

## Supporting Information

### **Noble Metal-Free Fe–N/C catalyst for Highly Efficient Oxygen Reduction Reaction Under Both Alkaline and Acidic Conditions**

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## EXPERIMENTAL SECTION

**Chemicals.** 11,11'-bis(dipyrido[3,2-a:2',3'-c]phenaziny)l (bidppz) was purchased from Jinan Henghua Sci. & Tec. Co., Ltd. Other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification.

**Catalyst Synthesis.** Fe–N/C catalyst was synthesized by pyrolysis of iron-complex precursor, which is described in detail below. To synthesize precursor, 0.0225 g (0.04 mmol) bidppz was added into 40 mL DMF and sonicated to form a homogenous solution, then, 0.0111 g (0.04 mmol) FeSO<sub>4</sub>•7H<sub>2</sub>O was added under vigorous stirring. After stirring for 10 min, the mixture was transferred into a 50 mL Teflon-lined stainless autoclave and heated at 160 °C for 8 h. The brown product was collected by centrifugation, then washed with DMF and ethanol for several times and dried in air at 60 °C overnight. Finally, the dried precursor was heated to 700, 750, 800, 850 and 900 °C for 1.5 h at a heating rate of 5 °C/min. The pyrolyzed product was ultrasonically leached in 6 M hydrochloride acid (HCl) for 8h to remove inactive iron species. The leached sample was washed to neutral with water for several times and dried in vacuum at 60 °C overnight.

**Catalyst characterization.** The X-ray powder diffraction (XRD) patterns of the samples were collected on a Rigaku/Max-3A X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ), the operation voltage and current was maintained at 40 kV and 200 mA, respectively. Raman spectra were recorded on a LabRAM HR Evolution Raman microscope with laser excitation at 514.5 nm. Scan electron microscopic (SEM) images were taken using a field-emission scanning electron microscope (JSM-6701F, JEOL) operated at an accelerating voltage of 5 kV. Transmission electron microscopic (TEM) images were taken on a Hitachi-7650 microscope with an accelerating voltage of 100 kV. The X-Ray photoelectron spectroscopy (XPS) was performed at a Perkin-Elmer RBD upgraded PHI-5000C ESCA system.

**Cyclic voltammetry (CV).** CV measurements of the catalysts were determined using a glassy carbon (GC) electrode. The GC electrode was polished using 0.05  $\mu\text{m}$  alumina slurry, rinsed with deionized water, then ultrasonically treated in water for 30 s for three times and washed with distilled water. A catalyst ink was prepared by dispersing 2 mg of the catalyst into 1 mL ethanol containing 10  $\mu\text{L}$  5% Nafion (D520, Dupont Inc., USA). Ten microliters of the catalyst ink was then deposited on a GC electrode with a surface area of 0.196  $\text{cm}^2$  with an overall catalyst loading of 0.1  $\text{mg cm}^{-2}$ . Electrochemical activities was conducted with a CHI 660D potentiostat in a three-electrode electrochemical cell with a platinum counter electrode, an Ag/AgCl reference electrode and with 0.1 M KOH or HClO<sub>4</sub> as the electrolyte. Electrolyte was saturated with oxygen by bubbling O<sub>2</sub> prior to each experiment. A flow of O<sub>2</sub> was maintained over the electrolyte during the measurements in order to ensure O<sub>2</sub> saturation. The scan rate was 10  $\text{mV s}^{-1}$ , and at least 10 cycles were performed before collecting the data. In control experiments, measurements were also performed in N<sub>2</sub> flowing through the electrochemical cell.

**Linear sweep voltammetry (LSV).** LSV measurements of the catalysts were determined using a rotating disk electrode (RDE) (Pine Research Instrumentation).

The working electrode was prepared by the same method as for CV. The scan rate of working electrode was  $10 \text{ mV s}^{-1}$  with varying rotating speed from 400 to 1600 rpm. The number of electrons transferred ( $n$ ) during ORR was calculated by Koutecky-Levich equation, at various electrode potentials:

