Supporting Information

Carbon for oxygen reduction reaction: A defect mechanism

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Experimental Summary

Computational Method. All calculations were carried out within the scheme of spin-polarized DFT, under the generalized gradient approximation method.[1-2] The Perdew-Burke-Ernzerhof functional was employed for the exchange-correlation term, which has been embedded in the Vienna ab-initio Simulation Package (VASP). During the calculation, the projector augmented wave method[3] with a cutoff energy of 400 eV was applied to achieve high computational efficiency. The free energy changes associated with the elementary reactions were calculated based on the hydrogen electrode scheme proposed by Nørskov et al.[4]

Materials Synthesis. Commercial Pt/C catalyst (20 wt% platinum on Vulcan XC72) and cyanuric chloride were purchased from Aldrich Chemical Co., p-nitroaniline was obtained from Sinopharm Chemical Reagent Co., Ltd. All other materials and solvents, unless otherwise specified, were bought from Aldrich Chemical Co. and used without further purification.

2,4,6-Tris(p-aminoanilino)-1,3,5-triazine, the starting material for PAF-40, was synthesized using the published procedures.[5] All reactions were performed at ambient laboratory conditions, and no precautions were taken to exclude oxygen or atmospheric moisture, unless otherwise specified.

For the preparation of PAF-40, a Teflon-lined stainless steel autoclave with the volume of 30 mL was charged with terephthaldehyde (50 mg), 2,4,6-Tris(p-aminoanilino)-1,3,5-triazine (100 mg), 5 mL of anhydrous dioxane and 2 mL of 3 M aqueous acetic acid water. The reaction was carried out in the oven at 120 ºC for 7 days to produce a yellow jelly which was separated by filtration and washed with anhydrous dioxane and anhydrous THF. The obtained powder was Soxhlet extracted in anhydrous THF for 72 h and dried at room temperature for 12 h and then 70 ºC for 2 h to receive a yellow powder. Yield: 102 mg.

In the carbonization process, PAF-40 was firstly loaded into a quartz boat and then placed into the central area of a quartz tube furnace, followed by heating up at a ramp rate of 2 °C min^{-1} to the final temperature of 400 to 1000 °C and holding for 5 hours under N_2 atmosphere. The final products were collected from the quartz boat directly. For sample C-1000-O_2, PAF-40 was heated at a ramp rate of 5 °C min^{-1} to 1000 °C for 2 hours under N_2/O_2 (99.5/0.5, v/v) mixture.

Characterizations. X-ray Powder diffraction (XRD) data were collected on a Bruker Advance-D8 with Cu-Kα radiation (λ = 1.5418 Å) at 40 kV and 35 mA in the range of $4° < 2\theta < 40°$ with a step of 0.02° (2θ) for PAF-40 and the starting materials, and in the range of $4° < 2\theta < 80°$ with 1 s counting time per step for the ORR catalysts. The structural and elemental characteristics of the synthesized products were investigated by TEM (FEI Tecnai F20, acceleration voltage: 200 kV) equipped with a Gatan Image Filter (GIF) system. Raman spectra were recorded using a Renishaw spectrometer, excited by a 514.5 nm Argon laser. X-ray photoelectron spectroscopy (XPS) was recorded using the ESCALAB250 spectrometer with Al Kα radiation (15 kV, 150 W). The XPS survey was collected over 0-1200 eV with pass energy of 160 eV and an energy interval of 1 eV step^{-1}. The high resolution XPS spectra were measured with pass energy of 30 eV and an energy interval of 0.05 eV step^{-1}. Perkin-Elmer Diamond instrument was used to obtain thermogravimetric analysis (TGA) curves under air atmosphere with a ramp rate of 10 °C min^{-1}.

Electrochemical Measurements. ORR activity and 4-electron selectivity of the catalysts were evaluated via cyclic voltammetry (CV) and rotating disk electrode (RDE), respectively. CV/RDE measurements were performed on the CHI Electrochemical Station (CHI 760D) in a conventional three-electrode electrochemical cell. Pt wire was used as the counter electrode and Ag/AgCl electrode in 3.0 M KCl was used as the reference electrode. The data were obtained at room temperature (~25 °C) with a catalyst loading of 0.12 mg cm^{-2} in 0.1 M KOH at the rotating speed of 1600 rpm.

2 mg catalyst and 20 µL 5 wt% Nafion® solution were dispersed into 1 mL of 15:1 v/v water/ethanol mixed solvent followed by sonication for at least 30 min to form a homogeneous ink, then 12 µL of the catalyst ink (containing 24 µg of catalyst) was loaded onto a glassy carbon (GC) electrode of 5 mm in diameter (loading ~ 0.12 mg cm^{-2}) for CV and RDE test. The reference Pt/C data were recorded with the same mass loading, which equals to 24 µgPt cm^{-2}. For rotating ring-disk electrode (RRDE) measurements, 20 µL of the ink (the prepared samples and Pt/C) was dropped onto the RRDE with a Pt ring.

