## **Supporting information**

## 1. Experimental Section

## 1.1 Materials

Flake graphite and 20% Pt/C used in this study were purchased from Sigma-Aldrich. Cyclohexane (Sinopharm Chemical Reagent Co., Ltd) was freshly distilled before using. Ferrocene, aluminum, aluminum powder were purchased from Aladdin (Shanghai, China) and used without further purification.

## 1.2 Preparation of rGFeCp via ligand exchanging.

Graphene oxide (GO) was prepared from flake graphite by a modified Hummer's method.<sup>1</sup> More related literature on graphene preparation by chemical exfoliation, electrochemical exfoliation please see the reference.<sup>2,3,4</sup> Reduced graphene oxide (rG) was prepared by hydrate reduction of GO in presence of sodium dodecylbenzenesulphonate. First, ferrocene (7.44 g, 40.0 mmol), AlCl<sub>3</sub> (13.33 g, 100 mmol), Al powder (1.36 g, 50mmol), cyclohexane (500.0 mL), and rG (0.5 g) were added to a round bottom flask under inert atmosphere. The mixture was then heated to

80°C under vigorous stirring for 36h. After centrifugation and washed with methanol,

acetone, and ether in turn and at last dried at 60°C under vacuum for 5h, iron (II) 1cyclopenta-2,4-dienyl reduced graphene oxide (denoted as rGFeCp) was produced.

Iron (II) 1-cyclopenta-2,4-dienyl graphite (GFeCp) was prepared under the same condition as rGFeCp using graphite flake as starting material for comparison.

# **1.3 Pyrolysis and activation**

rGFeCp was pyrolyzed at a heating rate of 5  $^{\circ}$ C min<sup>-1</sup> and held at the 800  $^{\circ}$ C for 2h under nitrogen flow. The obtained rGFe-800 was further activated under NH<sub>3</sub> flow

(30 ml/min) for 10 min under 800  $^{\circ}$ C to produce iron/nitrogen co-doped porous graphene (rGFe-800a). Similarly, GFe-800 and GFe-800a were prepared under the same procedure. Besides, rG was also activated under the same condition to produce nitrogen-doped graphene (rG-800a).

## 1.4 Characterization

Atomic force microscopy (AFM) images were obtained with a microscope MUL TIMODE NANOSCOPE (DI Co., USA). Transmission electron microscope (TEM) was performed on a JEOL-2100 (JEOL Ltd., Japan) electron microscope operated at an acceleration voltage of 200kV. Scanning electron microscopy (SEM) was carried out with an FEI Sirion-200 (FEI Co., USA). Thermogravimetric analysis (TGA) of the samples(S1) was undertaken using a Q5000IR (TA Instruments, USA) thermogravimetric analyzer with a heating rate of 20°C min<sup>-1</sup> from room temperature up to 800°C under nitrogen flow. Fourier transform infrared spectroscopy (FT-IR) was performed on a Spectrum 100 (Perkin Elmer, Inc., USA) spectrometer with a scan range of 4000-400 cm<sup>-1</sup>. Raman measurements were recorded on an Invia/Reflrx Lasser Micro-Raman spectroscope (Renishaw, England) with excitation laser beam wavelength of 532 nm. The powders were placed on a clean glass substrate that was

used for the Raman measurement. X-ray photoelectron spectra (XPS) were determined by an AXIS Ultra DLD system (Kratos Co., Japan) using Al Ka radiation as the X-ray source.

#### 1.5 Electrochemical measurements

All the electrochemical measurements including cyclic voltammetry (CV), rotating disk electrode (RDE) measurements and rotating ring disk electrode (RRDE) were carried out in a conventional three-electrode cell and O2-saturated 0.1 M KOH solution using AFMSRCE2759 electrochemical system (Pine Instrument Co., USA) at room temperature. Reference and counter electrodes are Ag/AgCl and platinum wire, respectively. A RRDE electrode with a Pt ring and a glassy carbon disk loading the electrocatalyst was used as the working electrode. The electrocatalyst sample was synthesized as follows: 5mg catalyst was dissolved in 500µL of 0.25% Nafion ethanol solution, and then stirred overnight to form homogeneous solution. 10µL of the solution was pipetted onto glassy carbon electrode which has a diameter of 5.61 mm, leading to a catalyst loading of 0.6 mg/cm<sup>2</sup>. The solution was dried in the air and ultimately a sample film was formed on the glassy carbon surface. In order to measure for comparison, a working electrode loaded commercial 20wt.% platinum was prepared with the same procedure as above except adding 2 mg of Pt/C (20wt.%Pt) into 500ml 0.25% Nafion ethanol solution. After that, CV was conducted under alkaline condition (N<sub>2</sub>- and O<sub>2</sub>-saturated 0.1 M KOH as well as O<sub>2</sub>-saturated 0.1 M KOH solution with 1.0 M methanol) to test the electric catalytic properties of the materials. The voltage range was set between -1.0 to 0 V with a scan rate of 100 mV s<sup>-1</sup> at room temperature after bubbling  $O_2$  or  $N_2$  for 30 min.

