

## Supporting information

### Experimental section

#### Characterization

The phase structure was determined by X-ray diffractometer (BRUCKER D8 ADVANCE, CuK $\alpha$  radiation). The morphologies were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) on SU8020 and FEI Tecnai G2 F200X instruments. X-ray photoelectron spectroscopy (XPS) measurements were conducted on the Thermo ESCALAB 250Xi device, using a monochromatic Al K $\alpha$  (h $\nu$ =1486.6 eV) X-ray source and contaminated carbon C1s=284.8 eV for charge correction. The atomic force microscope (AFM) was carried out on Bruke's MULTIMODE 8 device. The scanning mode is Scanasyst, the scanning area is 200 nm, and the scanning frequency is 1 Hz. Inductively coupled plasma atomic optical emission spectroscopy (ICP-OES) was obtained on agilent ICPOES730. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed using an aberration corrected electron microscope (JEM ARM 200F). X-ray absorption spectra (XAS) of the sample were collected on spring-814b2, including X-ray absorption near-side structures (XANES) and extended X-ray absorption fine structures (EXAFS). The storage ring was working at the energy of 8.0 GeV with average electron current of 99.5 mA. Raman spectra were recorded using a Renishaw inVia microscope with a 633 nm laser. Radio frequency (RF) discharge was produced by a RF Power Generator (KVMEN) with a RF matcher (K-mate) at a frequency of 13.56 MHz.

#### Electrochemical measurements

The catalytic activity was tested in 1.0M KOH solution using CHI660E electrochemical workstation in a standard three-electrode system. A glass carbon electrode (GCE, diameter 5 mm) was used as the working electrode, a platinum plate as the counter electrode, and Hg/HgO as the reference electrode. Before

measurement, the glassy carbon electrode was polished and cleaned with 0.5  $\mu\text{m}$ , 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  powder, respectively. For preparation of catalyst ink, 4 mg catalyst and 1.5 mg carbon source (CABOT BP2000) were ultrasonically dispersed in 20  $\mu\text{L}$  Nafion(5 wt%) mixed with 480  $\mu\text{L}$  ethanol to form a uniform suspension. Then, 15  $\mu\text{L}$  of suspended liquid drops were placed on the polished GC electrode surface and dried to obtain a catalytic load of 0.611  $\text{mgcatcm}^{-2}$ .

All measured potentials are converted according to RHE calibration conversion equation:

$$E (\text{V vs. RHE}) = V \text{ vs. (Hg / HgO)} + 0.098 + 0.059 \cdot \text{pH}$$

To ensure complete catalyst stability, cyclic voltammetry curves (CV) were cycled 20 times before data acquisition at a scan rate of 100  $\text{mVs}^{-1}$ . Linear sweep voltammetry (LSV) of OER was measured at a sweep rate of 5  $\text{mVs}^{-1}$ . Electrochemical impedance spectroscopy (EIS) measurements are made by applying an AC voltage of 5 mV amplitude over a frequency range of 0.01 to 100 kHz. Cyclic voltammetry (cv) curves were tested at sweep rates of 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100  $\text{mVs}^{-1}$  in the range of 1.15-1.25 V to calculate electrochemical surface area (ECSA).

The turnover frequency (TOF) is calculated from the equation below:

$$TOF = \frac{I}{4Fn}$$

Where I is the current (A) during linear sweep measurement, F is the Faraday constant (96485.3  $\text{Cmol}^{-1}$ ), and n is the mole number of active metals on the electrode. The factor 1/4 is based on the consideration that four electrons are needed to form an oxygen molecule. The mole number of active metals on the electrode(n) is calculated from the equation below:

$$n = \frac{m}{M} = \frac{0.004 \text{ g} \times \frac{15}{500} \times 0.66\%}{192.217 \text{ g/mol}} = 4.12034 \times 10^{-9} \text{ mol}$$

Where m is the mass of Ir loaded on the GCE, M is the molar mass of Ir (192.217  $\text{g/mol}$ ). The content of Ir in Ir-Cu /C was determined to be 0.66 wt% by ICP-OES.

