

Supporting Information

Ion-exchanged route synthesis of Fe₂N/N-doped graphitic nanocarbons composite as advanced oxygen reduction electrocatalyst

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Experimental section

Synthesis of Fe₂N/NGC composites

In a typical synthesis, 2.54 g FeCl₂ was dissolved in 120 mL deionized water and then 8.5 g of polyacrylic weak-acid cation-exchanged resin (PWAR) were added. After magnetic stirring 6 h at room temperature, the process of Fe²⁺ ions coordinated with PWAR to form Fe²⁺-PWAR precursor was achieved. The Fe²⁺-PWAR precursor was firstly carbonized in a tube furnace at 1000 °C for 1h with a flowing argon rate of 80 mL min⁻¹, then ammonia was introduced to the tube furnace and further kept at this temperature for 2 h (the v/v ratio of NH₃/Ar is 1:2). Finally, the Fe₂N/NGC1-1000 was obtained. In order to study the effect of heated temperature and catalyst content on the ORR performance, the samples of Fe₂N/NGC1-900, Fe₂N/NGC1-1100, Fe₂N/NGC2-1000, Fe₂N/NGC3-1000 were also synthesized (the detailed experimental parameters were displayed in **Table S1**). Besides, the NGC was prepared by using 3 mol L⁻¹ HCl to remove the metal nanoparticles in Fe₂N/NGC1-1000 for comparison.

Table S1 The experimental parameters of the synthesized Fe₂N/NGC composites.

Samples	The dosage of catalyst (FeCl ₂ , g)	Heated temperature (°C)	Fe ₂ N content calculated from TG analyses (%)
Fe ₂ N/NGC1-900	2.54	900	26.3
Fe ₂ N/NGC1-1000	2.54	1000	26.3
Fe ₂ N/NGC1-1100	2.54	1100	26.3
Fe ₂ N/NGC2-1000	1.27	1000	10.8
Fe ₂ N/NGC3-1000	3.81	1000	56.2

Materials Characterization

X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advance diffractometer equipped with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation and a LynxEye Detector. X-ray photoemission spectroscopy (XPS) studies were carried out on a Kratos-AXIS ULTRA DLD with Al K α radiation source. The X-ray absorption spectra at Fe K-edge near the edge structure was recorded at a transmission mode by using ion chambers at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF) of China. The station was operated with a Si (111) double-crystal monochromator. The data were processed by using the program ATHENA, and all fits of the EXAFS data were performed with the program ARTEMIS.^[S1] Raman spectra were taken out with a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. Transmission electron microscopy (TEM) characterization was tested on a JEM-2100 electron microscope (JEOL) with an acceleration voltage of 200 kV. The weigh percents of Fe₂N in Fe₂N/NGC samples were analyzed by thermogravimetric (TG, SDTQ600).

Electrochemical measurements

The catalytic activity of the electrocatalysts for the ORR was carried out with a three-electrode system by using a Pine Instrument biopotentiostat. A rotating ring-disk electrode (RRDE) with a Pt ring (inner/outer-ring diameter: 6.25/7.92 mm) and a glassy carbon disk (diameter: 5.61 mm) was used as the working electrode. A home-made reversible hydrogen electrode (RHE) and platinum foil (1.0 cm²) were used as the reference electrode and the counter electrode, respectively. All electrochemical data were obtained at 25 °C. The working electrode was prepared as follows: A mixture of the electrocatalyst (5.0 mg), ethanol

(1.9 mL), and Nafion suspension (0.1 mL, 0.5 wt.%, DuPont, USA) was placed in an ultrasound bath for 30 min to obtain a well-dispersed electrocatalyst “ink”. Then, 30 μL of the electrocatalyst as-prepared ink was dropped onto the surface of the glassy carbon disk of the RRDE by using a microsyringe. After drying under an IR lamp, a thin-layer electrocatalyst was obtained. The ORR activities of the electrocatalysts were tested in O_2 -saturated 0.1 mol L^{-1} KOH aqueous solution in the potential range of $0.1\sim 1.1 \text{ V}$ (vs RHE) with a scan rate of 5 mV s^{-1} . The ring potential was held at 1.2 V versus RHE. The specific kinetic current densities (j_k) associated with the intrinsic activity of the catalysts can be obtained by Koutecky-Levich equation (eq 1):

