Supporting Information

Metal-organic Framework-loaded Carbon-encapsulated Nano-catalyst as pH-universal Oxygen Reduction Reaction Electrocatalyst for Various Fuel Cell Devices

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Catalogue

S1. Experimental

1.1. Chemicals

Commercial Pt/C (20 *wt* %), Nafion solution (5 %) were purchased from Sigma-Aldrich (US). Iron chloride (FeCl$_3$), absolute methanol (CH$_3$OH), 2-methylimidazole, zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) were got from Sinopharm Chemical Reagent Co., Ltd (China). Methanol and Sodium borohydride were purchased from Chinese Medicine Chemical Reagent Co., Ltd (China). All chemicals were used as received without any further purification.

1.2. Synthesis of the catalysts

1.2.1. Preparation of ZIF-8

Typically, 4.800 g Zn(NO$_3$)$_2$·6H$_2$O　and 9.400 g 2-methylimidazole are dispersed in 150.00 mL methanol and 200.00 mL methanol, and then the former solution is added dropwise to the latter under stirring. Stir at 25 °C for 12 h. The product was then centrifuged, washed with methanol, and finally dried under vacuum at 60 °C for 12 h.

2.2.2. Preparation of FeN$_{0.056}$/BNC-X (X=700,800,900) and NC-800

0.0288 g of FeCl$_3$ was dissolved in 40 mL of methanol, and then 0.500 g of ZIF-8 was dispersed in the resulting solution. The mixture was stirred for 12 h, and then 0.100 g of sodium borohydride was added. After 30 minutes, the resulting product was collected by suction filtration, and then vacuum dried at 60 °C for 12 h. Put the dried mixture into a high-temperature tube furnace, and first pass 30 minutes of N$_2$ to remove the air in the tube. Under N$_2$ conditions, the temperature was increased to 700°C,800°C and 900 °C at 5 °C min^{-1}. High-temperature calcination at different temperatures for 2 h. For comparison, NC was prepared by the pyrolysis of ZIF-8 at 800 °C under the same process. After the high-temperature carbonization is completed, the material is ground into powder and recorded as FeBNCs without acid wash. Then the materials treated with 3 M HCl solution for 12 hours to remove the residual metal salt in the material. After washing with deionized water and suction filtration, it is stored in a vacuum drying oven at 60 °C for 12 hours, which is recorded as FeN$_{0.056}$/BNCs-X (X represents

temperature).

S2. Physical characterizations

X-ray diffraction (XRD) patterns were collected on a Model D8 Avance X-ray diffractometer (Bruker, Germany) with Cu Kα radiation. The morphology and structure of the samples were characterized by a field emission scanning electronmicroscopy (SEM) (JSM-6700F). The transmission electron microscope (TEM; FEI TF20, 200 kV) equipped with an X-ray spectrometer detector. The 3D high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) tomography was acquired by an FEI Titan 80-300 LB field emission TEM operated at 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS system (PHI, USA) with a monochromatic Al Kα source and a charge neutralizer. BET surface area test was carried out on an ASAP2020M apparatus (Micromeritics Instrument Corp., USA). The Raman spectroscopy was performed using an invia-Reflex Micro-Raman Spectroscopy system (Renishaw Co.) with 532 nm line of an Ar ion laser at room temperature.

S3. Electrochemical characterization

3.1. Electrochemical measurements

Electrochemical measurements were performed at room temperature (25 °C) on the CHI760E electrochemical workstation (CH Instrument Company) with a three-electrode system. A platinum wire electrode was used as counter electrode. At the same time, in alkaline medium, Hg/HgO in 1 M KOH solution is used as reference electrode, and in neutral and acidic medium, Ag/AgCl electrode in saturated KCl is used as reference electrode. A rotating disk electrode (RDE) with a glassy carbon disk of 3 mm in diameter and a rotating ring-disk electrode (RRDE) with a glassy carbon disk (4.0 mm diameter) and a Pt ring (5.0 mm inner diameter and 7.0 mm outer diameter) served as the substrate for the working electrode. The O_2-saturated 0.1 M KOH solution,0.1 M PBS solution and 0.5 M H_2SO_4 solution were used as alkaline, neutral, and acidic media. For the CV measurements, the scan rate was 50 mV s^{-1}, while it was 5 mV s^{-1} for the RDE/RRDE test.

The potential in all these jobs will convert the Hg/HgO electrode or Ag/AgCl electrode into the potential of the reversible hydrogen electrode (RHE), and the potential conversion formula as following:

$$E_{RHE} = E_{Hg/HgO\ or\ Ag/AgCl} + 0.059\ V \times pH\ (medium)$$

The Koutecky-Levich (K-L) equation can be used to calculate the electron transfer number (n) and the limiting diffusion current (J_k) during the oxygen reduction reaction. The K-L equation is as follows:[1]

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

$$B = 0.2nFC_0D_0^{2/3}v^{-1/6}$$

$$J_K = \frac{1}{nkFC_0}$$

Among them, J, J_K, J_L represent the measured current density, kinetic current density, limiting diffusion current density (mA cm^{-2}), ω is the rotation speed of the rotating disk electrode (rpm min^{-1}); F is the Faraday constant (F=96485 C mol^{-1}); C_0 and D_0 are the volume concentration and diffusion coefficient of O_2 respectively (in 0.1M KOH solution, C_0=1.2×10^{-3}mol cm^{-3}, D_0=1.9×10^{-5}cm^2 s); v is the kinematic viscosity of the electrolyte (in 0.1M KOH solution, v=0.01 cm^2 s^{-1}), k is the electron transfer rate constant.

After the RRDE test, the collected data is processed. The H_2O_2 yield and the electron transfer number(n) are calculated by the following equation:[2]

$$H_2O_2\% = 200 \times \frac{I_r/N}{I_d + I_r/N}$$

$$N = 4 \times \frac{I_d}{I_d + I_r/N}$$

In the above formula, I_r and I_d are ring current and disk current respectively, and the collection efficiency(N) in this experiment is 0.125.

Under the same settings as the RDE test in the O_2-saturated aqueous electrolyte,

the resistance of the material to methanol and its stability were tested. The stability test was carried out at room temperature under static potential, and the working electrode was rotated at 1600 rpm in O_2-saturated solution.

