Electronic supplementary information

Air plasma etching towards rich active sites in Fe/N-porous carbon for oxygen reduction reaction with superior catalytic performance

Experimental

Synthesis of chitin-based carbons

The raw material chitin (practical grade) was purchased from Sigma Chemical. To prepare porous carbons, chitin was first pre-oxidized at 250°C for 2h in air (labeled as PC-250), which was then mixed with FeCl₃ and ZnCl₂ with a mass ratio of 1:3:1 (PC-250 : FeCl₃ : ZnCl₂). The mixture was then treated in a tubular furnace in a N₂ atmosphere by heating at a rate of 5°C min⁻¹ and held at 800°C for 2h. Subsequently, the sample was soaked in 2M hydrochloric acid and washed with deionized water to remove iron compounds until a neutral pH was reached. The product was then dried at 80°C for 12 h and the final product was labeled as Fe-N/C.

The pre-oxidized chitin (PC-250) was also mixed with only $ZnCl_2$ with a mass ratio of 1:1 and carbonized under the same conditions as Fe-N/C. The obtained carbon was labeled as N/C.

Plasma treatment of the obtained catalyst samples

A plasma cleaner (PCE-6, MTI Co. Ltd.) was reconfigured for the plasma irradiation process. The plasma is ignited by the radio frequency (RF) power introduced by the coil. A typical process of plasma irradiation is as follows: the Fe-N/C catalyst was placed on the sample stage and the chamber was evacuated and then a gas flow of air was introduced to the chamber to reach 80 Pa for the plasma ignition. A radio frequency power of 29.6 W was applied for a desired period of time, ranging from 30 s to 240 s. The resultant samples were denoted as Fe-N/C-0, Fe-N/C-30, Fe-N/C-60, Fe-N/C-120 and Fe-N/C-240. The N/C catalyst was also etched under the same conditions as denoted as N/C-0, N/C-30, N/C-60 and N/C-120, respectively.

Structural characterization

The crystallite structure was investigated by XRD (Bruker/D8 Advance) with Cu Ka radiation. The morphology and microstructure were inspected using an field emission SEM (FESEM, JEOL JSM-7800F) and TEM (JEM-2100), respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed on an Ultra DLD using a monochromic Al X-ray source. Raman spectra were obtained using a Renishaw/INVIA REFLEX spectrometer coupled with a 633 nm laser. FTIR spectra were collected using a Nicolet 6700 spectrometer. Nitrogen adsorption-desorption isotherms were measured using a BELSORP-max. The specific surface area and pore size distribution were determined using the Brunauer-Emmett-Teller (BET) theory and the nonlocal density functional theory (NLDFT) method, respectively. Mössbauer spectra were recorded in transmission mode with a ⁵⁷Co source in a rhodium matrix. The Mössbauer spectrometer of the electromechanical type was fixed absorber and operated source on constant-acceleration mode, which was calibrated by using an α -Fe foil. Mössbauer spectra were least squares fitted, giving the values of isomer shift (δ_{iso}), electric quadrupole splitting (ΔE_0), full-width at half maximum (fwhm), and relative area of Fe ions.

Electrocatalytic activity measurements

To prepare electrodes for electrochemical measurements, 4 mg of the Fe-N/C catalyst was dispersed into the 4 ml ethanol and sonicated for 30 min to form a stable suspension. Then, 50 μ L of 5% Nafion solution was added into the suspension and sonicated for 20 min to form a "paste-ink" for the electrochemical measurement.

Their ORR activities were investigated using a rotating-ring disk electrode (RRDE) in both 0.1 M HClO₄ and 0.1M KOH. The electrochemical measurements were conducted using a standard three-electrode cell. Cyclic voltammogram (CV) and linear sweep voltammogram (LSV) measurements were performed. A Pt wire and an Ag/AgCl electrode in saturated KCl solution served as the counter electrode and reference electrode, respectively. All potential values refer to that of a reversible hydrogen electrode (RHE). The potential, measured against a Ag/AgCl electrode, was converted to a potential versus RHE according to E (vs. RHE) = E (vs. Ag/AgCl)+0.197+0.059pH. To prepare the working electrode, desired amount of the

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suspension was applied onto a glassy carbon disk (with a disk diameter of 4 mm, A_{disk} = 0.126 cm²) surrounded by a Pt ring (inner/outer-ring diameter: 5.0/7.0 mm, A_{ring} = 0.188 cm²) of a rotating-ring disk electrode (RRDE). The catalyst loading was changed in the range of 0.1 mg cm⁻² to 0.6 mg cm⁻². A suspension of 20% Pt/C was also prepared using the same procedure and applied on a glassy carbon disk of RRDE, yielding a catalyst loading of 80 µg cm⁻². Prior to measurements, the solutions were purged with high purity O₂ gases at a constant flow rate of 50 mL min⁻¹ for at least 30 min. The O₂ gas was kept flowing over the electrolytes to maintain the saturation O₂, respectively, during the measurements. In order to remove the double layer capacity term, the current recorded in an N₂-saturated electrolyte under the same scan conditions was subtracted.

