

# A neural-network-like catalyst structure for oxygen reduction reaction: carbon nanotubes bridged hollow PtCo alloy nanoparticles in MOF-like matrix for energy technologies

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## SUPPORTING INFORMATION

### Experimental Procedures

#### Synthesis of PVP-Pt<sup>1</sup>

2.5 nm PVP-stabilized Pt nano-particles (NPs) were prepared by refluxing a mixture of PVP (533 mg, Mw=30,000), methanol (180 ml), and aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> (6.0 mM, 20 ml) in a flask (500 ml) for 3 hours under air. Methanol was removed by rotary evaporator. The NPs in the remaining solution were precipitated by acetone and then collected by centrifugation at 6,000 rpm for 5 minutes. The sample was cleaned several times with methanol and acetone to remove excess free PVP. Finally the obtained Pt NPs were dispersed in methanol (90 ml) to give a Pt content of 0.26 mg/ml according to the amount of H<sub>2</sub>PtCl<sub>6</sub>.

#### Synthesis of Pt@ZIF-67

As our thought to simulate the neural network structure, the polyvinyl pyrrolidone (PVP) and dimethyl imidazole (20mM 100ml) capped Pt NPs (30ml) were used as center species, and connected them together by adding 5mM Co<sup>2+</sup> ions to form Pt@ZIF-67. And then kept at room temperature for 24 hours without stirring, during the formation of ZIF-67, the Pt NPs are uniformly inlaid inside the whole ZIF-67 crystals. The product was collected by centrifugation, washed several times with methanol, and vacuum dried overnight.

#### Synthesis of PtCo@CNTs-MOF, Co/CNTs-MOF and PtCo/C

The obtained Pt@ZIF-67 powders were put into quartz tube and then pyrolyzed under  $N_2+H_2$  (9:1) atmosphere with different procedure.