S4. Zn-air Battery Assembly and measurement

In this paper, a simple zinc-air battery is made to measure the performance of the catalyst in the zinc-air battery. Cathode preparation: 10.0 mg of catalyst, mix with 840 µL of water, 60 µL of ethanol, and 100 µL of 5 % Nafion solution for 30 minutes to form a concentration of 10 mg/mL catalyst ink. Then use a pipette to suck 100 µL of catalyst ink, apply the slurry to hydrophobic carbon paper and dry it as a cathode (catalyst coating area is 1cm×1cm, loading capacity is 1mg m^{-2}), zinc flakes with an area of 1 cm × 1 cm is used as the anode, the electrolyte is a mixed solution of 6 M potassium hydroxide and 0.2 M zinc nitrate. The Zn-air battery is tested at room temperature. The polarization curves were obtained by LSV technique with CHI760E electrochemical working station. Open circuit voltage curve, constant current discharge curve, rate discharge curve, constant current charge and discharge cycle curve are obtained on the LAND test system. Among them, the open circuit voltage data is obtained by continuously measuring the battery connected to the LAND test system and selecting the standing program; the constant current discharge curve data is obtained by discharging 10 h at a discharge current density of 10 mA cm^{-2}; the rate discharge curve data is obtained at different discharge current densities (2, 5, 10, 20, 2 mA cm^{-2}) under discharge for 5 h; the constant current charge and discharge cycle process charge and discharge current density of 10 mA cm^{-2}, each cycle 20 min (10 min

charge, 10 min discharge). The specific capacitor of Zn-air fuel cell was calculated from the following equation:

$$C_{sp} = \frac{i \times t}{\Delta m}$$

Among them, i, t, Δm represent the discharge current, discharge time and the quality of zinc consumed respectively.[3]

S5. Operation and configuration of Microbial fuel cell (MFCs)

Take 20 mg of catalyst, 25 µL of Nafion solution, 125 µL of deionized water, and 50 µL of absolute ethanol in a centrifuge tube for 0.5 h to form a uniformly dispersed catalyst ink. Then evenly spread the catalyst ink on both sides of carbon cloth (1 cm × 2 cm), and fix the carbon cloth on the titanium wire, then the cathode electrode is successfully prepared. In this paper, a traditional two-chamber MFCs reaction vessel is used, and the volume of each vessel is about 150 mL. The two reaction vessels are separated by a proton exchange membrane (PEM, Membrane International Inc., Ringwood, NJ, USA), and then fix the two reaction vessels with clamps to build the reaction. The electricity-producing microorganisms in the experiment originated from the sludge of a sewage treatment plant (Xianghu Sewage Treatment Plant in Nanchang City, Jiangxi Province). In order to fairly compare the oxygen reduction performance of cathode catalysts in MFCs, the cathode catalysts to be compared can be installed in the same cathode chamber and connected to the same anode.

Every 5 minutes, use a digital multimeter (2700, Keithley Instruments, Inc., Cleveland, OH) to record the battery voltage and cathode potential at both ends of the external circuit. A potentiostat (Reference 600, Gamry Instruments, Warminster, PA) is used to obtain the polarization curve at a scan rate of 0.5 mV s^{-1}. The maximum power/current density is calculated by normalizing the cathode surface area.

S6. Operation and configuration of direct methanol fuel cell (DMFCs)

The anolyte is a mixed solution of 0.5 M H_2SO_4 and 1 M CH_3OH, and the catholyte is a 0.5 M H_2SO_4 solution. Preparation of cathode electrode and anode electrode: 10