## **Materials**

All chemicals (1-4 Terephthalic acid, DMF, CH<sub>3</sub>CN, CuNO<sub>3</sub>·4H<sub>2</sub>O, Ethylene glycol, ethanol, H<sub>2</sub>IrCl<sub>6</sub>·6H<sub>2</sub>O, KOH, Nafion) are of analytical grade and were used as received without further purification. High purity deionized water was used in the whole experiment.

## **Preparation of Cu-BDC**

Cu-BDC was prepared by a three-layer solution method. First, dissolve 150 mg of 1-4 terephthalic acid in a mixture of 10 mL DMF and 5 mL CH<sub>3</sub>CN and pour at the bottom of the test tube. Subsequently, a mixture of 5 mL DMF and 5 mL CH<sub>3</sub>CN is carefully added as an intermediate buffer layer to prevent premature mixing of the top and bottom solutions. Then 150 mg CuNO<sub>3</sub>·4H<sub>2</sub>O was dissolved in a mixture of 5 mL DMF and 10 mL CH<sub>3</sub>CN, and finally the metal precursor solution formed in this mixture was added to the tube as the top layer. Cu ions coordinate with organic ligands in the intermediate buffer layer by diffusion. The reaction was carried out at 40°C for 48 h. At the end of the reaction, the formation of blue precipitates was observed at the bottom of the tube. The precipitates were collected by centrifugation at 8000 RPM, washed three times with DMF, and finally dried at 80°C.

## **Preparation of Ir/Cu-BDC**

The prepared 50 mg Cu-BDC was added to a 200 mL beaker and ultrasonic dispersed in 100 mL glycol for about 30 minutes. 400 μL of H<sub>2</sub>IrCl<sub>6</sub>·6H<sub>2</sub>O (10 mg/mL, dissolved in deionized water) was then added to the dispersion. After 20 min of ultrasound, the beaker was moved into a water bath at a constant temperature of 65°C for 5 h. The precipitate was centrifuged, washed with ethanol 3 times, and dried in an oven at 60°C. The final product Ir/Cu-BDC was obtained.

## **Preparation of Ir-Cu/C**

20 mg Ir/Cu-BDC powders were spread on a quartz boat and inserted into a plasma reactor. The RF-induced plasma came from a RF reactor with the water-cooled copper coil and the reaction chamber. The reactor was pumped down in Ar atmosphere (keep a flowing rate of 40

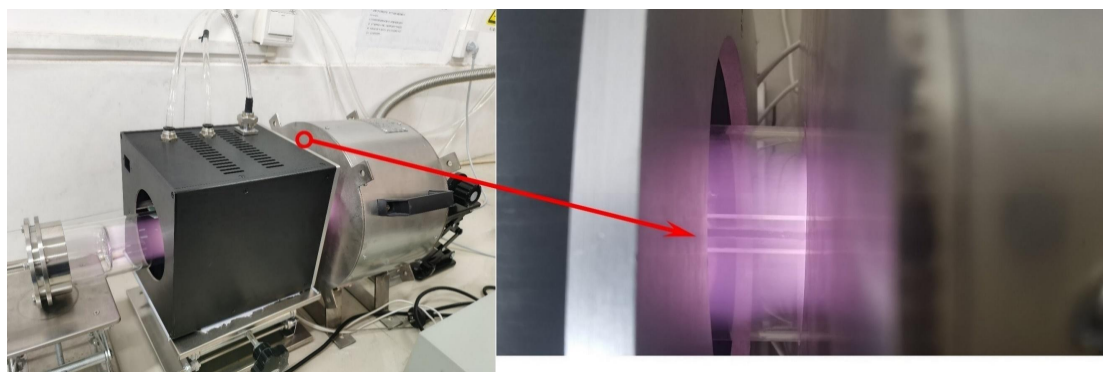
mL min<sup>-1</sup> ). The Ir/Cu-BDC nanosheets were treated by Ar plasma with 40 min at the power of 100 W and the black Ir-Cu/C powders were obtained.