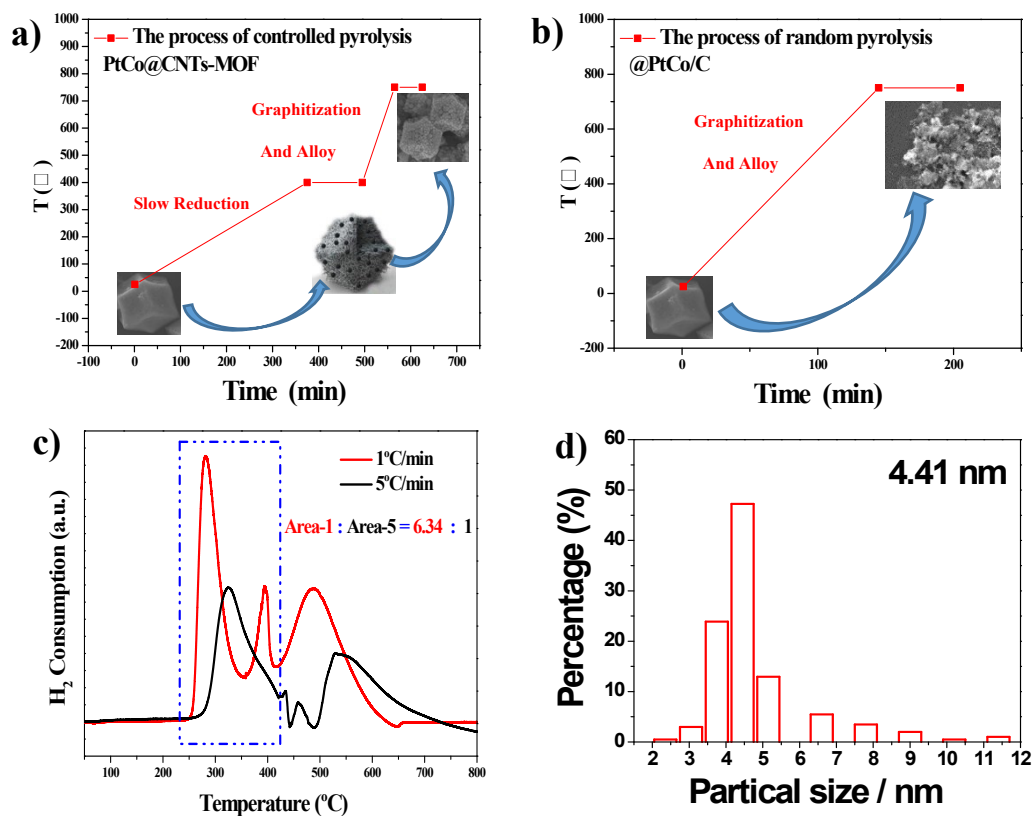


Figure S1. a) The process of controlled pyrolysis for Pt@ZIF-67, b) the process of random pyrolysis for Pt@ZIF-67, c) the  $H_2$ -TPR profiles of catalysts with different temperature rate, d) the particle size distribution map of PtCo@CNTs-MOF.

Figure S1a. shows the two process of controlled pyrolysis for Pt@ZIF-67, under the first controlled pyrolysis process with a relative low heating up rate ( $1\text{ }^\circ\text{C min}^{-1}$ ), the  $Co^{2+}$  species were firstly reduced by  $H_2$ , and then reduced Co NPs would catalyze the organic ligands to form carbon nanotubes; under the second controlled pyrolysis process with a relative high heating up rate ( $5\text{ }^\circ\text{C min}^{-1}$ ), the Co NPs would diffuse outward at high temperature, a part of them would form large particles, the other part would diffuse into the encapsulated Pt NPs to form PtCo alloy. At last, the polyhedral morphology could be preserved effectively consist of carbon nanotubes, Co large particles and PtCo alloy. After acid-leached ( $0.5M\ H_2SO_4$ ) at  $80^\circ\text{C}$  for 24h, the surplus Co NPs would be removed. Finally, the MOF-like neural network structure products consisting of the interconnected carbon nanotubes and hollow  $Pt_3Co$  NPs could be obtained (PtCo@CNTs-MOF). Similarly process, the Co/CNTs-MOF composites was prepared by one-pot thermal annealing by using ZIF-67 as precursors.

Figure S1b. shows the process of random pyrolysis for Pt@ZIF-67, the  $Co^{2+}$  species would be firstly reduced by organic ligands of ZIF-67 during the random pyrolysis at a high heating up rate of  $5\text{ }^\circ\text{C min}^{-1}$ , leading to an uncontrollable collapse in structure and morphology, the part of reduced Co NPs also would aggregate to form large particles, the other would diffuse into the encapsulated Pt NPs to form PtCo alloy. After acid-leached ( $0.5M\ H_2SO_4$ ) at  $80^\circ\text{C}$  for 24h, the surplus Co NPs would be removed, and the final products consisting of the  $Pt_3Co$  NPs and ruleless carbon material could be obtained (PtCo/C).

### Physical Characterization

Xray diffraction (XRD) patterns were recorded on a XRD6000 using Cu Kr radiation ( $\lambda=1.5418\text{ \AA}$ ) at a step rate of  $2^\circ\text{ s}^{-1}$ . Low-resolution transmission electron microscopy (TEM) was carried out on a FEI Tecnai G220S-TWIN instrument operating at 120 kV. High-resolution transmission electron microscopy (HRTEM) was carried out on a Zeiss LIBRA 200 FETEM instrument operating at 200 kV. XPS was acquired using a Kratos XSAM800 spectrometer

equipped with monochromatic Al X-ray source (Al KR, 1.4866 keV), the vacuum in the analysis chamber was maintained at  $10^{-7}$  Pa, and the binding energy was calibrated by using 284.5 eV as the C 1s peak energy.

### Electrochemical measurement

The catalysts were evaluated electrochemically in three-electrode one-compartment cell, in which 0.1M HClO<sub>4</sub> was used as the electrolyte, a saturated Ag/AgCl electrode and a carbon rod were used as reference and counter electrodes, respectively.

