Electronic Supplementary Information

Nitrogen-self-doped graphene-based non-precious metal catalyst with superior performance to Pt/C catalyst toward oxygen reduction reaction

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Experimental details

Materials synthesis

The N-doped graphene was prepared by a novel resin-based self-assembly growth methodology at large-scale. 20 g nitrogen-containing resin (N-resin), poly(acrylonitrile-divinylbenzene-triallyl isocyanurate), was immersed in 200 ml 1.0 mol L^{-1} HCl solution in order to remove impurities, and then washed by de-ionized water until the PH is 7, put the N-resin in a vacuum oven at 80 °C until the N-resin was dry. FeCl₂.6H₂O (3.76 g) was dissolved in 200 ml deionized water, and 20 g N-resin was added in the solution with magnetic stirring at 80 °C until the mixed slurry was dried. Then, the Fe-containing N-resin was heated in tube furnace at 900

 $^{\circ}$ C in the flowing high-purity gaseous argon (30 ml min⁻¹) for 1 h. For comparison, we adjusted the heating temperature from 700 $^{\circ}$ C to 1100 $^{\circ}$ C.

Material Characterization

The X-ray diffraction (XRD) analysis was performed on a D/Max-III (Rigaku Co., Japan) using Cu K α radiation, and operating at 40 kV and 30 mA. The 2 θ angular regions between 15° and 80° were explored at a scan rate of 6° min⁻¹. The Raman spectroscopic measurements were carried out on a Raman spectrometer (Renishaw Corp., UK) using a He/Ne laser with a wave length of 514.5 nm. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a XPS apparatus (ESCALAB 250, Thermo-VG Scientific Ltd.). Structural and morphological characterizations were carried out on a transmission electron microscopy (TEM, JOEP JEM-2010, JEOL Ltd.) operating at 200 kV, a field emission scanning electron microscope (FESEM,JSM-6330F, JEOL Ltd.) and the electron energy loss spectroscopic (EELS) mapping was carried on Field emission transmission electron microscopy (FETEM, FEI Tecnai G2 F30).

Electrochemical measurements

A bipotentiostat (Pine Instrument Company, USA) with rotating ring/disk electrode (RRDE) was used to perform the electrochemical measurements in a thermostat-controlled standard three-electrode cell at room temperature with a reversible hydrogen electrode (RHE) as the reference electrode (in a separate chamber and connected by a salt bridge), a piece of graphite $(10 \times 1 \text{ cm}^{-2})$ as the counter

electrode to avoid any possible contamination by Pt, and a rotating ring/disk electrode with a glassy carbon disk (5 mm in diameter) as working electrode. A suspension made with 10.0 mg electrocatalysts, 1.0 mL ethanol and 1.0 mL Nafion solution (0.05 wt %, DuPont, USA) was ultrasonicated for half an hour to form a well-dispersed ink. A pre-calculated amount of the ink was transferred onto the surface of the glass carbon electrode followed by drying under infrared lamp for 5 mins to form an electrocatalyst thin film.

The oxygen reduction reaction (ORR) experiments were carried out in an oxygen-saturated 0.1 mol L^{-1} KOH solution and 0.1 mol L^{-1} HClO₄ solution. The standard three-electrode cell was performed at 25[°]C in a thermostatic water both. The potential range was controlled between 0.05 and 1.1 V (vs. RHE) with a scan rate of 5 mV s⁻¹. For the ORR polarization curve, the rotating rate is 1600 rpm. Methanol-resistant and CO-resistant test of Fe-N-graphene and Pt/C were carried by *i-t* chronoamperometric responses technology. First the solutions were cleaned by the N₂, when the systems come to steady-state, we pumped O₂ into the solution, and the systems come to ORR steady-state after twenty minutes. And after for a while, we introduced 1.0 mol L-1 methanol or 3% CO into the solutions. The potential was hold at 0.7 V (vs RHE), and the rotating rate is 1600 rpm. The durability of the Fe-N-graphene electrode toward ORR was also performed by *i-t* chronoamperometric responses technology. The durability tests of the Fe-N-graphene and Pt/C electrodes were performed in O₂-saturated 0.1 mol L⁻¹ KOH and 0.1 mol L⁻¹ HClO₄ solution for

6 hours. The potential was hold at 0.7 V (vs RHE), and the he rotating rate is 1600 rpm.

