Electronic Supplementary Information

Experimental sections

Synthesis of CoIr-MOF /NF

Firstly, a piece of commercial nickel foam $(2 \text{ cm} \times 4 \text{ cm})$ was sonicated with 3M hydrochloric acid, then washed with ethanol and deionized water several times, respectively, after which it was dried and set aside in an oven. Next, 0.3 g of Co(NO₃)₂·6H₂O, 0.033 g of triethylenediamine (TED), and 0.105 g of 1,4-benzenedicarboxylic acid (BDC) were dissolved in 30 mL DMF solvent and left to sonicate until completely dissolved, 2 mL of IrCl₃ aqueous solution (20 mM) was added, followed by strong stirring for 15 min. Then the above solution was transferred to a 50 mL autoclave lined with stainless steel Teflon, placed in an oven and heated to 130°C, and kept at this temperature for 12 h. After natural cooling to room temperature, the formed CoIr-MOF/NF composites were washed 3 times with ethanol and dried in an oven at 60 °C.

Synthesis of Ir-Co₃O₄ /NF

First, the CoIr-MOF/NF precursor prepared above was placed in the middle part of the porcelain boat. Subsequently, the tube furnace was heated from room temperature to 300 °C (heating rate of 10 °C min⁻¹) under an air atmosphere and kept at this temperature for 4 hours. The Ir-Co₃O₄/NF material was collected after the tube furnace was cooled to room temperature. The Co₃O₄/NF composite was prepared using Co-MOF/NF as precursors and by similar steps. Moreover, the contrastive samples with lower Ir content (Ir-Co₃O₄/NF(L)) and higher Ir content (Ir-Co₃O₄/NF(H)) were synthesized by adjusting the adding amount of IrCl₃ in the MOF synthesis process (see Table S1).

Characterization

Scanning electron microscopy (SEM) was performed on a Zeiss SUPRA 55. Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on a JEM-2010 microscope. X-ray powder diffraction (XRD) patterns were obtained by Cu K α radiation ($\lambda = 0.154056$ nm). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB MK II spectrometer (VG Scientific, UK), using Al K α X-ray radiation excitation. Nuclear magnetic resonance (NMR) was performed on an Avance III HD 500 (Bruker). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurement was performed on a Thermo Fisher iCAP PRO.

Electrochemical measurements

We performed all electrochemical measurements at room temperature on a CHI 760E workstation. To construct a standard three-electrode system, the Ir-Co₃O₄/NF (1 x 1 cm²) was as working electrode, along with Ag/AgCl reference electrode and graphite rod counter electrode. HER, OER, and GOR performance were evaluated by the above three-electrode system, and the electrolyte for HER and OER is a 1 M KOH aqueous solution, while that for GOR is a 1 M KOH aqueous solution containing 0.1 M glycerol respectively. Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s⁻¹. All LSV data were iR (95%) corrected. The potentiometric voltages in this work were all based on the Nernst equation ($E_{vs RHE} = E_{vs Ag/AgCl} + E^{\theta}_{Ag/AgCl} + 0.0596$ *pH). Electrochemical impedance spectroscopy (EIS) tests were performed in the frequency range of 0.1–100 kHz.

The HER||GOR hybrid water electrolysis system was constructed by using Ir-Co₃O₄/NF electrodes as the anode and cathode and tested in a 1 M KOH solution containing 0.1 M glycerol). The Faraday efficiency (FE) of HER electrocatalytic production of H_2 was also tested by the drainage method. the Faraday efficiency of GOR conversion to formate was tested by ¹H NMR spectroscopy.

The calculation equation is as follows.^{1, 2}

$$FE(H_2) = \frac{N(H_2 \text{ production})}{Q_{totl1}/(Z_1 \times F)} \times 100\%$$
(1)

$$FE(formate) = \frac{N(formate \text{ yield})}{Q_{totl2}/(Z_2 \times F)} \times 100\%$$
(2)

Where Q_{tot1} and Q_{tot2} are the total charges passing through the electrodes during HER and GOR, respectively, Z_1 and Z_2 are the number of electrons to generate one molecule of H₂ and one mole of H₂ formate, respectively, where Z_1 takes 2, Z_2 takes 8/3, and *F* is the Faraday constant (96,485 C mol⁻¹).



Fig. S1 SEM images of the CoIr-MOF/NF.



Fig. S2 XRD patterns of the CoIr-MOF and Co-MOF.

The comparison between the XRD patterns of the Co-MOF and CoIr-MOF clearly showed that the diffraction spectrum of the CoIr-MOF is similar to that of Co-MOF except for the slight shift in the diffraction peak positions. These results suggested that doing of Ir cations into Co-MOF structure caused a small lattice distortion to the parent Co-MOF structure, resulting in the formation of binary CoIr-based MOF structure.



Fig. S3 Scheme illustrating the synthesis process of the Ir-Co₃O₄/NF.



Fig. S4 (a) Nitrogen-adsorption and-desorption isotherm and (b) Barrett–Joyner–Halenda pore distribution curve of the $Ir-Co_3O_4$ sample.

BET analysis shows that a specific surface area of 63.9 m2·g-1 for the Ir-Co3O4 porous nanosheets together with mesoporous features can be obtained.



Fig. S5 (a) SEM image and (b) TEM image the Co_3O_4/NF .

The Co_3O_4/NF without Ir incorporation was also prepared by the same calcination conditions using Co-MOF/NF as precursors.



Fig. S6 The XPS survey spectrum of Ir-Co₃O_{4.}



Fig. S7 (a) SEM image and (b) EDX spectrum of Ru-Co₃O₄. (c) SEM image and (d) EDX spectrum of Os-Co₃O₄.