The electrocatalytic activity of catalysts for oxygen reduction was determined by cyclic voltammetry (CV) at a sweep rate of 50mV s<sup>-1</sup> followed by liner sweep voltammetry (LSV) at a sweep rate of 10mVs<sup>-1</sup> with a rotational disk electrode (RDE). The measurements were performed at 25 °C after purging O<sub>2</sub> or N<sub>2</sub> for 30 min. RDE measurements were conducted with a varying rotating speed of 1600 rpm. A glassy carbon disk of 5 mm diameter coated with a film of catalyst was used as working electrode. To prepare the working electrode, 2mg of PtCo@N-MCF catalyst and a drop of 0.1wt% Nafion solution were ultrasonically dispersed in 800μL of a water-ethanol (1:1 v/v) mixed solvent to form a homogeneous ink. As a comparison, 2 mg of JM-Pt/C was ultrasonically dispersed in 800μL of EtOH with a drop of a 0.1wt % Nafion solution. Then a certain amount of the catalyst ink were loaded onto a RDE, respectively. Finally, the RDE was dried at air temperature. All potentials in this study are given relative to the potential of the reversible hydrogen electrode (RHE).

The electrical double layer capacitance was measured in 0.1M HClO<sub>4</sub> aqueous solution, the scanning potential range of 0.36-0.46 V versus Reversible hydrogen electrode (RHE) reference at a step of different scan rate (20, 40, 60, 80, 100 mV/s), the chosed potential range should ensure only non-faradic activity occurs. On the basis of the surface area from BET and the weight of catalyst on the electrode, we could obtain the real catalyst surface area and current density on the electrode. The value of imposed current density is divided by the slope of the lineal chronopotentiogram plot, taking the average value between charge and discharge process at 0.41 V. Finally, the slope is the electrical double layer capacitance.

The chronopotentiometry curves were recorded in O<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> solutions at a different constant current (2 mA cm<sup>-2</sup>, 10 mA cm<sup>-2</sup>, 30 mA cm<sup>-2</sup>, 50 mA cm<sup>-2</sup>), particularly using a self-made working electrode. Firstly, a viscous suspension consisting of catalyst, nafion solution, and ethanol (with mass ratio of nafion to catalyst = 0.35:1) was pipetted onto the carbon paper to reach Pt loading of 0.025 mg cm<sup>-2</sup> (absolute amount of Pt = 0.025 mg; effective area = 1.0 cm<sup>2</sup>). The catalyst was naturally dried at room temperature and loaded into the ring groove of the working electrode. Specially, the side loaded with catalyst faces outside, allowing that O<sub>2</sub> molecules enter into the catalyst layer through carbon paper. When testing, the head of the "rattle-drum" was sealed with Vaseline and totally soaked in the HClO<sub>4</sub> solution as working electrode. And the three-electrode systems also include a carbon rob counter electrode and an Ag/AgCl (in 3.0 M KCl) reference electrode. Flowing rate of O<sub>2</sub> is maintained at 10 mL/min during the test.

### Koutecky-Levich equation<sup>2</sup>

The slopes of the best linear fit lines were used to calculate the transferred electron number (n) per oxygen molecule in the ORR process on the basis of the Koutecky–Levich equations:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.2nFC_0 (D_0)^{2/3} \nu^{1/6} \quad (2)$$

Where  $J$  is the measured current density,  $J_k$  and  $J_L$  are the kinetic- and diffusion-limiting current densities,  $\omega$  is the electrode rotating speed in rpm,  $n$  is the electron transfer number in oxygen reduction,  $F$  is the Faraday constant ( $F=96485\text{C mol}^{-1}$ ),  $C_0$  is the bulk concentration of O<sub>2</sub> ( $C_0=1.13 \times 10^{-6} \text{ mol cm}^{-3}$ ),  $D_0$  is the diffusion coefficient of O<sub>2</sub> ( $1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),  $\nu$  is the kinematic viscosity of the electrolyte ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ ), The constant 0.2 is adopted when the rotating speed is in rpm

The specific kinetic current densities ( $J_k$ ) associated with the intrinsic activity of the catalysts can be obtained by the following relation:

$$J_k = \frac{J_d * J}{J_d - J}$$

Where  $J$  is the measured current density,  $J_k$  is the kinetic current density;  $J_d$  is the diffusion-limited current density, respectively.

