Supporting Information

Ultrathin iridium carbonyl formate for efficient and durable acidic oxygen evolution electrocatalysis

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Experimental Section

Materials. Iridium chloride hydrate ($IrCl_3$ xH_2O, metals basis, Ir > 52%) was purchased from Aladdin Scientific Corp and was dissolved in the ultrapure water to a concentration of 10 mg mL^{-1} for the further use. 1,3,5-benzenetricarboxylic acid (BTC, 98%) was purchased from J&K Scientific Co., Ltd. Perchloric acid ($HClO_4$, analysis reagent, 72%), N, N-Dimethylformamide (DMF, reagent grade, 99.8%) and formic acid (reagent grade, 98%) were provided by the Sinopharm Chemical Reagent Co., Ltd. Ethanol anhydrous (reagent grade, 99.7%) was purchased from the Lingfeng Chemical Reagent Co. Commercial Pt/C (40%), iridium black and iridium oxides nanomaterials were obtained from Shanghai Hesen Electric Co., Ltd. Nafion 115 was used as proton exchange membrane in the electrolyzer test.

Sample preparation. Microwave synthesis was adopted to prepare catalytic materials on the XH-300UL+ device equipped with a temperature-controlled unit. For IrCF-BTC sample synthesis, 3.5 mL $IrCl_3$ aqueous solution was mixed with 5 mL DMF and 5 mL formic acid, and 7 mg BTC was then dissolved by ultrasonic. The mixture solution was transferred into microwave synthesis device and heated to 100 ℃ in 5 min, following reaction for several minutes. The sample was collected after cooling by high-speed centrifugation with 10000 rpm for 10 min, using water and ethanol to wash the residual solvents. The additive amounts of BTC were 0 mg and 70 mg for samples of IrCF and IrCF-10BTC, correspondingly. IrCF-hydrothermal sample was prepared by heating the precursor of IrCF in a baking oven at 80 ℃ for 12 h instead of microwave synthesis. All the samples were dried in a vacuum oven at 80 ℃.

Characterizations. The crystal structure was analyzed by X-ray diffraction (XRD, D8 ADVANCE, BRUKER) equipped with the Cu k radiation source, operating at voltage of

40 kV and current density of 40 mA. Fourier Transform - Infrared Spectrometer (FT-IR, Nicolet 7000-C) was operated to probe the function group in materials. The morphology was observed by the scanning electron microscopy (SEM, Hitachi S-4800) and aberration-corrected scanning transmission electron microscopy (STEM, Thermo Fisher Themis Z microscope) with accelerating voltage of 300 kV. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer thermogravimetric analyzer with air atmosphere. Element analysis (EA) was tested on the equipment of vario EL cube (Elementar, Germany). X-ray absorption fine structure (XAFS) spectra were collected at the BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF), China. For iridium element, the L3-edge (11215 eV) was selected as absorption edge for measurement, in which Ir foil and commercial IrO_2 were as reference samples of metallic and oxidation states.

Electrochemical measurements. Three-electrode system and proton exchange membrane (PEM) electrolyzer device were used to estimate materials' performance of the acidic oxygen evolution catalysis. In three electrode system, electrolyte was 0.1 M $HClO_4$ solution. The catalysts were loaded onto glass carbon (diameter 3 mm) to form a working electrode. Catalysts ink contained 5 mg samples, 25 μL Nafion (5 vol.%), and 475 μL ethanol, which was prepared by ultrasonic. 4 μL ink was drop-coated onto glass carbon electrode, drying naturally under ambient conditions. A Pt mesh with size of 1 cm × 1 cm and Ag/AgCl (packing with 3.5 M KCl solution) were used as the counter electrode and reference electrode, respectively. Measurements were operated on an electrochemical workstation of CHI 660e. Linear sweep voltammetry (LSV) was performed with a scanning rate of 5 mV s^{-1} to determine the overpotential of water oxidation reaction. Electrochemical impedance spectroscopy (EIS) was performed with frequency range from 0.01 Hz to 10^5 Hz.