mg of cathode catalyst, 50 μL of Nafion solution, 150 μL of deionized water, and 100 μL of ethanol in a centrifuge tube and sonicate for 0.5 h to form a mixed ink. Spread it on both sides of the carbon cloth (1 cm × 2 cm), dry it naturally and use titanium wire to string the carbon cloth as the cathode chamber electrode; similarly, 10 mg 30 % PtRu/C catalyst is dispersed in the same solution as above, coated on both sides of the carbon cloth (area 1 cm × 2 cm), and dried naturally. Use titanium wire to string the carbon cloth together as the anode chamber electrode. Finally, a 100 Ω resistor is connected to the external circuit to form a fuel cell. An oxidation reaction of methanol occurs at the anode; oxygen reduction reaction occurs at the cathode. The open circuit voltage curve data of DMFCs is obtained by the LAND test system; the power density polarization curve data is obtained by LSV on the electrochemical workstation; The cell voltage is measured by a digital multimeter (Keithley 2700 Instruments, Inc. Cleveland, USA). When the collected voltage value drops to 0, it indicates that the anode methanol is exhausted and the anode electrolyte needs to be replaced. It is a cycle from the replacement of the anolyte (voltage reaches the maximum value) to the complete consumption of the anolyte (voltage reaches the minimum value).
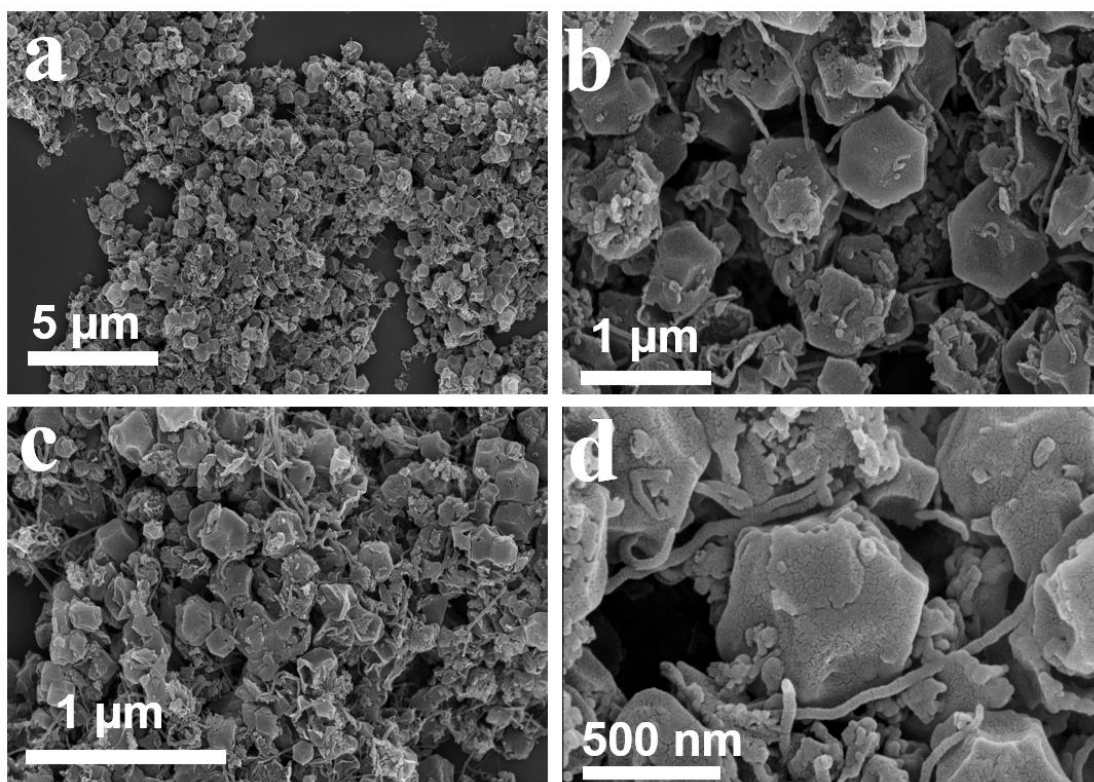
Figure S1.SEM images of FeN$_{0.056}$/BNCs-700.
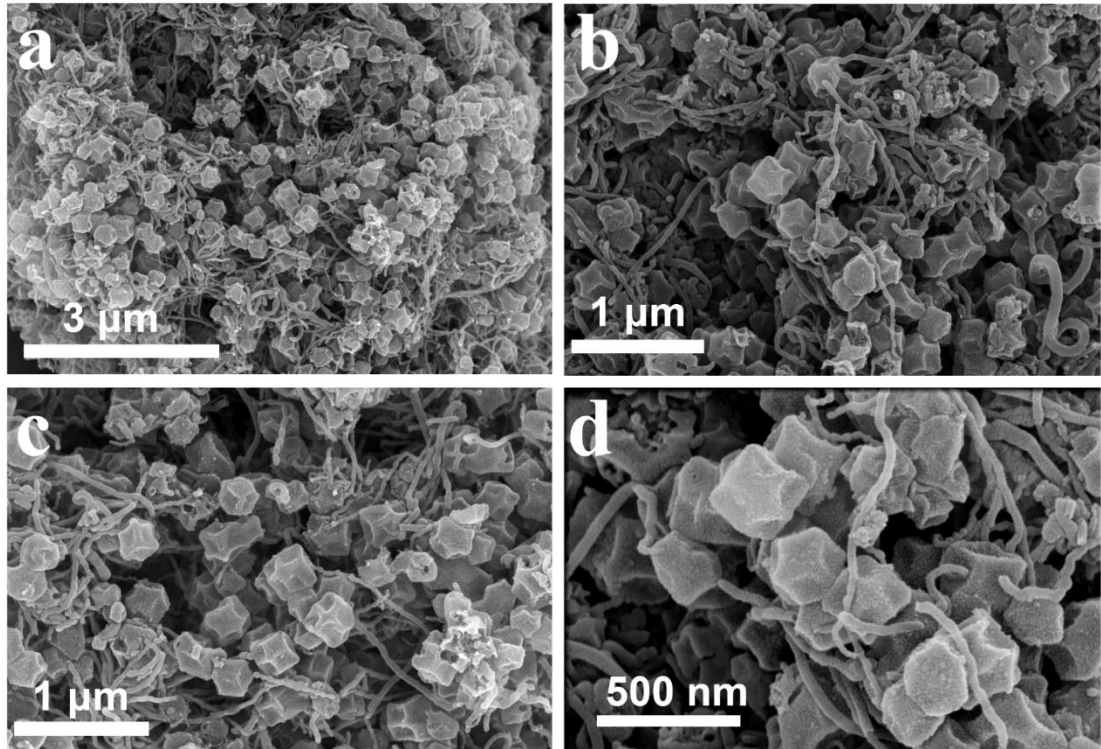
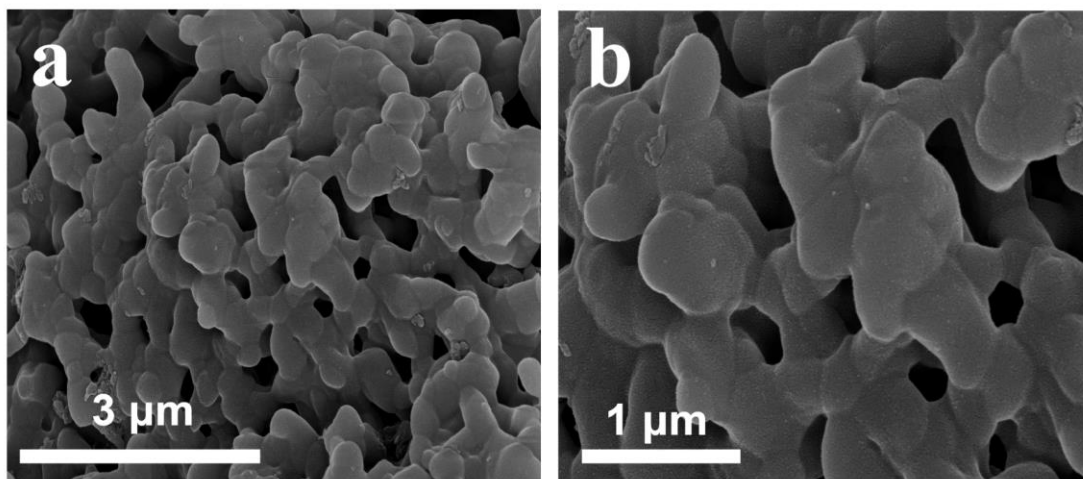**Figure S2**.SEM images of FeN$_{0.056}$/BNCs-900.