The RHE was made by ourselves. In Figure 1, A and B are electrolysis electrodes for produce hydrogen, C is the stopcock valve, D is a fixed air inlet, E is for a counter electrode, G is for a working electrode and F is for the electrolyte. According to this design, the installation steps are shown below. Firstly, turn on the stopcock valve C, and then fill glass tube A and B with the same electrolyte as that in electrochemical cell, turn off the stopcock valve C immediately after the tube A and B are filled. Secondly, the electrode A and B, which both are Pt or Pt-black electrodes, will be connected to the positive and negative sides of a potentiostat or power supply, respectively. According to the reaction of electrolysis of water, hydrogen will generate in B electrode and A electrode produces oxygen. The oxygen produced in tube A should be released during the electrolysis. The liquid level in tube B will be at the position of half of the Pt electrode. It is prohibited that the whole Pt electrode disconnects with the electrolyte. Then, stop the electrolysis and close tube A to keep H₂ in a stable state. Thus, a fresh RHE is prepared. Lastly, opening the stopcock valve C, the electrolyte in the tube U is connected to the electrochemical cell by Luggin capillary.



Figure S1 The electrochemical cell for a rotating electrode and a reversible hydrogen electrode.

Additional characterization and analysis results

Figure S² shows the powder X-ray diffraction (XRD) patterns of samples derived from the samples with heated-treatment between 700 °C and 1100 °C. The diffraction peak at 20=26.2° is the characteristic of the graphite (002) plane, with the *d* value of 0.346 nm, while, the natural graphite is 0.335 nm. The slightly positive shift of the (0 0 2) peak probably is resulted from the enhancement of the compartment structure with nitrogen incorporation.^[S1] In the XRD patterns, the peak at 20 = 44.7° corresponds to the (110) basal plane differaction in the iron. The Figure 1a also indicates that the formation of Fe₃O₄ which is identified by the peaks at the 20 of 18.30°, 30.01°, 35.45°, 43.09°, 53.46°, 56.98° and 62.57°, corresponding to the (111), (220), (311), (400), (422), (511)and (440) facets of Fe₃O₄. The Fe-N-graphene composite was obtained at 900 °C.



Figure S2. The XRD patterns of samples derived from the samples with heated-treatment between 700 $^{\circ}$ C and 1100 $^{\circ}$ C.

Figure S³a shows the full scan spectra of the samples derived from the samples with heated-treatment between 700 °C and 1100 °C. The peaks at binding energy of 84.6 eV, 400.0eV, 533.15 eV and 720.0eV are ascribed to C1s, O1s, N1s and Fe2p3, respectively. The high-resolution N1s XPS spectra of the samples (Figure S3b) show that the nitrogen in the samples. Through curve deconvolution, the peaks at 398.55, 400.04 and 401.10 eV, assigned to pyridinic, pyrrolic and graphitic nitrogen species,^[S2] respectively. Figure S3c shows high-resolution XPS spectra of Fe2p3 in Fe-N-graphene. The atomic percentage of nitrogen in the samples decreased as the heated-treatment temperature increased (Table S1).



Figure S3. (a) The full scan XPS spectra of the samples derived from the samples with heated-treatment between 700 $^{\circ}$ C and 1100 $^{\circ}$ C. (b) High-resolution N1s XPS spectra of the samples with heated-treatment between 700 $^{\circ}$ C and 1100 $^{\circ}$ C, the N1s peak can be fitted by there Lorentzian peaks at 398.55, 400.05 and 401.10 eV, which

are pyridinic nitrogen, pyrrolic nitrogen and graphitic nitrogen., respectively. (c) High-resolution Fe2p3 XPS spectrum of the samples with heated-treatment between 700 °C and 1100 °C. The Fe2p3 peaks at 711.2, 720.1 and 725.3.3 eV, assigned to Fe2p_{3/2}, Fe2p₁ and Fe2p_{1/2} iron species, respectively.