PEMWE assembly and test. For PEMWE device test, membrane electrode assemblies (MEAs) were fabricated with Pt/C (40 wt.%) cathodic materials and target anodic samples by hot-press method. Pt/C materials were air-sprayed onto Nafion 115 membrane with a loading of about 1 mg cm^{-2} before hot-pressing. The anodic catalyst samples were air-sprayed onto PTEF film with about 1.4 mg cm^{-2} loading mass, and transferred onto proton exchange membrane in the pressing procedure, leading to a three-layer MEA. Two porous transport layer (PTL) was covered on the catalyst layers of MEAs, and a five-layer MEAs were formed after clamping between the two Ti plate current collectors equipped with the serpentine flow channel. Pure water was heated to 80 °C to feed anodic reagent by a thermostat water bath and a peristaltic pump. The polarization curves were collected from 0.1 A cm^{-2} to 1.5 A cm^{-2}. The stability of the PEM electrolyzers were evaluated by measuring chronopotentiometry at 1.0 A cm^{-2}.

DFT calculation method. All the spin-polarized DFT computations were performed by using the Vienna Ab initio simulation package (VASP)[S1] and the ion cores represented by the projector augmented wave (PAW) potentials. The generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) functionalwas used in this work.[S2] A cutoff energy of 450 eV for the plane-wave basis set were adopted. The convergence threshold for the structure relaxation was set to be 0.05 eV*Å^{-1} in force and 10^{-5} eV in energy, respectively. A vacuum space exceeding 15 Å was employed. The 2 × 2 × 1 Monkhorst–Pack k-point mesh was performed for all the calculation models. The van der Waals (vdW) interactions were taken into consideration using method of Grimme (DFT-D3).[S3]

The adsorption energy (Eads) can be calculated using the following equation:

$$\Delta E_{ads} = E_{ads/slab} - E_{ads} - E_{slab}$$

where $E_{ads/slab}$, E_{ads} and E_{slab} are the total energies for adsorbed species on slab, adsorbed species and isolated slab, respectively.

