Electronic Supplementary Information

MIL-100 Derived Nitrogen-Embodied Carbon Shells Embedded with Iron Nanoparticles

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Experimental Sections

1. Materials Preparation

1.1 Preparation of MIL-100-Fe
MIL-100-Fe-F was prepared by hydrothermal reactions following the procedures reported by Ferey et al.[1] A reaction mixture of molar composition 1.0 Fe: 0.66 trimesic acid: 2.0 HF: 1.2 HNO_3: 280 H_2O was held at 150°C in a Teflon-lined autoclave for 12h. The light-orange solid product was recovered by filtration and washed with deionized water, followed by treatment in hot DI water (80°C) and hot ethanol (60°C) sequentially to remove residual trimesic acid. The as-prepared material was degassed under vacuum at 150°C overnight before further treatment.

1.2 Preparation of Fe-NC-X
MIL-100-Fe (200 mg) was mixed with 5-aminotetrazole (400 mg) and grounded with pestle and mortar for 30 min. The mixture was sealed in the quartz tube and moved to the tube furnace, followed by a heating in the Ar flow for 3 h. The ramp was 6 °C /min and target temperature was set as X °C, where X= 600, 700, 800 and 900 respectively. The as-obtained samples were named as Fe-NC-600, 700, 800 and 900, respectively.

1.3 Preparation of NC-X
The as-obtained Fe-NC-X was placed in 5 M HCl aqueous solution and kept under stir for 24 h. The sample was then recovered by filtration and washed with H_2O and ethanol. The as-obtained samples were named as NC-600, 700, 800 and 900, respectively.

1.4 Preparation of MIL-dicyandiamide, urea and melamine

200 mg MIL-100-Fe was mixed with 400 mg dicyandiamide, urea or melamine and grounded with pestle and mortar for 30 min. The mixture was sealed in the quartz tube and moved to the tube furnace, followed by a heating in the Ar flow for 3 h. The ramp was 6 ^{o}C /min and target temperature was set as 800 ^{o}C. The as-obtained samples were placed in 5 M HCl aqueous solution and kept under stir for 24 h. The sample was then recovered by filtration and washed with H_2O and ethanol. The as-obtained samples were named as MIL- dicyandiamide, urea and melamine respectively.

1.4 Preparation of MIL-C

400 mg MIL-100-Fe was grounded with pestle and mortar for 30 min. The solid was sealed in the quartz tube and moved to the tube furnace, followed by a heating in the Ar flow for 3 h. The ramp was 6 ^{o}C /min and target temperature was set as 800 ^{o}C. The as-obtained samples were placed in 5 M HCl aqueous solution and kept under stir for 24 h. The sample was then recovered by filtration and washed with H_2O and ethanol. The as-obtained sample was named as MIL-C.

2. Electrochemistry measurement

Cyclic voltammetry (CV) experiments were carried out in O_2 or N_2 saturated 0.1 M KOH solution. The potential was varied from 0 V to 1.2 V at a scan sweep of 10mV/s. In rotating disk electrode (RDE) tests, the linear sweep voltammograms (LSVs) were carried out in O_2 or N_2 saturated 0.1 M KOH solution. The potential was scanned from 1.2 V to 0 V at a scan sweep of 10mV/s at various rotating speeds from 400 to 2500 rpm.

All the potentials are calibrated to the RHE potential according to the method reported in the literatures. The ORR current density is obtained by subtracting the current density measured in N_2-saturated electrolyte from the current density measured in O_2-saturated electrolyte. The onset ORR potential was defined as the electrode potential where ORR current density is 3 μA cm^{-2} in RDE polarization curves. The Koutecky-Levich (K-L) equations have been used to calculate the kinetic parameters:

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

$$B=0.62nFC_0D_0^{\frac{2}{3}}v^{-\frac{1}{6}}$$

$$J_K=nFkC_0$$

, Where J, J_K and J_L are the measured current density, kinetic- and diffusion-limiting current densities, respectively; ω is the angular velocity of the rotating disk, n is the electron-transfer number in ORR, F is the Faraday constant (F=96485 C/mo), C_0 is the bulk solubility of O_2, D_0 is diffusion coefficient of O_2, ν is the kinetic viscosity of the electrolyte, and k is the electron transfer rate constant. The number of electrons transferred (n) and J_K can be obtained from the slope and intercept of the K-L plots (In 0.1 M KOH, C_0=1.2×10^{-3} mol L^{-1}, D_0=1.9×10^{-5} cm s^{-1}, ν= 0.01 cm^2 s^{-1}).

Durability test was carried out in O_2 saturated 0.1 M KOH solution. The working electrode with active materials was rotating at a speed of 1600 rpm for over 11h

and the potential was set at 0.55 V. In methanol tolerance test, the reaction time was set as 2000 s while 3.5 mL methanol was added to KOH solution at 1000 s for NC-800. For Pt-C, the reaction time was set as 1500 s while 3.5 mL methanol was added to KOH solution at 500 s.

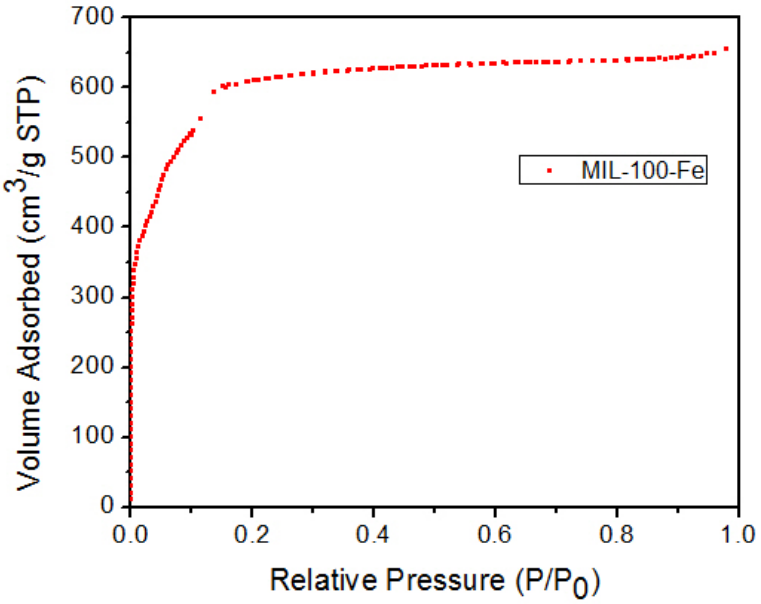


Figure S1 The nitrogen adsorption-desorption isotherms of MIL-100-Fe

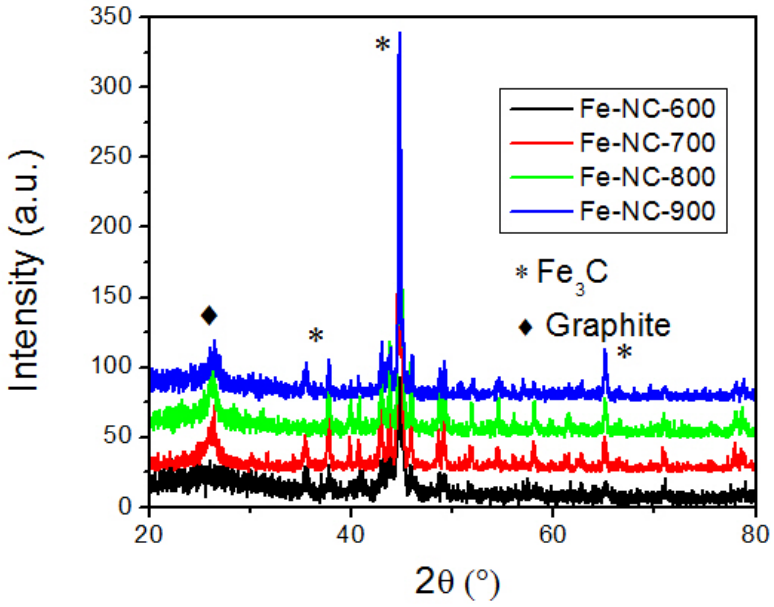


Figure S2 PXRD patterns of Fe-NC-600, 700, 800 and 900.