Figure S3.SEM images of ZIF-800 Precursor.
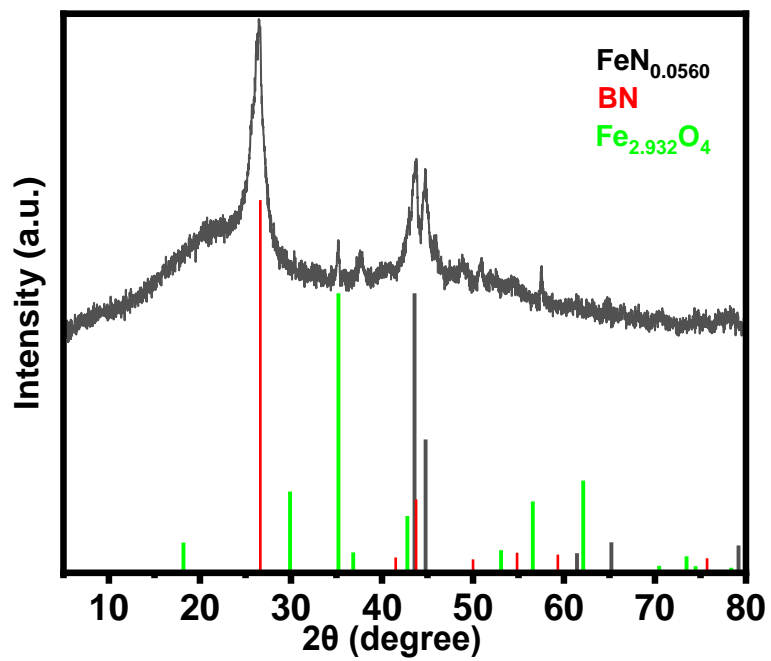
Figure S4. XRD patterns of FeBNCs-800 without acid wash.
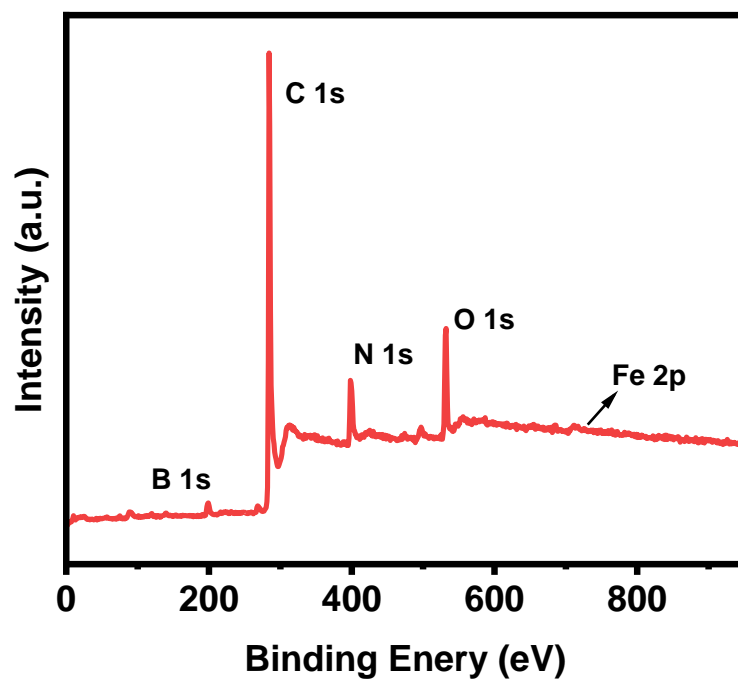
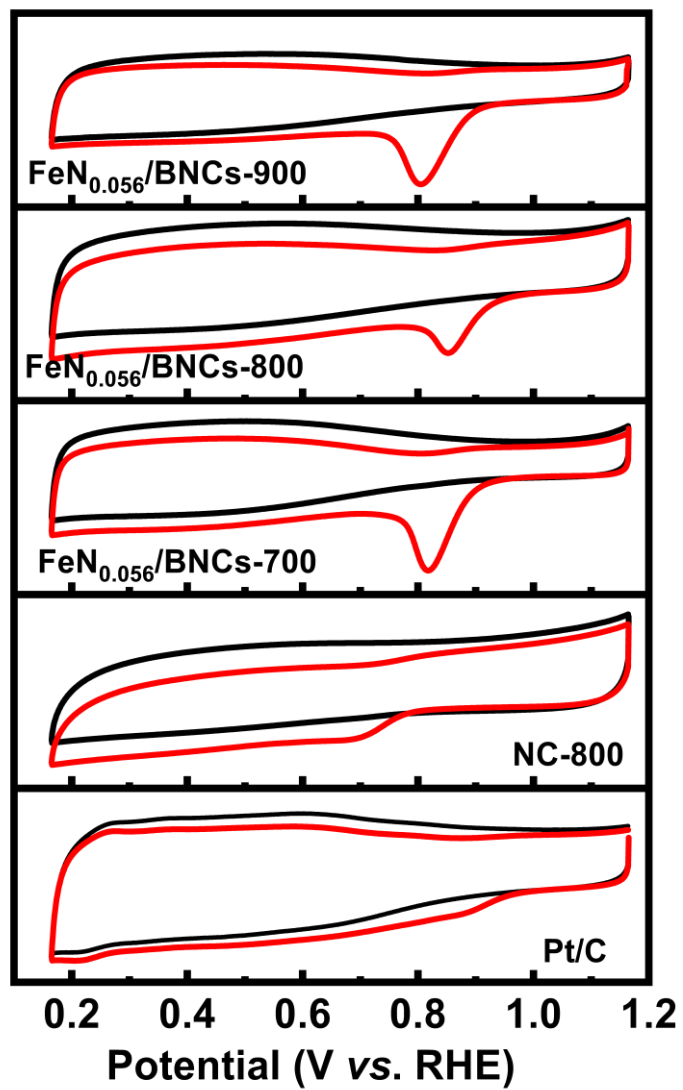**Figure S5**. XPS surface survey of FeN$_{0.056}$/BNCs-800.

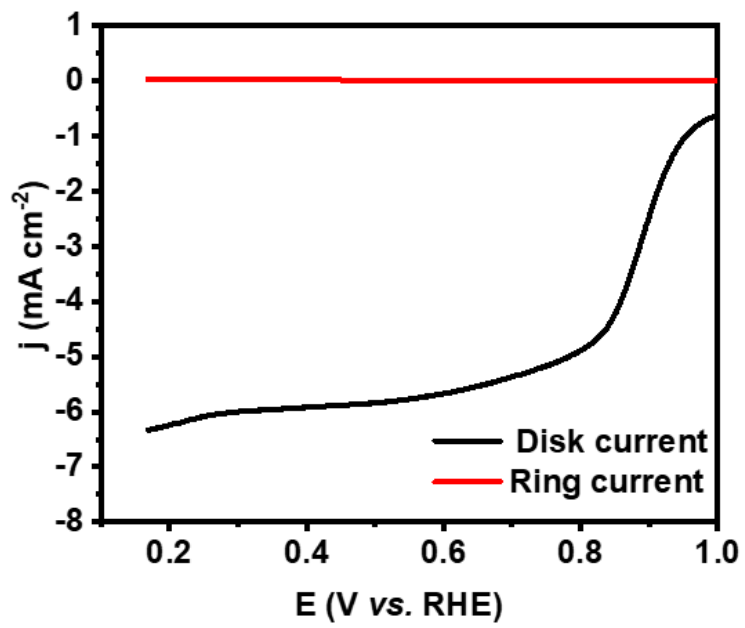**Figure S6**. CV curves of different catalysts in 0.1 M KOH solution.

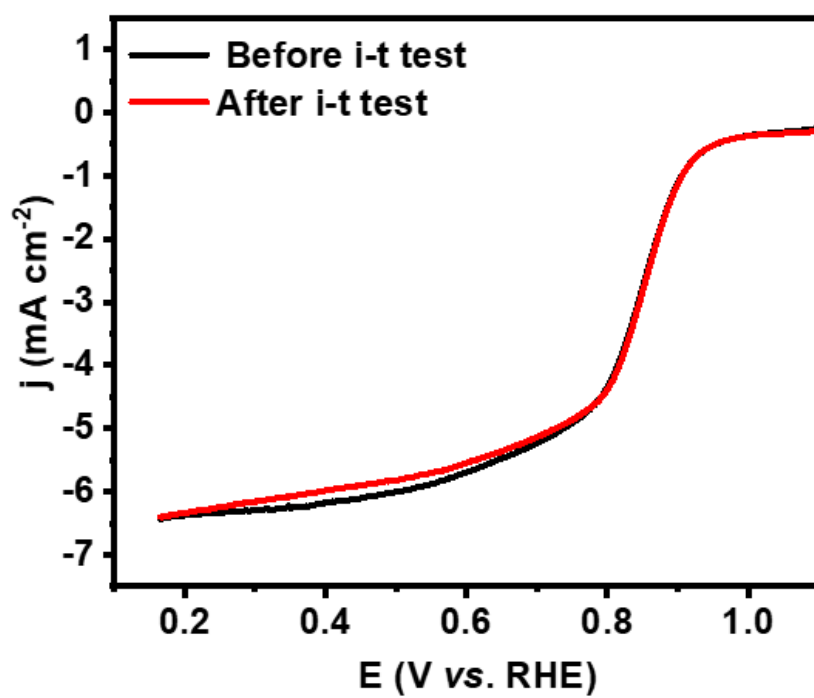**Figure S7**. The ring current and disk current of FeN$_{0.056}$/BNCs-800 recorded by RRDE in 0.1 M KOH.