The free energy of a proton/electron pair $(H^+ + e^-)$ is equal to half of the gaseous hydrogen $(1/2H_2)$ at an equilibrium potential for each process, namely the free energy variations for each process were calculated based on computational hydrogen electrode (CHE) model.
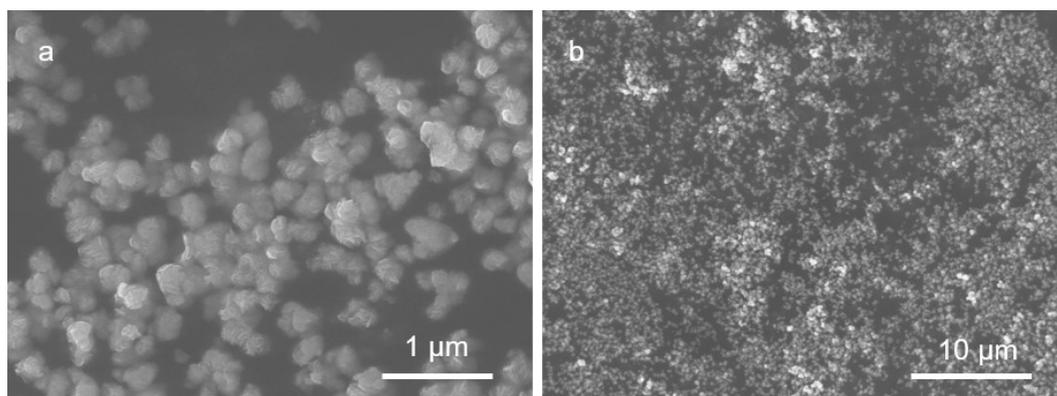
Fig. S1. (a) and (b) SEM images of IrCF-BTC samples at different magnifications.
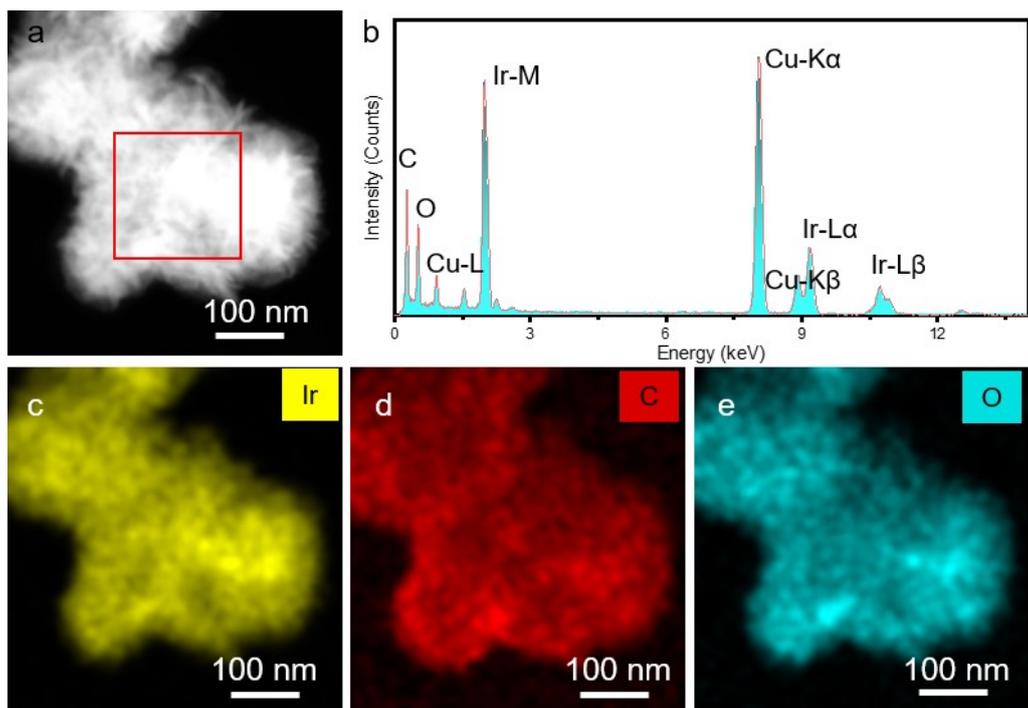
Fig. S2. (a) HAADF-STEM image of IrCF-BTC sample for energy dispersive spectroscopy analysis. (b) EDS spectrum of IrCF-BTC for the selected area in (a). (c-e) Element maps of Ir, C, and O based on the surface scanning results, revealing the uniform distribution of elements in the sample.
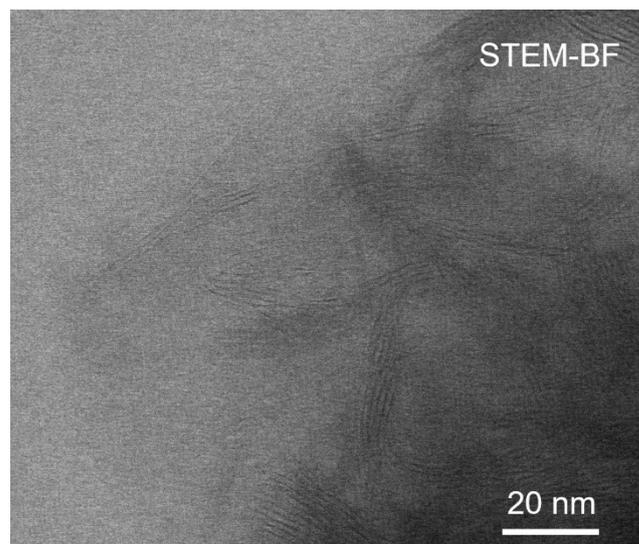
Fig. S3. Bright field (BF)-STEM image of IrCF-BTC sample, in which ultrathin stacked

flakes could be observed.
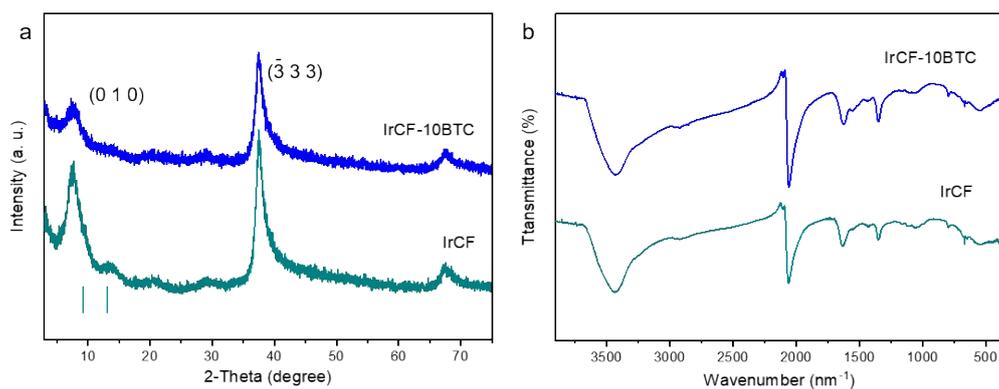
Fig. S4. (a) XRD patterns and (b) FTIR spectra of IrCF and IrCF-10BTC samples. Similar