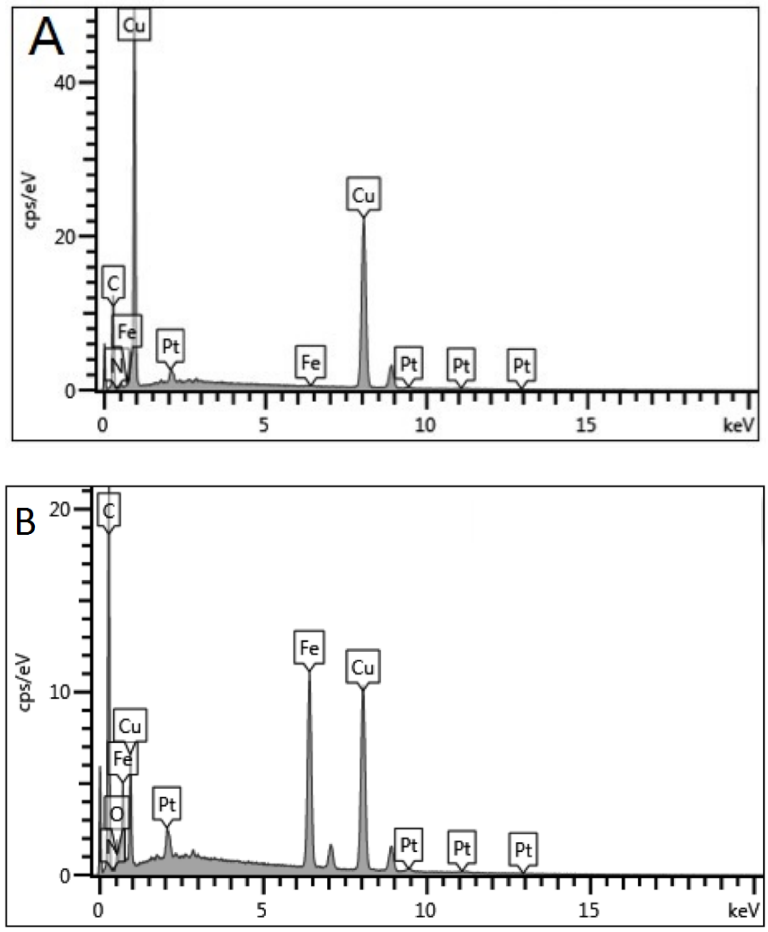


Figure S3 (A) The EDS spectrum of NC-800. (B) The EDS spectrum of Fe-NC-800. Pt signal comes from coating during SEM sample preparation and Cu signal comes from the SEM sample substrate we used.

