

Defect-driven Oxygen Reduction Reaction (ORR) of Carbon without Any Element Doping

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Detailed Experimental Section

Reagents and Materials. All chemicals purchased are reagent grade or better and are used without further purification. 2,6-Naphthalenedicarboxylic acid (2,6-NDC, 99%), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), platinum on graphitized carbon (Pt/C, wt 20%) and Nafion® 117 solution (5%) are purchased from Sigma-Aldrich. N, N-diethylformamide (DEF, 99%) is purchased from Alfa Aesar.

Preparation of IRMOF-8. IRMOF-8 compound was synthesized basing on the reported literature. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.55 g) and 2,6-NDC (0.15 g) were dissolved in 50 mL DEF and dispensed to 100 mL Teflon-lined stainless steel vessels, the reaction was carried out at 95 °C for 20 hours under autogenous pressure. After filtering and washing with 5 mL DEF for three times, the cubic crystals of IRMOF-8 were collected.¹⁻⁴

Synthesis of PC-I8-950 porous carbon. Under nitrogen flow and with a heating rate of 5 °C·min⁻¹, 500mg of IRMOF-8 crystals were heating at 150 °C for 90 minutes to remove guest molecules, and then the treatment temperature raised to 550 °C and remained for 180 minutes. Finally, the sample was heated at 950 °C for 240 minutes and lower to room temperature. The black powerful product were collected directly and denoted as PC-I8-950.

Instruments and characterization

The N₂ adsorption and desorption isotherm was measured on a Micromeritics Tristar II 3020 analyser. X-ray photoelectron spectroscopy (XPS) was recorded by an ESCALAB-M II 250 photoelectron spectrometer with Al-K α X-ray radiation as the X-ray source for excitation. X-ray diffraction (XRD) pattern was recorded by a PANalytical Empyrean Diffractometer using Ag-K α radiation, 60 kV, 30 mA with a scanning rate of 1°·min⁻¹ and the data were calibrated with respect to Cu-K α radiation. Raman spectrum was measured on a Renishaw in Via Raman Microscopy with 514 nm laser. All electrochemical experiments were carried out with a CHI 760E electrochemical workstation (CH Instruments) in a three-electrode electrochemical cell.

Electrochemical Measurements

Electrochemical performance of PC-I8-950 and Pt/C catalysts were measured in the three-electrode

electrochemical cell, which employed Pt wire, Ag/AgCl (filled with saturated KCl aqueous solution) and glassy carbon (GC) electrode as the counter electrodes, reference electrodes and working electrode respectively.

The inks of carbon catalysts and Pt/C were prepared by same method. The catalyst powder (1 mg) was dispersed in 1 mL mixed solution of Nafion, ethanol and deionized water with the volume ratio of 1: 15: 34.

12 μL catalyst inks were loaded onto a GC electrode of 4 mm in diameter and dried at 60 $^{\circ}\text{C}$ for 10 min. Before beginning each measurement, the electrolyte, which is 0.1 M KOH aqueous solution, was saturated with O_2 or N_2 , and O_2 or N_2 flow kept bubbling during the period of electrochemical measurement in order to maintain saturated state of KOH electrolyte.

Cyclic Voltammetry (CV). The catalyst modified working electrode was prepared by the method as above. The GC electrode as a working electrode was scanned at a rate of 50 $\text{mV}\cdot\text{s}^{-1}$ in the potential range from 0.20 to -1.20 V (vs. Ag/AgCl).

Rotating Disk Electrode (RDE) Measurement. The catalyst modified working electrode was prepared by the same method. The working electrode rotated with varying speed from 400 to 2500 rpm at a scanned rate of 10 $\text{mV}\cdot\text{s}^{-1}$.

LSV curves are investigated by Koutecky–Levich plots (J^{-1} vs $\omega^{-1/2}$) at different electrode potentials from -0.30 to -0.60 V (vs. Ag/AgCl). The slopes of the best linear fit lines are used to calculate the diffusion-limiting and kinetic current density (J_K) and the number of electrons transferred (n) per O_2 molecule from Koutecky–Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_k} \quad (B = 0.2nF(D_{\text{O}_2})^{2/3}(\nu)^{-1/6}C_{\text{O}_2})$$

J is the measured current density, J_L and J_K are the diffusion-limiting and kinetic current densities, and ω is the rotating speed. n represents the number of electrons transferred per O_2 molecule, F is the Faraday constant ($F = 96485 \text{ C}\cdot\text{mol}^{-1}$), D_{O_2} is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9\times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$), ν is the kinetic viscosity of electrolyte ($0.01 \text{ cm}^2\cdot\text{s}^{-1}$), C_{O_2} is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol}\cdot\text{cm}^{-3}$).

