

## Electronic Supplementary Information

# Fe induction strategy for hollow porous N doped carbon with superior performance in oxygen reduction

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## 1. Experiment section

### Materials

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (>99.0%), FeSO<sub>4</sub>·7H<sub>2</sub>O (>99.0%), Co(NO<sub>3</sub>)<sub>2</sub>·6(H<sub>2</sub>O) (>99.0%), 2-methylimidazole (>99.0%), and methanol (>99.5%), which were of AR grade, were bought from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were used as received without any further purification.

### Synthesis

#### Synthesis of ZnCo-ZIF and ZnCoFe-ZIF.

0.7 mmol of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 1.2 mmol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in 20 mL of methanol, and 0.1 mmol of FeSO<sub>4</sub>·7H<sub>2</sub>O was added to the solution to study etching mechanism during the synthesis. Another 20 mL of methanol with 8 mmol of 2-methylimidazole dissolved was then added into the prepared Zn/Co/Fe-containing solution under a 2 h vigorous stirring, and the mixture was aged for 24 h at room temperature to form ZIF precursors containing Fe, Zn, and Co. After filtration, the product was collected, washed with methanol for three times, and then dried at the temperature of 60 °C in an oven overnight. The obtained product with Fe addition was denoted as ZnCoFe-ZIF. The ZnCo-ZIF was synthesized in the same way as ZnCoFe-ZIF without the addition of Fe<sup>2+</sup> salt.

#### Synthesis of Co-N/C and CoFe-HN/C.

The prepared ZnCoFe-ZIF was carbonized in a tube furnace from room temperature to 800 °C at a rate of 5 °C min<sup>-1</sup>, then maintained at 800 °C for 2 h and finally cooled naturally, with an atmosphere of Ar/H<sub>2</sub> (90/10, v/v). The cooled

pyrolyzed product was treated in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for 12 h to remove the remains (e.g., ZnO, Co and Fe), and then collected by filtration, washed with deionized water, and dried at 60 °C in an oven overnight to obtain the final product, named as CoFe-HN/C. The Co-N/C was obtained by carbonizing the pre-prepared ZnCo-ZIF in the same way.

### **Physicochemical Characterizations.**

The morphologies of the precursors and their carbonization product samples were characterized by using a scanning electron microscope (SEM, JEOL JSM-7610F) at an accelerating voltage of 15.0 kV and a high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) operated at 200.0 kV. The X-ray diffraction (XRD) patterns of the precursors and their corresponding derivatives were obtained from the  $2\theta$  angle of 5 to 80° at a scan rate of 5° min<sup>-1</sup> by using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) on a Rigaku D/max 2500 X-ray diffractometer. The pyrolysis processes of the precursors were characterized by thermogravimetric/differential thermal analysis (TG/DTA) on a thermal analyzer (DTA-50) from room temperature to 1000 °C with a heating rate of 5 °C min<sup>-1</sup> in an Ar/H<sub>2</sub> atmosphere. The bonding states and compositions of the ZnCoFe-ZIF precursors treated under different temperatures were characterized by Fourier transform infrared (FT-IR) spectroscopy in the range of 2000 to 400 cm<sup>-1</sup> on a Nicolet-5700 spectrometer. N<sub>2</sub> adsorption–desorption isotherms for Brunauer-Emmett-Teller (BET) measurements for specific surface area were recorded on an Autosorb-iQ (Quantachrome) analyzer at 77 K. Raman spectra of the synthesized Co-

N/C and CoFe-HN/C were obtained from 200 to 3500  $\text{cm}^{-1}$  on a Raman spectrometer (LabRAM HR, HORIBA) with a laser power of 10 % and acquisition time of 10. The X-ray photoelectron spectroscopy (XPS) study was carried out on a ThermoFisher ESCALAB 250Xi spectrometer using an Al  $K\alpha$  source (1486.6 eV) and a multidetection analyzer under  $10^{-8}$  Pa residual pressure with an acquisition time of 68 seconds. Surface charging effects were revised with a C 1s peak at 284.8 eV as a reference. Peak areas were converted to total intensities using a Shirley background correction and Gaussian-Lorentzian fitting.

