Supporting Information

for

Ligand effects enhancing low-temperature oxygen reduction kinetics in neutral conditions

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Experimental Section Synthesis of the ZIF-8(Cl) precursor:

First, ZnCl₂ (1.13 g, 8 mmol) and 2-methylimidazole (7.9 g, 96 mmol) were separately dissolved in ultrapure water (160 mL). The above solutions were then mixed and stirred at room temperature for 12 hours. The resulting powder was washed by centrifugation several times and dried in an oven at 60 °C. The sample obtained was named ZIF-8(Cl).

Synthesis of NC:

Typically, ZIF-8(Cl) (400 mg) was thoroughly mixed with KCl (1.4 g, 19 mmol) and ZnCl₂ (2.6 g, 19 mmol) in an agate mortar. The mixture was heated from room temperature to 900 °C at a heating rate of 5 °C min⁻¹ under flowing Ar gas and maintained for 2 hours. After naturally cooling to room temperature, the mixture was washed with ultrapure water at 80 °C overnight to remove the remaining salts. The sample was then re-annealed at 900 °C (with a heating rate of 5 °C min⁻¹) for 1 hour under flowing Ar gas. The sample obtained was termed as NC.

Synthesis of CNP-x (where x = 800, 900, 1000):

Triphenylphosphine was used as the P source. A mixture of NC (30 mg) and triphenylphosphine (250 mg, 0.95 mmol) was first homogeneously ground. The mixture was then heat treated under flowing Ar gas at 900 °C (with a heating rate of 5 °C min⁻¹) for 1 hour. The sample obtained was named CNP-900. CNP-800 and CNP-1000 were prepared using the same procedure except that their heat treatment temperatures were set to 800 °C and 1000 °C, respectively.

Synthesis of P-doped Carbon (PC):

PC was prepared through one-step pyrolysis. A mixture of acetylene black (30 mg) and triphenylphosphine (250 mg, 0.95 mmol) was thoroughly mixed. The mixture was heated from room temperature to 900 °C (with a heating rate of 5 °C min⁻¹) under flowing Ar gas and maintained for 1 hour. The sample obtained was named as PC.

Material characterizations

Atomic force microscopy (AFM) was performed using a Bruker Dimension Icon microscope in ScanAsyst mode. N2 adsorption-desorption isotherms were measured using an ASAP 2460 N₂ adsorption apparatus. X-ray powder diffraction (XRD) analysis was performed using a PANalytical Empyrean instrument with Cu Ka radiation ($\lambda = 0.154$ nm) in the range of 10° to 80° (2 θ) (scan rate: 10°/min). The surface morphology of the samples was examined using field emission scanning electron microscopy (FESEM, JSM-7800F). High-resolution topography of the samples was obtained using transmission electron microscopy (TEM, JEOL F200). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging and the corresponding energy-dispersive X-ray spectroscopy (EDX) analysis were performed using an aberration-corrected TEM (ACTEM, FEI Titan Cubed Themis G2 300). X-ray photoelectron spectroscopy (XPS) was performed using a Microlab350 at 15 kV and 300 W. The work function of the samples was determined from the ultraviolet photoelectron spectroscopy (UPS) spectra using an ESCALABXi with a bias of 10 V. Raman spectra were obtained using a HORIBA LABRAM HR spectrometer with a 532 nm wavelength laser. IR spectra were collected on a Nicolet 8700 spectrometer (MCT-A detector, spectral resolution of 8 cm⁻¹).

Electrochemical measurements

The electrochemical performance of the catalysts was evaluated using a traditional three-electrode setup on a CHI 760E electrochemical workstation. A glassy carbon rotating disc electrode (GC-RDE) with an inner diameter of 5 mm was used as the working electrode. Graphite rod was used as the counter electrode for stability test to prevent the dissolution and electroplating of Pt. The reference electrode used in 0.1 M HClO₄ and 0.1 M PBS solutions was Ag/AgCl electrode filled with saturated KCl solution. In 0.1 M KOH solution, an Hg/HgO electrode filled with 0.1 M KOH solution was used. All the reference electrodes were calibrated before use, and the standard potential relative to the reversible hydrogen electrode (RHE) was determined as the average of the two potentials at zero current (Figure S1-S3, scanning rate: 1 mV s⁻¹).