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

where j_k is the kinetic current density, j_d is the diffusion-limited current density, ω is the angular frequency of rotation. The B parameter is defined as eq 2:

$$B = 0.62nFC_o D_o^{3/2} \nu^{-1/6} \quad (2)$$

where n is the overall number of electrons, F is the Faraday constant (96485 C mol^{-1}), C_o is the concentration of molecular oxygen in the electrolyte ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_o is the diffusion coefficient of the molecular O_2 in 0.1 M KOH solution ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and ν is the viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$).^[S2] The electron transfer number (n) were determined by the followed equations (eq 3):

$$n = 4 \times \frac{I_d}{I_d + I_r / N} \quad (3)$$

where I_r is ring current, I_d is disk current, and N is current collection efficiency of the Pt ring ($N=0.37$).

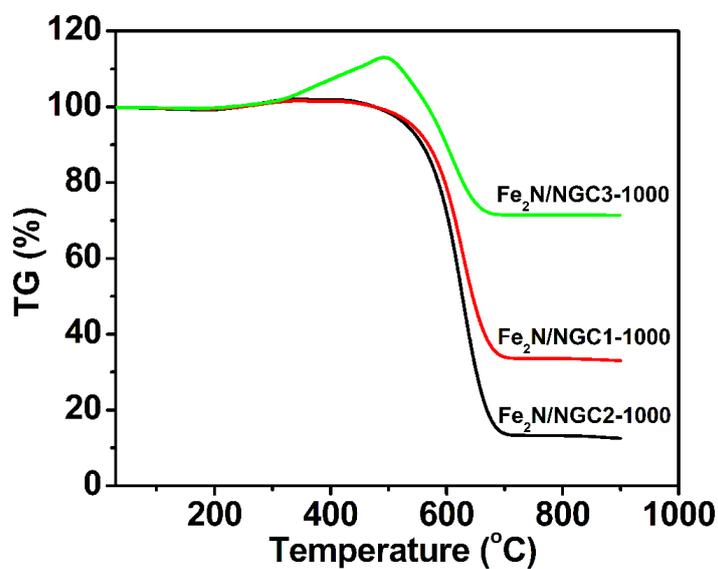


Fig. S1. TG curves of the Fe₂N/NGC samples in air at 5 °C min⁻¹ (30~900 °C).

Table S2 TG analyses results derived from **Fig. S1**.

Sample	Final residual mass after	Fe content calculated	Fe ₂ N content calculated
	TG tests (Fe ₂ O ₃ , %)	based on Fe ₂ O ₃ (%)	based on Fe ₂ O ₃ (%)
Fe ₂ N/NGC1-1000	33.4	23.4	26.3
Fe ₂ N/NGC2-1000	13.7	9.6	10.8
Fe ₂ N/NGC3-1000	71.4	49.9	56.2

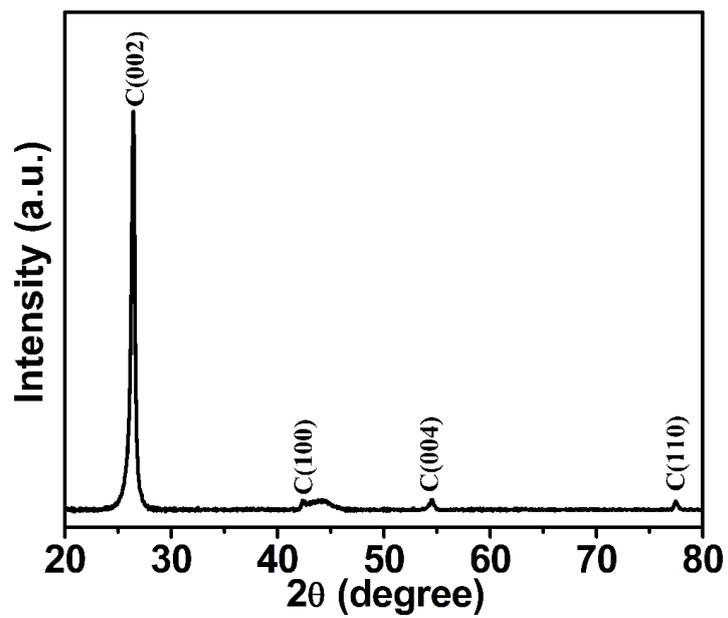


Fig. S2. XRD pattern of the NGC sample. NGC is prepared by using 3 M HCl to remove the metal NPs in Fe₂N/NGC1-1000.