Reference

[1] W. Kohn et al. Phys. Rev. 140, A1133–A1138 (1965).
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[3] G. Kresse, G. et al. Phys. Rev. B 59, 1758–1775 (1999).
[4] J. K. Nørskov et al. J. Phys. Chem. B 108, 17886 (2004).
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1. The relationship between the electrochemical activities vs. N concentration for N-doped carbon-based ORR catalysts.

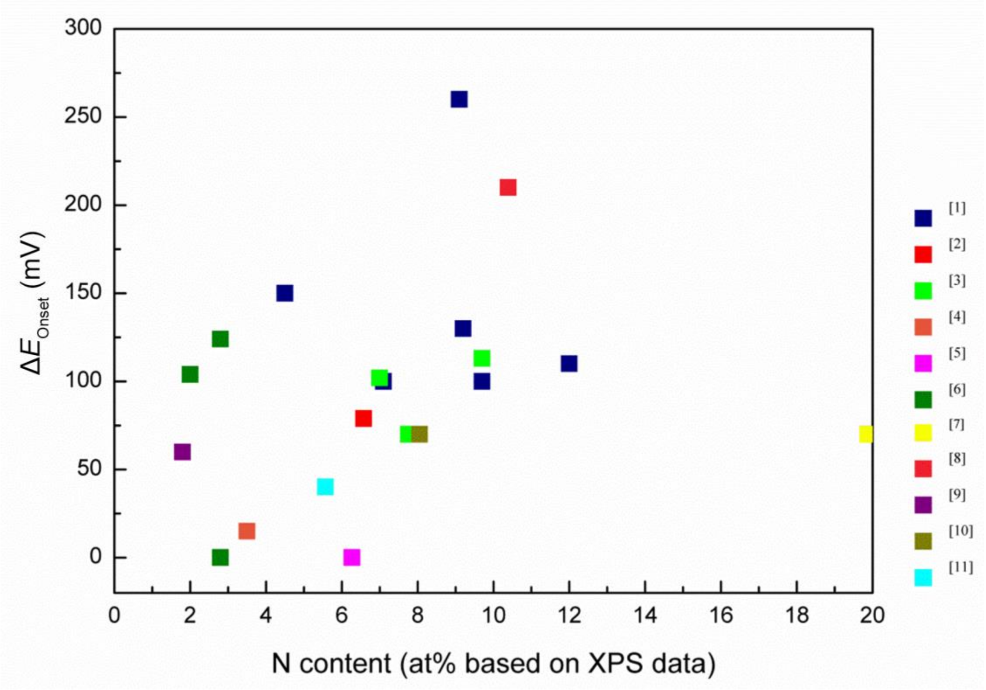

Figure S1. Electrochemical activity (onset potential difference between the reported samples and Pt/C catalysts) vs. N concentration for 21 reported N-doped carbon-based ORR catalyst samples[1-11] satisfying the criteria listed in the text.

The samples were selected by the following criteria to assure their comparability:

(a) Electrochemical measurements were performed in O_2-saturated 0.1 M KOH ;

(b) Commercial carbon supported 20 wt% platinum (Pt/C) catalyst was selected as the reference catalyst and the onset potential value for both the Pt/C and resulting ORR catalysts were given in the reports.

(c) N concentration data were given in at.% according to the XPS test.

2. Summary of the physical parameters and electrochemical properties

Table S1. XPS analysis and texture properties and ORR electrocatalysis properties of C-PAF-40s and control samples

Samples	Texture properties			ORR electrocatalysis properties			Yield (%)
	N content[a] (atom %)	S_{BET}[b] (m^2/g)	Pore size [c] (nm)	Onset potencial[d] (V)	Electron transfer number[e]	J_K ($mAcm^{-2}$)	
PAF-40	12.14	94	1.48				
C-700	2.11	489	1.18	-0.258	3.07	5.33	48.0
C-800	1.96	581	1.09	-0.245	3.32	4.53	41.2
C-900	0.72	995	1.45	-0.153	3.94	7.81	38.4
C-1000	0.56	1095	1.09	-0.144	3.87	8.73	37.1
C-1000-O_2	0.21	950	1.18	-0.109	~4.0	9.78	20.0
Pt/C(20%)				-0.066	~4.0		

a N atom % was calculated from XPS data. b SBET was calculated in the partial pressure (p/p_0) in range of 0.01 to 0.1 which gives the best liner. c Maxima of the pore size distribution calculated using the DFT method and slit-shaped pores. d Onset potential has been defined as a potential required for generating an ORR current density of 0.1 mA cm^{-2} in a steady-state RDE experiment in this research. e The transferred electron number (*n*) is calculated Electron transfer number (*n*) on the basis of the Koutecky-Levich equations according to RDE data.