The electron transfer number (*n*) can be determined using Koutecky–Levich (K–L) equations as given by:

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

in which

$$B = 0.2nFC_0(D_0)^{2/3} v^{-1/6}$$
(2)

$$J_K = nFkC_0 \tag{3}$$

where *J* is the measured current density, J_K is the kinetic limiting current densities, ω is the angular velocity of the disk ($\omega = 2\pi N$ where *N* is the linear rotation speed), and *n* is the overall number of electrons transferred in oxygen reduction. F is the Faraday constant (F = 96,485 C mol⁻¹), C₀ is the bulk concentration of O₂, *v* is the kinematic viscosity of the electrolyte, *k* is the electron transfer rate constant, and D₀ is the diffusion coefficient of O₂ in the electrolyte. The constant 0.2 is adopted when the rotating speed is expressed in rpm.

The electron transfer number (*n*) and the corresponding peroxide yield (HO₂⁻ in alkaline solution and H₂O₂ in acidic solution) can also be determined on the basis of the disk and ring currents using the following equations:

$$n = 4 \times \frac{I_{disk}}{I_{disk} + I_{ring}/N} \tag{4}$$

$$peroxide\% = 100 \times \frac{2I_{ring}/N}{I_{disk} + I_{ring}/N}$$
(5)

where I_{disk} and I_{ring} are the faradic disk and ring currents, respectively. N is the collection efficiency of the ring electrode, which is determined to be 0.43 herein.

Results

Structural characterizations



Fig. S1 EDS elemental mapping of Fe-N/C taken from the area in (a) showing the distribution of (b) all elements, (c) carbon, (d) oxygen, (e) nitrogen, and (f) iron.



Fig. S2 SEM images for catalysts treated by plasma for different durations: (a) 30 s, (b) 60 s, and (c) 240s.



Fig. S3 HRTEM images for Fe-N/C-120.



Fig. S4 Pore size distributions for catalysts treated by plasma for different durations.



Fig. S5 XPS spectra for catalysts treated by plasma for different durations.



Fig. S6 XPS peaks for the Fe-N/C catalysts and the variation of contents of different elements as a function of treatment duration: (a-c) oxygen, (d-f) carbon and (g-i) nitrogen.



Fig. S7 Fe2p XPS peaks for catalysts treated by plasma for different durations.

Table S1 Elemental composition and content of various nitrogen-bonding states (atom %) for Fe-N/C-0, Fe-N/C-30, Fe-N/C-60, Fe-N/C-120, and Fe-N/C-240 obtained from XPS quantitative analysis.

Elemental composition				on	Ratio percentage (%)/Content				
Samples	(atom %)				(atom %)				
	C O N Fe		Fe	Pyridinic-N Pyrollic-N		Graphitic-			
							Ν		
Fe-N/C-0	80.58	11.43	7.15	0.84	20.0/1.43	48.3/3.45	31.7/2.27		
Fe-N/C-30	78.41	12.87	7.94	0.78	27.5/2.18	45.9/3.65	26.6/2.11		
Fe-N/C-60	77.79	14.61	6.96	0.64	28.8/2.00	45.4/3.16	25.8/1.80		
Fe-N/C-120	70.13	22.00	7.13	0.74	28.8/2.05	37.5/2.68	33.7/2.40		
Fe-N/C-240	71.73	19.74	7.72	0.81	29.8/2.30	39.0/3.01	31.2/2.41		

Table S2 Mössbauer absorption spectrum and its deconvolution for the Fe-N/C-800 catalyst treated at: (a) Fe-N/C-0 and (b) Fe-N/C-120. The measurement was performed at room temperature and calibrated vs. α -Fe foil.

Summary of the Mössbauer parameters, the assignment of iron species, and the transmission of Fe-N/C-0 and Fe-N/C-120							
Mössbauer site		D1	D2	D3			
assignment		Fe ^{II} N ₄ , LS	Fe ^{II} N ₄ , HS	Fe ³⁺			
$\delta_{iso}\!/mm\;s^{-1}$		0.420(0.084)	1.23(0.11)	0.132(0.046)			
$\Delta E_Q/mm \ s^{-1}$		0.90(0.21)	2.13(0.23)	0.574(0.086)			
fwhm/mm s ⁻	I	0.36(0.12)	0.31(0.11)	0.203(0.092)			
areas/%	Fe-N/C-0	47	20	33			
	Fe-N/C-120	46	26	28			
Errors are given between parentheses.							