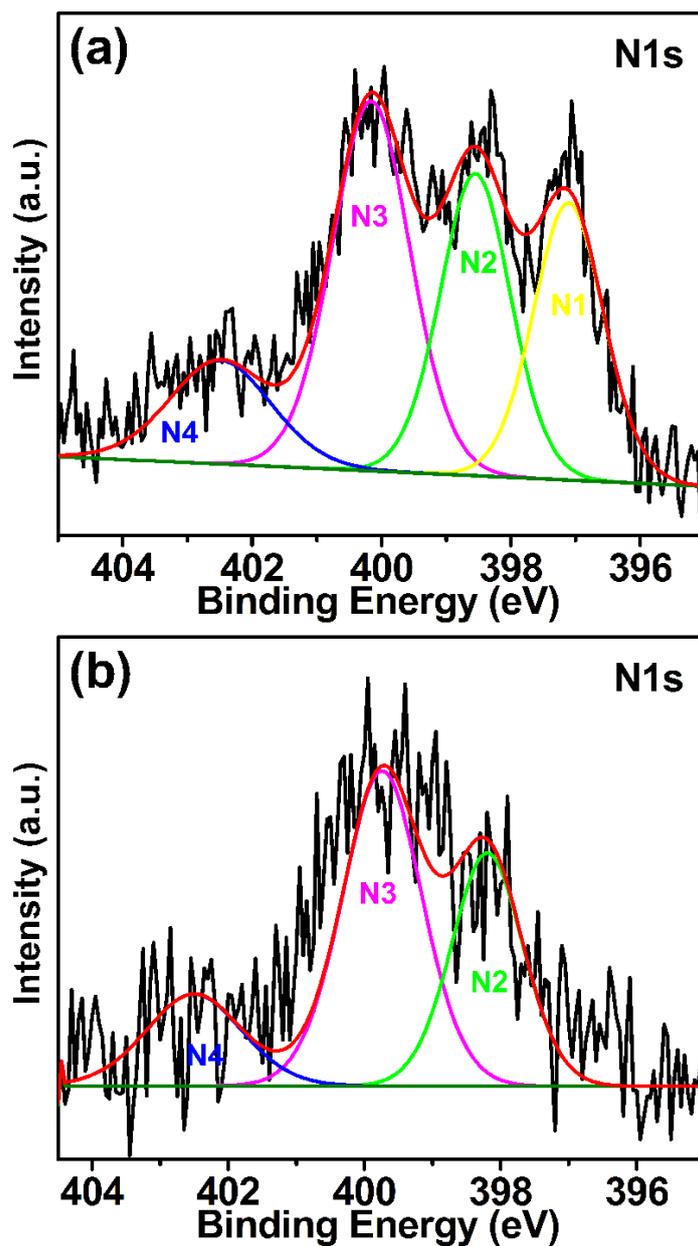


Fig. S3 The high-resolution N1s XPS spectra of (a) Fe₂N/NGC1-1000 and (b) NGC.

In order to confirm the existence of N-doping of graphitic carbon in the synthesized Fe₂N/NGC sample, the high-resolution N1s XPS spectra of Fe₂N/NGC1-1000 and NGC were analyzed as shown in Fig. S3. Compared to NGC, the N1s XPS spectra of Fe₂N/NGC1-1000 exhibits the extra N1 peak at 397.1 eV,

which is the typical characteristic of metal nitride. After removal of Fe₂N in Fe₂N/NGC1-1000 by HCl, the N1s XPS spectra of NGC also exhibited the three major peaks of N2, N3 and N4, implying the nitrogen could be doped into the graphitic carbon during the ammoniated process. The peaks of N2 (398.5 eV) and N3 (400.2 eV) are assigned to pyridinic-N and pyrrolic-N, respectively.^[S3, S4] The N4 peak at 402.5 eV is attributed to the nitrogen oxide functionalities (pyridinic-N⁺O⁻).^{[S5,}

S6]