crystal structure could be demonstrated for samples with and without BTC regulators.
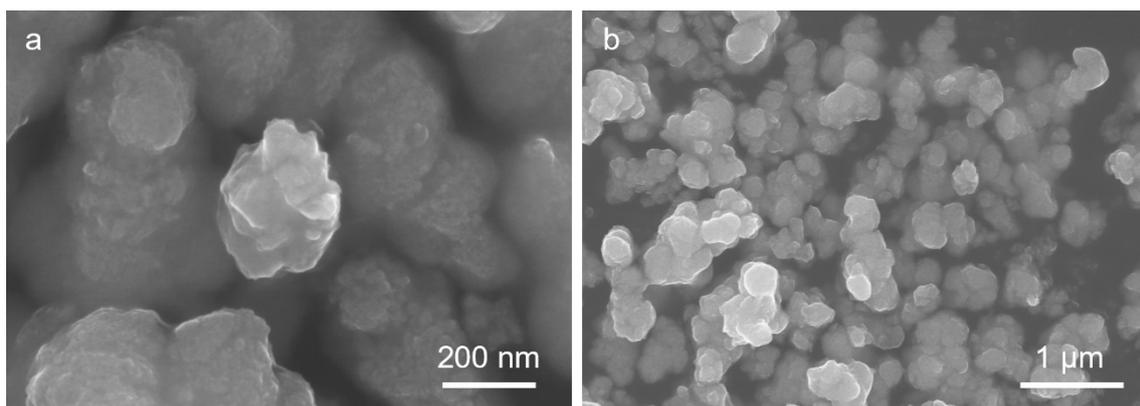
Fig. S5. (a, b) SEM images of IrCF-hydrothermal sample with the nanoparticles structure.
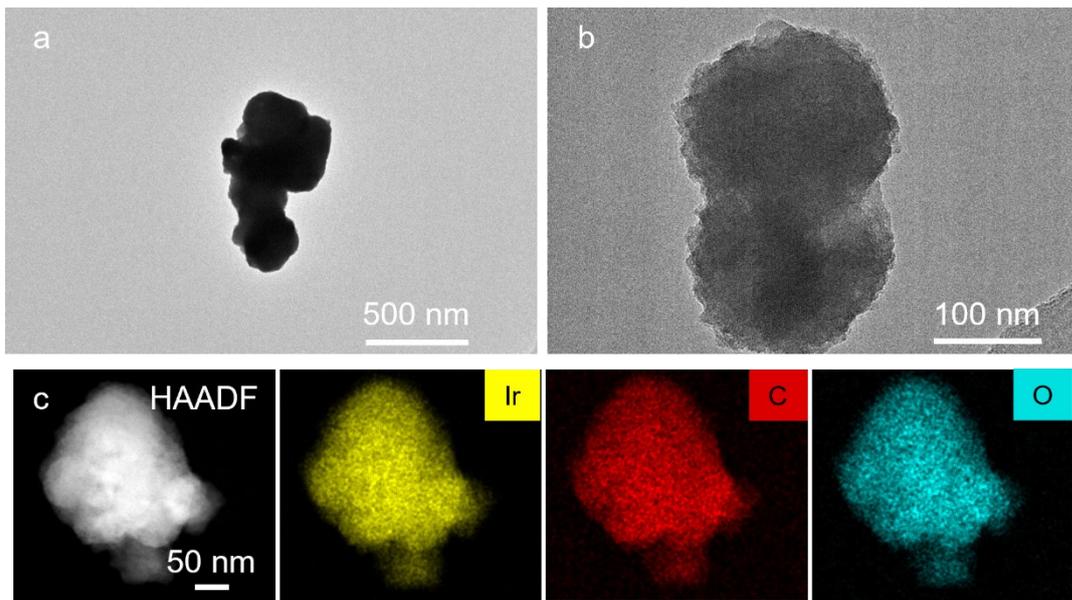
Fig. S6. TEM characterizations of IrCF-hydrothermal sample. (a) Low magnification image. (b) High magnification image. (c) Element