The catalyst ink was prepared by dispersing 2.5 mg of catalyst in 500 μ L of a mixed solution containing 475 μ L of ethanol and 25 μ L of Nafion solution (5 wt%). After a 30-minute ultrasonic treatment, 25 μ L of ink was uniformly coated on the GC-RDE, resulting in a loading of 0.63 mg cm⁻². For the 20 wt% commercial Pt/C catalyst, the loading is 0.26 mg cm⁻².

The linear sweep voltammogram (LSV) and cyclic voltammogram (CV) were obtained in O_2 or N_2 saturated electrolytes (alkaline, acidic, and neutral) with a rotation rate of 1600 rpm and scan rates of 5 mV s⁻¹ (Note: 50 mV s⁻¹ was used for activation and stabilization tests). Chronoamperometry (i-t) and accelerated aging tests (AAT) were used to assess the stability of the catalysts. For the accelerated aging test, 25 µL of the CNP-900 catalyst ink was coated onto a GC-RDE, achieving a catalyst loading of 0.63 mg cm⁻². Prior to electrochemical measurements, the solution was saturated with oxygen through continuous bubbling for 30 min. To assess electrochemical stability, accelerated aging tests were then conducted by applying 10,000 CV cycles (100 mV s⁻¹, 0.6-1.0 V vs. RHE) in 0.1 M PBS, with comparative testing performed using 35,000 cycles in 0.1 M KOH.

The electron transfer number (n) and hydrogen peroxide yield (H_2O_2 %) during ORR were measured using the rotating ring-disk electrode (RRDE). The following equations were used to calculate n and H_2O_2 %:

$$n = \frac{4I_{disk}}{\frac{I_{ring}}{N} + I_{disk}}$$
$$H_2O_2\% = \frac{200\frac{I_{ring}}{N}}{\frac{I_{ring}}{N} + I_{disk}}$$

where I_{disk} is the disk current, I_{ring} is the ring current, and N is the collection coefficient of the ring (N = 0.43).

Calibration reference electrode measurements

We calibrated the reference electrodes using a three-electrode system, with a reversible hydrogen electrode serving as the reference. Pt foil was used as the counter electrode. Glassy carbon loaded with commercial Pt/C was used as the work electrode. The H₂-saturated electrolytes (0.1 M KOH, 0.1 M PBS or 0.1 M HClO₄ solution) were first obtained by bubbling H₂ (500 mL min⁻¹) for 30 minutes. The calibration curves were then obtained by cyclic voltammetry with a scan rate of 1 mV s⁻¹.

DFT calculations

All the DFT calculations were conducted using the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method. The exchange-functional was treated using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. The energy cutoff for the plane wave basis expansion was set to 400 eV.^[1] Partial occupancies of the Kohn-Sham orbitals were allowed by employing the Gaussian smearing method with a width of 0.2 eV. The graphene layer with edges was constructed to accurately represent the observed vacancies from the experiment. The P atoms were placed on the edge of graphene, where PO₂, PO(OH), and PO groups were established. The Monkhorst mesh of $1 \times 2 \times 1$ was used for all surface structure optimizations. The self-consistent calculations used a convergence energy threshold of 10^{-4} eV, and the force convergence was set to 0.05 eV Å⁻¹. The energy of the electrochemical steps for ORR was calculated using the computational hydrogen electrode (CHE) approximation. The free energy corrections were set at 298 K, following:

 $\Delta G = \Delta E + \Delta G_{ZPE} + \Delta G_U - T\Delta S$

where ΔE , ΔG_{ZPE} , ΔG_U , and ΔS refer to the DFT calculated energy change, the correction from zero-point energy, the correction from inner energy and the correction from entropy. The solvent effect was taken into account for the OH* and OOH* adsorbates due to the H-network at the solid-liquid interface, and a stabilization of 0.17 and 0.20 eV was considered for OH* and OOH*, respectively.