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

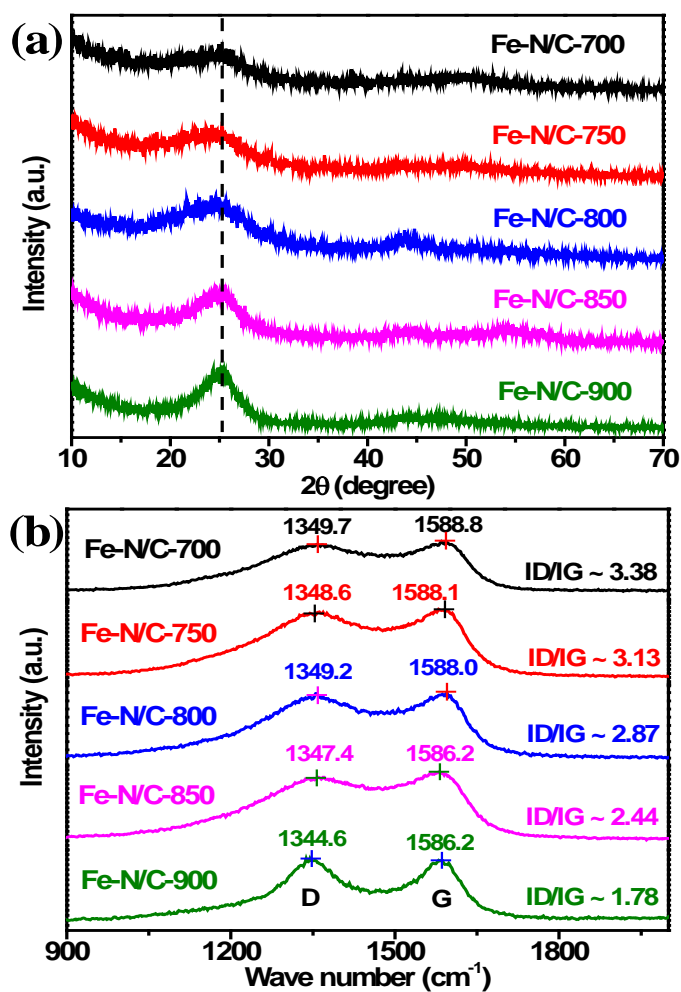
$$B = 0.62nFC_0D_0^{2/3} \nu^{-1/6}$$

where  $J$  is the measured current density,  $J_K$  and  $J_L$  are the kinetic and diffusion-limiting current densities,  $\omega$  is the angular velocity,  $n$  is transferred electron number,  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ),  $C_0$  is the bulk concentration of  $\text{O}_2$  ( $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ ),  $D_0$  is the diffusion coefficient of  $\text{O}_2$  in 0.1 M KOH and 0.1 M  $\text{HClO}_4$  ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), and  $\nu$  is the kinematic viscosity of the electrolyte ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ ). Rotating ring-disk electrode (RRDE) measurements was carried out to determine the four-electron selectivity. Before the experiments, the Pt ring electrode was activated through CV in 0.5 M  $\text{HClO}_4$  from 0 to 1.4 V vs. RHE at a scan rate of  $100 \text{ mV s}^{-1}$  for 10 minutes. For measurements, the electrolytes were 0.1 M KOH and 0.1 M  $\text{HClO}_4$ . The disk electrode was scanned at a rate of  $10 \text{ mV s}^{-1}$ , and the ring electrode potential was set to 1.2 V vs. RHE. The Hydrogen peroxide yield ( $\% \text{H}_2\text{O}_2$ ) and the electron transfer number ( $n$ ) were calculated by the followed equations:

$$\% \text{H}_2\text{O}_2 = 200 \frac{i_r/N}{i_d + i_r/N}$$

$$n = 4 \frac{i_d}{i_d + i_r/N}$$

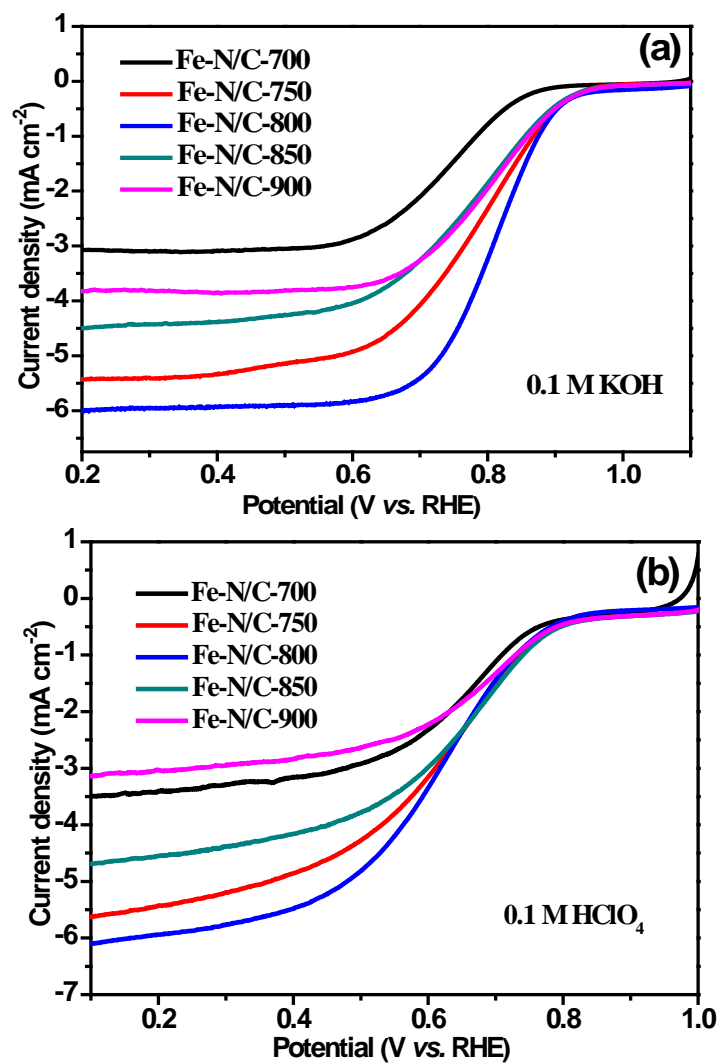
where  $i_d$  and  $i_r$  are the disk and ring currents, respectively.  $N$  is the ring current collection efficiency which was determined to be 37% by the reduction of 10 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  in 0.1 M  $\text{KNO}_3$ .



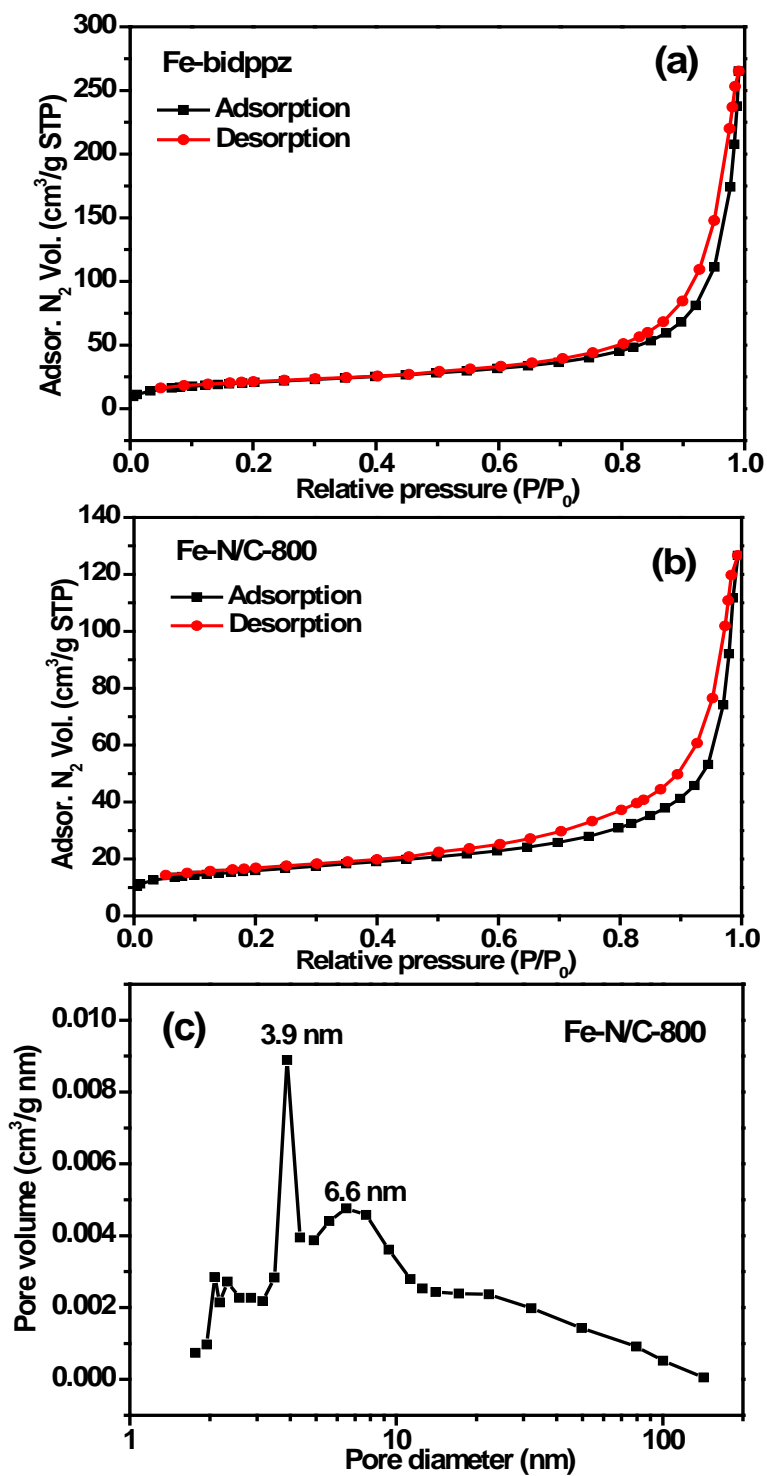
**Figure S1.** XRD patterns (a) and Raman spectra (b) of Fe-N/C catalysts pyrolyzed at different temperatures.