Figure S8. Polarization curve comparison of $FeN_{0.056}$/BNCs-800 before and after i-t stability test in 0.1

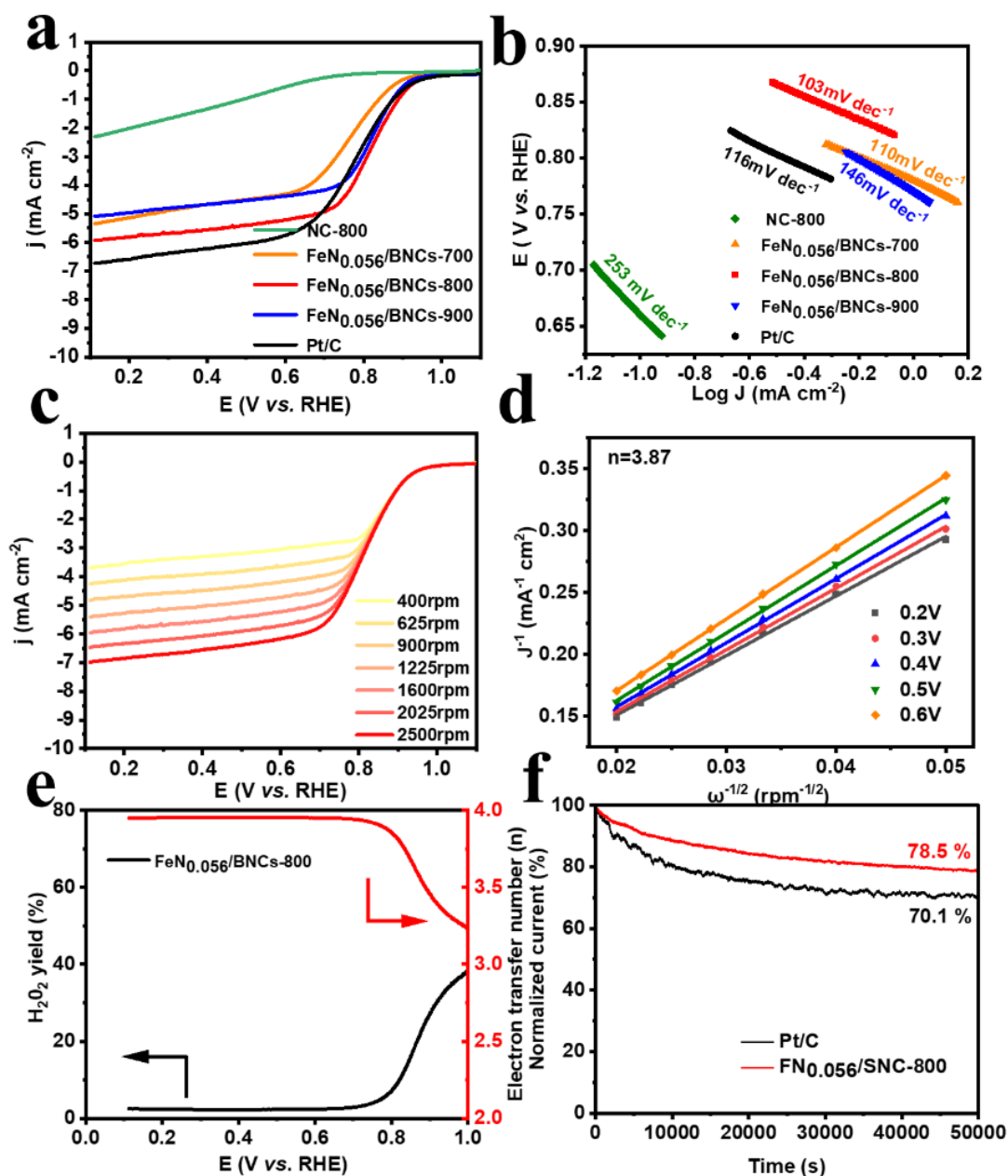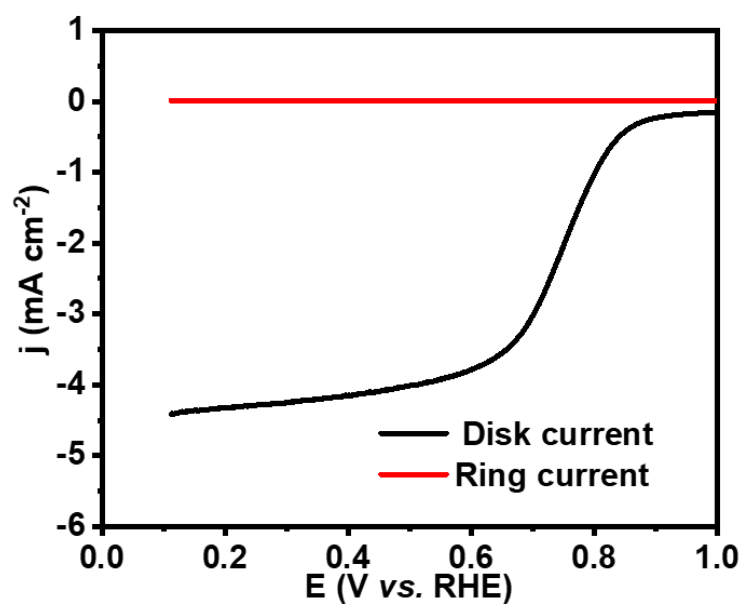M KOH.
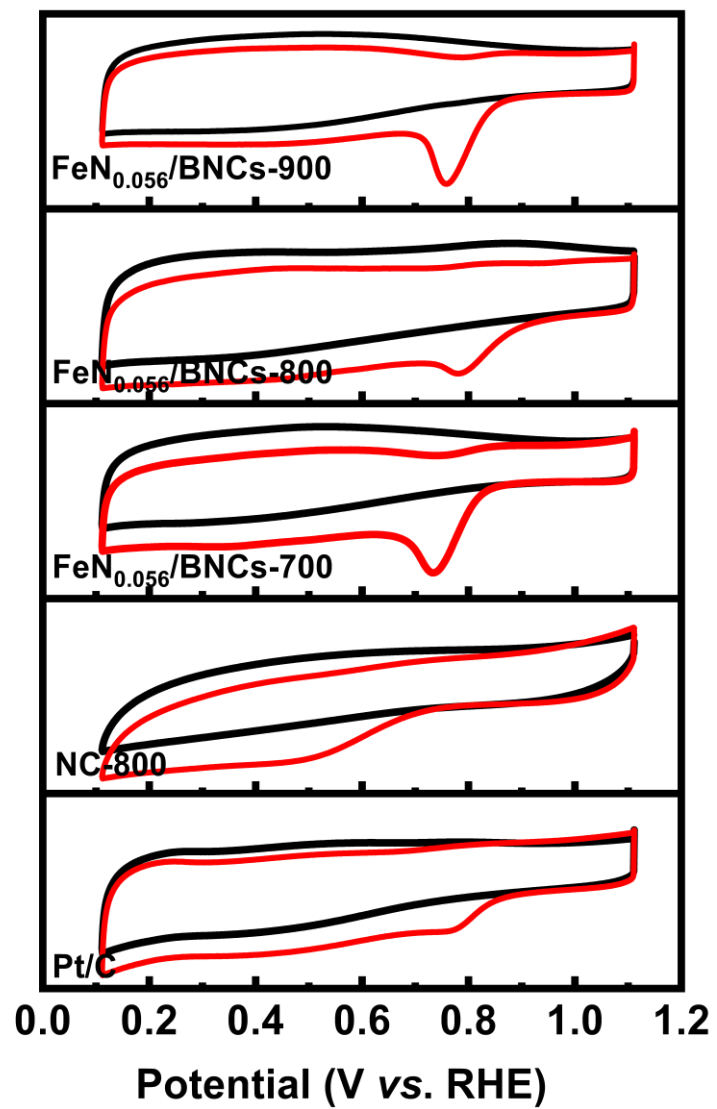
Figure S9. CV curves of different catalysts in 0.1 M PBS solution.