mapping images of Ir, C, and O in IrCF-hydrothermal.
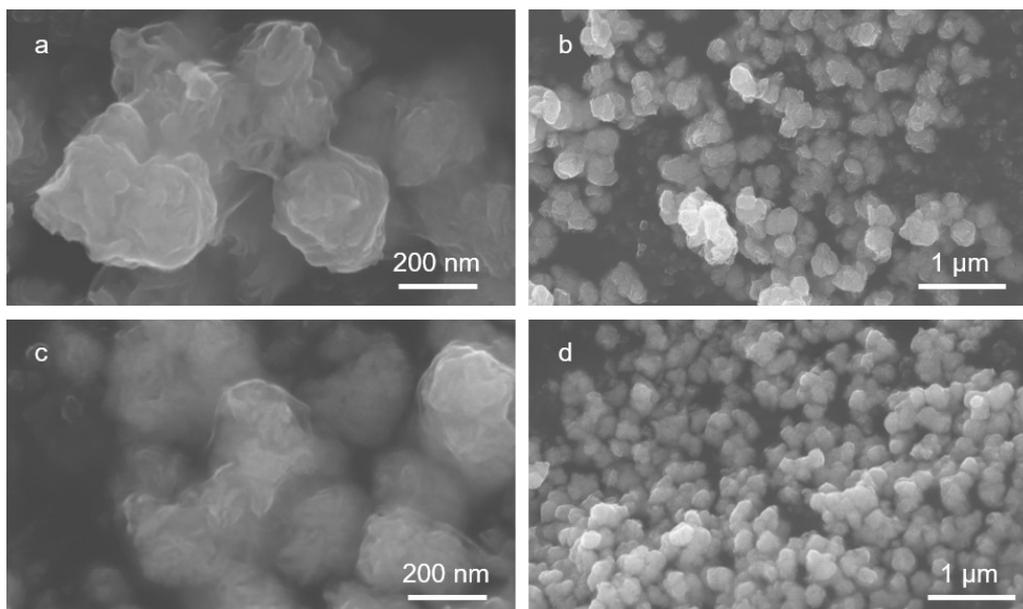
Fig. S7. (a, b) SEM images of IrCF sample with absence of BTC ligands in synthesis. (c, d) SEM images of IrCF-10BTC with more addiction of BTC regulators.
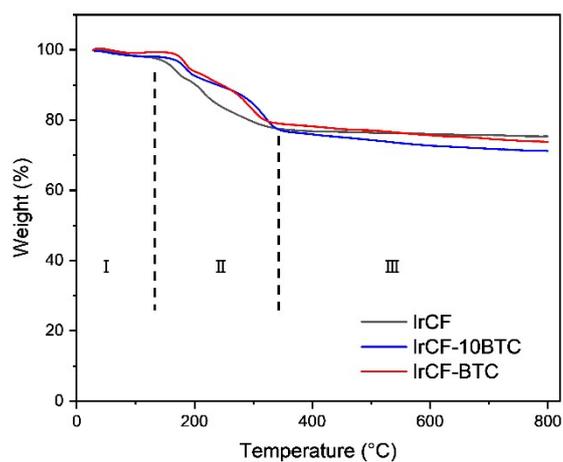
Fig. S8. TGA curves of IrCF, IrCF-BTC, and IrCF-10BTC samples under air atmosphere.