### Single Fuel cell testing.

The PtCo@CNTs-MOF catalyst “ink” was prepared by ultrasonically mixing the catalyst powder with 5wt% Nafion solution (DuPont) and anhydrous alcohol for approximately 15 min. The Nafion content in the dry catalyst layer was 33wt%. The gas diffusion layer heated at 80 °C for 3 hours under vacuum or not. The weight difference was measured and used to calculate the loading of the catalysts. The Pt loading was 0.06 mg cm<sup>-2</sup> when the PtCo@CNTs-MOF catalyst used as cathode, respectively. After spray deposition process, let the gas-diffusion electrode dry under vacuum condition or ordinary pressure. A suspension consisting of 60wt% PtRu/C catalysts (Johnson-Matthey In. UK), 5 wt% Nafion solution (DuPont), and isopropyl alcohol was used to prepare the opposite catalyst layer. The Pt loading was controlled at 0.04 mg cm<sup>-2</sup> or 0.06 mg cm<sup>-2</sup> on the anodic side. The MEA was prepared by hot-pressing the cathode, Nafion 212 membrane (DuPont, 50 μm), and the anode at 135°C and 5 MPa for 150s. The Nafion HP membrane (DuPont) was pretreated with 3 vol. % H<sub>2</sub>O<sub>2</sub> and 0.5M H<sub>2</sub>SO<sub>4</sub> for 1h to remove impurities. The membrane was then washed several times with hot ultrapure water. Pure hydrogen and oxygen/air were supplied to the anode and cathode at a flow rate of 150 and 200mL min<sup>-1</sup>, respectively.

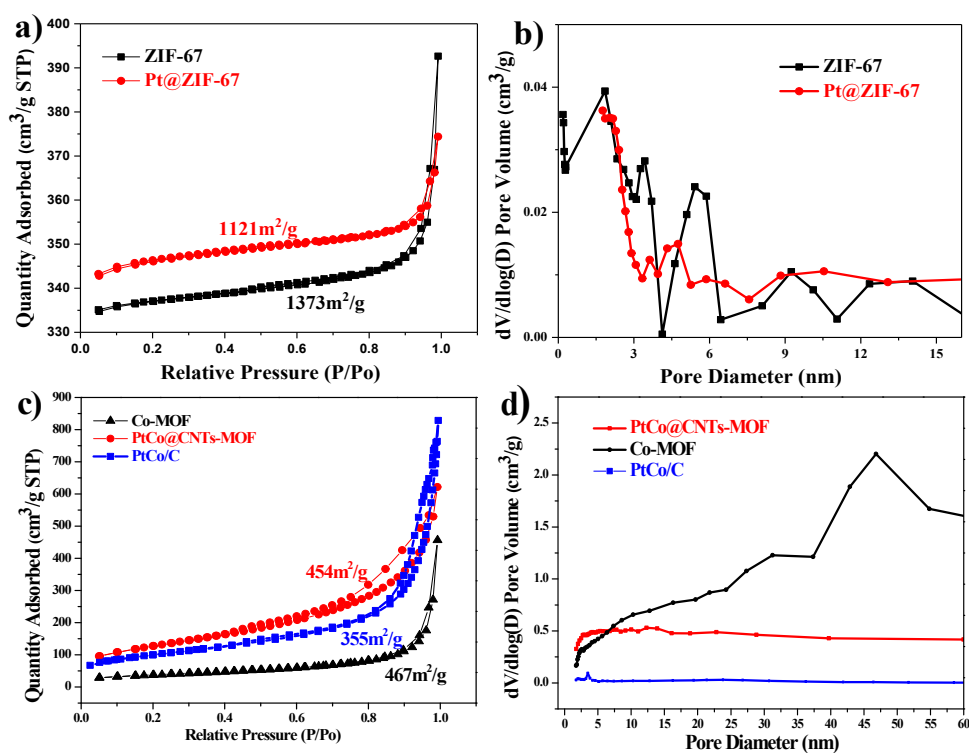


Fig S2. Nitrogen adsorption and desorption isotherms of a) ZIF-67, Pt@ZIF-67 and c) PtCo@CNTs-MOF, Co-MOF, b) and d) the pore size distribution of ZIF-67, Pt@ZIF-67 PtCo@CNTs-MOF and Co-MOF composites, respectively.