In-situ ATR-SEIRAS test

All in-situ SEIRAS tests are performed in a three-electrode system consisting of gold film as the working electrode, Ag/AgCl as the reference electrode, and carbon rod as the counter electrode. The catalyst ink was prepared by dispersing 5 mg catalyst in a mixture of 950 μ L ethanol and 50 μ L Nafion (5 wt%). Then, the dispersed catalyst ink droplets are cast on the surface of the gold film. The oxygen reduction reaction is carried out in an O₂-saturated 0.1 M PBS electrolyte, continuously purging O₂ at 20 cc/min. The background spectra are collected at open circuit potential (OCP). The real-time spectra are collected at different potentials ranging from 1.1 to 0.3 V (vs. RHE). The step width is 100 mV.

In-situ Raman spectra test

In-situ Raman spectra test was conducted using a three-electrode in-situ Raman epoxy pool cell. 1 mg of catalyst sample was uniformly applied onto a 1 cm² piece of carbon paper, which served as the working electrode. Platinum wire was used as the counter electrode, an Ag/AgCl electrode as the reference, and 0.1 M O₂-saturated PBS solution as the electrolyte (the reference electrode calibration curve in 0.1 M PBS is shown in Fig. S12). A 50X long-working-distance objective and a 532 nm laser (set to 25%) were used to focus on the sample surface without contacting the electrolyte. The applied potential range was 1.0 to 0.0 V (vs. RHE).

Preparation of the PVA/SA hydrogel:

First, Polyvinyl alcohol (PVA) (0.9 g) and sodium alginate (SA) (0.1 g, 5 mmol) were dissolved in water (10 mL) and stirred 30 min at 90 °C to obtain a homogeneous solution. Afterward, 1 mL of a mixed solution containing 18 M KOH and 0.6 M Zn(CH₃COO)₂ was added. The solution was poured into a glass dish and frozen at -20 °C. The alkaline PVA/SA hydrogel was finally obtained by soaking it in a mixed solution of 6 M KOH and 0.2 M Zn(CH₃COO)₂ for ion exchanging overnight. For neutral PVA/SA hydrogel, 1 mL of a mixed solution containing 5 M NH₄Cl and 0.6 M

ZnCl₂ was added into the PVA/SA solution. And the final gel product was obtained by soaking in a mixed solution of 4 M NH₄Cl and 0.2 M ZnCl₂.

Assembly of the flexible zinc-air battery (FZAB)

Carbon cloth loaded with 2 mg cm⁻² of CNP-900 or 1 mg cm⁻² of 20 wt% Pt/C was used as the air cathode. Zn foil and PVA/SA hydrogel were used as the anode and the electrolyte, respectively. For rechargeable FZABs, CNP-900 and RuO₂ with a mass ratio of 1:1 were loaded in carbon cloth. The charge/discharge current density was set at 1 mA cm⁻² (20 min/cycle). The rate capabilities test was to discharge at 2, 5, 10 and 20 mA cm⁻² current density for 10 min, respectively.



Fig. S1. SEM images of (a-c) NC, (d-f) CNP-800, (g-i) CNP-900, (j-l) CNP-1000.



Fig. S2. The (a, c) plane and (b, d) stereo AFM images of the CNP-900.



Fig. S3. (a-c) TEM images and (d) corresponding SAED pattern of the CNP-900.



Fig. S4. Raman spectra of NC and CNPs. The Raman spectra are deconvoluted into four peaks corresponding to the I, D, D" and G at 1184, 1350, 1510 and 1600 cm⁻¹, respectively. The peak I is associated with sp³-C at the edges. The peak D" can be attributed to the presence of amorphous carbons such as C_5 ring, heteroatoms or C-H vibrations in hydrogenated carbons.