3. Characterization of PAF-40

X-ray diffraction analysis

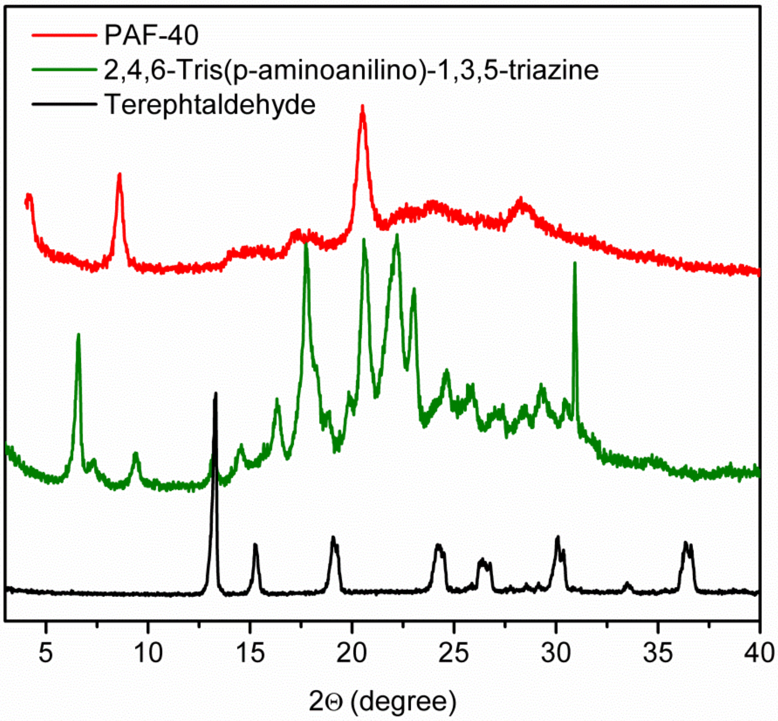

Figure S2. XRD pattern of PAF-40 (red), compared to those of 2,4,6-Tris(p-aminoanilino)-1,3,5-triazine (green) and terephtaldehyde (black).

Solid-State ^{13}C CP-MAS Nuclear Magnetic Resonance Spectroscopy

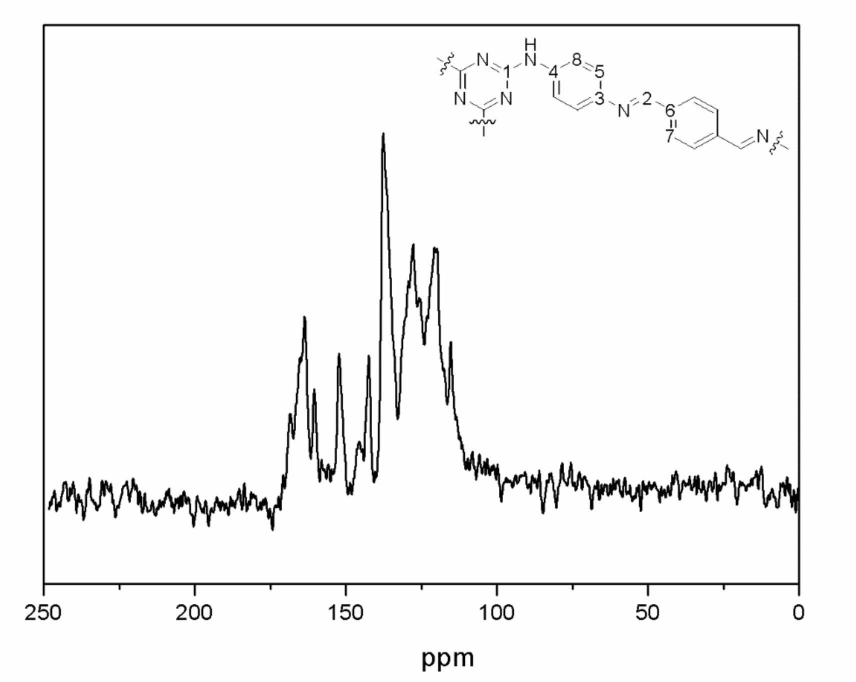

Figure S3. Solid-state ^{13}C CP-MAS NMR spectrum of synthesized PAF-40

X-ray photoelectron spectroscopy (XPS)