### **Electrochemical Measurements**

The catalytic performance of the as-prepared catalysts was evaluated by the rotating disk electrode (RDE) system on an Autolab PGSTAT204 electrochemical workstation in a three-electrode configuration at room temperature with a carbon rod as the counter electrode, an Ag/AgCl (in 3.5 M KCl) electrode as the reference electrode, and a  $\text{O}_2$ -saturated 0.1 M KOH (or  $\text{N}_2$ -saturated 0.1 M KOH) as the electrolyte. The working electrode, i.e., a glassy carbon (GC) RDE with a 5 mm diameter loaded with the as-prepared catalysts, was prepared as follows. 6.0 mg of the prepared catalyst was added into 1 mL of the solution composed of 950  $\mu\text{L}$  of anhydrous ethanol and 50  $\mu\text{L}$  of 5% Nafion solution. Then the mixture was placed under ultrasonication for at least 30 min to form a homogeneous ink. After that, 8  $\mu\text{L}$  of the ink was dropped onto the surface of a glassy carbon RDE and dried at room temperature naturally. The loading of the catalyst was about  $0.245 \text{ mg cm}^{-2}$ . A linear sweep voltammetry (LSV) study was performed by scanning the potential from 0.20

to -0.90 V (vs. Ag/AgCl) at a rate of 10 mV s<sup>-1</sup> with different rotating rates (i.e., 400, 625, 900, 1225, and 1600 rpm). A cyclic voltammetry (CV) test was executed without electrode rotation in the same potential range while the scan rate was 50 mV s<sup>-1</sup>. The commercial 20 wt% Pt/C (named as Pt/C for short) catalyst was prepared under the same conditions as Co-N/C and CoFe-HN/C for comparison.

RRDE test was carried out to measure the electron transfer number during the catalysis, with working electrode prepared in the same way as RDE except for loading 8 μL ink on the ring-disk electrode. It was also recorded in an O<sub>2</sub>-saturated 0.1 M KOH solution at 1600 rpm with the scan rate of 10 mV s<sup>-1</sup>, and 0.2 V to -0.9 V was set as potential range while the ring was 0.5 V (vs. Ag/AgCl).

The peroxide yield (HO<sub>2</sub><sup>-</sup>%) and the electron transfer number (n) were calculated using the following equations, where  $I_d$  denotes disk current,  $I_r$  represents ring current and  $N$  is 0.37, i.e., the current collection efficiency by the Pt ring on RDE.

$$HO_2^-(\%) = 200 \times \frac{I_r/N}{I_d + I_r/N}$$

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

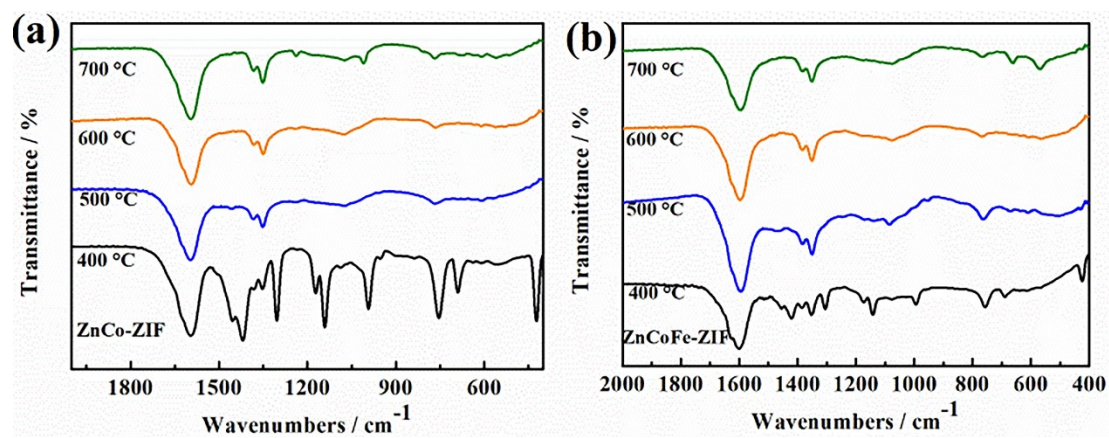
#### **Preparation of air cathodes for Mg-air batteries.**