Table S1. Component test result of the samples based on element analysis equipment.

Sample\Element	H [wt.%]	C [wt.%]	O [wt.%]
IrCF	0.746	9.980	14.375
IrCF-BTC	0.747	9.960	13.943
IrCF-10BTC	0.601	8.570	14.229
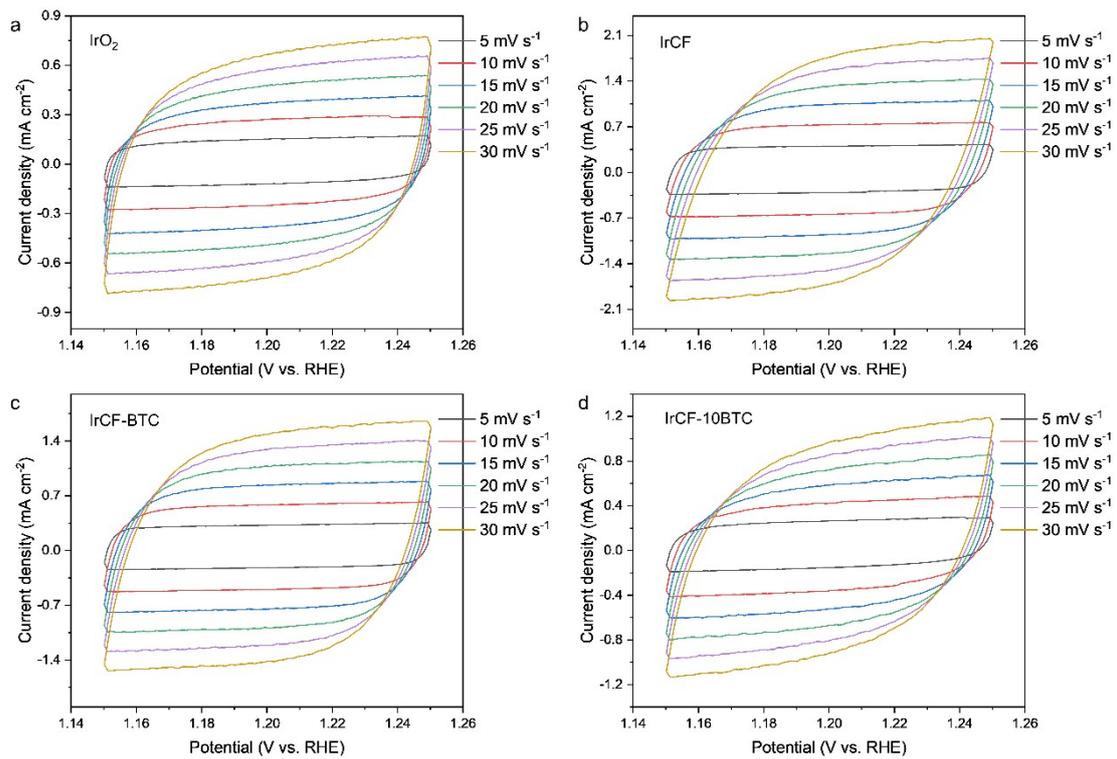
Fig. S9. Cyclic voltammetry curves of commercial IrO_2, as-prepared IrCF, IrCF-BTC, and IrCF-10BTC samples at the varied scan rates.
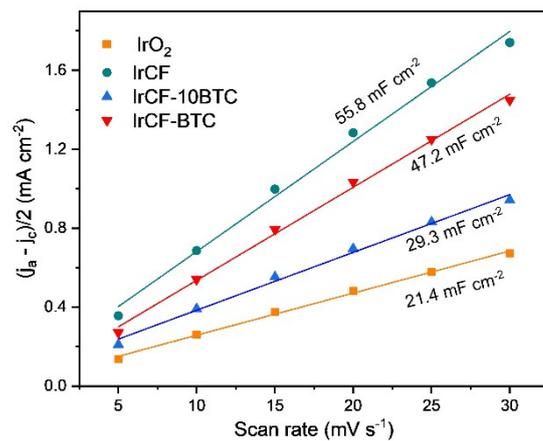
Fig. S10. Electric double-layer capacitances obtained by fitting the non-faradaic current and scan rates from the CV results.
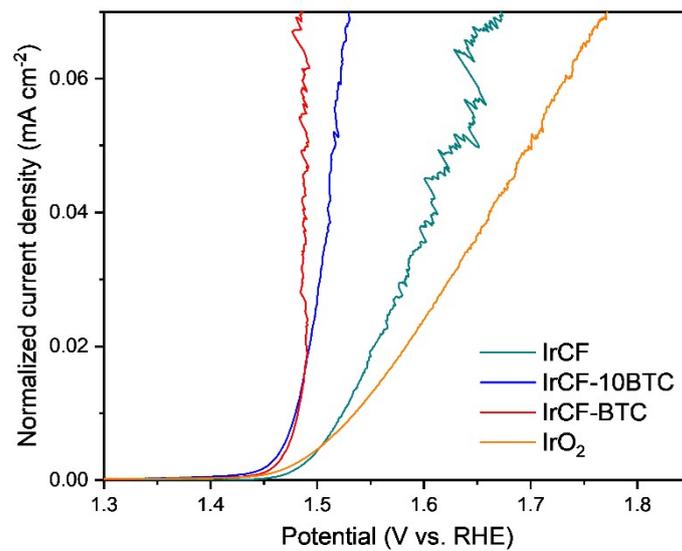