Fig. S5. N₂ adsorption-desorption isotherms and the corresponding pore size distributions of (a-b) NC, (c-d) CNP-800, (e-f) CNP-900 and (g-h) CNP-1000.



Fig. S6. (a) XPS survey, (b) C 1s and (c) N 1s spectrum of NC.



Fig. S7. (a) XPS survey, (b) C 1s, (c) N 1s and (d) P 2p spectrum of CNP-800.



Fig. S8. (a) XPS survey, (b) C 1s, (c) N 1s and (d) P 2p spectrum of CNP-900.



Fig. S9. (a) XPS survey, (b) C 1s, (c) N 1s and (d) P 2p spectrum of CNP-1000.



Fig. S10. The calibration curve of the reference electrode in 0.1 M KOH. E (vs. RHE) = E (vs. Hg/HgO) + 0.938 V.



Fig. S11. The calibration curve of the reference electrode in 0.1 M HClO₄. E (vs. RHE) = E (vs. Ag/AgCl) + 0.259 V.



Fig. S12. The calibration curve of the reference electrode in 0.1 M PBS. E (vs. RHE) = E (vs. Ag/AgCl) + 0.599 V.



Fig. S13. (a) CV curves of Pt/C, NC and CNPs in O₂/N₂-saturated 0.1 M PBS solution.
(b) LSV curves of the samples. (c) LSV curves and the corresponding K-L plots of CNP-900 at different rotation rates in O₂-saturated 0.1 M PBS solution.



Fig. S14. The CV and LSV curves of acetylene black and PC.



Fig. S15. LSV curves of Pt/C before and after 10,000 cycles in 0.1 M PBS solution.



Fig. S16. Methanol tolerance test of CNP-900 and Pt/C in 0.1 M PBS solution.



Fig. S17. (a, b) SCN⁻ and (c, d) Cl⁻ poisoning tests of NC and CNP-900 in 0.1 M PBS, respectively.



Fig. S18. (a) CV curves of Pt/C, NC and CNPs in O₂/N₂-saturated 0.1 M KOH solution.
(b) LSV curves of all the samples. (c) LSV curves and the corresponding K-L plots of CNP-900 at different rotation rates in O₂-saturated 0.1 M KOH solution.



Fig. S19. (a) Tafel slopes of Pt/C, NC and CNP-900. (b) H_2O_2 yield and electron transfer number of CNP-900 and Pt/C. (c) Chronoamperometric plots of CNP-900 and Pt/C. CV and LSV curves of (d) CNP-900, (e) Pt/C and (f) NC before and after extended cycling in 0.1 M O_2 -saturated KOH solution.



Fig. S20. Methanol tolerance test of CNP-900 and Pt/C in 0.1 M KOH solution.



Fig. S21. (a) CV curves of Pt/C, NC and CNPs in O_2/N_2 -saturated 0.1 M HClO₄ solution. (b) LSV curves of the samples. (c) LSV curves and the corresponding K-L plots of CNP-900 at different rotation rates in O_2 -saturated 0.1 M HClO₄ solution.



Fig. S22. (a) Tafel slopes of Pt/C, NC and CNP-900. (b) Chronoamperometry curves and (c) methanol tolerance test of CNP-900 and Pt/C in 0.1 M HClO₄ solution.



Fig. S23. Structural illustration of the (a) C-(P=O)₂, (b) C-P=O/OH and (c) C-P=O models. White (H), blue (N), red (O), brown (C), purple (P).



Fig. S24. The calculated adsorption energy of O_2 adsorbed on the C-(P=O)₂, C-P=O/OH and C-P=O models via "end-on", "side-on" and bridge chemisorption configurations.



