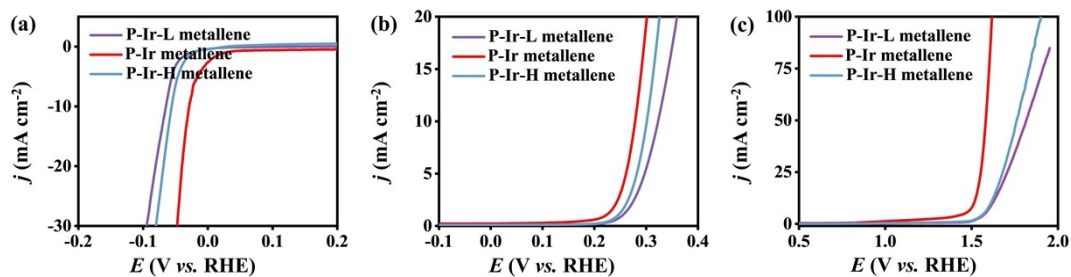


Fig. S13 (a) HER polarization curves, (b) OER polarization curves and (c) OWS polarization curves for P-Ir-L metallene, P-Ir metallene and P-Ir-H metallene in 0.5 M H₂SO₄.

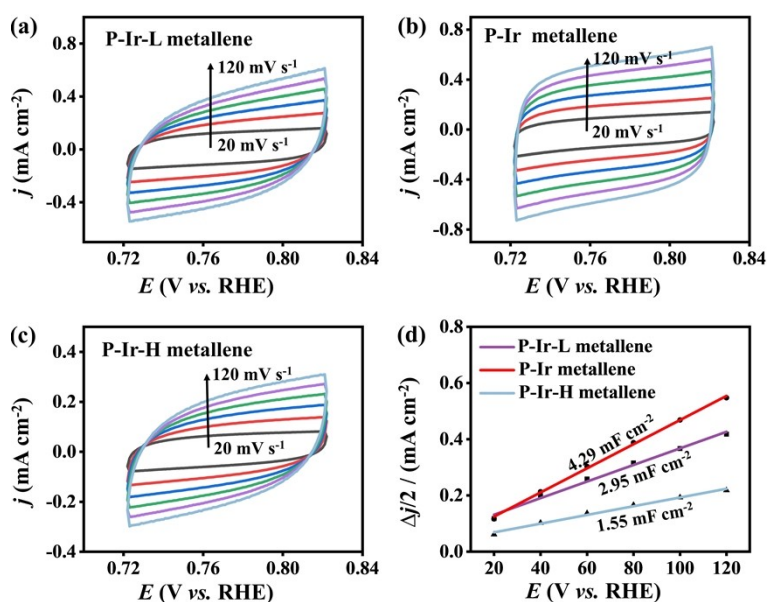


Fig. S14 Cyclic voltammograms for (a) P-Ir-L metallene, (b) P-Ir metallene and (c) P-Ir-H metallene recorded in the same potential range with increasing scan rates, and (d) corresponding capacitive current densities at 0.55 V.

Table S1. The comparisons of the HER performance of P-Ir metallene with the representative reported catalysts.

Electrocatalysts	Electrolytes	Overpotential at 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Ref.
P-Ir metallene	0.5 M H₂SO₄	28	37	This work
IrNi-N-C	0.5 M H ₂ SO ₄	28	38	1
Ir-mCNFs	0.5 M H ₂ SO ₄	39	181	2
Ir NPs/siloxene	0.5 M H ₂ SO ₄	31	29.4	3
Rh@Ir	0.5 M H ₂ SO ₄	169	112	4
Ir-NCNSs	0.5 M H ₂ SO ₄	46.3	52	5
Co-Ir/C	0.5 M H ₂ SO ₄	44	33	6
Ir/C-1	0.5 M H ₂ SO ₄	50.4		7
Pd _{83.5} Ir _{16.5}	0.5 M H ₂ SO ₄	73	43.6	8
Ir-Au-Si	0.5 M H ₂ SO ₄	38.2	24	9
Ir ₃ -CoP / CC	0.5 M H ₂ SO ₄	38	48	10

Table S2. The comparisons of the OER performance of P-Ir metallene with the representative reported catalysts.

Electrocatalysts	Electrolytes	Overpotential at 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Ref.
P-Ir metallene	0.5 M H ₂ SO ₄	279	63	This work
Pt ₇₀ Ru ₁₅ Ir ₁₅	0.5 M H ₂ SO ₄	450	118	11
IrRu _x @Ir	0.5 M H ₂ SO ₄	288	66.2	12
Au/Ir NCs	0.5 M H ₂ SO ₄	300	52.94	13
Ir/g-C ₃ N ₄ /NG	0.5 M H ₂ SO ₄	287	72.8	14
FeCoNiIrRu/CNFs	0.5 M H ₂ SO ₄	280	154	15
IrCo-N-C	0.5 M H ₂ SO ₄	340	79	16
PdCu/Ir/C	0.1 M HClO ₄	283	59.6	17
Ir ₃ CeO _x /C	0.1 M HClO ₄	299	49	18
Pt-Ir-Pd	0.5 M H ₂ SO ₄	408	128.7	19
Pt ₆₂ Co ₂₃ /Ir ₁₅ FBNWs/C	0.1 M HClO ₄	308		20

Table S3. The comparisons of the OWS performance of P-Ir metallene with the representative reported catalysts.

Electrocatalysts	Electrolytes	Voltage at 10 mA cm ⁻² (V)	Ref.
P-Ir metallene	0.5 M H ₂ SO ₄	1.5	This work
Au@AuIr ₂	0.5 M H ₂ SO ₄	1.55	21
Ir ₂ Ni/C	0.5 M H ₂ SO ₄	1.597	22
IrCo@NCNT/PC	0.5 M H ₂ SO ₄	1.51	23
IrTe NTs	0.5 M H ₂ SO ₄	1.53	24
Ir/Fe@NCNT	0.5 M H ₂ SO ₄	1.52	25
Ir-doped WO ₃	0.5 M H ₂ SO ₄	1.56	26
Ir-NSs	0.5 M H ₂ SO ₄	1.586	27
RuIrTe NTs	0.5 M H ₂ SO ₄	1.511	28
Ir ₁ Co ₁ HNPs	0.5 M H ₂ SO ₄	1.52	29
AuIr @ CNT	0.5 M H ₂ SO ₄	1.51	30

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