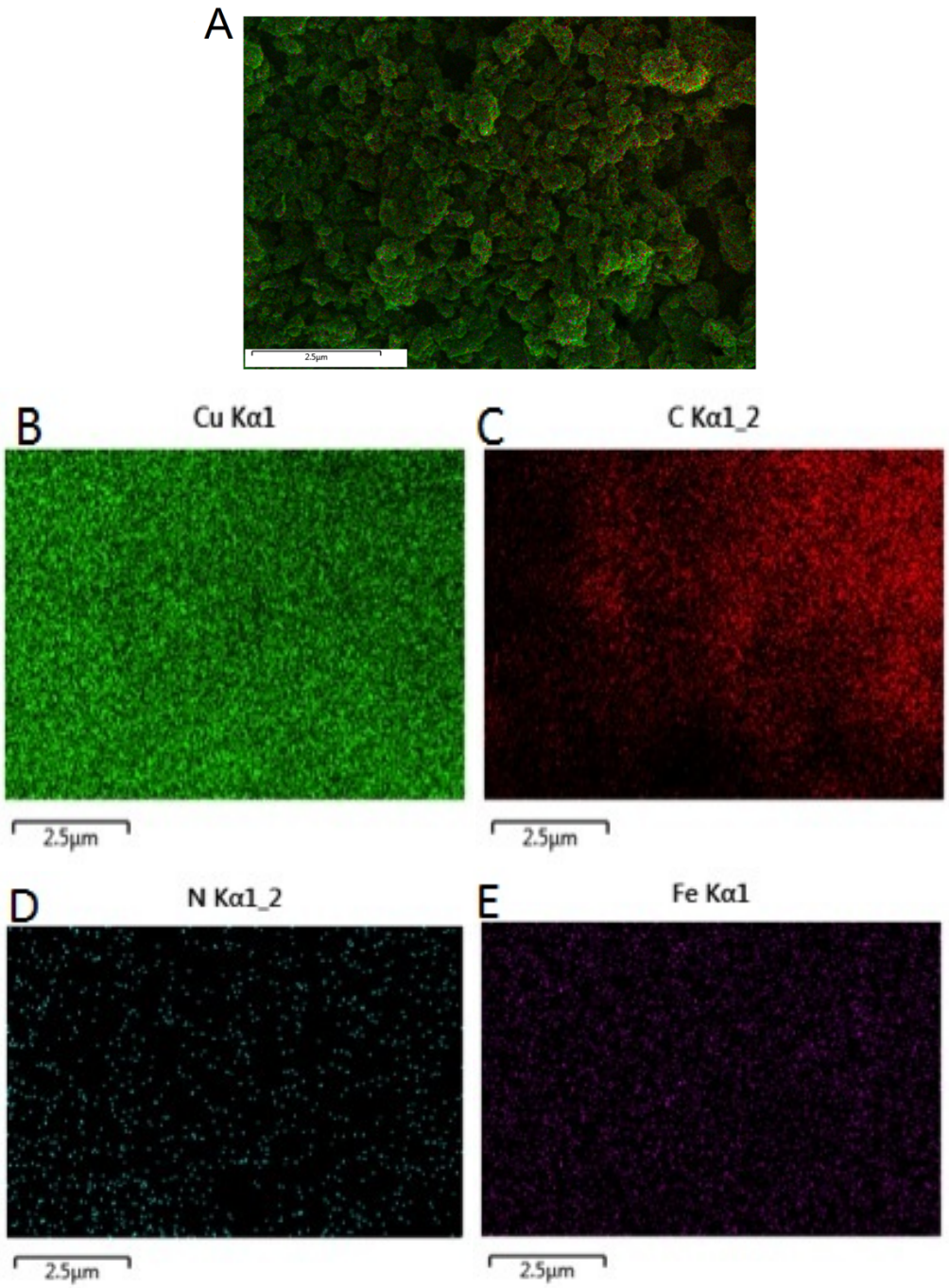
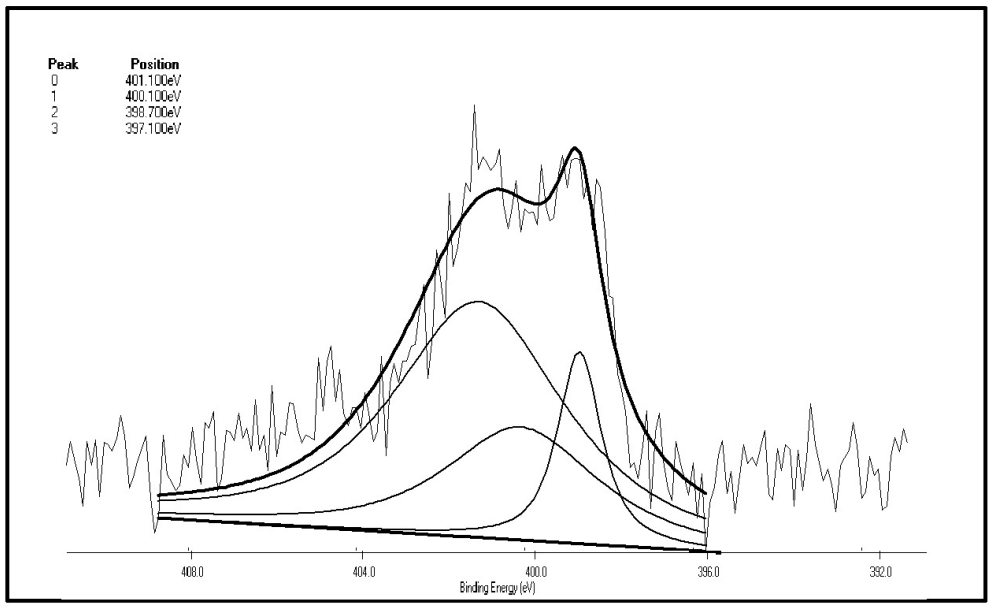