Figure S10. (a) LSV polarization curves at 1600 rpm in 0.1 M PBS, and corresponding (b) Tafel slopes; (c) LSV curves of FeN$_{0.056}$/BNCs-800 and corresponding (d) K-L plots at 0.2- 0.6 V $vs.$ RHE; (e) Electron transfer number and H$_2$O$_2$ yield of FeN$_{0.056}$/BNCs-800; (f) Durability test of the FeN$_{0.056}$/BNCs-800 and Pt/C catalyst (saturated O$_2$, 0.1 mol L^{-1} PBS, 1600 rpm).

Figure S11. The ring current and disk current of $FeN_{0.056}$/BNCs-800 recorded by RRDE in 0.1 M PBS.
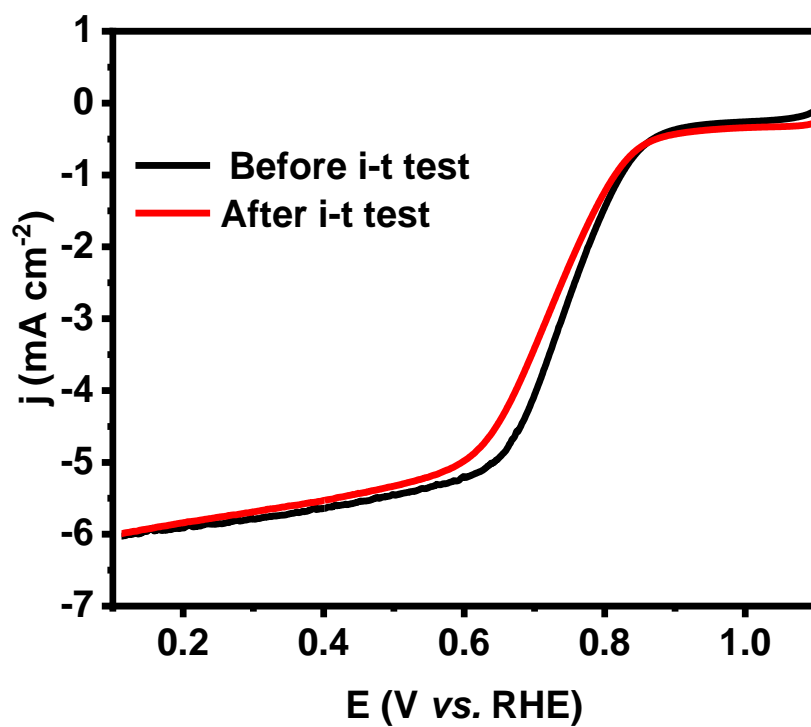
Figure S12. polarization curve comparison of $FeN_{0.056}$/BNCs-800 before and after it stability test in 0.1 M PBS.
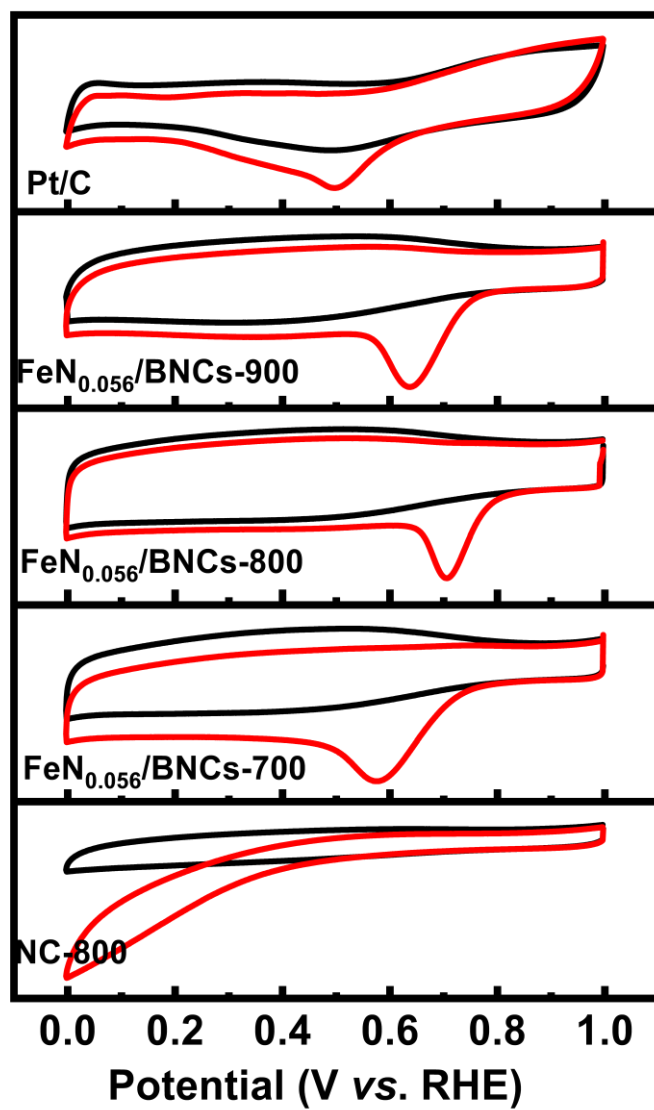