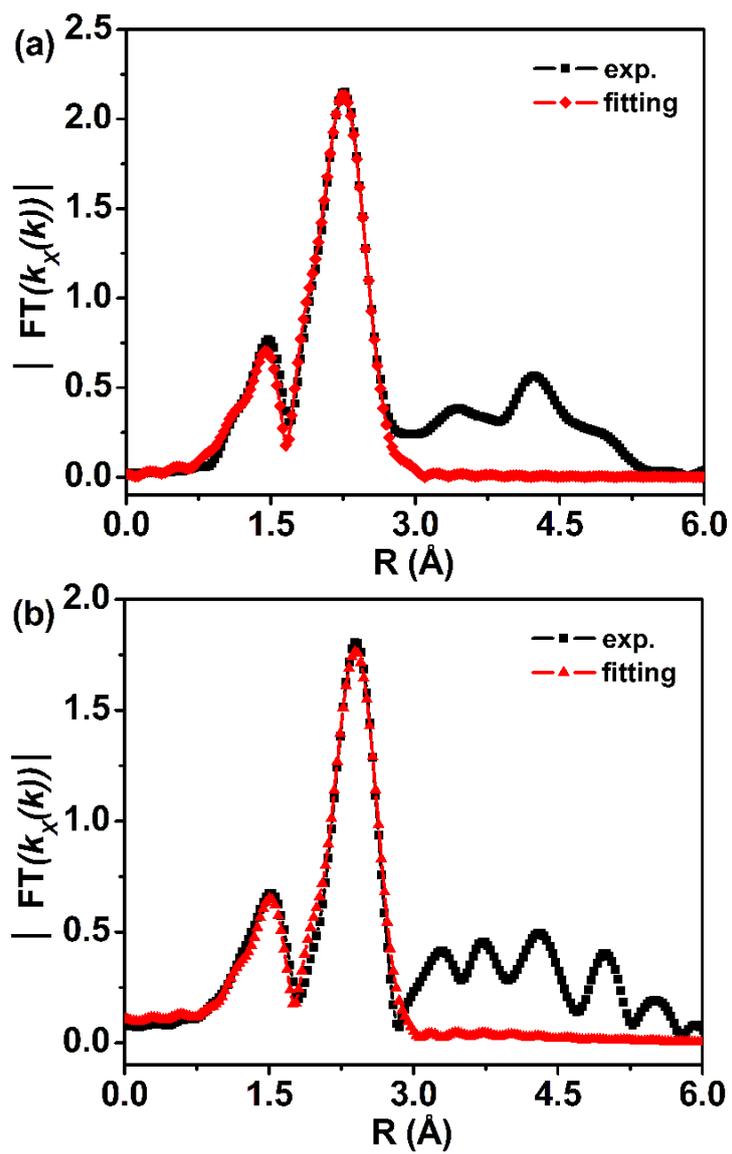


Fig. S4. Fourier transforms of experimental data (black line) and fit data (red line) for (a) $Fe_2N/NGC1-1000$ and (b) Fe_2N .

Table S3 Fit parameters of EXAFS spectra for Fe₂N/NGC1-1000 sample and standard Fe₂N.

samples	Shell	$N^{[a]}$	$R^{[b]}$	$\sigma^2 (10^{-3} \text{ \AA}^2)^{[c]}$	$\Delta E_0 (\text{eV})^{[d]}$
Fe ₂ N/NGC1-1000	Fe-N	1.1±0.2	1.93±0.03	6.0±5.0	1.4±0.8
	Fe-Fe	0.9±0.1	2.35±0.01	10.3±1.5	-10.1±1.5
	Fe-Fe	8.3±1.3	2.72±0.01	10.3±1.5	-10.1±1.5
Fe ₂ N	Fe-N	0.9±0.2	1.93±0.01	1.9±1.6	-3.8±0.8
	Fe-Fe	6.5±1.1	2.73±0.02	8.7±0.5	10.8±2.2

[a] Coordination number; [b] Distance between absorber and backscatterer atoms; [c] Debye–Waller factor; [d] Inner potential correction. Error bounds (accuracies) characterizing the structural parameters obtained by EXAFS spectroscopy are estimated as follows: coordination number $N \pm 20\%$; distance $R \pm 0.02 \text{ \AA}$, Debye–Waller factor $\sigma^2 \pm 10\%$; and inner potential correction $\Delta E_0 \pm 20\%$.