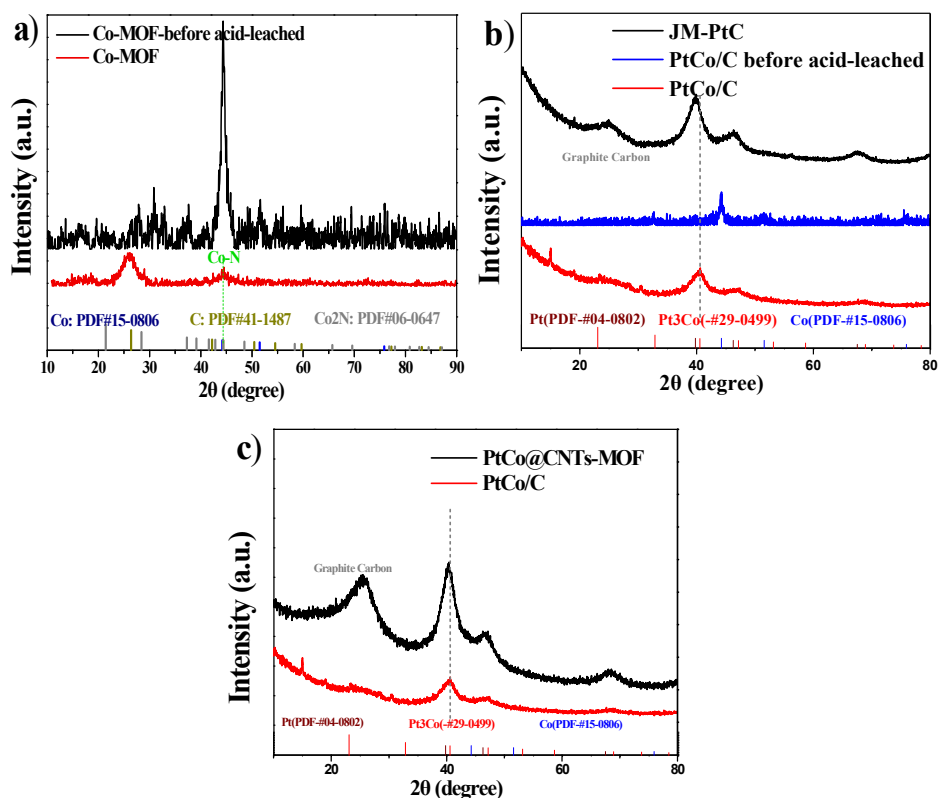


Fig S3. The XRD of Co-MOF (a) and PtCo/C in random pyrolysis (b) before and after acid-leaching treatment, (c)

XRD pattern for the PtCo@CNTs-MOF catalyst in comparison to that of PtCo/C. The XRD patterns show a relatively strong diffraction peak around 25° for the PtCo@CNTs-MOF catalyst obtained at the low heating rate pyrolysis (1 °C min<sup>-1</sup>) but a weak peak for the PtCo/C, indicating a much higher graphitization degree for PtCo@CNTs-MOF than that for PtCo/C. Besides, the diffraction peaks at 40° and 47° attributing to intermetallic Pt<sub>3</sub>Co (111) and (200) were also more sharpened for PtCo@CNTs-MOF than those for PtCo/C, demonstrating a relatively higher crystallization degree obtained at the low heating rate in PtCo@CNTs-MOF.