Figure S13. CV curves of different catalysts in 0.5 M H_2SO_4 solution.
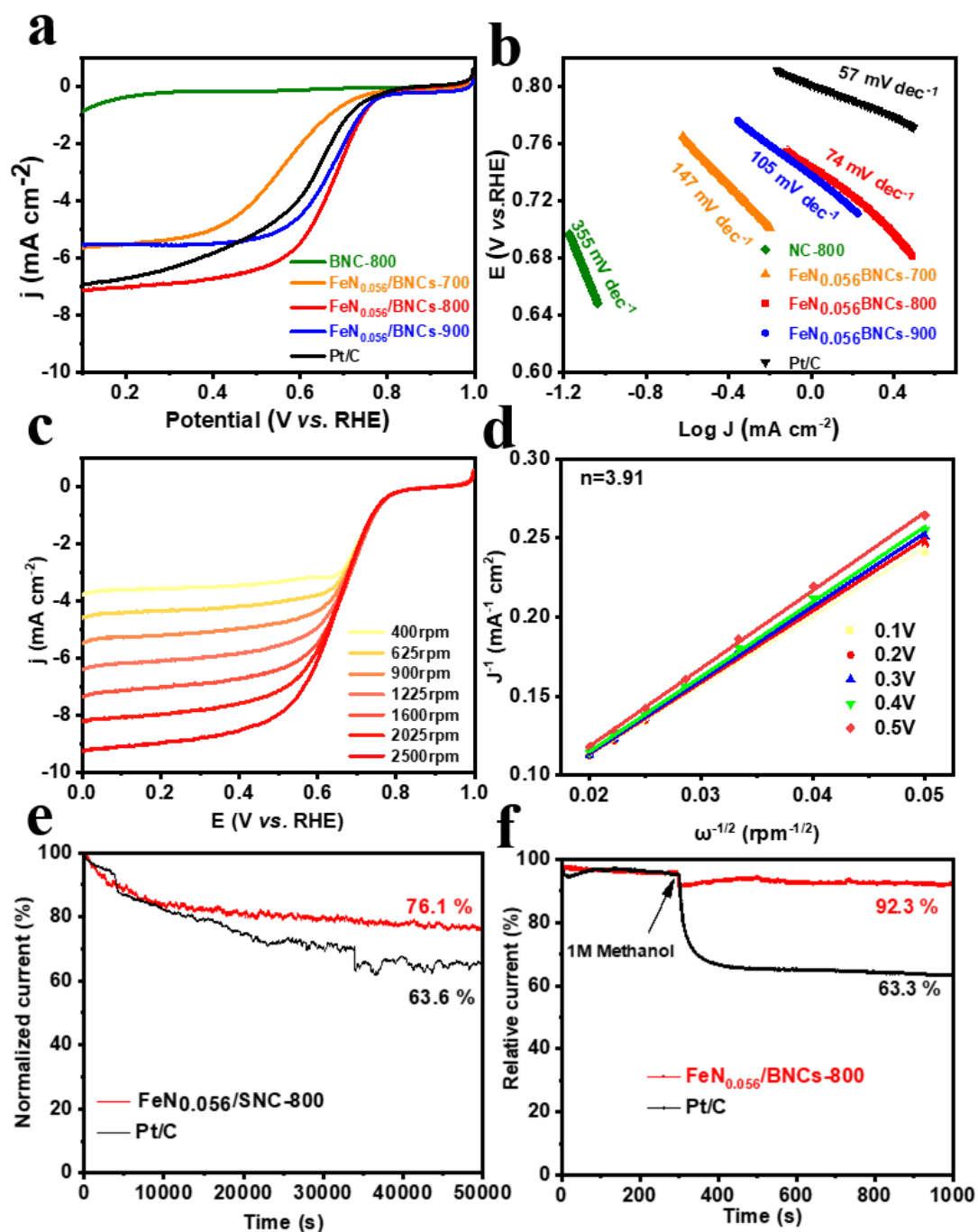
Figure S14. (a) ORR LSV polarization curves at 1600 rpm in 0.5 M H_2SO_4, and corresponding (b) Tafel slopes; (c) LSV curves of $FeN_{0.056}$/BNCs-800 and corresponding (d) K-L plots at 0.2-0.6 V *vs.* RHE; (e) i-t stability test of $FeN_{0.056}$/BNCs-800 and 20% Pt/C in 0.5 M H_2SO_4 solution; (f) Methanol tolerance (with 1 M methanol) of $FeN_{0.056}$/BNCs-800 and 20% Pt/C.
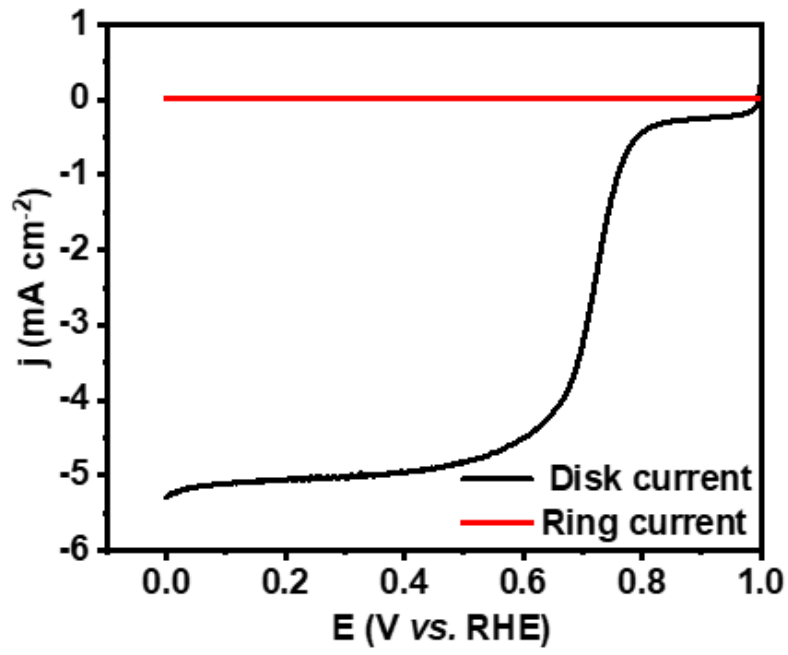
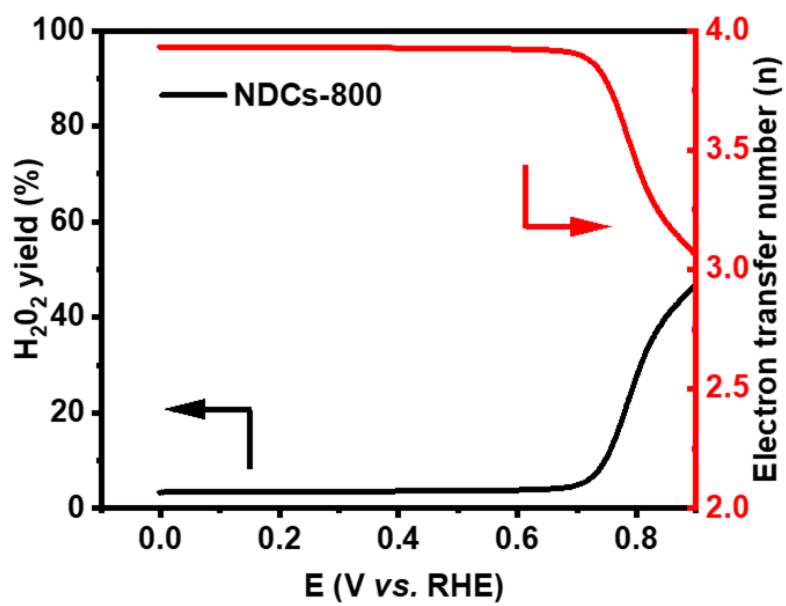**Figure S15**. The ring current and disk current of $FeN_{0.056}$/BNCs-800 recorded by RRDE in 0.5 M H_2SO_4.