Methanol crossover effect response. The catalyst modified GC electrode was prepared by same method as above. At a voltage of -0.30 V (vs. Ag/AgCl), the current-time (i-t) chronoamperometric response was recorded in O_2 -saturated 0.1 M KOH aqueous solution for Pt/C and PC-I8-950 catalysts. The methanol was added into the electrochemical cell with a volume ratio of 1:10.

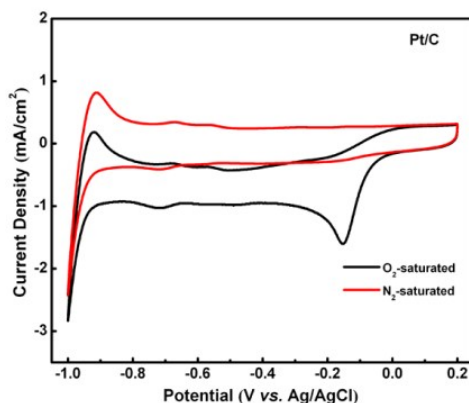


Figure S1. CV curves of Pt/C in 0.1 M KOH solution.

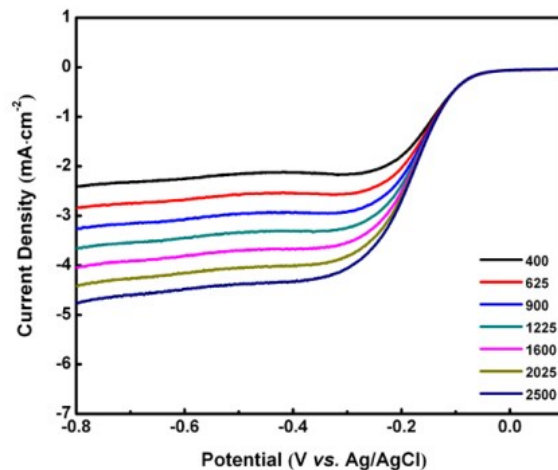


Figure S2. Linear sweep voltammogram (LSV) curves of PC-I8-950 catalyst in oxygen -saturated 0.1M KOH solution. The rotation speed of GC electrode is varied from 400 to 2500 rpm and the scan rate is $10 \text{ mV} \cdot \text{s}^{-1}$.

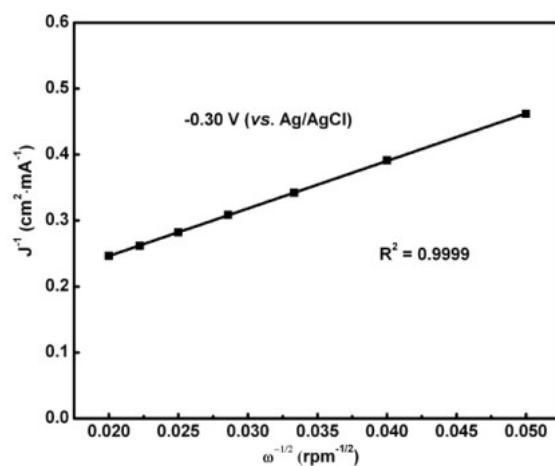


Figure S3. Koutecky–Levich plot of the carbon products at a potential of -0.30 V. The plots are generated from the LSV curves of PC-I8-950 tested in oxygen-saturated 0.1 M KOH solution with different rotating speeds.

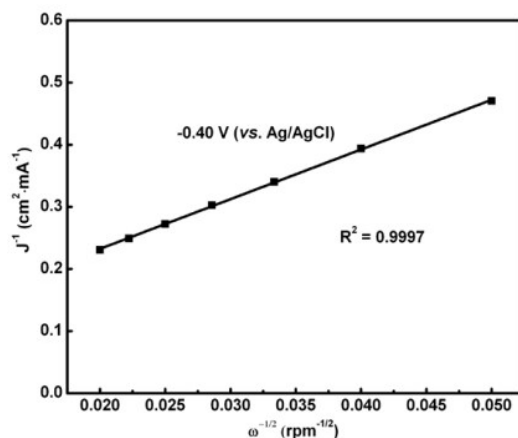


Figure S4. Koutecky–Levich plot of the carbon products at a potential of -0.40 V. The plots are generated from the LSV curves of PC-I8-950 tested in oxygen-saturated 0.1 M KOH solution with different rotating speeds.