The porous air cathode was composed of a current collector, a waterproof breathable layer, and a catalyst layer. The current collector was a piece of copper adhesive tape, and the waterproof breathable layer consists acetylene black and polytetrafluoroethene (PTFE 60 wt%), which were mixed in ethanol with a weight ratio of 6/4. The catalyst layer was fabricated as follows. About 4 mg of the prepared

catalyst was added into 1 mL of the solution which is composed of 950  $\mu\text{L}$  of anhydrous ethanol and 50  $\mu\text{L}$  of 5% Nafion solution, and was then placed under ultrasonication for at least 30 min to form a homogeneous ink. Then, the resultant mixture was homogeneously sprayed on the waterproof breathable layer under a  $\text{N}_2$  current. After being dried at 60  $^\circ\text{C}$  for 1 h, the air cathode electrode was well prepared and the catalyst mass loading was about 1  $\text{mg cm}^{-2}$ .

The Mg-air battery was assembled by using the as-prepared air electrode (1 cm  $\times$  1 cm) as the cathode, a 2 M NaCl aqueous solution as the electrolyte, and a piece of AZ31 Mg foil as the anode. The discharge tests of the battery were performed on a CHI660D electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). The power density, i.e.,  $P$  ( $\text{mW cm}^{-2}$ ), of the materials was calculated from the discharge curves based on  $P=V \times i$ , where  $V$  represents the voltage (V) and  $i$  represents the discharge current density ( $\text{mA cm}^{-2}$ ).