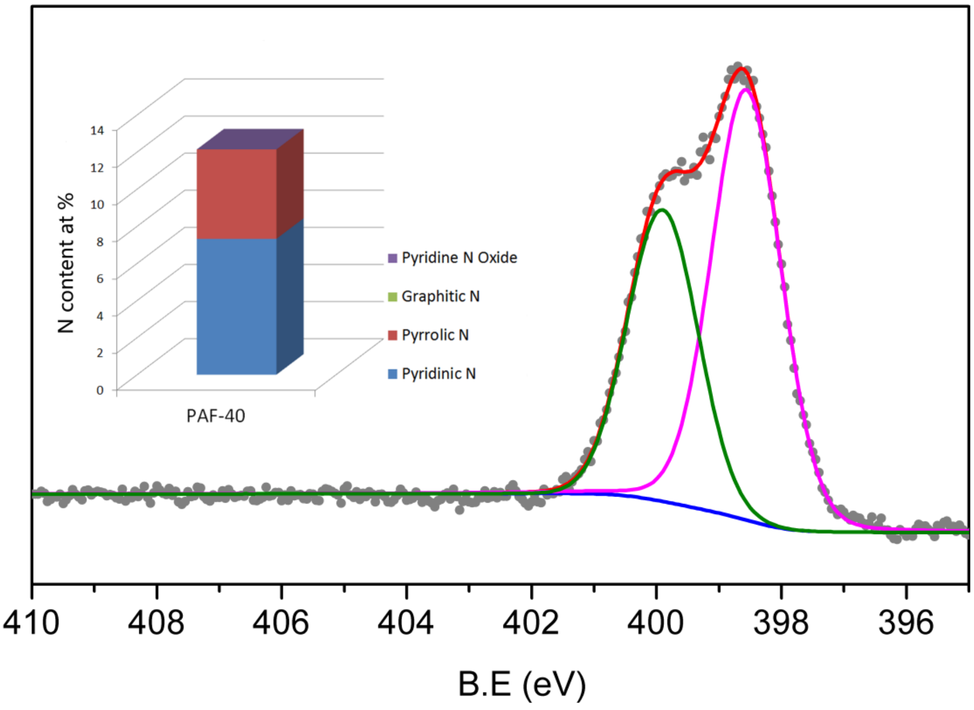

Figure S4. The XPS of the N1s regions for PAF-40 and total N content (insert)