Figure S4. (A) EDS mapping result of NC-800 and (B, C, D, E) corresponding elements of Cu, C, N and Fe. Cu comes from the substrate we use.

A



B

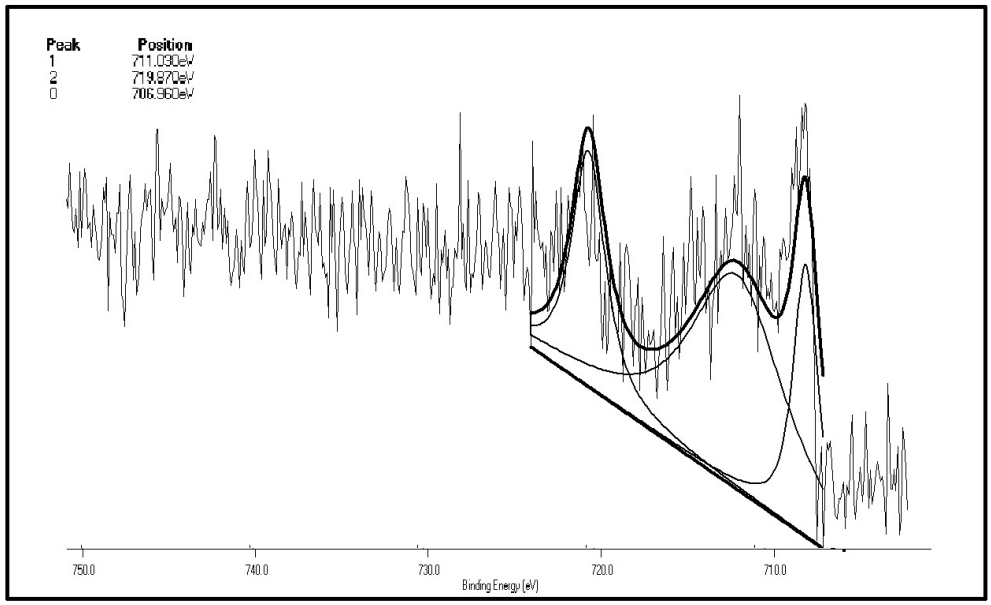


Figure S5. Deconvoluted XPS spectra of (A) N 1s and (B) Fe 2p from NC-800