**Table S1.** Elemental compositions of Fe-N/C samples pyrolyzed at different temperatures determined by XPS.

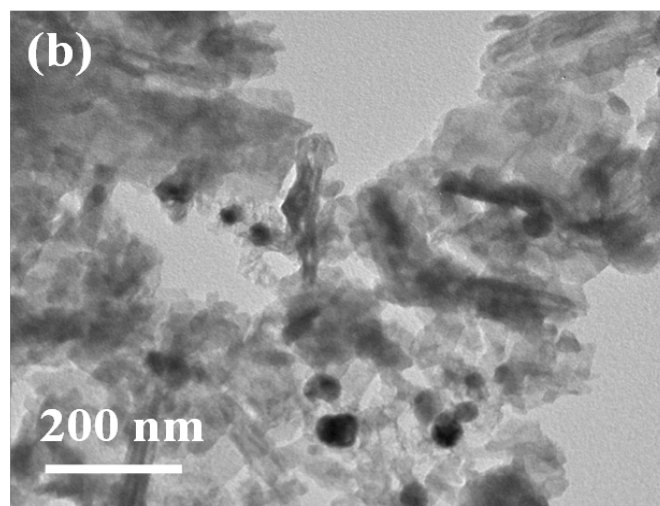
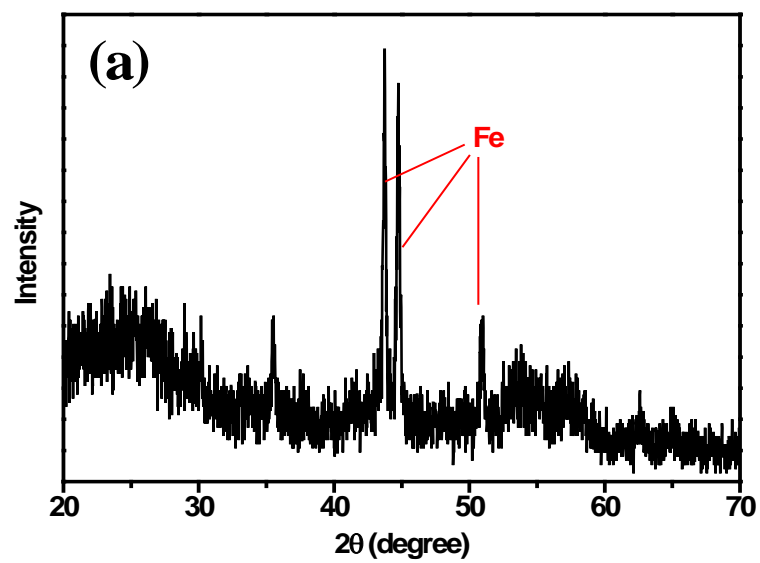
Temp/°C	C atom %	N atom %	O atom %	Fe atom %
700	82.45	12.54	4.42	0.59
750	84.02	11.78	3.69	0.51
800	87.25	9.62	2.85	0.28
850	92.22	6.23	1.38	0.17
900	96.04	3.12	0.73	0.11