Thermogravimetry

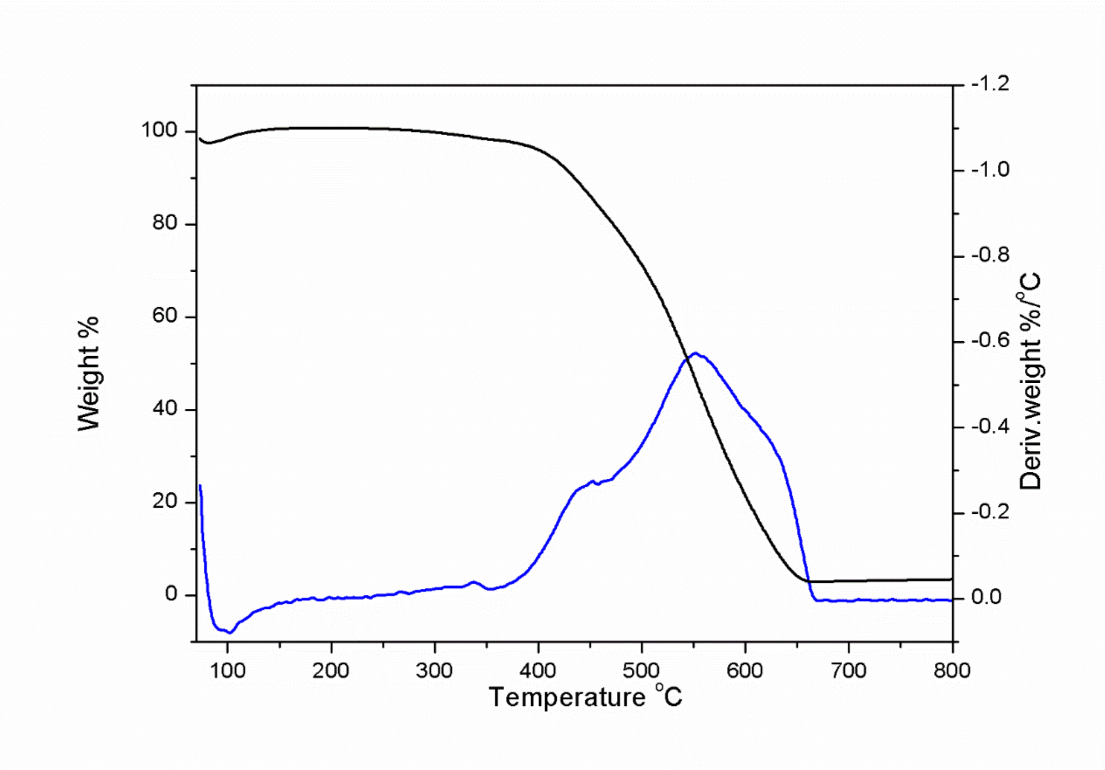

Figure S5. Thermogravimetric data of PAF-40 sample in air. Scan rate 20 °C/min

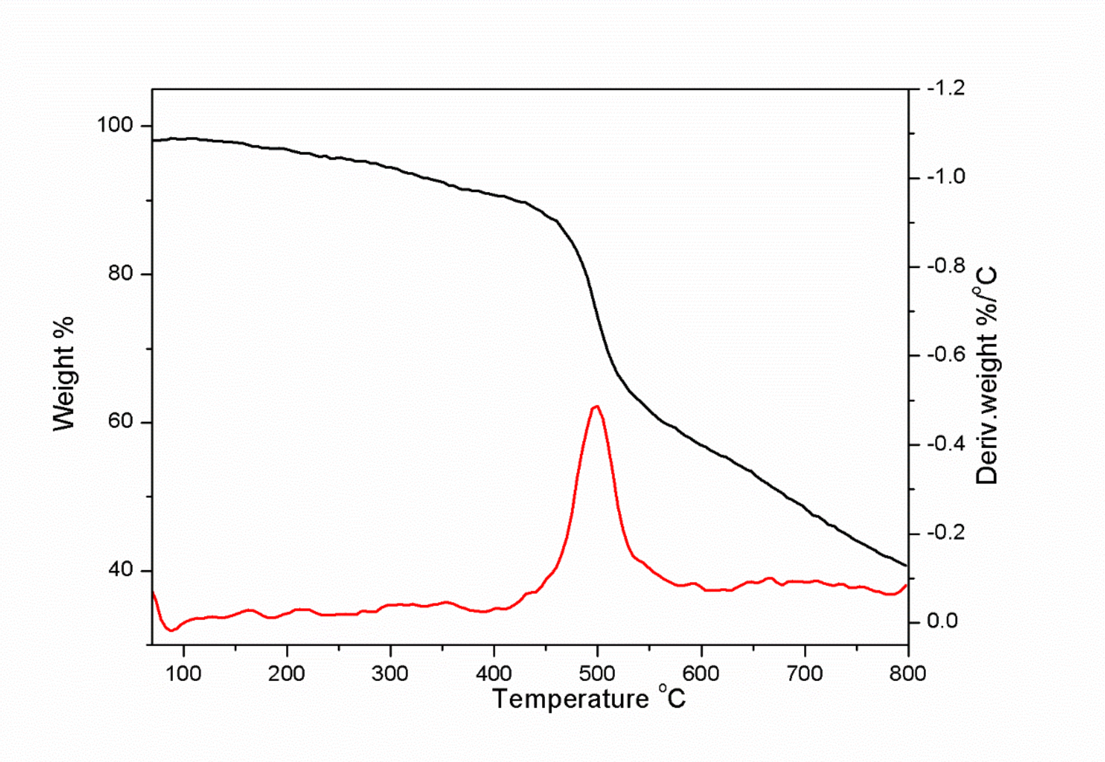

Figure S6. Thermogravimetric data of PAF-40 sample in Ar atmosphere. Scan rate 20 °C/min

4. Electrochemical Measurements

ORR steady-state RDE

Polarization plots were recorded in O_2-saturated electrolyte at scan ramp of 10 mVs^{-1}. The disk rotation rate was varied from 400 to 2000 rpm. The working electrode was scanned cathodically at a rate of 10 mVs^{-1} with varying rotating speed from 400 rpm to 2000 rpm. Koutecky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) were analyzed at various electrode potentials. The slopes of their best linear fit lines were used to calculate the number of electrons transferred (n) on the basis of the Koutecky-Levich equation

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

$$B=0.62nFC_o(D_o)^{2/3}v^{-1/6} \qquad J_K=nFkC_o$$

where J is the measured current density, J_K and J_L are the kinetic and diffusion-limiting current densities, ω is the angular velocity, n is transferred electron number, F is the Faraday constant, C_o is the bulk concentration of O_2, v is the kinematic viscosity of the electrolyte, and k is the electron-transfer rate constant. For the Tafel plot, the kinetic current was calculated from the mass-transport correction of RDE by:

$$J_K=\frac{J\times J_L}{(J_L-J)}$$

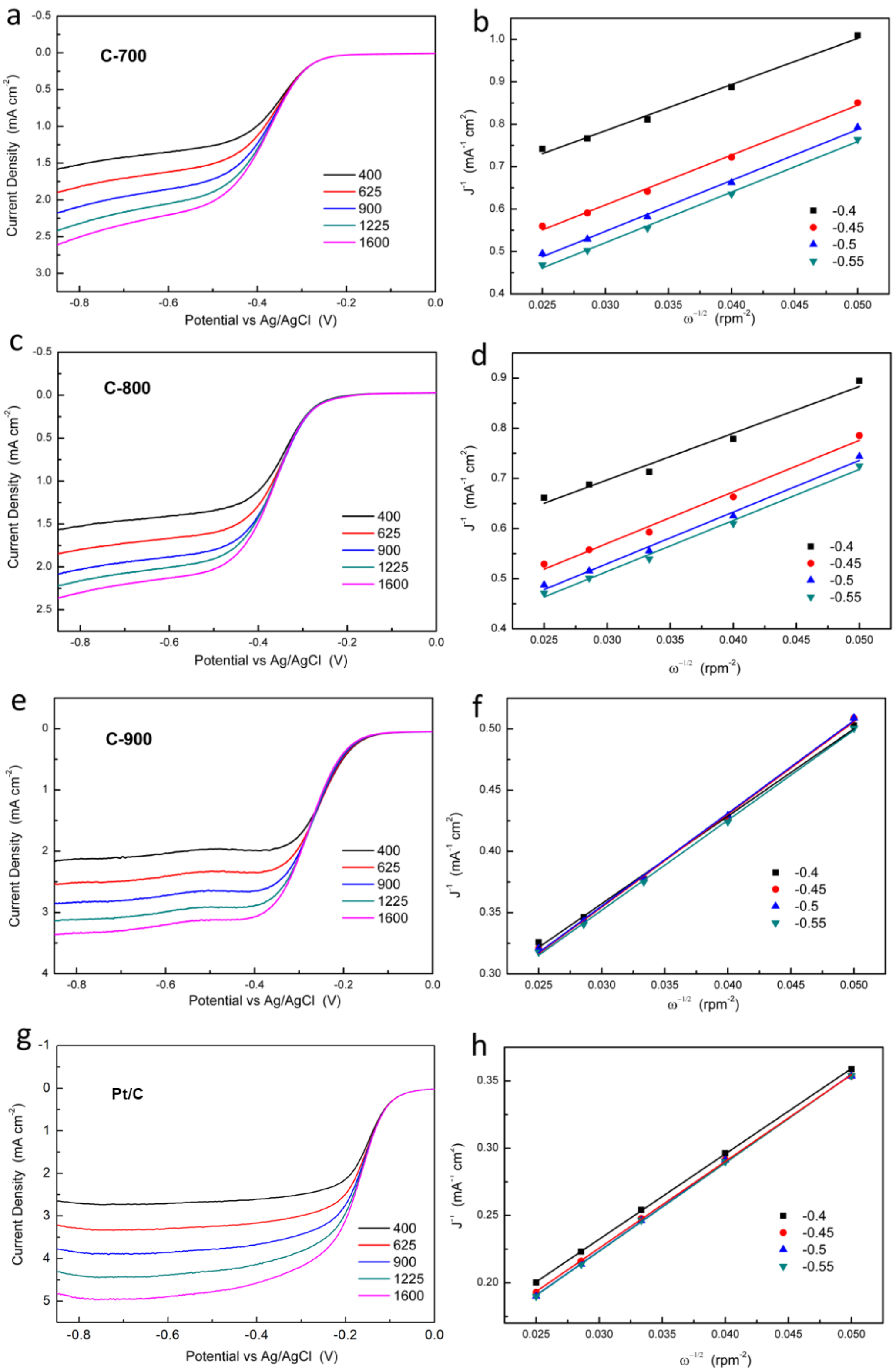

Figure S7. Rotating-disk voltammogram (catalyst loading: 0.12 mg cm^{-2}) in O$_2$-saturated 0.1 M KOH at a sweep rate of 10 mV s^{-1} and different rotation rates and corresponding Koutecky-Levich plot (J^{-1} vs. $\omega^{-0.5}$) at different potentials on C-700/GC (a) (b), C-800/GC (c) (d), C-900/GC (e) (f) and Pt-C/GC electrode.

