Integrating Multifunctional Catalytic Sites in COF@ZIF-67 Derived

Carbon for HER and ORR

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Experimental section

Materials: 2-Methylimidazole and Iridium(III) chloride were purchased from Aladdin. 2,4,6-Trihydroxyben-zene-1,3,5-tricarbaldehyde (TP) and [2,2'-bipyridine]-5,5'-diamine (BPY) were purchased from Alfa. Cobalt nitrate hexahydrate, methanol (MeOH), tetrahydrofuran (THF), ethanol (EtOH) and potassium hydroxide (KOH) were from Sinopharm Chemical Reagent Co., Ltd.

Catalyst preparation: In a typical synthesis of ZIF-67, 4 mmol 2-methylimidazole and 1 mmol cobalt nitrate hexahydrate were dissolved in 25 mL MeOH, respectively, which were mixed and stirred at 25°C for 24 hours to obtain purple solid. The ZIF-67 solid was washed with MeOH and THF in sequence and then dried in vacuum.

For the synthesis of COF@ZIF-67, 63 mg of TP in 50 mL THF and 83.7 mg of BPY in 50 mL THF were added into the mixture of ZIF-67 (500 mg) and MeOH (200 mL), which were then sonicated for 30 minutes and stirred at 25°C for 24 hours to obtain ZIF-67-supported TP-BPY-COF (named as COF@ZIF-67). The collected COF@ZIF-67was washed with MeOH and THF in sequence and then dried in vacuum to obtain 506 mg COF@ZIF-67.

For the synthesis of Ir-ZIF, 500 mg ZIF-67 was well-dispersed in 200 mL EtOH, followed by adding 10mg $IrCI_3$ in 10 mL MeOH and stirring for 24 h at room temperature. The products were washed with EtOH and then dried in vacuum to obtain 156.55 mg Ir-ZIF.

For the synthesis of Ir-COF@ZIF, 400 mg COF@ZIF-67 in 200 mL MeOH and 8 mg $IrCl_3$ in 10 mL MeOH were well-dispersed respectively. Then they were mixed up and stirred at 25°C for 24 hours to obtain 331.51 mg Ir-COF@ZIF.

For the synthesis of Ir-COF@ZIF(1%), 400 mg COF@ZIF-67 in 200 mL MeOH and 4 mg IrCl₃ in 10 mL MeOH were well-dispersed respectively. Then they were mixed up and stirred at 25°C for 24 hours to obtain Ir-COF@ZIF(1%).

For the synthesis of Ir-COF@ZIF(5%), 400 mg COF@ZIF-67 in 200 mL MeOH and 20 mg IrCl₃ in 10 mL MeOH were well-dispersed respectively. Then they were mixed up and stirred at 25°C for 24 hours to obtain Ir-COF@ZIF(5%).

For the synthesis of Ir-ZIF₈₀₀ and Ir-COF@ZIF₈₀₀. The as-prepared Ir-ZIF and Ir-COF@ZIF were heated to 800°C with a rate of 5°C min⁻¹ and kept for 1 hour in N₂ to yield Ir-ZIF₈₀₀ and Ir-COF@ZIF₈₀₀, respectively.

For the synthesis of Ir-COF@ZIF₈₀₀(1%) and Ir-COF@ZIF₈₀₀(5%), the as-prepared Ir-COF@ZIF (1%) and Ir-COF@ZIF (5%) were heated to 800°C with a rate of 5°C min⁻¹ and kept for 1 hour in N₂ to yield Ir-COF@ZIF₈₀₀(1%) and Ir-COF@ZIF₈₀₀(5%), respectively.

Electrochemical performance tests:

The catalyst (4 mg) was ultrasonic dispersed in a Nafion ethanol solution (0.25 wt%, 500 μ L) for 2 h to yield a homogeneous ink. The ink of Ir-COF@ZIF₈₀₀ (9 μ L) was pipetted onto a glassy carbon electrode (d = 4.00 mm, S = 0.125 cm²) with a loading amount of 0.54 mg cm⁻². The commercial Pt/C catalyst (20 wt% platinum on carbon black, BASF) and Ir-ZIF₈₀₀ were employed as references. The Pt/C catalyst ink (13.3 μ L), Ir-ZIF₈₀₀ (13.3 μ L) and electrode were prepared by the same conditions to that of Ir-COF@ZIF₈₀₀. All the electrochemical measurements were conducted in a conventional three-electrode cell using the PINE electrochemical workstation (Pine Research Instrumentation, USA) at room temperature. The Ag/AgCl (3 M KCl) and platinum wire were used as reference and counter electrodes, respectively. A rotating ring disk