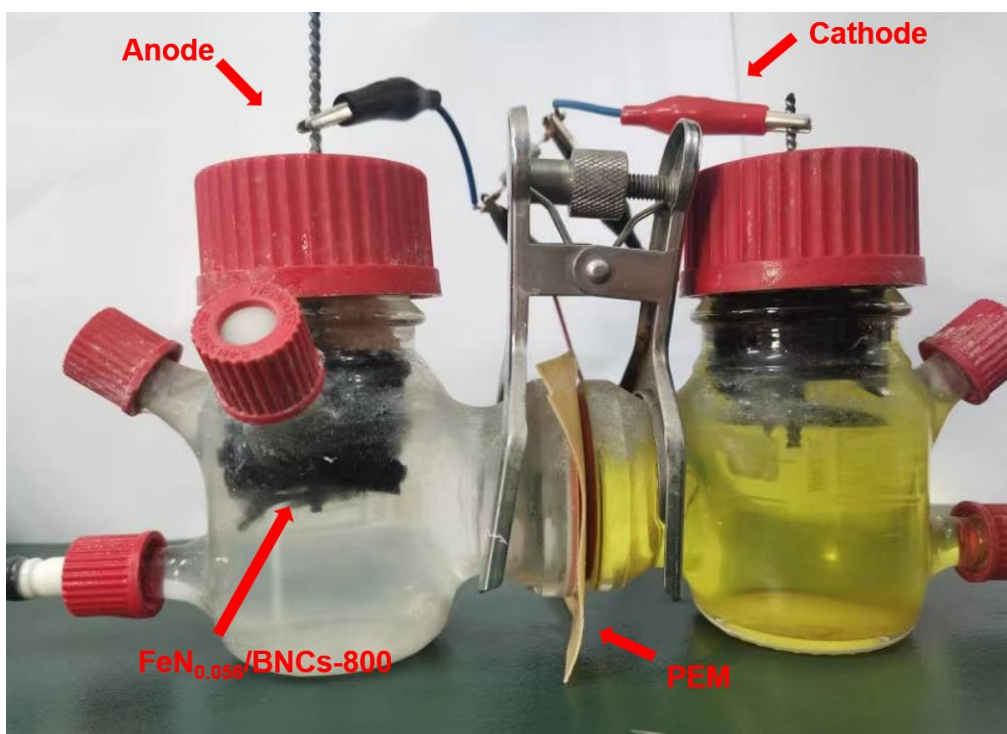**Figure S16.** The electron transfer number and hydrogen peroxide production of $FeN_{0.056}$/BNCs-800 in 0.5 M H_2SO_4.

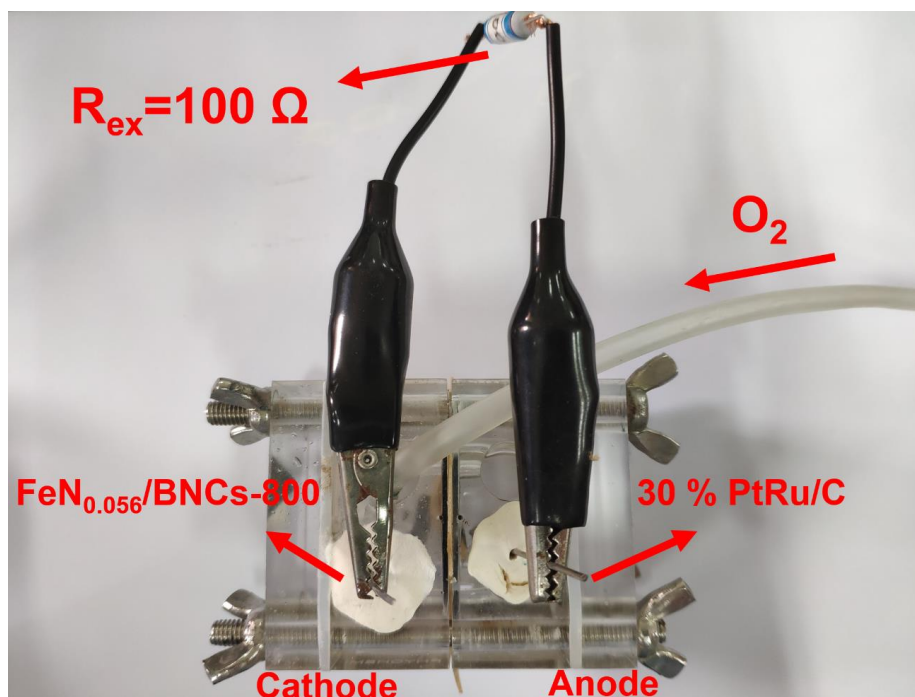**Figure S17**. Device of double-chamber MFC schematic diagram.

Figure S18. Device of DMFC schematic diagram.

Catalysts	Surface Area (cm^2g^{-1})	Pore Volume (cm^3g^{-1})	Pore Size (nm)
FeN$_{0.056}$/BNCs -700	448	0.30	7.20
FeN$_{0.056}$/BNCs -800	508	0.72	8.20
FeN$_{0.056}$/BNCs -900	450	0.55	7.38
NC-800	275.45	0.13	1.83

Table S1. Surface Area, Pore Volume, Pore Size of FeN$_{0.056}$/BNCs-700, FeN$_{0.056}$/BNCs-800, FeN$_{0.056}$/BNCs-900, NC-800.

Catalysts	Onset potentials (V)	Half wave potentials (V)	Reference
FeN$_{0.056}$/BNCs - 800	0.996	0.887	This work
Fe$_3$O$_4$@FeNC	0.946	0.852	Applied Catalysis B: Environmental, 2019, 251: 240-246.
Fe$_2$N/C	1.000	0.860	Nano Research, 2021, 14: 122-130
Czif-Fe(acac)$_3$-6		0.805	Journal of energy chemistry, 2018, 27(6): 1668-1673.
NC15-900 °C		0.848	Small, 2018, 14(52): 1804183.
FeNi-NPC	0.970	0.869	Israel Journal of Chemistry, 2023: e202200058
ZP 0.1 F/NC	0.974	0.861	Journal of The Electrochemical Society, 2022, 169(6): 060547.
D-NCNS	1.050	0.873	Carbon, 2023, 203: 76-87.
Fe0.06-N/C-900	0.980	0.890	Catalysis Science & Technology, 2018, 8(20): 5368-5381.

Table S2. Summary of some recently reported representative ORR Fe/NC electrocatalysts in 0.1 M KOH.

References

1. K. Chen, Z. Wen, P. Cai, G. Wang, S. Ci and K. Li, *Applied Catalysis B: Environmental*, 2021, **295**.

2. Y. Dong, Z. Fang, D. Ou, Q. Shi, Y. Ma, W. Yang, B. Tang and Q. Liu, *Chemical Engineering Journal*, 2022, **444**.

3. L. Fan, X. Wei, X. Li, Z. Liu, M. Li, S. Liu, Z. Kang, F. Dai, X. Lu and D. Sun, *Nano Research*, 2022, DOI: 10.1007/s12274-022-4939-5.