5. Characterization and Electrochemical Measurements of C-1000-O_2

X-ray photoelectron spectroscopy

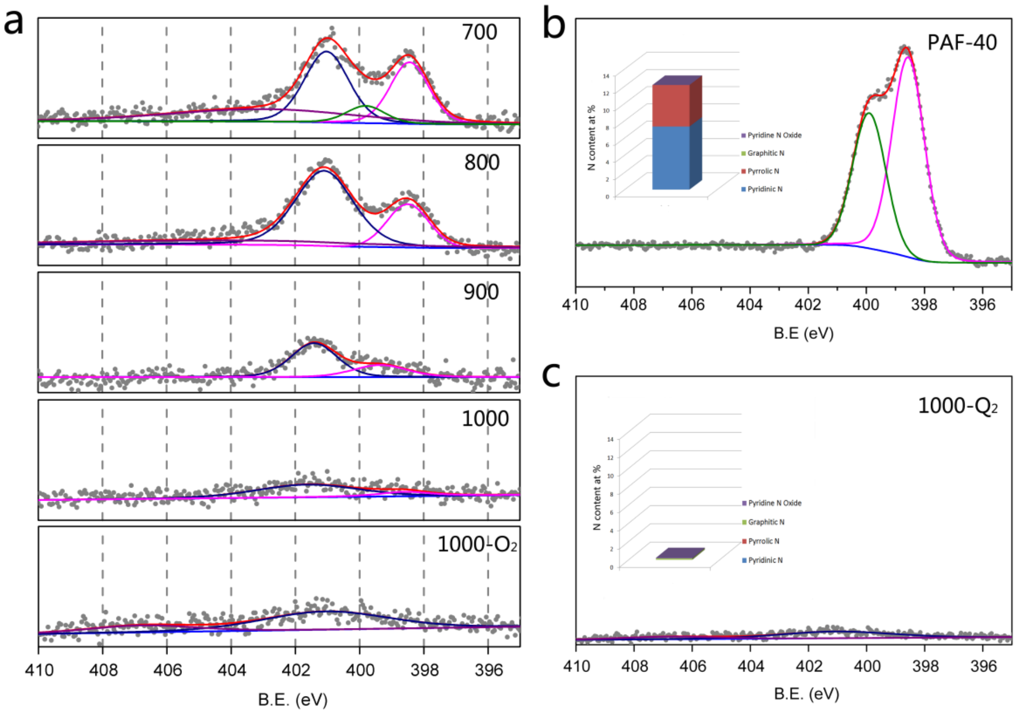

Figure S8. (a) X-ray photoelectron spectroscopy (XPS) of the N1s regions for C-700, 800, 900, 1000 and 1000-O_2. BE is the binding energy. (b) and (c) XPS of the N1s regions and total N content (insert) for PAF-40 and C-1000-O_2 catalysts.