## 2. FT-IR analysis

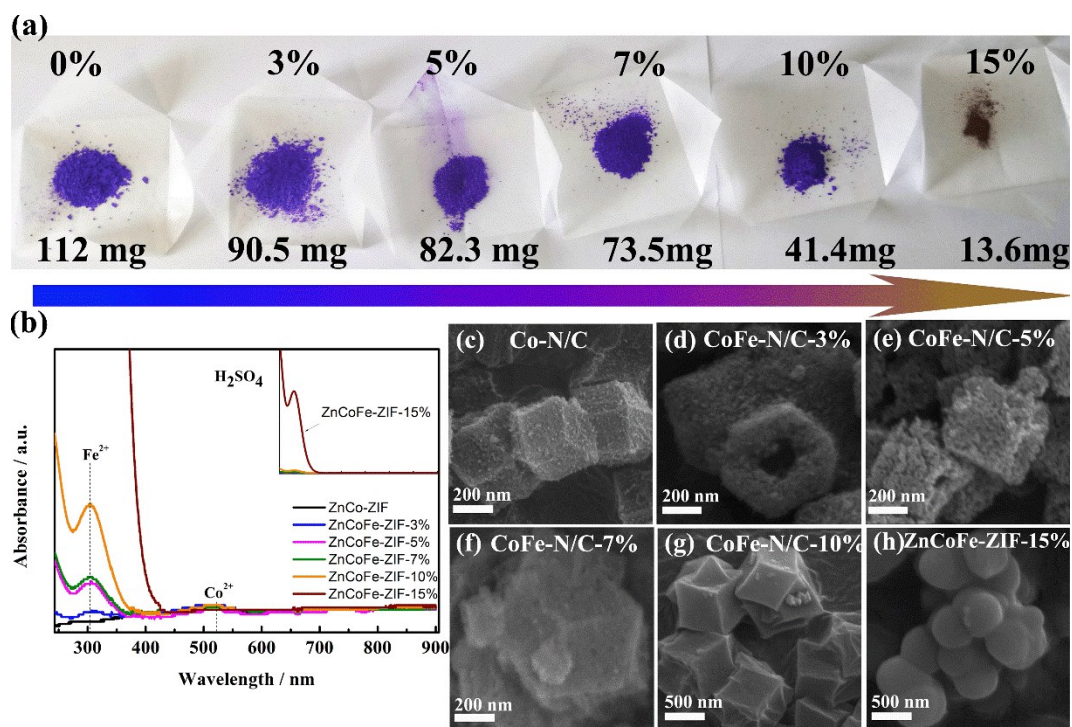


**Figure S1.** FT-IR spectra for (a) ZnCo-ZIF and (b) ZnCoFe-ZIF treated at 400, 500, 600 and 700 °C for 2 h.

### 3. Analysis of influences of Fe addition.

To analyze the effects of Fe addition level on the composition, structure and properties of the material, ZnCoFe-ZIF precursors with different Fe additions, with molar ratios of  $\text{Fe}^{2+}/(\text{Zn}^{2+}+\text{Co}^{2+}+\text{Fe}^{2+})$  ranging from 3% to 15%, were prepared and then carbonized. The experimental results show that the yield of the synthesized precursor decreases and the color darkens as Fe addition increases (Fig. S2a). As the addition of Fe reaches to 15%, ZnCoFe-ZIF-15% precursor becomes amorphous, accompanied with the destruction of polyhedral structure and displaying the color of iron oxides. The relative contents of Fe addition were detected by UV-vis to analysis the absorbance of  $\text{Fe}^{2+}$  by dissolving the precursors in a 0.5 M  $\text{H}_2\text{SO}_4$  solution. The relative content of Fe in the precursors increases as the added Fe content increases (Fig. S2b). SEM images of the metal, nitrogen co-doped carbon materials derived from ZnCoFe-ZIF with different Fe addition show that the particle size of pyrolyzed materials enlarges with the increase of Fe content in precursor. Apart from that, the materials display a hollow dodecahedral structure when Fe addition is between 3% and 5%. But the structure is ruined as the content continues increasing, until it turns into an amorphous compound (ZnCoFe-ZIF-15% cannot be pyrolyzed to obtain carbon material due to exorbitant Fe addition) (Fig. S2c-h).





**Figure S2.** (a) Images and yield of ZnCoFe-ZIF with different Fe content in at%. (b) UV-vis spectra of precursors dissolved in 0.5 M  $\text{H}_2\text{SO}_4$ . SEM images of (c) Co-N/C, (d) CoFe-N/C-3%, (e) CoFe-N/C-5%, (f) CoFe-N/C-7%, (g) CoFe-N/C-10% and (h) ZnCoFe-ZIF-15%.

#### 4. Analysis of the specific surface area of Co-N/C and CoFe-HN/C.

**Table S1.** Summary of porosity parameters of Co-N/C and CoFe-HN/C.

Samples	$S_{\text{BET}} / \text{m}^2 \cdot \text{g}^{-1}$	$S_{\text{Langmuir}} / \text{m}^2 \cdot \text{g}^{-1}$	Pore size distribution / nm
Co-N/C	557	820	4.84(4)
CoFe-HN/C	509	783	8.68(4,30)

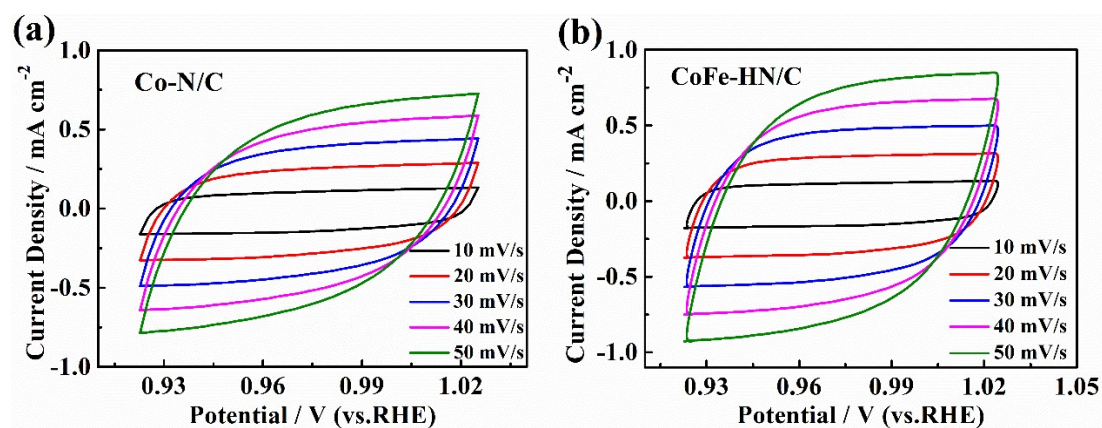
#### 5. XPS analysis of Co-N/C and CoFe-HN/C.