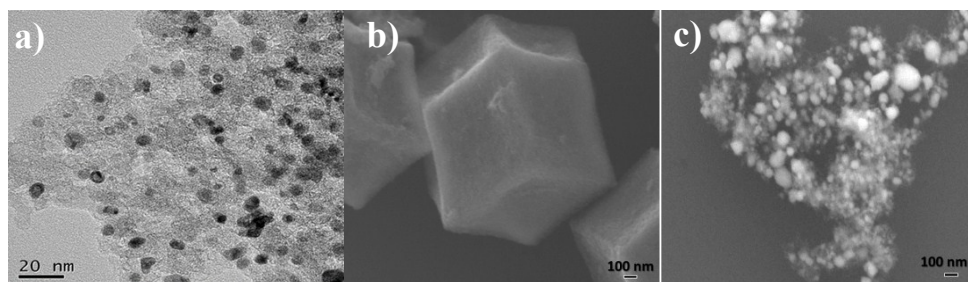


Fig S4. a) The TEM of PtCo/C after acid-leaching treatment, b) the SEM of PtCo@CNTs-MOF, c) the SEM of PtCo/C. According to the SEM and TEM images, the PtCo@CNTs-MOF catalyst exhibited a porous MOF-like structure, which consisted of interconnected CNTs with a diameter of 8 nm and hollow Pt<sub>3</sub>Co NPs with a wall thickness of 1.5 nm (figure 2f-i). However, for PtCo/C, the original polyhedral MOF morphology was completely destroyed during the pyrolysis at heating rate of 5 °C min<sup>-1</sup>; and the BET surface area decreased from 454 m<sup>2</sup> g<sup>-1</sup> for PtCo@CNTs-MOF to 355 m<sup>2</sup> g<sup>-1</sup> for PtCo/C, when the heat rate increased from 1 to 5 °C min<sup>-1</sup>. The collapsed

structure and decreased BET surface area in PtCo/C may bring relatively higher resistance for mass transfer during the catalysis.

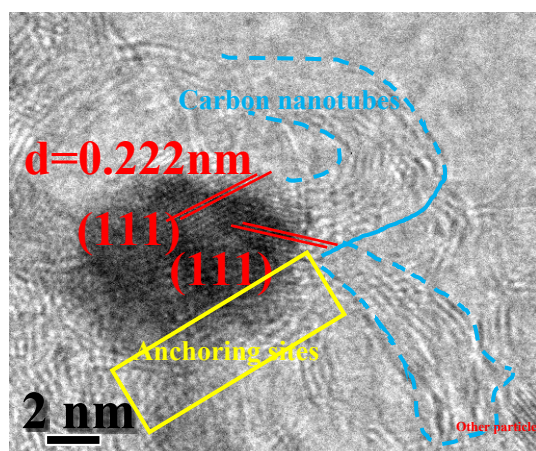


Fig S5. The TEM of PtCo@CNTs-MOF after acid-leaching treatment.

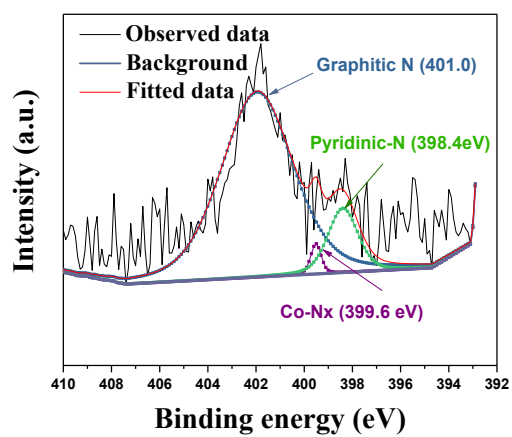


Fig S6. The XPS of PtCo@CNTs-MOF for N elements.