Transmission electron microscope

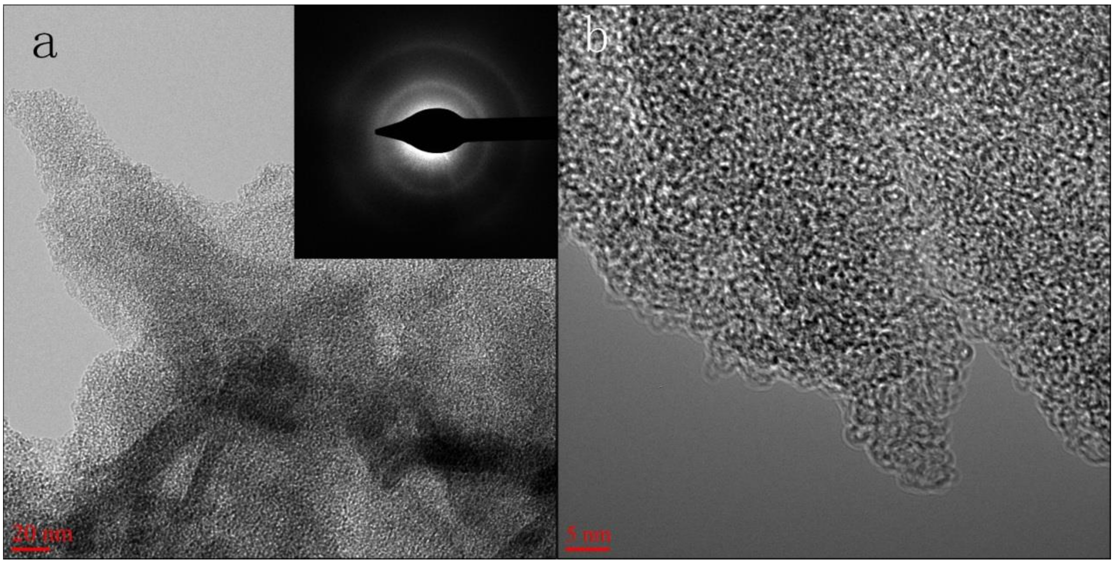

Figure S9. HRTEM images and SAED pattern (insert) of C-1000-O_2

X-ray diffraction analysis

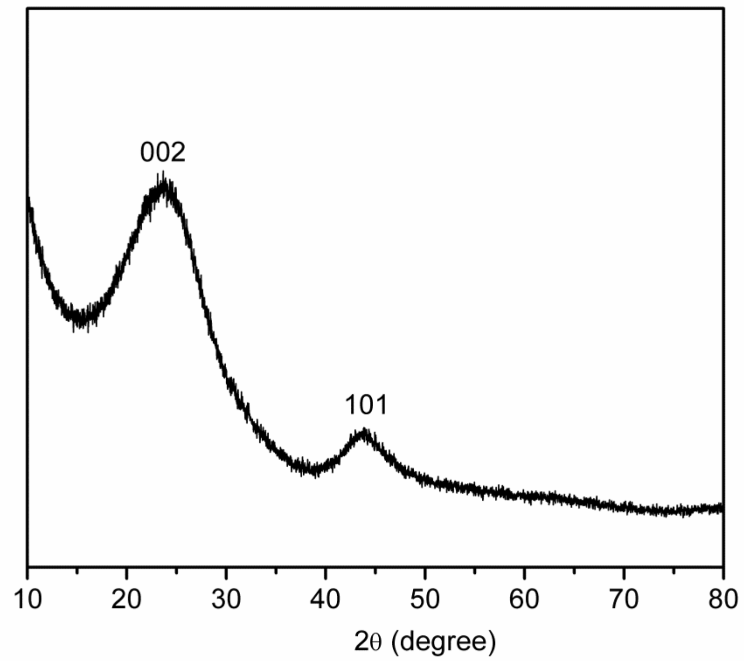

Figure S10. XRD pattern for C-1000-O_2

Raman spectrum

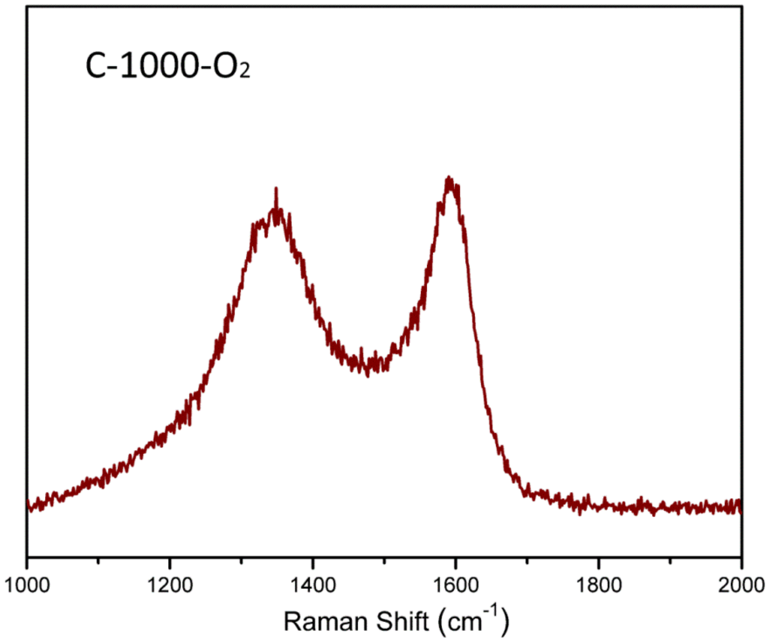

Figure S11. Raman spectrum for catalyst of C-1000-O_2, I_D/I_G=0.90.

Cyclic voltammetry

Characterization of the catalysts was typically carried out in the potential range from -0.2 to 1.2 V at a scan rate of 100 mV s^{-1} in in the oxygen-saturated or nitrogen-saturated 0.1 KOH electrolyte. All loaded on glassy carbon electrode with the same mass loading.

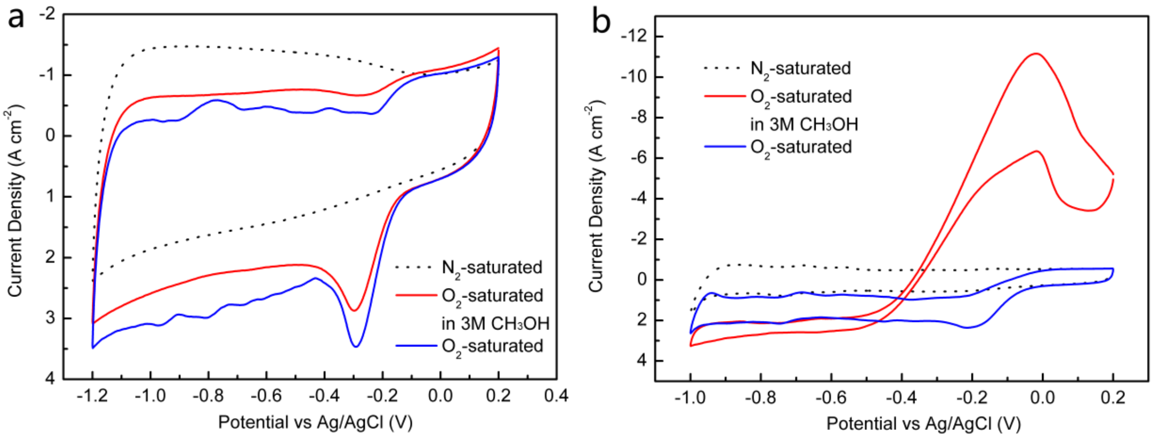

Figure S12. Cyclic voltammetry of C-1000-O_2/GC electrode (a) and Pt/C /GC electrode in oxygen (blue), nitrogen (dash) saturated 0.1 M KOH and oxygen saturated 0.1 M KOH with 3 M CH_3OH (red). Scan rate: 100 mV s^{-1}; cell temperature: 25 °C.

6. Reference

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