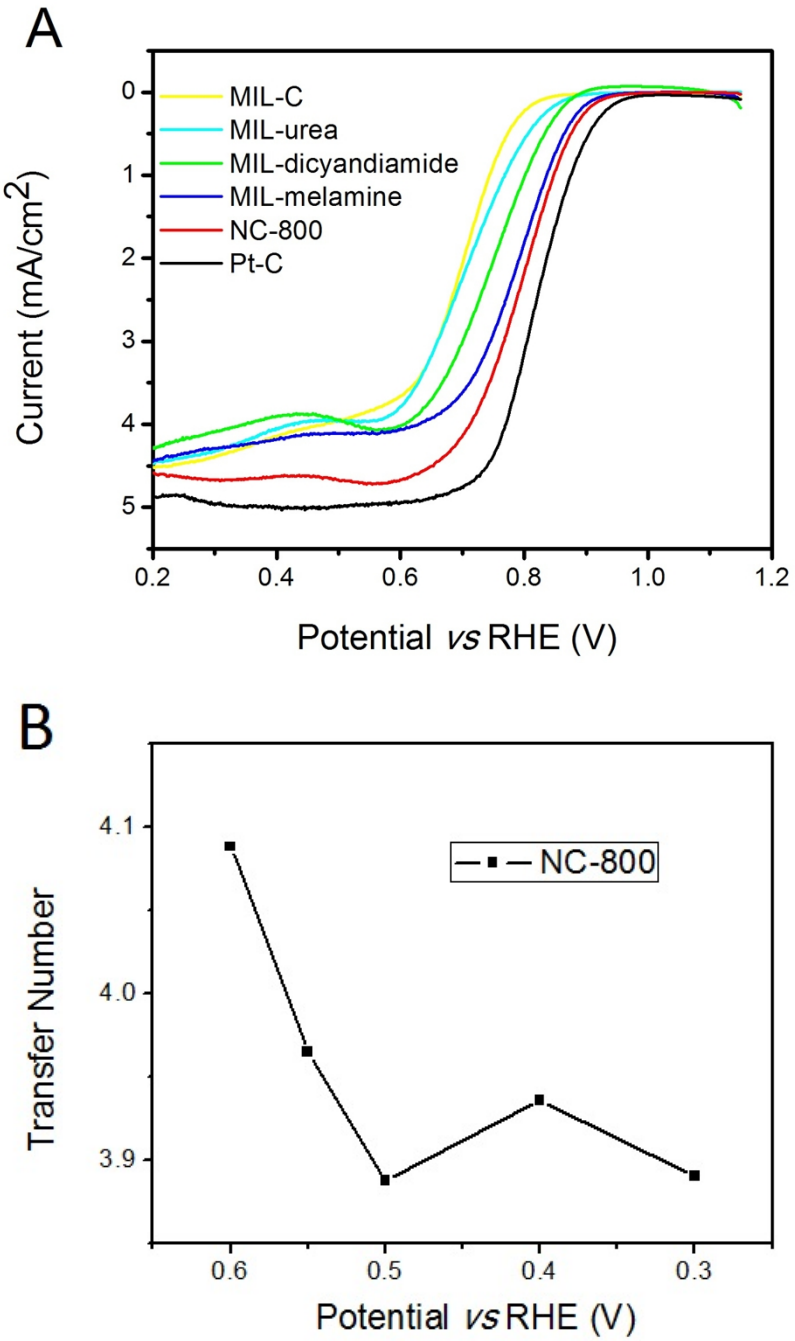


Figure S6 (A) Polarized curves of MILs annealed with different nitrogen-containing organics at a rotation speed of 1600 rpm (B) Electron transfer number of NC-800 at various potentials.