Fig. S25. DOS of the 2p orbitals of carbon adjacent to the P dopant.



Fig. S26. In-situ Raman spectra of (a) CNP-900 and (b) NC.



Fig. S27. DOS of the 2p orbitals of P, C (adjacent to P) and O₂ after O₂ chemisorption on (a) C-(P=O)₂, (b) C-P=O/OH and (c) C-P=O.



Fig. S28. Correlation between the bond length of O–O (L_{O-O}), P-O (L_{P-O}), C-O (L_{C-O}) and the ORR activity of C-(P=O)₂ (red ball), C-P=O/OH (blue triangle) and C-P=O (orange pentagram).



Fig. S29. (a) Free energy profile of the electrochemical steps during ORR on the C- $(P=O)_2$ model. (b) Schematic diagram showing the structural failure of C- $(P=O)_2$ if ORR follows the dissociative pathway. White (H), blue (N), red (O), brown (C), purple (P).



Fig. S30. (a) OCV and (b) Power density of Pt/C-based FZABs in neutral medium.



Fig. S31. Image of a mini-fan powered by two neutral FZABs in series



Fig. S32. OCV of (a) CNP-900 and (b) Pt/C in alkaline FZABs. (c) Power densities of CNP-900-based alkaline FZABs under difference operating temperatures. (d) Power density of Pt/C-based alkaline FZABs at room temperature.

Catalyst	$\mathbf{J}_{\mathbf{L}}$	Eonset	E _{1/2}
	(mA cm ⁻²)	(V vs. RHE)	(V vs. RHE)
Pt/C	-5.32	1.00	0.68
NC	-5.69	0.86	0.70
CNP-800	-5.10	0.93	0.75
CNP-900	-5.54	0.94	0.77
CNP-1000	-5.60	0.94	0.76

Table S1. The LSV parameters of Pt/C and CNPs in O_2 -saturated 0.1 M PBS solution.

Catalyst	E _{onset} (V vs. RHE)	E _{1/2} (V vs. RHE)	J_{L} (mA cm ⁻²)	Reference
CNP-900	0.94	0.77	-5.54	This work
WSC-1	0.89	0.71	-6.03	[2]
Fe-N-HCS-900	0.90	0.76		[3]
1@Fe ₃ O ₄ NR/TM	0.81	0.57		[4]
N-HPCs		0.61	~-4.80	[5]
NPS-1&10&2	0.85	0.71	-5.62	[6]
Fe ₁ /d-CN	0.75	0.605	~ -5.20	[7]
NMCS-rGO-Co		0.72	~ -5.00	[8]
NiFe ₂ O ₄ /FeNi ₂ S ₄ HNSs	0.715	0.507	~ -4.00	[9]
Co–N/C+N _G	0.93	0.73	0.73 ~ -5.25	
FeS/Fe ₃ C@N-S-C- 800		0.56	-5.50	[11]

Table S2. Comparison of ORR performance of CNP-900 with reported representative noble-metal-free electrocatalysts in O₂-saturated 0.1 M PBS solution.

Catalyst	$\mathbf{J}_{\mathbf{L}}$	Eonset	E _{1/2}
	(mA cm ⁻²)	(V vs. RHE)	(V vs. RHE)
Pt/C	-5.18	1.03	0.86
NC	-6.35	0.99	0.86
CNP-800	-6.10	1.00	0.88
CNP-900	-6.62	1.02	0.91
CNP-1000	-6.67	1.00	0.90

Table S3. The LSV parameters of Pt/C and CNPs in O_2 -saturated 0.1 M KOH solution.