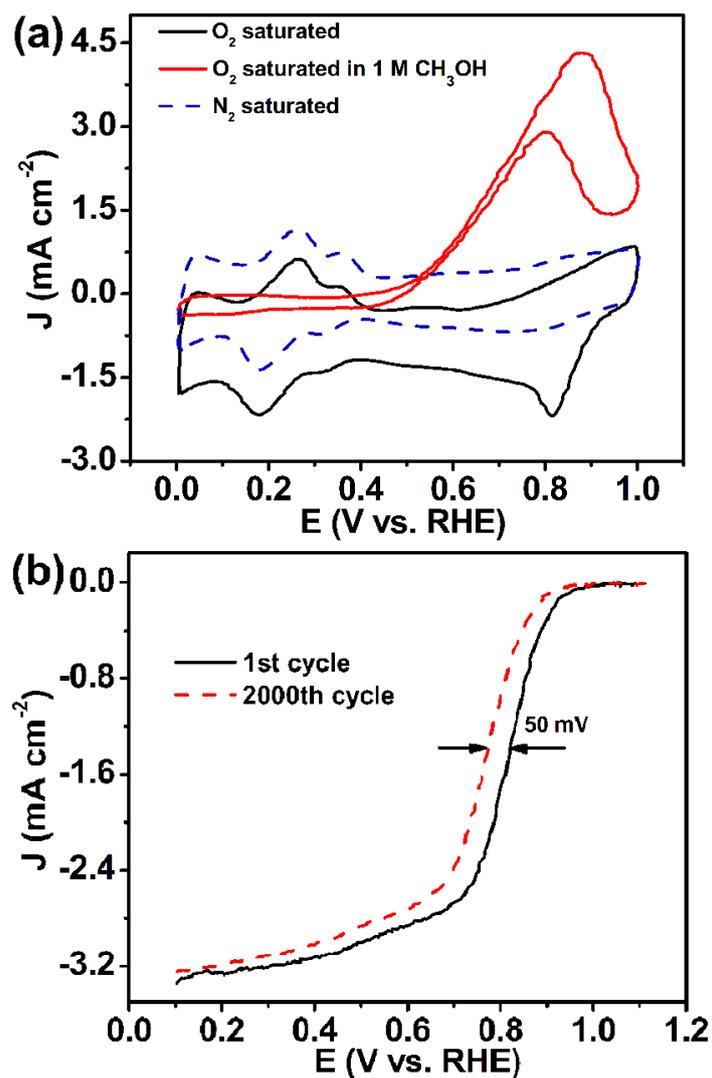


Fig. S5. (a) CV curves of commercial 20% Pt/C catalyst at a scan rate of 50 mV s⁻¹ in O₂- or N₂-saturated 0.1 M KOH solutions as well as O₂-saturated 0.1 M KOH solution with 1 M CH₃OH. (b) RDE voltammograms of Pt/C catalyst before and after 2000 cycles (rotation rate: 1600 rpm, scan rate: 5 mV s⁻¹).