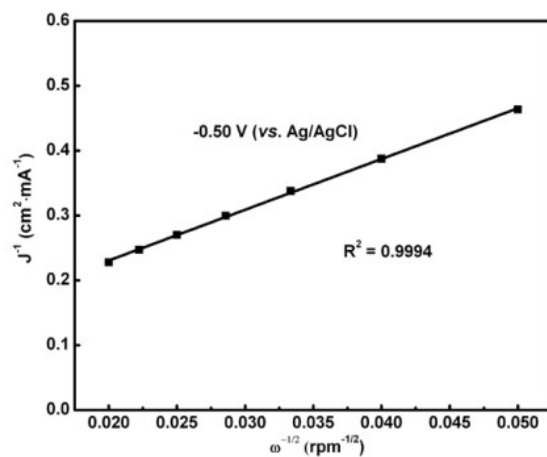


Figure S5. Koutecky–Levich plot of the carbon products at a potential of -0.50 V. The plots are generated from the LSV curves of PC-I8-950 tested in oxygen-saturated 0.1 M KOH solution with different rotating speeds.

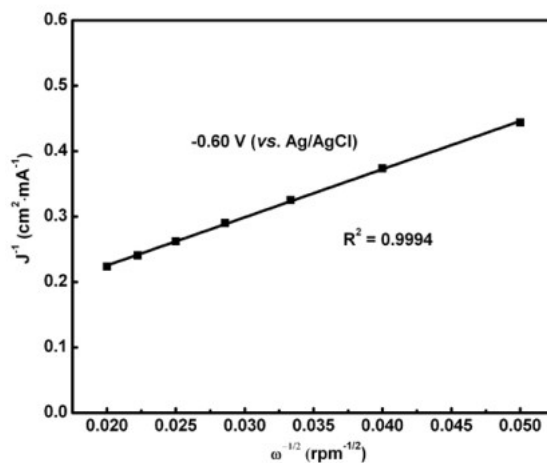


Figure S6. Koutecky–Levich plot of the carbon products at a potential of -0.60 V. The plots are generated from the LSV curves of PC-I8-950 tested in oxygen-saturated 0.1 M KOH solution with different rotating speeds.

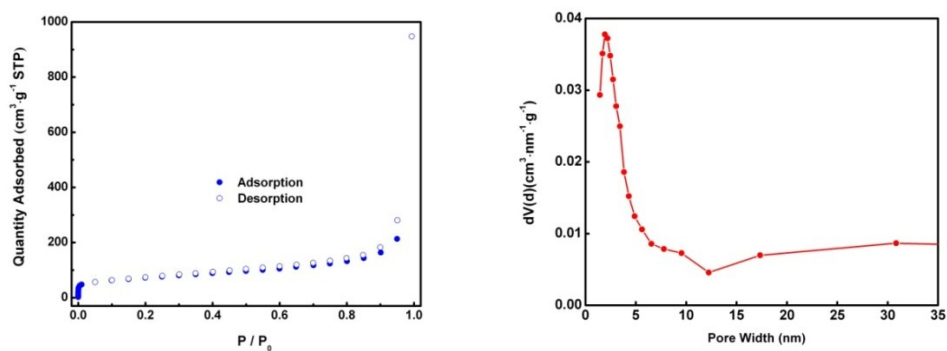


Figure S7. Nitrogen adsorption isotherms (left) and pore distribution curve (right) of XC-72.

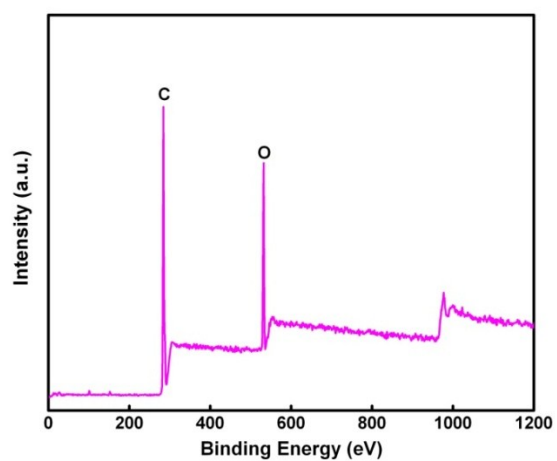


Figure S8. XPS survey spectrum of XC-72.

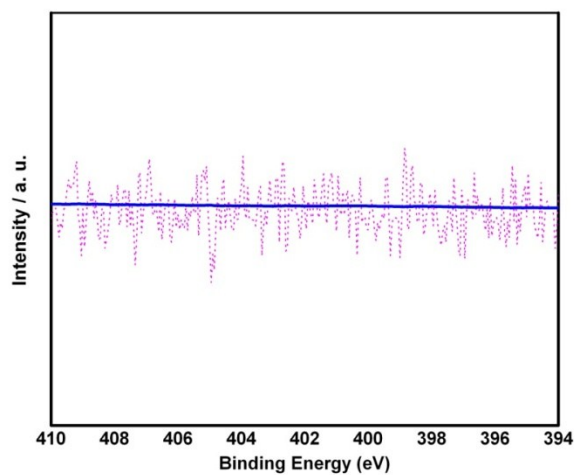


Figure S9. High-resolution N 1s spectra of XC-72.