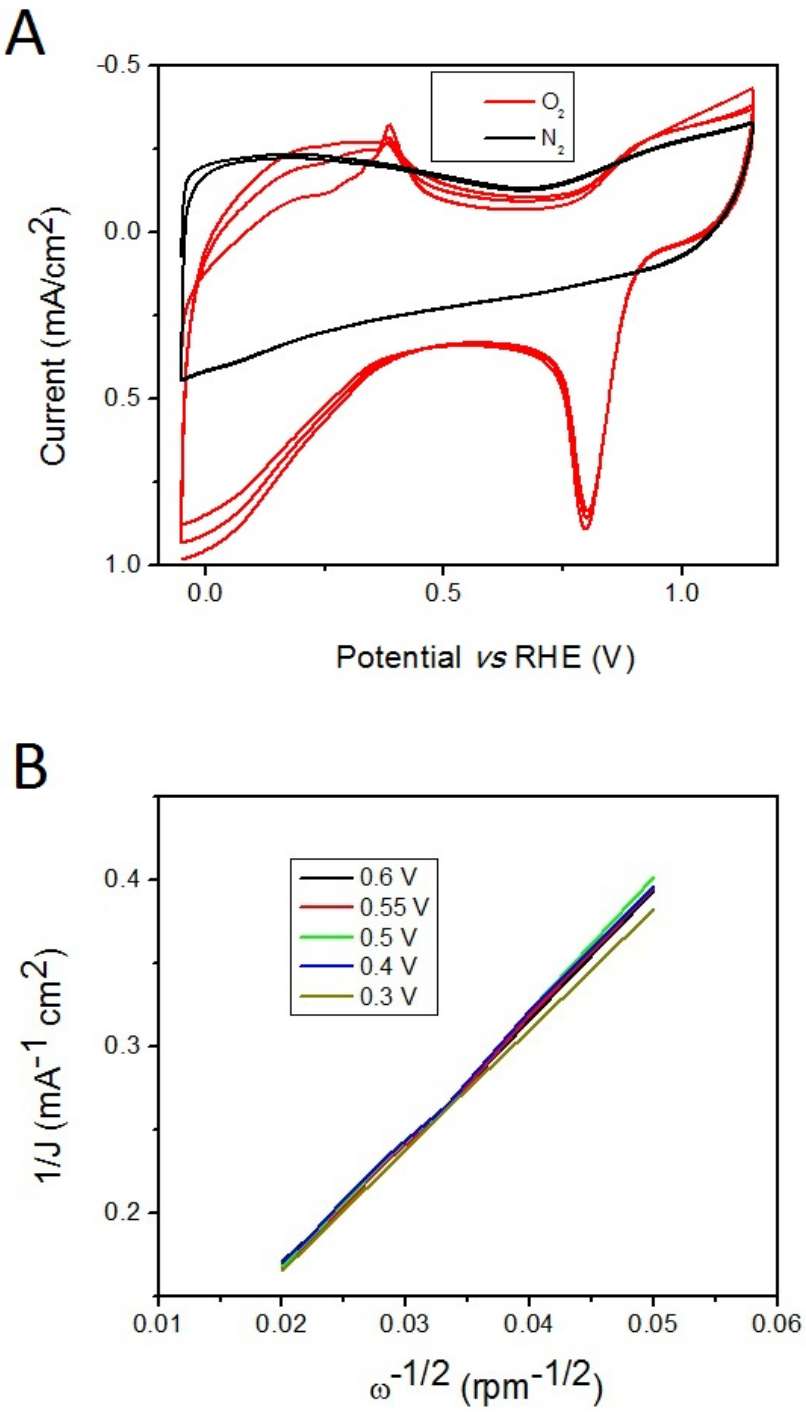


Figure S7 (A) CV curves of Fe-NC-800 in nitrogen and oxygen saturated 0.1M KOH electrolyte (B) K-L plots on Fe-NC-800 electrode.

Table S1 Elemental content of NC-800 obtained by EDS analysis.

Element	Line Type	Apparent Concentration	Atomic %	Standard Label	Factory Standard
C	K series	7.75	94.65	C Vit	Yes
N	K series	0.70	4.80	BN	Yes
Fe	K series	0.26	0.55	Fe	Yes
Total:			100.00		

REFERENCES

1. J. W. Yoon, Y.-K. Seo, Y. K. Hwang, J.-S. Chang, H. Leclerc, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, E. Bloch, P. L. Llewellyn, C. Serre, P. Horcajada, J.-M. Grenèche, A. E. Rodrigues and G. Férey, Angew. Chem., Int. Ed., 2010, 49, 5949–5952