**Table S2.** The content and chemical state of C, N, O and Co in Co-N/C and CoFe-HN/C.

Sample	C at%	N at%	O at%	Co at%	Fe at%
Co-N/C	87.95	3.01	7.14	1.9	—
CoFe-HN/C	92.45	3.37	3.73	0.45	undetected

## 6. CV technique for $C_{dl}$ measurements.

The ECSA of the prepared Co-N/C and CoFe-HN/C samples were estimated based on the measured  $C_{dl}$  using CV technique (Fig. S3). The CV curves were tested at scan rates of 10, 20, 30, 40, and 50  $\text{mV s}^{-1}$  in a  $\text{N}_2$ -saturated 0.1 M KOH solution from 1.025 to 0.925 V (vs. RHE). The corresponding average current densities of the two samples were taken at the open circuit potential (OCP) on the CV curves.  $C_{dl}$  of each sample is decided by the slope of the linear fits to the current density (at OCP) vs. scan rate plot based on the CV curves, as shown in Fig. 3c.



**Figure S3.** CV curves of (a) Co-N/C and (b) CoFe-HN/C at different scan rates in  $\text{N}_2$ -saturated 0.1 M KOH solution.

## 7. The Koutechy-Levich plots (K-L) to calculate electron transfer number ( $n$ ).

The LSV measurement was carried out in O<sub>2</sub>-saturated 0.1 M KOH aqueous solution at 5 mV s<sup>-1</sup> with various rotating rates of 400, 625, 900, 1225, and 1600 rpm. The electron transfer number ( $n$ ) per oxygen molecule for ORR was determined on the basis of the Koutechy-Levich equations below.

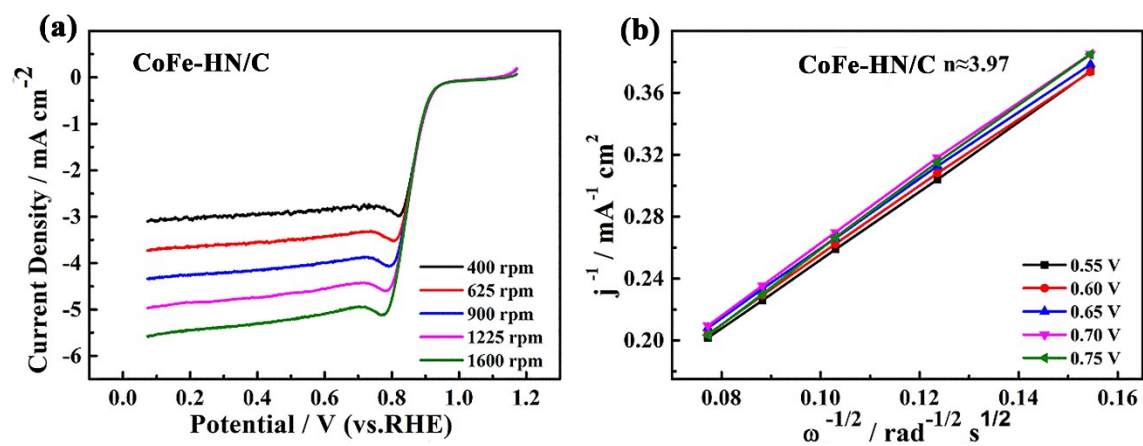
$$1/J = 1/J_L + 1/J_K = 1/B\omega^{0.5} + 1/J_K$$

$$B = 0.62n FC_0(D_0)^{2/3}\nu^{-1/6}$$

$$J_k = nFkC_0$$

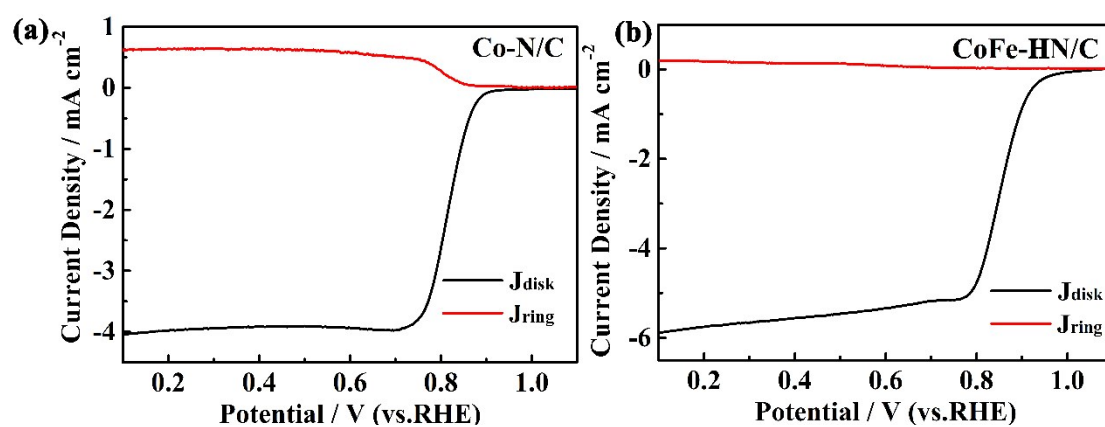
In the K-L equations,  $J$  represents the measured current density,  $B$  is called the Levich constant which is determined from the slope of the Koutechy-Levich (K-L) plot.