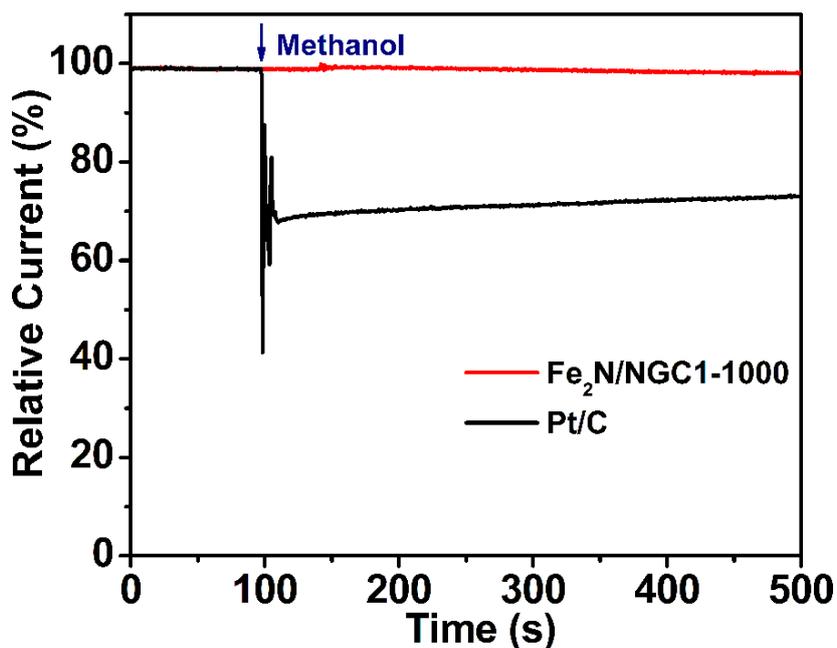


Fig. S6 The relative ORR cathodic current–time response (1600 rpm) of the Fe₂N/NGC1-1000 and Pt/C catalysts at 0.6 V in O₂-saturated 0.1 M KOH before and after adding 1 M methanol.

Resistance to crossover effects and stability of the cathodic catalyst are greatly important considerations for their practical application to fuel cells. The current–time responses to methanol introduced into an O₂-saturated electrolyte were measured for Fe₂N/NGC1-1000 and Pt/C catalysts, respectively. As shown in Fig. S7, no noticeable change was observed in the ORR current at the Fe₂N/NGC1-1000 catalyst after the addition of 1 M methanol to the O₂-saturated 0.1 M KOH electrolyte. In contrast, the ORR current for the Pt/C catalyst decreased sharply. The above results indicate that Fe₂N/NGC1-1000 exhibits high ORR selectivity and has a good ability for avoiding crossover effects, which is consistent with the CV curves (Fig. 3a).