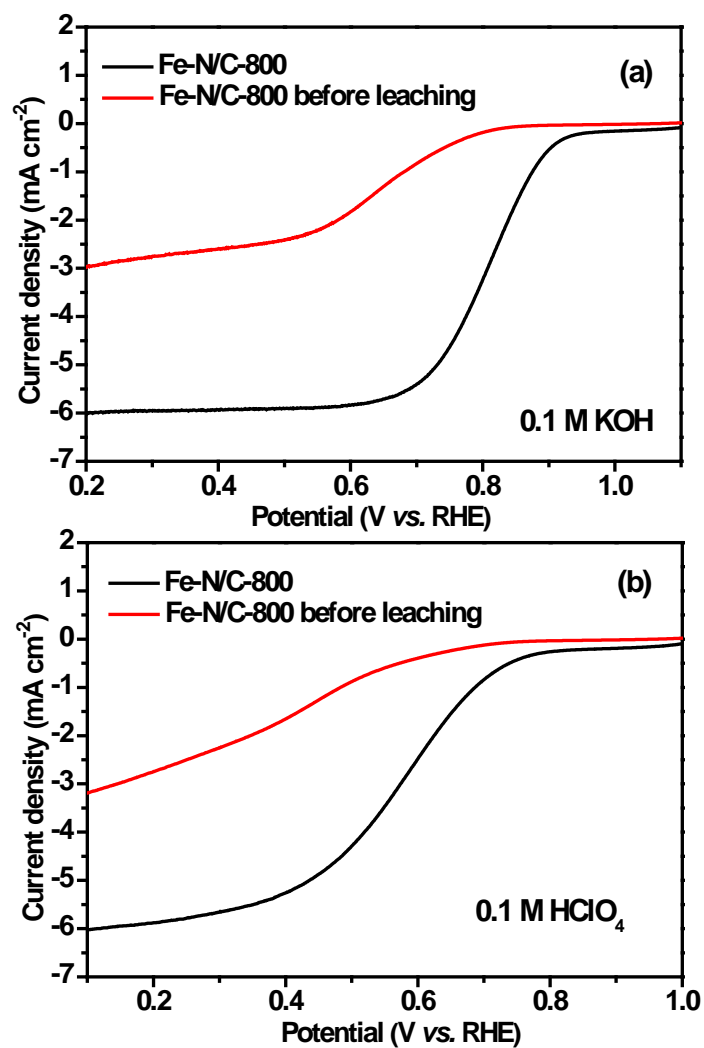
**Figure S2.** RDE voltammograms of Fe–N/C catalysts pyrolyzed at different temperatures in O<sub>2</sub>-saturated 0.1 M KOH (a) and 0.1 M HClO<sub>4</sub> (b). For all experiments, the rotating speed is 1600 rpm, the catalyst loading is 0.1 mg cm<sup>-2</sup> and the scan rate is 10 mV s<sup>-1</sup>.



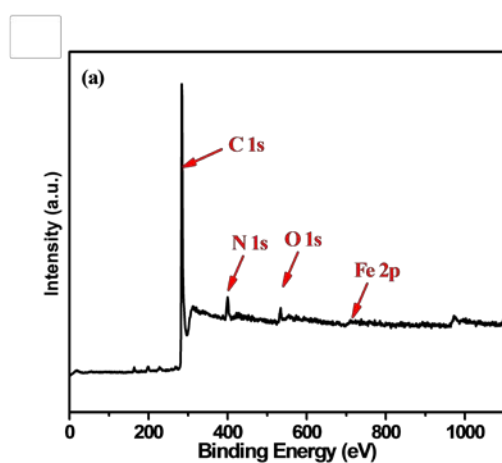
**Figure S3.** Nitrogen adsorption/desorption isotherms of Fe-bidppz (a), Fe-N/C-800 catalyst (b) and pore distribution in Fe-N/C-800 catalyst (c).