### Computational Details

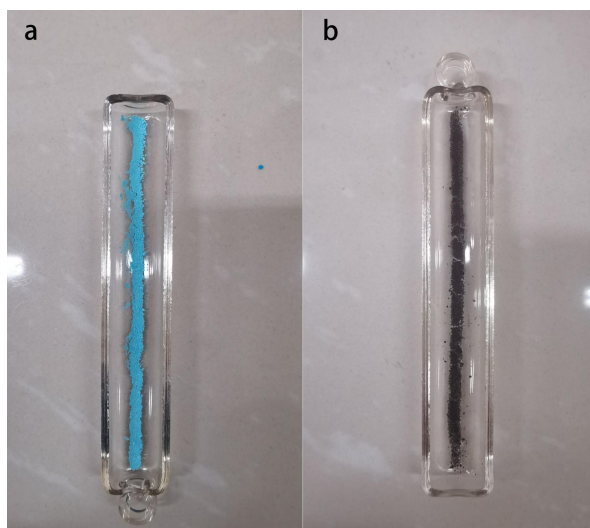
First-principles calculations were performed using the Vienna ab initio simulation package (VASP). The ion-electron wave function of the ground state is described by using the projection enhanced wave (PAW) method. The electron exchange correlation is expressed by Perdew-burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA). The cutoff energy of the plane wave base group is 400 eV. The iterative convergence of energy in the optimization process is 10<sup>-6</sup> eV.

Four layers of Cu (111) units are cut from the bulk phase Cu, and vacuum layers of 20 Å are taken along the z axis to minimize periodic interactions. Then, the Cu (111) unit is expanded into a 3×4 super unit and the top layer contains 12 Cu atoms. One of the top Cu atoms is replaced by an Ir atom, and the Ir-doped Cu surface model is constructed. In the optimization process of Cu (111) supercell, a 3×2×1 k-point meshes is used accordingly. The OH, O, and OOH atoms are then placed in different positions on the optimized surface.

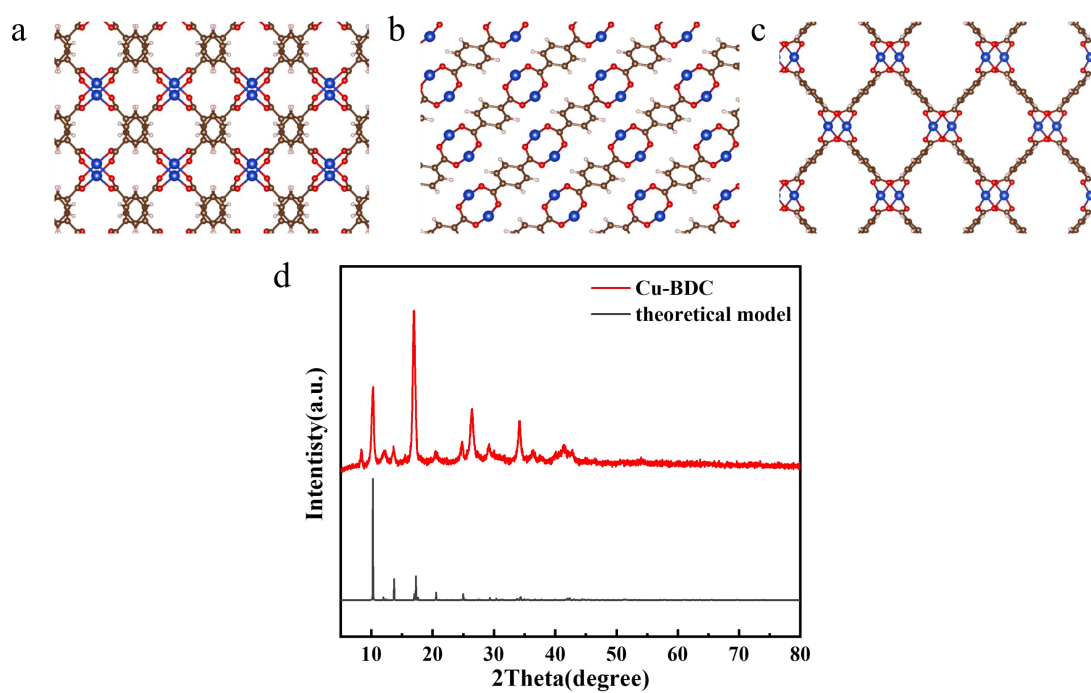
Gibbs free energy ( $\Delta G$ ) was selected as a standard catalytic activity, defined as  $\Delta G = \Delta E + \Delta ZPE - T\Delta S$ ,  $\Delta E$  is the adsorption energy,  $\Delta ZPE$  is the zero-point energy change of adsorbed atoms relative to free atoms, and  $\Delta S$  is the entropy difference between adsorbed atoms and free atoms at room temperature (298.15K).