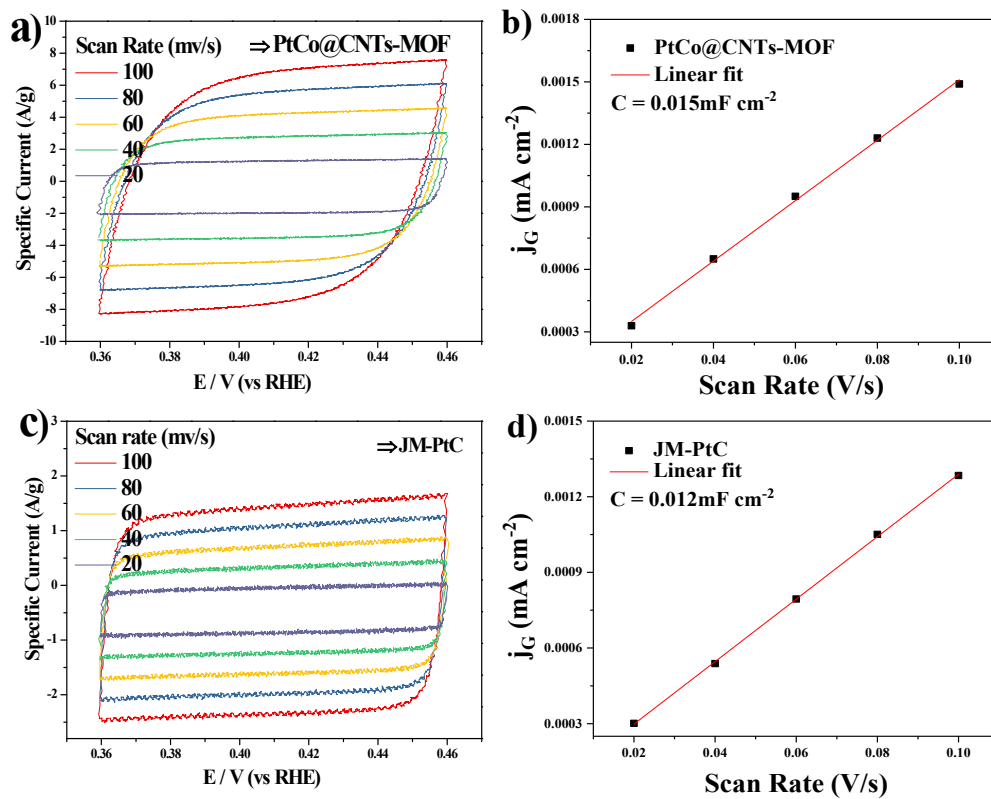


Fig S7. a), c) Cyclic voltammograms within the range of no faradaic reactions. b), d) Variation of double layer charging currents at +0.41 V as a function of scan rate, respectively

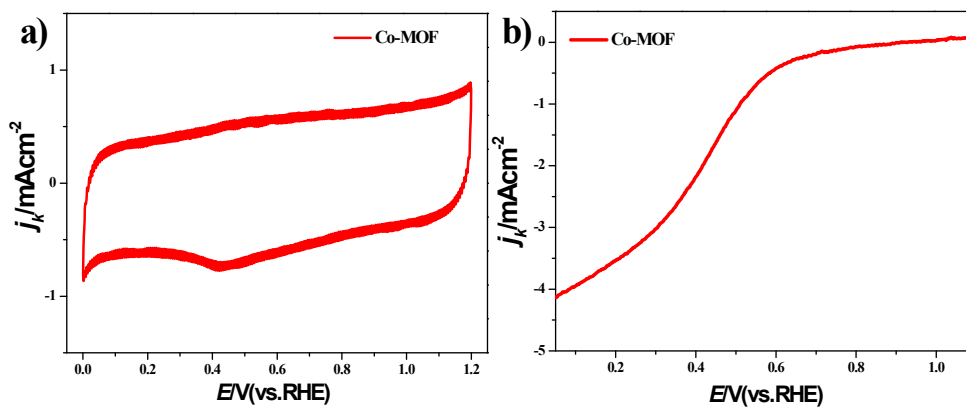


Fig S8. The CV and LSV curves of Co-MOF in 0.1M HClO<sub>4</sub> solution.