**Figure S4.** XRD pattern (a) and TEM image (b) of Fe-N/C-800 catalyst before leaching in 6 M HCl solution.

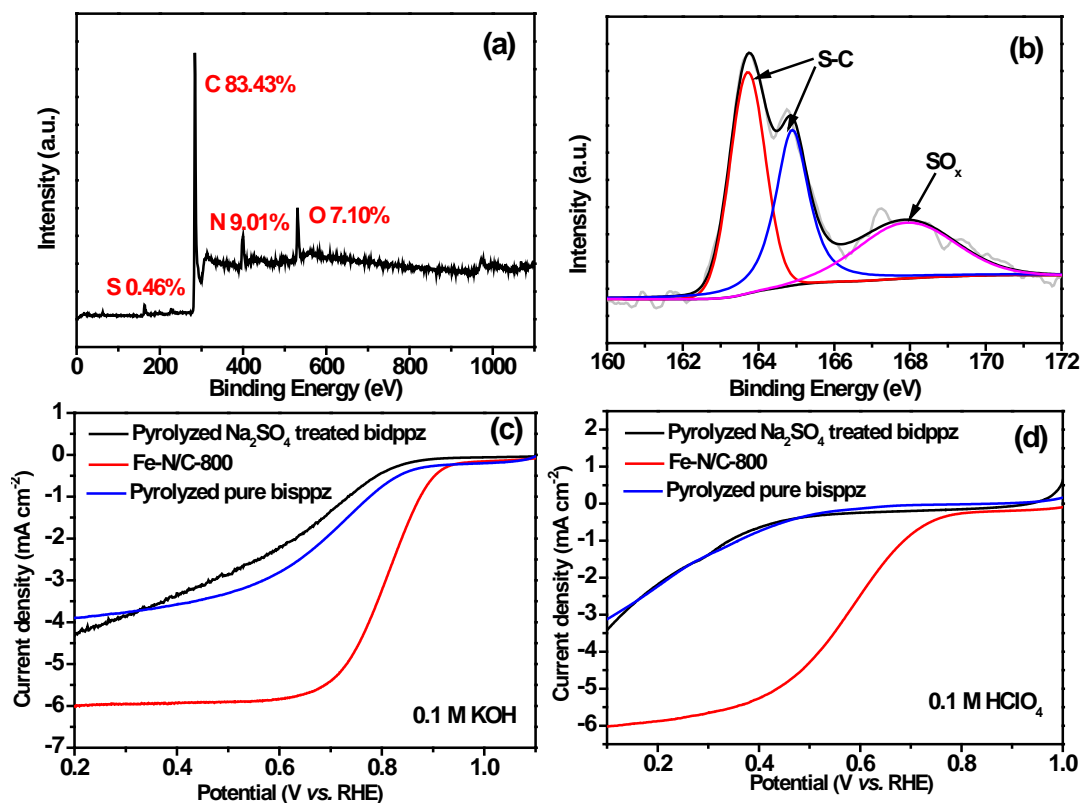


**Figure S5.** RDE voltammograms of Fe-N/C-800 catalyst in O<sub>2</sub>-saturated 0.1 M KOH (a) and 0.1 M HClO<sub>4</sub> (b) before and after being leached in acid. For all experiments, the rotating speed is 1600 rpm, the catalyst loading is 0.1 mg cm<sup>-2</sup> and the scan rate is 10 mV s<sup>-1</sup>.



**Figure S6.** XPS survey scan of Fe-N/C-800.



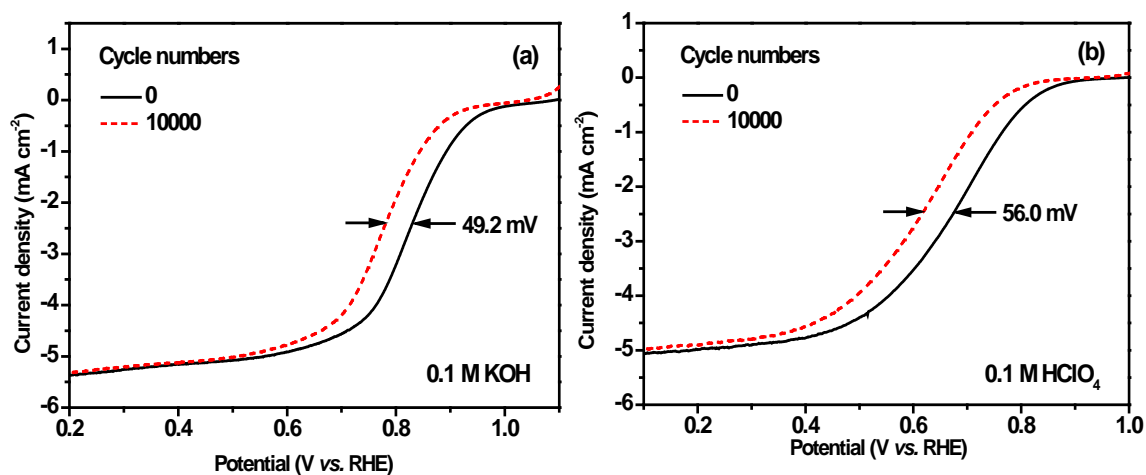


**Figure S7.** XPS survey scan (a) and S 2p XPS spectrum of pyrolyzed  $\text{Na}_2\text{SO}_4$  treated bidppz catalyst. RDE voltammogram of pyrolyzed  $\text{Na}_2\text{SO}_4$  treated bidppz catalyst, pyrolyzed pure bidppz catalyst and Fe-N/C-800 catalyst in  $\text{O}_2$ -saturated 0.1 M KOH (c) and 0.1 M  $\text{HClO}_4$  (d). For all experiments, the rotating speed is 1600 rpm, the catalyst loading is  $0.1 \text{ mg cm}^{-2}$  and the scan rate is  $10 \text{ mV s}^{-1}$ .