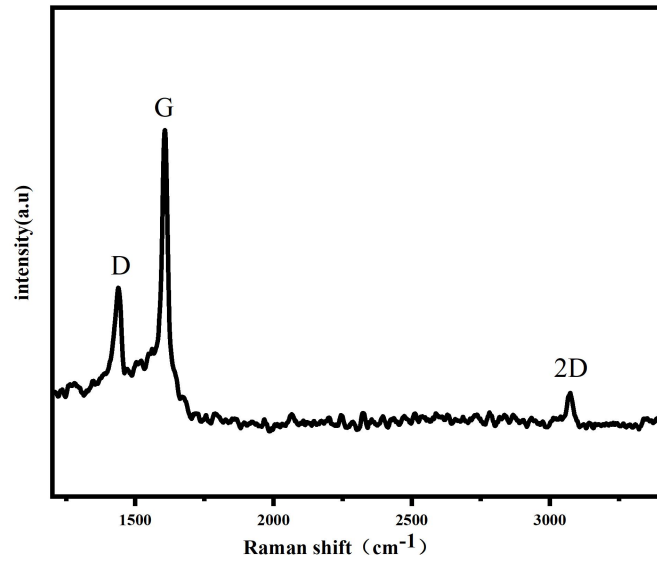
**Fig. S1** Ar gas luminescence during plasma carbonization process



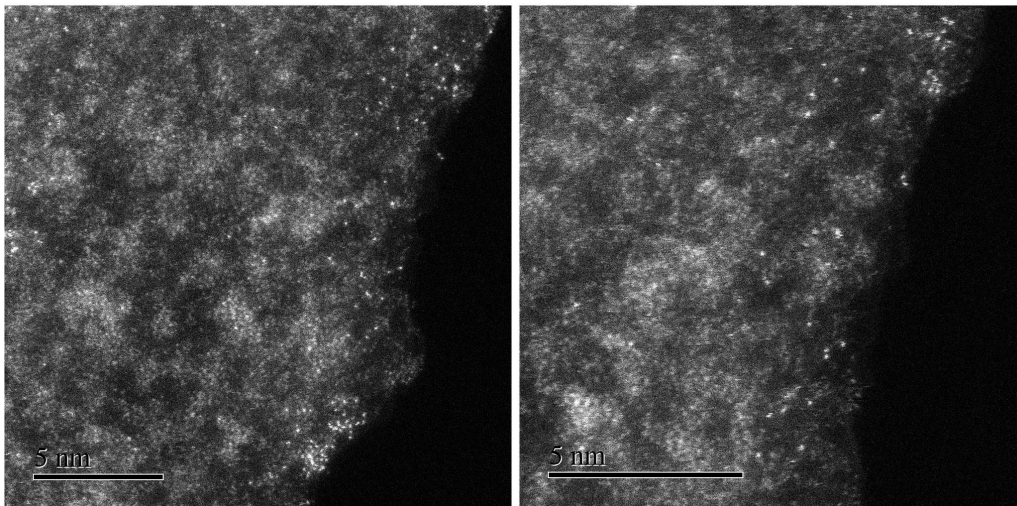
**Fig.S2** Comparison before and after plasma treatment: Ir/Cu-BDC(a); Ir-Cu/C(b)