Fig. S11. Normalized LSV curves by the calculated ECSA based on the IrO_2.
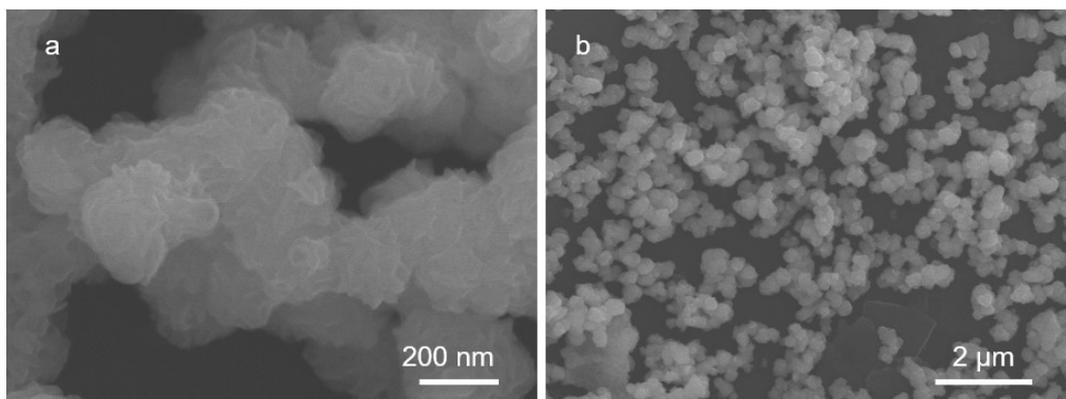
Fig. S12. (a, b) SEM images of IrCF-BTC samples after long term electrolysis at a current density of 10 mA cm^{-2} in 0.1 M HClO$_4$ solution.
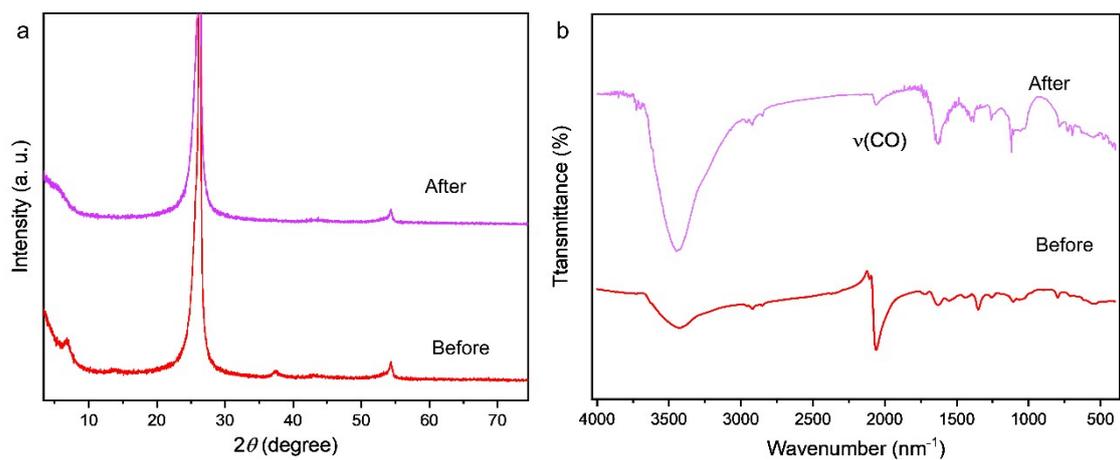
Fig. S13. (a) XRD patterns and (b) FTIR spectra of the IrCF-BTC materials before and after electrolysis in 0.1 M HClO₄ solution.
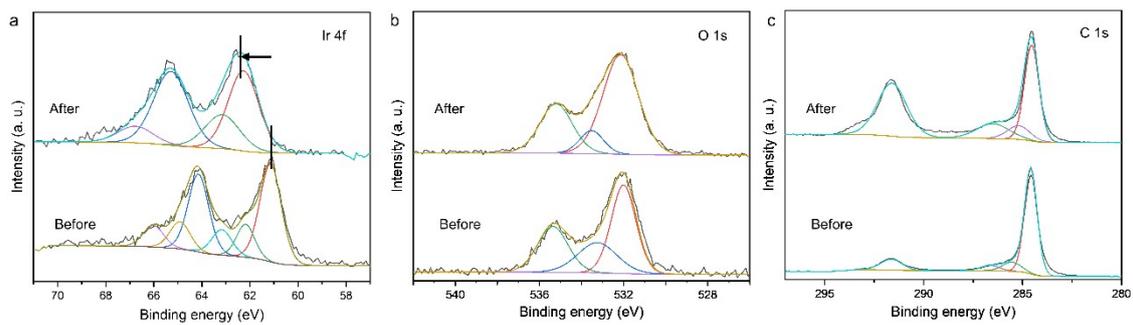
Fig. S14. X-ray photoelectron spectroscopy characterization of the IrCF-BTC sample before and after electrolysis. (a) Ir 4f, (b) O1s, and (c) C1s high-resolution spectra.