	Eonset	E _{1/2}	J_{L}	Df	
Catalyst	(V vs. RHE)	(V vs. RHE)	(mA cm ⁻²)	Kelerence	
CNP-900	1.02	0.91	-6.62	This work	
N, P, O-Carbon-PA	0.98	0.84	-5.43	[12]	
S, N, P-HPC-1		0.881	~ -5.00	[13]	
NPMC-1000	0.94	0.85	~ -4.20	[14]	
NSC/MPA-5		0.76	-3.30	[15]	
PNGF (op)		0.845	~ -5.60	[16]	
NPS-G-2		0.857	~ -5.80	[17]	
WSC-1	1.00	0.86	-6.52	[2]	
mf-pClNC	1.02	0.91	~-5.80	[18]	
Mn-SAS	0.99	0.85	-6.20	[19]	
CeNC-40	1.05	0.90	-5.60	[20]	
Te-Sl	0.87	0.76	-4.10	[21]	

Table S4. Comparison of ORR performance of CNP-900 with reported representativenoble-metal-free electrocatalysts in O_2 -saturated 0.1 M KOH solution.

Catalyst	$\mathbf{J}_{\mathbf{L}}$	Eonset	E _{1/2}
	(mA cm ⁻²)	(V vs. RHE)	(V vs. RHE)
Pt/C	-5.32	0.96	0.84
NC	-6.00	0.88	0.74
CNP-800	-6.00	0.86	0.75
CNP-900	-6.12	0.94	0.78
CNP-1000	-6.10	0.89	0.76

Table S5. The LSV parameters of Pt/C and CNPs in O_2 -saturated 0.1 M HClO₄ solution.

Catalyst	E _{onset} (V vs. RHE)	E _{1/2} (V vs. RHE)	J _L (mA cm ⁻²)	Reference
CNP-900	0.94	0.78	-6.12	This work
Ce SAS/HPNC		0.75	-5.50	[22]
SnNC		0.74	~ -5.90	[23]
β- FeOOH/PNGNs	0.84	0.68	-4.55	[24]
Fe-N-HCS-900	0.92	0.78		[3]
Cr/N/C-950		0.76	~-6.00	[25]
Co-N-C-10	0.92	0.79	~-6.00	[26]
PT-MnN ₄		0.73	~-5.80	[27]
CoTPP@bio-C	0.78	0.69		[28]

Table S6. Comparison of ORR performance of CNP-900 with reported representative noble-metal-free electrocatalysts in O₂-saturated 0.1 M HClO₄ solution.

 Lo-o
 Lp-o
 Lc-o

 C-(P=O)2
 1.5174 Å
 1.7017 Å
 1.4245 Å

 C-P=O/OH
 1.2589 Å
 3.6114 Å
 4.2083 Å

 C-P=O
 1.5198 Å
 1.6444 Å
 1.5867 Å

Table S7. The detail of bond lengths after O_2 bridge chemisorption on C-(P=O)₂, C-P=O/OH and C-P=O model.

Table S8. Comparison of the performance of CNP-900-based alkaline/neutral FZAB with reported representative alkaline/neutral FZABs using noble-metal-free air cathode.

Catalyst	Electrolyte	Open circuit voltage (V)	Power density (mW cm ⁻²)	Durability (h)	Ref.
CNP-900	KOH- PVA/SA	1.47	104.2	35	This work
CC-AC	KOH-PVA	1.36	52	16.6	[29]
N, S-CC	KOH-PVA	1.25	47	5	[30]
N-Co ₃ O ₄	KOH-PVA	1.1	32	28	[31]
Fe ₁ /d-CN	KOH-PVA	1.50	78	15	[7]
MnO _x -CC-400	КОН-РАА	1.47	32	45	[32]
MnO _x -GCC	КОН-РАА	1.43	32	~70	[33]
Co-NC@Al ₂ O ₃	КОН-РАА	1.41	72.4	10	[34]
Co@NCNTA- 700	KOH-PVA	1.48	38.6	12	[35]
CNP-900	NH4Cl- PVA/SA	1.37	47.1	13	This work
Fe ₁ /d-CN	NH ₄ Cl- PVA/SA	1.21	15.8		[7]
SA-Ir/NC	KNO ₃ -PVA	~ 0.80	31		[36]

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