For the RDE measurements, catalyst inks were prepared by the same method as CV's. The working electrode was scanned cathodically at a rate of 10 mV s<sup>-1</sup> with a varying rotating speed of 225-1600 rpm. Koutecky–Levich plots following of the main text were analyzed at various electrode potentials. The number of electrons

transferred (n) was calculated from the slopes of their best linear fit lines.<sup>5</sup>

$$1/J = 1/J_L + 1/J_k = 1/B\omega^{0.5} + 1/J_K \quad (1)$$
$$B = 0.62nFC_o(D_o)^{2/3}v^{-1/6} \quad (2)$$
$$J_K = nFkC_o \quad (3)$$

Where **J** is the measured current density,  $J_K$  and  $J_L$  are the kinetic- and diffusionlimiting current densities,  $\omega$  is the angular velocity, **n** is transferred electron number, **F** is the Faraday constant (96 486 C cm<sup>-1</sup>),  $C_0$  is the bulk concentration of  $O_2(C_0 = 1.2*10^{-3} \text{ mol } L^{-1})$ , **v** is the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>), and **k** is the electron-transfer rate constant.

For the RRDE measurements, catalyst inks and electrodes were also prepared by the same method as CV's. The disk electrode was scanned cathodically at a rate of 10 mV s<sup>-1</sup>, and the ring potential was constant at 0.5 V. Based on the RRDE result, the electron transfer number (*n*) and the *HO*<sub>2</sub><sup>-</sup> concentration (%) were calculated by the

following equations:

$$n = \frac{4I_D}{(I_D + I_R/N)}$$
 (4)

$$\%(HO_2^{-}) = \frac{200I_R/N}{\left(I_D + \frac{I_R}{N}\right)}$$
(5)

Where  $I_D$  and  $I_R$  are the disk and ring currents, respectively, and N = 0.37 is the ring collection efficiency.<sup>5,6</sup>



Figure S1. TGA spectra of Graphite(C), rG, ferrocene, rGFeCp and GFeCp.



**Figure S2.** (a) Digital pictures of Graphite (1) GFeCp, (2), and rGFeCp(3) in DMF (2 mg/ml), 2h after sonication.(b) AFM image of GFeCp.



Figure S3. XPS survey spectra.



**Figure S4**. Oxygen reduction polarization curves for rGFe-700, rGFe-800 and rGFe-900 on GC electrodes at 1600 rpm in 0.1 M KOH.



**Figure S5.** (a) Typical cyclic voltammograms for GFe-800a at a scan rate of 100 mV s-1in  $O_2$  and  $N_2$ -saturated 0.1 M KOH solution as well as in  $O_2$ -saturated 0.1 M KOH solution with 1.0 M methanol. (b) RRDE voltammogram for GFe-800a in 0.1 M KOH solution saturated with  $O_2$ ; the electrode rotation rate was 1600 rpm, and the Pt ring electrode was held at 0.5 V. (c) RDE voltammograms for GFe-800a in 0.1 M KOH solution saturated with  $O_2$ . (d) Koutecky – Levich plots calculated from the RDE

result.



Figure S6. XRD spectra of graphite, ferrocene and GFeCp.



Figure S7. XRD spectra of rG, ferrocene and rGFeCp.

	Total content	Ratios of different N-species				
Samples	(Atom%)	(Atom%)				
_	Nitrogen	Pyridinc	Pyrrolic	Graphitic	N-O	
		Ν	Ν	Ν		
GFe-800a	1.73	43.7	27.55	18.21	10.53	
rGFe-800a	2.94	18.51	34.04	33.24	14.21	

Table S1. Concentrations of different nitrogen and Fe in the prepared catalysts.

	ferrocene	rGFeCp	rGFe-800	rGFe-800a
Fe(wt.%)	2.964	2.912	8.104	3.667
Fe(at.%)	2.266	1.024	1.494	1.838

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