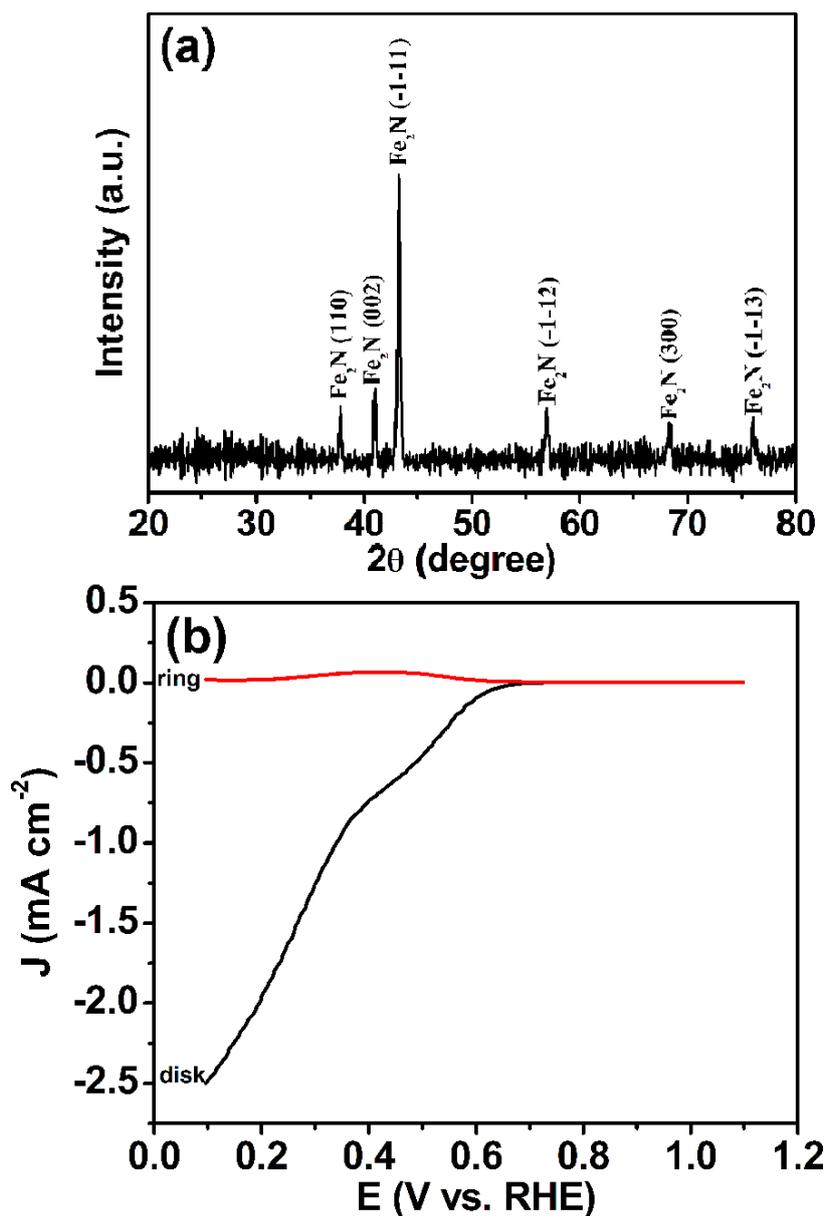


Fig. S7. (a) XRD pattern of the Fe_2N sample, which was prepared by treatment the commercial iron powder under ammonia at 1000 °C. (b) RRDE polarization curves of the Fe_2N catalyst in O_2 -saturated 0.1 M KOH solution at a scan rate of 5 mV s^{-1} and a rotation rate of 1600 rpm.

Because the Fe_2N catalyst without graphene could not be obtained by the present

ion-exchanged method, so we prepare the Fe₂N catalyst by treatment the commercial iron powder under ammonia at 1000 °C. The XRD pattern indicates the formation of Fe₂N (Fig. S7a). The RRDE polarization curves of the synthesized Fe₂N catalyst towards ORR was shown in Fig. S7b. It can be seen that the onset potential of ORR on the Fe₂N electrode was only about 0.67 V (vs. RHE). The poor performance is attributed the following reasons: Firstly, the Fe₂N derived from iron powder by a high-temperature treatment, resulting in the aggregation of Fe₂N NPs because of without any support in it; Secondly, there is no NGC support in the catalyst, so the relative poor conductivity of Fe₂N is not beneficial to the electron transport. The above reasons lead to the poor ORR performance of Fe₂N catalyst.

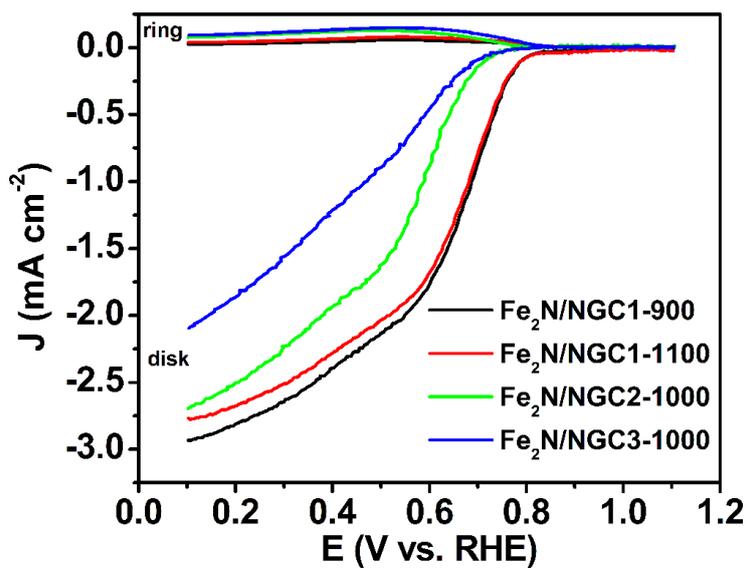


Fig. S8. RRDE polarization curves of the synthesized catalysts with different Fe_2N content and different heated temperature in O_2 -saturated 0.1 M KOH solution at a scan rate of 5 mV s^{-1} and a rotation rate of 1600 rpm.

Table S4 The ORR performance for the Fe₂N/NGC and NGC catalysts.

Catalysts	Onset potential (V)	Kinetic current at 0.6 V (<i>i_k</i>)	Electrons transfer number (n)
Fe ₂ N/NGC1-900	0.83	7.9	3.62
Fe₂N/NGC1-1000	0.84	13.8	3.98
Fe ₂ N/NGC1-1100	0.83	6.5	3.56
Fe ₂ N/NGC2-1000	0.77	2.3	3.41
Fe ₂ N/NGC3-1000	0.76	1.5	3.26
NGC	0.73	1.3	3.02
Pt/C	0.95	13.6	4.0

References:

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