electrode (RRDE) electrode with a Pt ring and a glassy carbon disk served as the substrate for the working electrode for evaluating the ORR activity and selectivity of various catalysts. The electrochemical experiments were conducted in O₂ saturated aqueous solution of KOH (0.1 M) or H₂SO₄ (0.5 M) for ORR and in N₂ saturated aqueous solution of H₂SO₄ (0.5 M) for HER. The RRDE measurements were conducted at a rotation rate of 1600 rpm with a sweep rate of 10 mV s⁻¹. On the basis of ring and disk currents, the electron-transfer number (n) and fourelectron selectivity of catalysts based on the H₂O₂ yield (H₂O₂ (%)) were calculated from the equations of n = 4 I_D/[(I_R/N) + I_D] and H₂O₂ (%) = 200 (I_R/N)/[(I_R/N) + ID], where I_D and I_R are the disk and ring currents, respectively, and the ring collection efficiency N is 0.37. The Tafel slope was estimated by linear fitting of the polarization curves according to the Tafel equation (h = b×log*j* + a, where *j* is the current density and b is the Tafel slope). For the cyclic voltammetry (CV) tests, the potential range was circularly scanned between 0.15 and 1.1 V at a scan rate of 50 mV s⁻¹ after purging O₂ gas for 30 min. To estimate the double layer capacitance, the electrolyte was deaerated by bubbling with nitrogen, and then the voltammogram was evaluated again in the deaerated electrolyte.

Characterization: Powder X-ray diffraction (PXRD) data were recorded on an Ultima IV diffractometer with Cu K α radiation by depositing powder on glass substrate, from 2 θ = 1.5° up to 60° with 0.02° increment. Nitrogen sorption isotherms were measured at 77 K with a TriStar II, Micromeritics. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha XPS spectrometer using Al K α X-ray source for radiation. Raman spectra were obtained from a Bruker SEN TERRA spectrometer employing a semiconductor laser (λ = 532 nm). High-resolution transmission electron microscope images were obtained by transmission electron microscopy (TEM, FEI Tecnai G2) installed with energy dispersive spectrometer (EDS, Oxford). The morphology was measured by a scanning electron microscope (SEM, Zeiss SUPRA 55 SAPPHIRE).



Figure S1. FT-IR spectra of ZIF-67 (purple), Ir-ZIF (blue), COF@ZIF-67 (green) and Ir-COF@ZIF (red).

With introducing the Ir in the COF@ZIF-67, the FT IR spectra showed all the peaks from COF@ZIF-67 were retained, and the peak at 1275 cm⁻¹ from the C-N of bipyridine units, which negatively shifted to 1270 cm⁻¹, suggesting the Ir ions were coordinated with bipyridine units (Fig. S1, red curve).



Figure S2. PXRD patterns of ZIF-67 (purple) and COF@ZIF-67 (green).



Figure S3. SEM images of COF@ZIF.



Figure S4. TEM images of COF@ZIF.



Figure S5. (a) PXRD patterns of Ir-ZIF (blue), Ir-COF@ZIF(red) and the simulation of ZIF-67 (black). (b) Nitrogen sorption profiles at 77K of Ir-ZIF (blue), Ir-COF@ZIF (red).



Figure S6. SEM images of Ir-ZIF (a, b) and Ir-COF@ZIF (c, d).



Figure S7. TEM images of Ir-ZIF (a, b) and Ir-COF@ZIF (c, d).



Figure S8. EDX-mapping images of Ir-ZIF.



Figure S9. EDX-mapping images of Ir-COF@ZIF.



Figure S10. Pore size distribution curves of Ir-ZIF (a) and Ir-COF@ZIF (b).



Figure S11. XPS spectra of Ir-ZIF (blue curve) and Ir-COF@ZIF (red curve). The chemical nature and atomic states of Ir-ZIF-67 and Ir-COF@ZIF-67 were then investigated by X-ray photoelectron spectroscopy (XPS). The peaks from C, N, O, Co and Ir in Ir-ZIF-67 and Ir-COF@ZIF were clearly identified. And the weight contents calculated by XPS spectra for Co and Ir in Ir-ZIF-67 were 18.14 wt% and 16.67 wt%, respectively. In contrast, Ir-COF@ZIF showed a decreased weight contents of Co (9.54 wt%) and Ir (12.84 wt%) compared with that of Ir-ZIF, owing to the successful forming of Tp-Bpy-COF thin layer (Fig. S11).