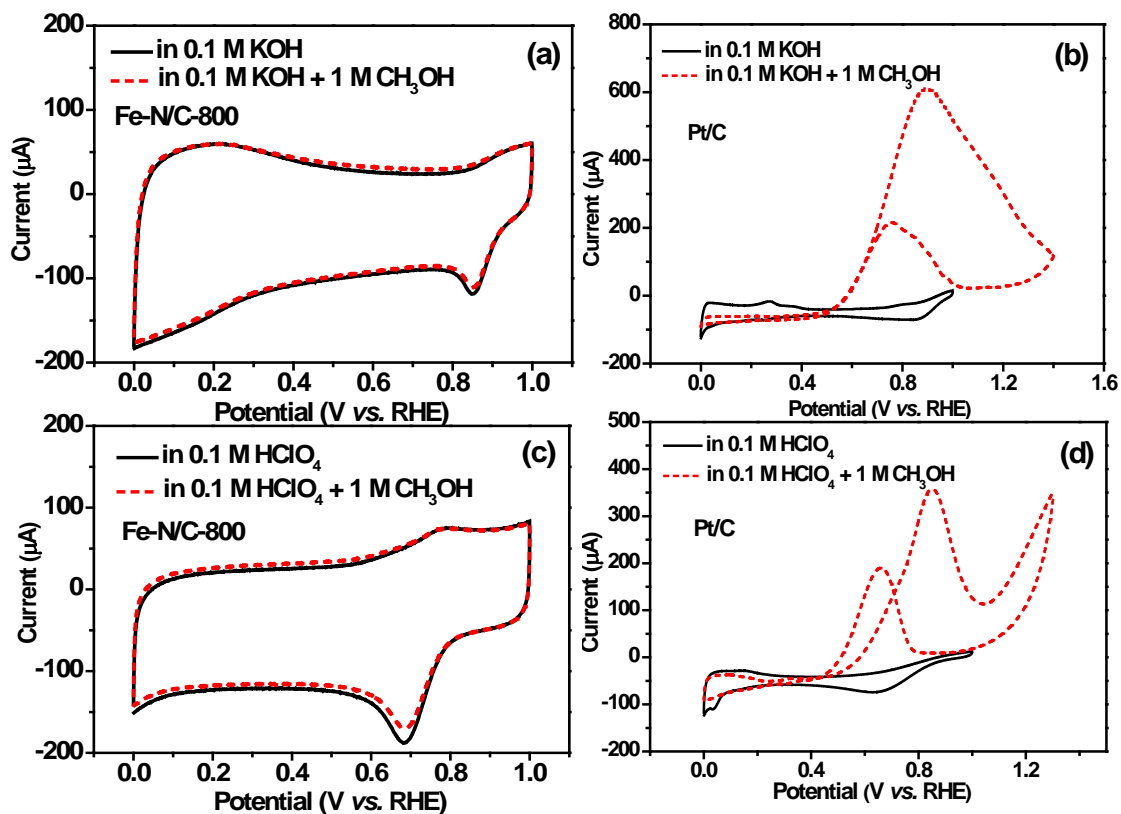
The XPS survey scan of pyrolyzed  $\text{Na}_2\text{SO}_4$  treated bidppz catalyst shows the presence of S. A detailed scan of S 2p shows three peaks: peaks at 163.7 and 164.8 eV belong to S-C species, and peak at 167.9 eV belongs to oxidized S ( $\text{SO}_x$ ), indicating S atoms are partially doped into carbon network. Similarly, the trace amount of S in our Fe-N/C-800 is likely to present in the form of S-C and  $\text{SO}_x$ , because our acid leaching process can remove all iron sulfide species. Electrochemical tests show that pyrolyzed  $\text{Na}_2\text{SO}_4$  treated bidppz catalyst shows an ORR activity comparable to pyrolyzed pure bidppz catalyst and much poorer than Fe-N/C-800 in both alkaline and acidic conditions. Therefore, the trace amount of S has no obvious contribution to our catalyst.