The Ru-Co₃O₄ and Os-Co₃O₄F samples were prepared by similar procedure to that of Ir-Co₃O₄, except that IrCl₃ was replaced with RuCl₃ and OsCl₃, respectively.



Fig. S8 Electrochemical impedance spectra of various catalysts in 1.0 M KOH solutions with and without 0.1 M glycerol and at different potentials: (a) -0.25 V (vs. RHE), without glycerol; (b) 1.35 V (vs. RHE), with 0.1 M glycerol.



Fig. S9 (a,b) SEM images, (c) TEM image, (d) HRTEM image, (e) HAADF-STEM and (f) corresponding elemental mapping images of the post-HER Ir- Co_3O_4 /NF. The inset in (d) show the lattice spacing.



Fig. S10 XRD patterns of fresh, post-HER, and post-GOR Ir-Co₃O₄ samples.



Fig. S11 (a) Co 2p high-resolution XPS spectra, (b) O 1s high-resolution XPS spectra, (c) Ir 4f high-resolution XPS spectrum for fresh and post-HER Ir-Co₃O₄ samples.



Fig. S12 (a) LSV curves (with iR compensation) of Ir-Co₃O₄/NF in 1 M KOH solution with and without 0.1 M glycerol and (b) corresponding Tafel plots. (c) ¹H NMR spectra (with maleic acid as an internal standard) of formate standard, methanol standard and electrolyte containing 1.0 M KOH and 0.1 M glycerol before and after 15 hours' chronoamperometric testing. (d) ¹H NMR measurements of oxidative conversion of glycerol to formate from 0 to 15 h (interval of 3 h). (e) Relative concentrations of glycerol, formate and methanol at various charges during the chronoamperometric testing form 0 to 15 h (interval of 3 h). (f) Glycerol conversion efficiency and formate FE for 5 consecutive cycles.



Fig. S13 (a) LSV curves measured for Ir-Co₃O₄/NF, Co₃O₄/NF/NF, RuO₂/NF, and NF in 1.0 M KOH solution containing 0.1 M glycerol. (b) The require applied potentials for various electrodes at a current density of 100 mA cm⁻².



Fig. S14 (a) HER polarization curves and (b) GOR polarization curves for various catalysts. It was found that the electrocatalytic performance of Ir-Co₃O₄/NF was affected by the Ir content. The typical Ir-Co₃O₄/NF showed higher GOR activity than those contrastive catalysts with lower or higher Ir content (Table S1).



Fig. S15 The ¹³C NMR spectra of the products of glycerol before and after 15 h of anodic oxidation, and the spectra of HCOO⁻ and CO_3^{2-} .



Fig. S16 Glycerol conversion and formate Faradaic efficiency at different potentials for Ir-Co₃O₄/NF tested in a 1 M KOH solution containing 0.1 M glycerol.



Fig. S17 (a) GOR polarization curves (iR compensation) of Ir-Co₃O₄/NF at initial and after 5000 cycles testing. (b) The V-t curves of Ir-Co₃O₄/NF measured at an anode current density of 10 mA cm⁻² for 24 h (without iR compensation).



Fig. S18 (a,b) SEM images, (c) TEM image, (d) HRTEM image, (e) HAADF-STEM and (f) corresponding elemental mapping images of the post-GOR Ir- Co_3O_4 /NF. The inset in (d) show the lattice spacing.



Fig. S19 (a) Co 2p high-resolution XPS spectra, (b) O 1s high-resolution XPS spectra, (c) Ir 4f high-resolution XPS spectrum for fresh and post-GOR Ir-Co₃O₄ samples.



Fig. S20 (a, c) Relative concentrations of glycerol and formate, and (b,d) ¹H NMR measurements at different time stages during the V-t testing for various two-electrode systems: (a, b) Ir-Co₃O₄/NF||Ir-Co₃O₄/NF system, (c, d) Co₃O₄/NF||Co₃O₄/NF system.

Sample names	Adding amount of IrCl ₃ Atomic ratio of Co	
Ir-Co ₃ O ₄ /NF	0.04 mmol	97.2 : 2.8
Ir-Co ₃ O ₄ /NF(L)	0.02 mmol	98.8 : 1.2
Ir-Co ₃ O ₄ /NF(H)	0.06 mmol	96.6 : 3.4

Table S1. The composition of various catalyst samples.

Table S2. Comparison of the hydrogen evolution and organic electrosynthesis performance of Ir- Co_3O_4/NF || Ir- Co_3O_4/NF systems and other reported bifunctional catalyst-based co-electrolysissystems.

Bifunctional catalysts	Electrolyte	Main anode product	Cell voltage at 10 mA cm ⁻ ² (V)	Ref.
Ir-Co ₃ O ₄ /NF	1.0 M KOH+ 0.1 M glycerol	Formate	1.40	This work
Co(OH)2@HOS/CP	1.0 M KOH+ 3 M methanol	Formate	1.497	3
Ni ₃ S ₂ /NF	1M KOH + 0.01 M 5- hydroxymethylfurfural	2,5- furandicarboxylic acid	1.46	4
Co ₃ S ₄ -NSs/Ni-F	1.0 M KOH + 0.5 M ethanol	Acetate	1.48	5
Ni ₂ P-UNMs/NF	1 M KOH + 0.125 M benzylamine	Benzonitrile	1.41	6
Co-S-P/CC	1.0 M KOH + 1.0 M ethanol	Acetic acid	1.63	7
Ni(OH) ₂ /NF	1 M KOH + 0.5 M methanol	Formate	1.52	8
Ni _{0.33} Co _{0.67} (OH) ₂ /NF	1 M KOH + 0.5 M methanol	Formate	1.5	9
MoO ₂ -FeP@C	1M KOH + 0.01 M 5- hydroxymethylfurfural	2,5- furandicarboxylic acid	1.486	10

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