$J_L$  and  $J_K$  stand for the diffusion current densities and the kinetic-limiting current densities, respectively.  $F$  is Faraday constant, i.e., 96485 C mol<sup>-1</sup>,  $n$  is the transferred electron number,  $C_0$  represents the initial O<sub>2</sub> concentration in the electrolyte, i.e., 1.26 × 10<sup>-6</sup> mol cm<sup>-3</sup>,  $D_0$  represents the diffusion coefficient of O<sub>2</sub> in the 0.1 M KOH, i.e., 1.93 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>, and  $\omega$  represents the angular velocity of the electrode, rad s<sup>-1</sup>. Apart from that,  $\nu$  represents the kinetic viscosity of the electrolyte, which is 0.01009 cm<sup>2</sup> s<sup>-1</sup>, and the constant 0.62 is adopted only when the rotation rate is expressed in the form of rad s<sup>-1</sup>.



**Figure S4.** (a) LSV curves of CoFe-HN/C at different rotating rate and (b) the K-L equation to calculate  $n$ .

## 8. Rotating ring-disk electrode (RRDE) measurement



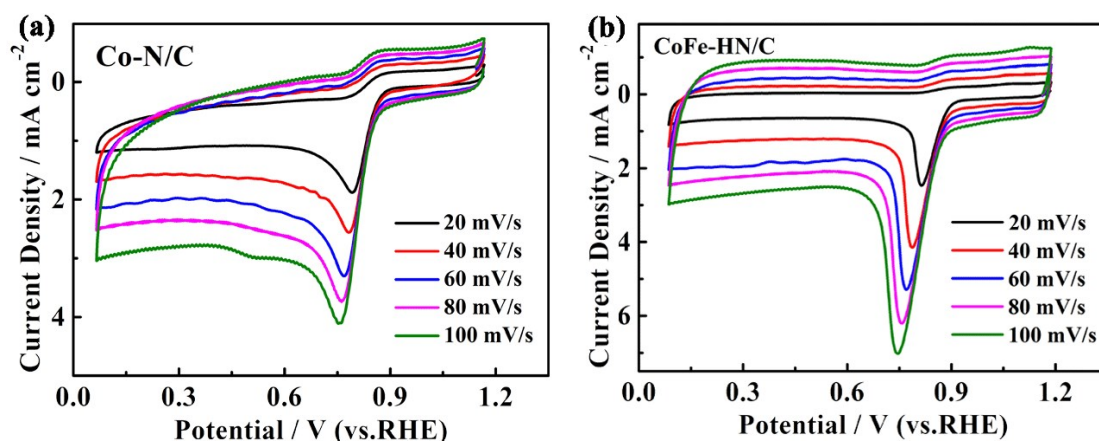
**Figure S5.** RRDE curves in  $\text{O}_2$ -saturated  $0.1 \text{ M KOH}$  at  $1600 \text{ rpm}$  for (a)  $\text{Co-N/C}$  and (b)  $\text{CoFe-HN/C}$ .

## 9. Mass transport

CV curves were measured at different scan rates from 10 to 100 mV s<sup>-1</sup>. The peak current is dictated by the mass diffusion coefficient as Randles–Sevcik equation as follows.

$$i_p = Bn^{3/2}AD^{1/2}C\nu^{1/2}$$

In the Randles–Sevcik equation,  $B$  is a constant equal to  $2.99 \times 10^5$ ,  $i_p$  stands for the peak current,  $n$  represents the number of transferred electrons, which has been mentioned above,  $A$  is the area of the electrode,  $D$  delegates the diffusion coefficient,  $C$  is on behalf of the concentration, and  $\nu$  represents the scan rate.



**Figure S6.** Cyclic voltammetry curves at various scan rates for (a) Co-N/C and (b) CoFe-HN/C.