Electrochemical performances in the HClO₄ solution



Fig. S8 CV curves for the Fe-N/C catalysts in 0.1 M HClO₄: (a) Fe-N/C-120 in both O_2 and N_2 -saturated solutions; (b) catalysts etched for different durations in O_2 -saturated solutions.

Table S3

Comparison of the literature data for the ORR performance of non-noble metal catalysts in acidic media.

No.	Catalyst type	Electrolyte	ORR onset	catalyst	Ref.
			potential vs.	loading/	
			RHE (V)	mg cm ⁻²	
1	Meso-Fe-N-C/G	0.1M HClO ₄	0.88	0.26	1
2	Fe-NC/C	$0.5M~\mathrm{H_2SO_4}$	0.83	0.20	2
3	5% Fe-N/C	$0.5M H_2 SO_4$	0.86	—	3
4	Fe-Co/Nf-GNF	0.5M HClO ₄	0.93	0.90	4
5	Fe-CNT-PA	$0.5M H_2 SO_4$	0.80	0.50	5
6	Co–	0.1M HClO ₄	0.83	0.40	6
	N _x /C/ZIF/rGO-				
7	700-AL	0.1M HClO ₄	0.90	0.08	This Work
8	20% Pt/C	0.1M HClO ₄	0.88	0.60	This Work
	Fe-N/C-120				

Table S4

The reduction peaks ($E_{reduction}$ vs. RHE), onset potential (E_{onset} vs. RHE), current density ($J_{0.20}$, mA cm⁻²) at +0.20 V (vs. RHE) and 1600rpm, and electron transfer number (*n*) at +0.20 V (vs. RHE) in 0.1M KOH and current density ($J_{0.30}$, mA cm⁻²) at +0.30 V (vs. RHE) and 1600rpm, and electron transfer number (*n*) at +0.30 V (vs. RHE) in 0.1M HClO₄ of the Fe-N/C-0, Fe-N/C-30, Fe-N/C-60, Fe-N/C-120, and Fe-N/C-240 catalysts at the same catalyst loading (0.14 mg cm⁻²)

	0.1M KOH				0.1M HClO ₄				
Samples	E _{reduction}	E _{onset} /V	J _{0.20} /mAcm ⁻²	n	 E _{reduction} /V	E _{onset} /V	J _{0.30} /mAcm ⁻²	n	
Fe-N/C-0	0.735	0.976	2.64	2.80	None	0.745	1.96	2.73	
Fe-N/C-30	0.787	0.979	3.19	3.16	0.586	0.746	2.60	3.18	
Fe-N/C-60	0.804	0.981	3.48	3.60	0.635	0.750	2.90	3.55	

Fe-N/C-120	0.805	0.996	4.00	3.67	0.694	0.812	3.56	3.77
Fe-N/C-240	0.789	0.987	3.84	3.63	0.663	0.759	3.25	3.69



Fig. S9 LSV curves, K-L plots and kinetic limiting current densities and transfer electrons (*n*) for the Fe-N/C catalysts in 0.1 M HClO₄: (a-c) Fe-N/C-0; (d-f) Fe-N/C-30; (g-i) Fe-N/C-60; (j-l) Fe-N/C-120; (m-o) Fe-N/C-240.



Effect of plasma etching on performance of carbons doped by Nitrogen only

Fig. S10 LSV curves for the chitin-derived carbon both containing and without Fe and etched for different durations. The loading was ~ 0.14 mg cm⁻², scan rate 10 mV s⁻¹ and rotation rate was 1600 rpm.

Electrochemical performances in the KOH solution



Fig. S11 CV curves for the Fe-N/C catalysts in 0.1 M KOH: (a) Fe-N/C-120 in both O_2 and N_2 -saturated solutions; (b) catalysts etched for different durations in O_2 -saturated solutions.



Fig. S12 Electrocatalytic performance evaluation in 0.1 M KOH: (a) LSV curves (loading ~0.14 mg cm⁻², scan rate 10 mV s⁻¹ and rotation rate 1600 rpm), (b) K-L plots , (c) LSV curves for Fe-N/C-120 (loading ~0.6 mg cm⁻²) and Pt/C (loading ~80 μ g cm⁻²), (d) the HO₂⁻ yields as a function of potential, (e) Durability evaluation at 0.4 V and a rotation rate of 1600 rpm for Pt/C and (f) Chronoamperometric responses on addition of 1M methanol after about 300 s.



Fig. S13 LSV curves, K-L plots and kinetic limiting current densities and transfer electrons (*n*) for the Fe-N/C catalysts in 0.1 M KOH: (a-c) Fe-N/C-0; (d-f) Fe-N/C-30; (g-i) Fe-N/C-60; (j-l) Fe-N/C-120; (m-o) Fe-N/C-240.

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