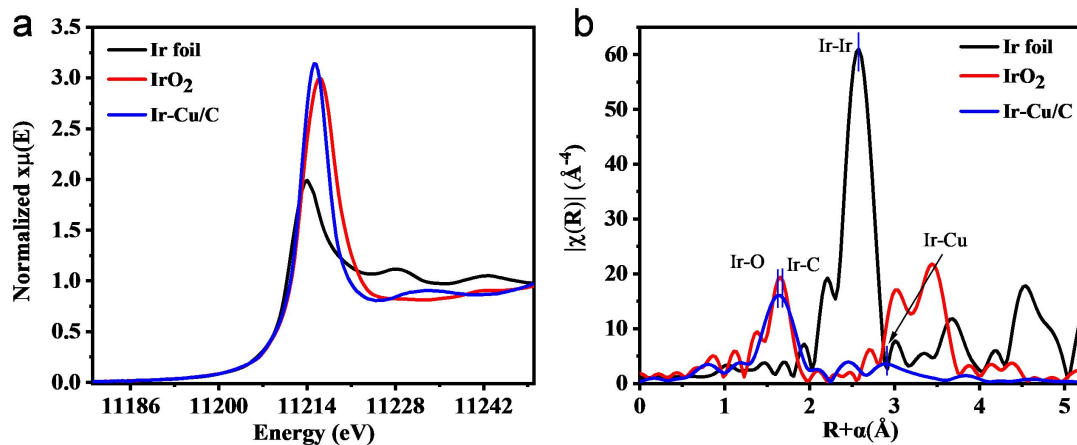
**Fig. S3** The atomic model of Cu-BDC: front view (a) side view (b) top view (c); The XRD results of Cu-BDC experiment are compared with the powder diffraction patterns calculated by atomic model