Figure S12. TGA profiles for Ir-ZIF (blue) and Ir-COF@ZIF (red) from 25 °C to 800 °C under N₂. The thermal gravimetric analysis (TGA) measurement showed the decomposition temperature (Fig. S12) for Ir-ZIF-67 and Ir-COF@ZIF were 440 and 495 °C under N₂.



Figure S13. Raman spectra of Ir-ZIF₈₀₀ (blue) and Ir-COF@ZIF₈₀₀ (red).

The defective and graphitic degree were revealed by the Raman spectra (Fig.S13). The intensity ratios between the D and G bands (I_D/I_G) for Ir-ZIF₈₀₀ and Ir-COF@ZIF₈₀₀ were 1.02 and 0.98. The lower I_D/I_G values for Ir-COF@ZIF₈₀₀ attributed to the COF-derived carbon improved the graphitic degree in pyrolysis process.



Figure S14. XPS spectra of Ir-ZIF $_{800}$ (blue curve) and Ir-COF@ZIF $_{800}$ (red curve).



Figure S15. EXAFS fitting curve for Co in Ir-COF@ZIF $_{800}$.



Figure S16. EXAFS fitting curve for Ir in Ir-COF@ZIF $_{\rm 800}.$



Figure S17. SEM images of Ir-ZIF_{800} (a, b) and Ir-COF@ZIF_{800} (c, d).



Figure S18. The EDX-mapping images of $\rm Ir\mathchar`zIF_{800}.$



Figure S19. The TEM images of Ir-COF@ZIF₈₀₀.



Figure S20. The CV curves of (a) Ir-ZIF₈₀₀ and (b) Ir-COF@ZIF₈₀₀ at scan rates of 50 mV s⁻¹ under N₂ and O₂ -saturated KOH (0.1 M) aqueous solution.



Figure S21. (a) Chronoamperometric curves of Ir-COF@ZIF₈₀₀ (red) and Pt/C (black) upon addition of methanol. The LSV curves for (b) Ir-COF@ZIF₈₀₀ and (c) Pt/C before (black) and after (red) adding MeOH to the electrolytes.



Figure S22. Long-term stability test of Ir-COF@ZIF $_{800}$ at 0.5 V vs RHE in 0.1 M KOH for 20 h.





The electrochemical impedance spectroscopy (EIS) was measured to study the mass and electron transport of the catalysts and investigate the different conductive behavior of Ir-ZIF₈₀₀ and Ir-COF@ZIF₈₀₀. As shown in Fig. S23, the semicircle in the high frequency region was associated with the internal resistance, while the medium-frequency semicircle was related to the charge transfer resistance (R_{ct}). The R_{ct} value of Ir-COF@ZIF₈₀₀ was 104.4 Ω , which was smaller than that of Ir-ZIF₈₀₀ (503.6 Ω), indicating the introduction of Tp-Bpy-COF can greatly enhance charge transfer capacity.



Figure S24. The LSV curves for ORR over Ir-COF@ZIF₈₀₀ (red curves) and addition of KSCN (green curves) to the electrolytes in 0.1 M KOH.



Figure S25. The LSV curves for HER over Ir-COF@ZIF₈₀₀ (red curves) and addition of KSCN (green curves) to the electrolytes in 0.5 M H_2SO_4 .



Figure S26. LSV curves for HER over COF@ZIF_{800} in 0.5 M H_2SO_4 solution.



Figure S27. (a) LSV curve of for ORR over Ir-COF@ZIF₈₀₀(1%) (yellow) and Ir-COF@ZIF₈₀₀(1%) (green) in oxygen-saturated KOH (0.1 M) aqueous solution. (b) LSV curve of for HER over Ir-COF@ZIF₈₀₀(1%) (yellow) and Ir-COF@ZIF₈₀₀(1%) (green) in N₂-saturated H₂SO₄ (0.5 M) aqueous solution.