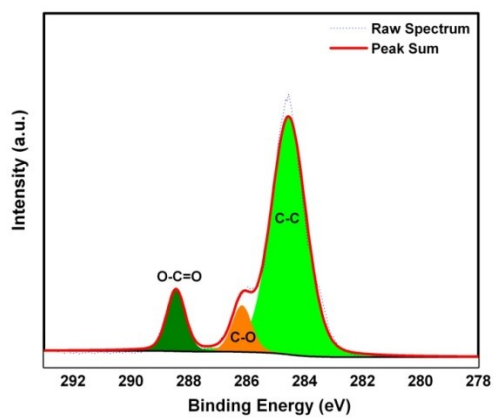


Figure S10. High-resolution C 1s spectra of XC-72.

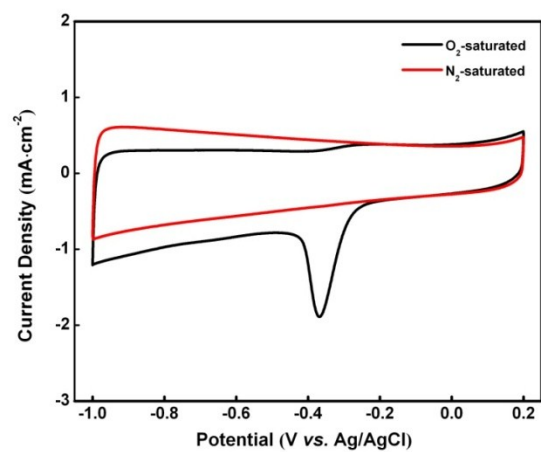


Figure S11. CV curves of XC-72 in 0.1 M KOH solution.

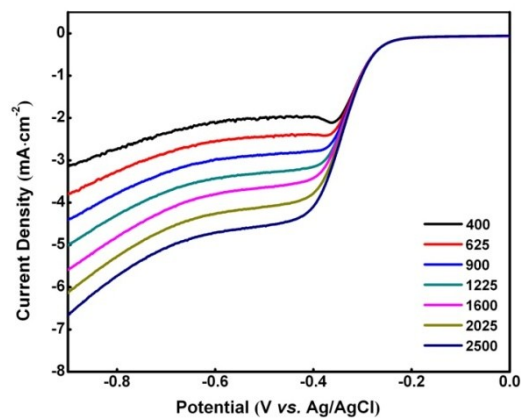


Figure S12. Linear sweep voltammogram (LSV) curves of XC-72 sample in oxygen -saturated 0.1M KOH solution. The rotation speed of GC electrode is varied from 400 to 2500 rpm and the scan rate is 10 mV·s⁻¹.

Table S1. Textural parameters of PC-I8-950 calculated by N ₂ adsorption				
	S _{BET} ^[a] (m ² ·g ⁻¹)	S _{micro} ^[b] (m ² ·g ⁻¹)	V _{total} ^[c] (cm ³ ·g ⁻¹)	V _{micro} ^[d] (cm ³ ·g ⁻¹)
PC-I8-950	836	275	1.09	0.12

^[a] S_{BET} is the surface area calculated by Brunauer-Emmett-Teller equation.

^[b] S_{micro} is microporous surface area calculated by t-plot method.

^[c] Total pore volume is calculated at a relative pressure of 0.96.

^[d] Micro-pore volume is calculated by t-plot method.

Table S2. The carbon state and content of PC-I8-950 and XC-72 calculated by XPS				
PC-I8-950	Peak (eV)	284.6	286.2	288.6
	State	C-C	C-O	O-C=O
	Content (%)	80.39	10.10	9.51
XC-72	Peak (eV)	284.6	286.2	288.5
	State	C-C	C-O	O-C=O
	Content (%)	80.39	8.84	10.77

Table S3. The number of electrons transferred (n) of Pt/C and PC-I8-950				
E (eV)	-0.30	-0.40	-0.50	-0.60
Pt/C	4.0	4.0	4.0	4.0
PC-I8-950	3.6	3.5	3.6	3.6

Supplementary Information References

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- (4) M. Miller, C. Wang, G. N. Merrill, *J. Phys. Chem. C*, 2009, **113**, 3222.