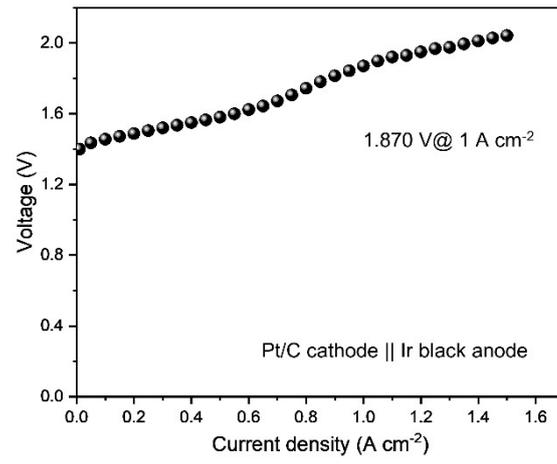
Fig. S15. PEM test using Ir black as anode and Pt/C cathode materials.
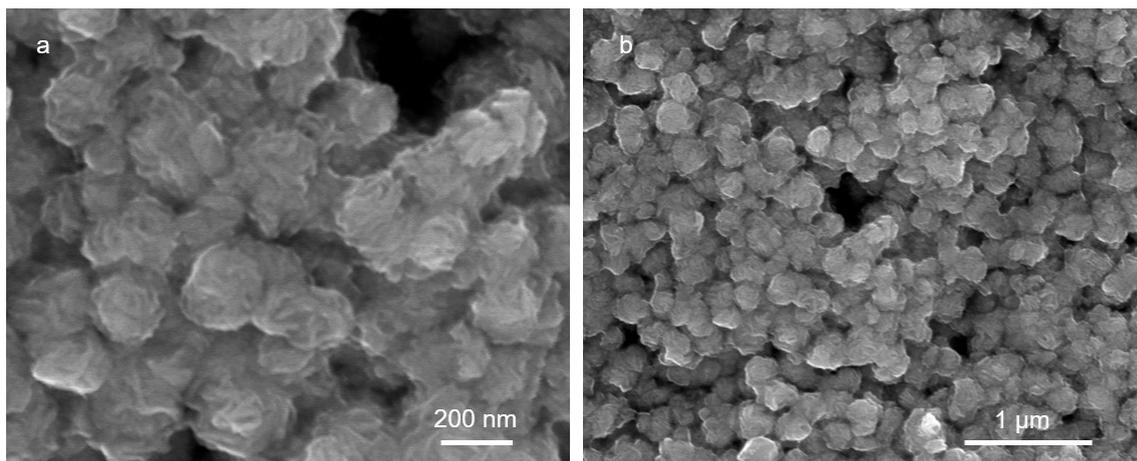
Fig. S16. (a, b) SEM images of IrCF-BTC loaded on the MEAs, after testing for more than 100 hours in the PEMWE device with operating current density of 1.0 A cm^{-2} under 80 °C.

Supporting References:

S1 G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, 59, 1758-1775.

S2 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.

S3 G. Stefan, *J. Comput. Chem.,* 2006, 27, 1787-1799.