To further confirm the roles of Ir nanoparticles in the catalysts, the catalysts with different contents of Ir have been synthesized (Ir-COF@ZIF₈₀₀ (1%) and Ir-COF@ZIF₈₀₀ (5%)). The E_{1/2} for Ir-COF@ZIF₈₀₀(1%) and Ir-COF@ZIF₈₀₀(5%) were 0.85 and 0.86 V, with J_{lim} of 4.86 and 6.25 mA cm⁻² for ORR (Fig. S27a). And the η_{10} Ir-COF@ZIF₈₀₀(1%) and Ir-COF@ZIF₈₀₀(5%) were 60 mV and 41 mV for HER (Fig. S27b). The higher contents of Ir resulted in higher activity in ORR and HER, and thus confirming important roles of Ir nanoparticles in ORR and HER.

Table S1. Co K-edge EXAFS fitting results for Ir-COF@ZIF_{800}.

Catalysts	Shell	Bond distance (R(Å))	Coordination number(CN)	ΔE₀ (eV)	σ ² (10 ⁻³ Å ²)	R - factor	
(Co)-Ir-	Co-N/O	2.08±0.13	1.0±1.5	11.1±1.36	3.8±11.0	1.7%	
	Co-Co	2.52±0.02	7.5±0.0	11.1±3.4	4.7±1.1		

Note: ΔE_0 , inner potential correction; σ^2 , Debye-Waller factor to account for both thermal and structural disorders; R-factor, indicating the goodness of the fit.

Table S2. Ir L3-edge EXAFS fitting results for (Ir)-Ir-COF@ZIF₈₀₀.

Catalysts	Shell	Bond	Coordination	ΔE_0	σ^2	R -	
		distance	number(CN)	(eV)	(10 ⁻³ Ų)	factor	
		(R(Å))					
(Ir)-Ir-COF@ZIF ₈₀₀	lr-N/C	1.90±0.13	1.5±1.7	-0.8	3.0	0.4%	
	lr-Ir	2.63±0.10	8.5±0.0	-0.8	4.2		

Note: ΔE_0 , inner potential correction; σ^2 , Debye-Waller factor to account for both thermal and structural disorders; R-factor, indicating the goodness of the fit.

Catalyst	Overpotential	Tafel slope	Reference
Catalyst	@J ₁₀ (mV)	(mV/dec)	
	(1	70	This work
II-ZIF ₈₀₀	01	70	This work
Ir-COF@ZIF ₈₀₀	48	44	This work
Pt/C(20%Pt)	43	40	This work
Pd NPs	59.6	30	1
Mo ₂ N–Mo ₂ C /HGr	157	55	2
P-WN/rGO	85	54	3
MoDCA-5	78	41	4
RuSA-Ti₃C₂Tx Mxene	151	90	5
Metallic WO ₂ -Carbon	58	46	6
Au@NC	130	76.8	7
FeIr alloy	19	32	8
Ir NPs/siloxene	31	29.4	9
RuP@NPC	15.6	31	10
Ir-NCNSs	46.3	52	11
IrNiTa	99	35	12

Table S3. Summary of electrocatalysts for HER in 0.5M H₂SO₄.

Catalyst	Electrolyte	E _{1/2} E ₀		J _{lim}	Tafel	Reference
		(V vs.	(V vs.	(mA cm ⁻²)	slope	
		RHE)	RHE		(mV/dec)	
Ir-ZIF ₈₀₀	0.1M KOH	0.79	0.89	3.36	102	This work
Ir-COF@ZIF ₈₀₀	0.1М КОН	0.86	0.96	5.64	80	This work
Pt/C	0.1M KOH	0.85	1.02	5.33	126	This work
Co-N3C1@GC	0.1 M KOH	0.846	0.913	5.16	46	13
Co-SAs/NSC	0.1 M KOH	0.86	0.95	4.50	46	14
Ir-SAC	0.1 M	0.864	0.97	-	41	15
	HCIO ₄					
L10-PtCo/C	0.1 M	0.94	0.99	-	-	16
	HCIO ₄					
IrO₂@CNT	0.1 M KOH	0.796	0.91	4.6	-	17
IrCo@NCNT/PC	0.1 M KOH	0.83	0.93	-	53	18
cal-CoZIF-VXC72	0.1 M KOH	0.84	0.92	5.9	45	19
Fe-N4 SAs/NPC	0.1 M KOH	0.885	0.972	5.5	123	20
GC@COF-NC0.08	0.1 M KOH	0.841	0.923	-	78.4	21

Table S4. Summary of electrocatalysts for ORR.

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