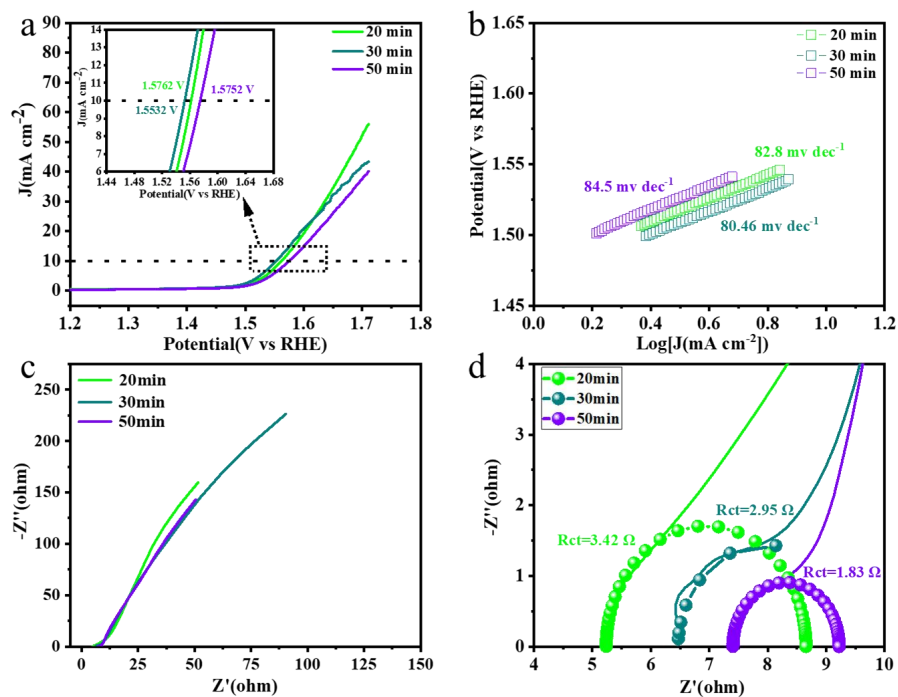
**Fig. S4** Raman spectra of Ir-Cu/C



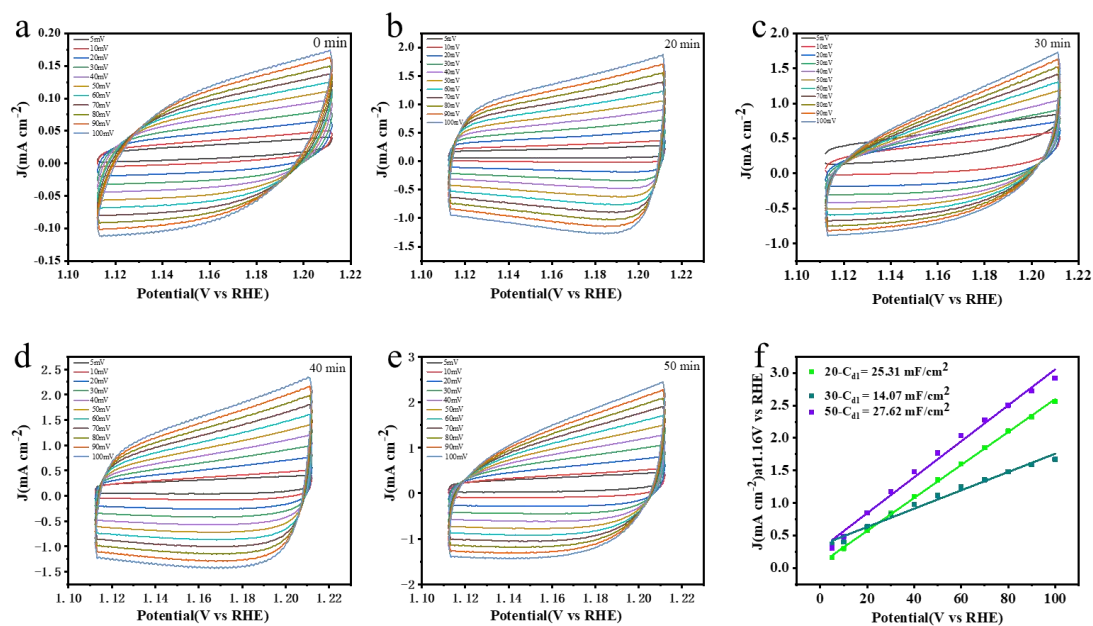
**Fig. S5** HAADF-STEM images of Ir-Cu/C



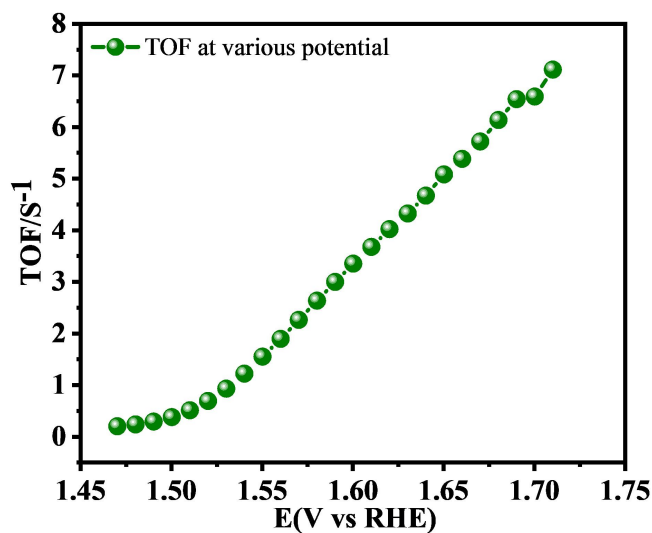
**Fig. S6** Ir L3-edge XANES profiles of Ir foil, IrO<sub>2</sub>, and Ir-Cu/C (a); Ir L3-edge EXAFS spectra in R space of Ir foil, IrO<sub>2</sub>, and Ir-Cu/C.



**Fig. S7** LSV curves (a); Tafel plots (b) and Nyquist plots (c,d) of Ir/Cu-BDC sample treated with Ar plasma for 20, 30, and 50 minutes



**Fig. S8** Cyclic voltammety curves of samples at different sweep rates in the range of 1.15-1.25 V(a-e); Double layer capacitance  $C_{dl}$  (f)



**Fig. S9** Plot of TOF as a function of potential for Ir-Cu/C

**Table S1** Atomic ratio in Ir-Cu/C based on XPS measurement

Atomic	Atomic ratio (%)
Ir	0.40
C	39.20
O	41.95
Cu	18.45