**Table S2.** Elemental compositions of pyrolyzed pure bidppz catalyst determined by XPS.

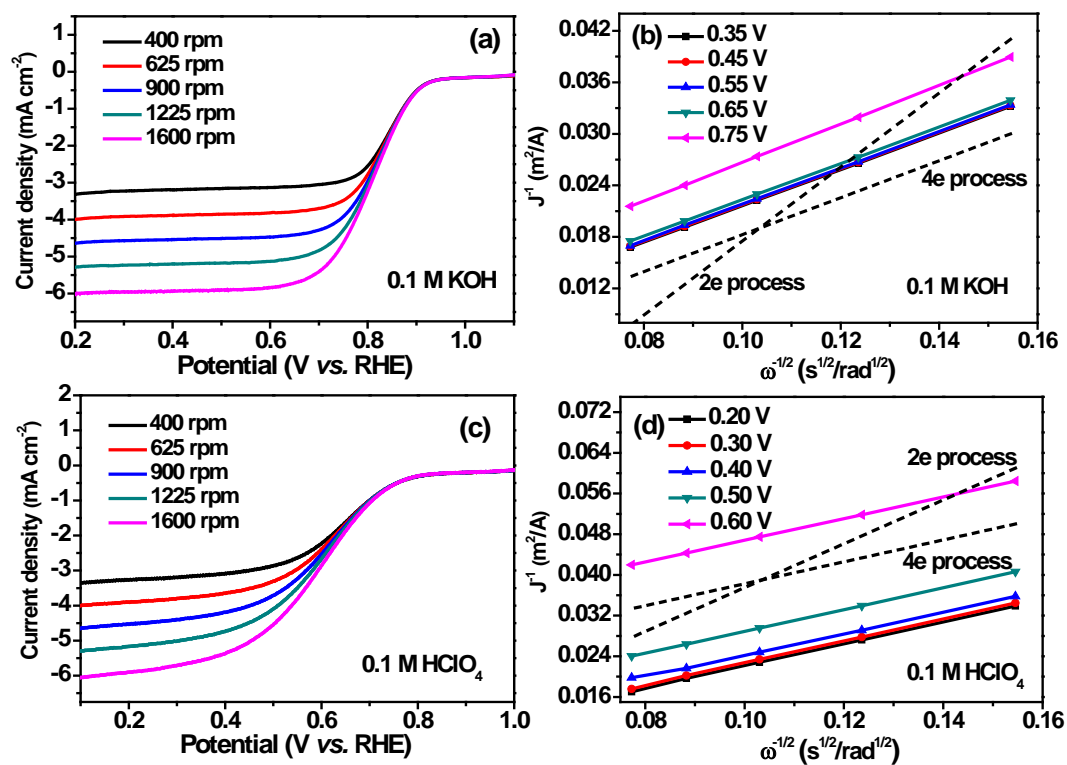
	C atom %	N atom %	O atom %	Fe atom %
Pyrolyzed bidppz	85.74	10.15	4.11	0



**Figure S8.** Endurance test of Pt/C catalyst for 10000 cycles in O<sub>2</sub>-saturated 0.1 M KOH (a) and 0.1 M HClO<sub>4</sub> (b). For all experiments, the rotating speed is 1600 rpm, the catalyst loading is 0.1 mg cm<sup>-2</sup> and the scan rate is 10 mV s<sup>-1</sup>.



**Figure S9.** Cyclic voltammograms of Fe-N/C-800 (a) and Pt/C (b) catalysts before and after adding 1 M CH<sub>3</sub>OH in O<sub>2</sub>-saturated 0.1 M KOH. Cyclic voltammograms of Fe-N/C-800 (c) and Pt/C (d) catalysts before and after adding 1 M CH<sub>3</sub>OH in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>. For all experiments, the catalyst loading is 0.1 mg cm<sup>-2</sup> and the scan rate is 10 mV s<sup>-1</sup>.



**Figure S10.** RDE voltammograms at different rotating speeds (a) and Koutecky-Levich plots (b) of Fe-N/C-800 in O<sub>2</sub>-saturated 0.1 M KOH. RDE voltammograms at different rotating speeds (c) and Koutecky-Levich plots (d) of Fe-N/C-800 in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>. For all tests, the catalyst loading is 0.1 mg cm<sup>-2</sup>, and the scan rate is 10 mV s<sup>-1</sup>.