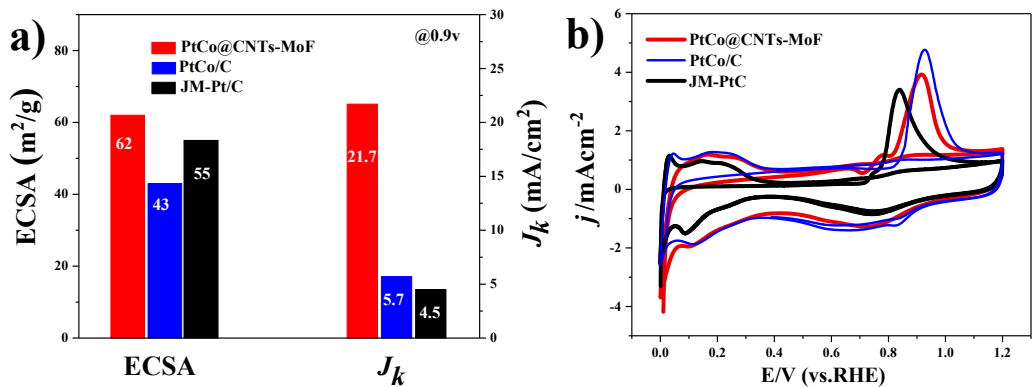


Fig S9. a) The ECSA and  $J_k$  of PtCo@CNTs-MOF, PtCo/C and JM-Pt/C, b) the CO-stripping curves of PtCo@CNTs-MOF, PtCo/C and JM-Pt/C were recorded at room temperature in CO-saturated 0.1 M  $\text{HClO}_4$  solution at scan rate of  $50 \text{ mVs}^{-1}$ .

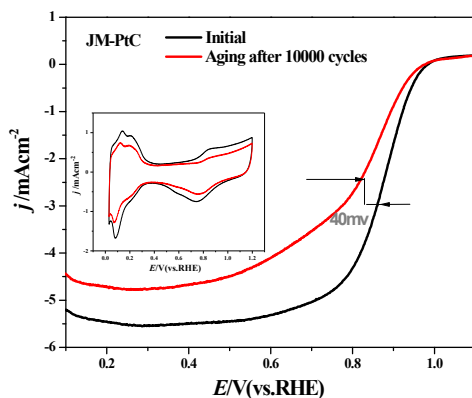


Fig S10. The CV and LSV curves of JM-Pt/C-20 wt% in  $\text{O}_2$ -saturated 0.1M  $\text{HClO}_4$  solution. The CV was recorded at a  $50 \text{ mVs}^{-1}$  scan rate before after aging.

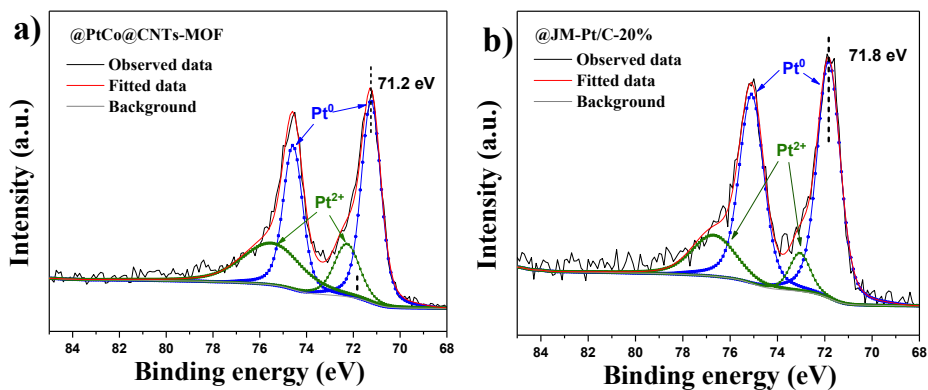


Fig S11. The XPS of PtCo@CNTs-MOF and JM-Pt/C-20% for Pt elements.



Table S1. The BET parameters of different samples.

Samples	Surface area (m <sup>2</sup> /g)	micropore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
ZIF-67	1372.70	0.66	14.84
Pt@ZIF-67	1121.03	0.52	9.56
Co-MOF-before acid-leached	133.90	0.0073	21.51
PtCo@CNTs-MOF-before acid-leached	146.67	0.0030	9.60
Co-MOF	467.29	0.0070	21.24
PtCo/C	354.67	0.0080	14.13
PtCo@CNTs-MOF	454.71	0.0075	8.28

#### Uncategorized References

1. Teranishi, T.; Hosoe, M.; Tanaka, T.; Miyake, M., Size control of monodispersed Pt nanoparticles and their 2D organization by electrophoretic deposition. *J Phys Chem B* **1999**, *103* (19), 3818-3827.
2. Chen, W.; Chen, S. W., Oxygen Electroreduction Catalyzed by Gold Nanoclusters: Strong Core Size Effects. *Angew Chem Int Edit* **2009**, *48* (24), 4386-4389.