Table S1. Nitrogen and iron content of the samples derived from the samples with heated-treatment between 700 $^{\circ}$ C and 1100 $^{\circ}$ C.

	Sample-70	Sample-80	Sample-90	Sample-100	Sample-110
	0	0	0	0	0
N1s At.%	6.80	6.66	2.47	1.04	0.86
Fe2p3	2.57	2.45	1.89	1.13	1.05
At.%					

Figure S4 shows the comparison of ORR performance of different resin-derived catalysts and Pt/C materials. The results show that the ample-900 (Fe-N-graphene) has the best ORR activity in the non- precious metal catalysts.



Figure S4. ORR polarization plots measured with different resin-derived catalysts and Pt/C materials: 1, sample-700; 2, sample-800; 3, sample-900 (Fe-N-graphene); 4, sample-1000; 5, sample-1100. non–precious metal catalyst loading: 0.4 mg_{cat} cm⁻². 6, Pt/C ($20 \mu g_{Pt} cm^{-2}$). Electrolyte: O₂-saturated 0.1 mol L⁻¹ KOH solution; temperature, 25°C. RDE rotating speed,1600 rpm. Scan rate: 5 mV s⁻¹.

The peroxide yield values were calculated with the following equation:^[S3]

$$n = \frac{4I_d}{I_d + (I_R / N)} \tag{1}$$

$$H_2O_2 \% = 100\frac{(4-n)}{2}$$
 (2)

The Figure S⁵a shows the ring current in the ORR test, from which the electron transfer number (n) and the peroxide yield can be calculated with above equations. The results are shown in Figure S⁵b. The n of Fe-N-graphene is the biggest at various potentials. And the percentage of the H_2O_2 generated on the Fe-N-graphene is the least of the three catalyst in the whole potential range.



Figure S5. (a) Ring currents of the N-doped graphene 0.4 mg_{cat} cm⁻²), Fe-N-graphene (0.4 mg_{cat} cm⁻²), and Pt/C ($20 \mu g_{Pt} cm^{-2}$) in O₂-saturated 0.1 mol L⁻¹ KOH solution. (b) The electron transfer number (n) (dotted line) and the percentage of the H₂O₂, based on the corresponding RRDE data in (a).



Figure S6. The comparison of the ORR performance of Fe-N-graphene and Pt/C catalyst under the same loading $(20\mu g_{metal} \text{ cm}^{-2})$ in O₂-saturated 0.1 mol L⁻¹ KOH at a rotating rate of 1600 rpm.



Figure S7. ORR polarization plots measured with different resin-derived catalysts and Pt/C materials: 1, sample-700; 2, sample-800; 3, sample-900 (Fe-N-graphene); 4, sample-1000; 5, sample-1100. non-precious metal catalyst loading: 0.4 mg_{cat} cm⁻². 6,

Pt/C (20 μ g_{Pt} cm⁻²). Electrolyte: O₂-saturated 0.1 mol L⁻¹ HClO₄ solution;





Figure S8. (a) Ring currents of the N-self-doped graphene (0.4 mg_{cat} cm⁻²), Fe-N-graphene (0.4 mg_{cat} cm⁻²), and Pt/C ($20 \mu g_{Pt} cm^{-2}$) in O₂-saturated 0.1 mol L⁻¹ KOH solution and (b) the electron transfer number (n) (dotted line) and the percentage of the H₂O₂, based on the corresponding RRDE data in (a).

References:

- [S1] J. W. Jang, C. E. Lee, S. C. Lyu, T. J. Lee, C. J. Lee, Appl. Phys. Lett. 2004, 84, 2877-2879.
- [S2] D. Yu, Q. Zhang, L. Dai, J. Am. Chem. Soc. 2010, 132, 15127-15129.
- [S3] H. Meng, N. Larouche, M. Lefèvre, F. Jaouen, B. Stansfield, J.-P. Dodelet,

Electrochim. Acta a 2010, 55, 6450-6461.