Supplementary Information

Bottom-Up Synthesis of Iron and Nitrogen Dual-Doped Porous Carbon Nanosheets for Efficient Oxygen Reduction

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Section 1. Experimental section

Synthesis of Fe, N-PCNs

In detail, PVP (Sigma-Aldrich) and Fe(NO₃)₃·9H₂O (J&K Scientific LTD.) were dissolved in deionized water at a ratio of 1:1.5 at room temperature. The above mixture was ground after being thoroughly dried at 100 °C in an oven. The resultant fine powder was annealed at 500 °C for 1 h at a heating rate of 5 °C/min under Ar gas flow, followed by immersion in HCl solution (2 M) overnight and thorough wash with deionized water and ethanol in sequence. At last, the acid-leached powder was subjected to secondary calcination at a higher temperature (800 °C, 900 °C or 1000 °C) for 1 h in Ar gas flow with the same heating rate of 5 °C/min. The fabricated sample was detonated as "Fe, N-PCNs-X", where X represents the 2nd calcination temperature.

Material characterization

The crystal structure of the sample was analyzed on a D2 Phaser (Bruker) X-ray powder diffractometer (XRD) with Cu-K_a radiation ($\lambda = 1.5406$ Å). The diffraction pattern was collected at a rate of 0.05° s⁻¹ to record the pattern in the 2 θ range of 10-70°. Scanning electron microscope (SEM) observations were carried out on a Philips XL-30 field-effect SEM operated at 20 kV. Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements were performed on a JEM-2100F microscope (JEOL) operated at 200 kV. For TEM observation, the samples were suspended in ethanol, dripped on the holey carbon film on a Cu grid, and then dried in air. An Atomic Force Microscope (AFM, Veeco), operated at tapping mode, was used to obtain the thickness of the graphitic carbon layer. The nitrogen adsorption experiment was measured at 77 K using the Quantachrome Nova 1200e Surface Area Analyzer. The samples were heated and vacuumed at 120 °C for over 6 hrs before measurement. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB 220i-XL photoelectron with a monochromatic Al K α X-ray beam (1486.6 eV). All binding energies were normalized to the

C1s peak energy at 284.6 eV. Raman spectra were measured using a Renishaw 2000 microscope equipped with a He-Ne Laser (632.8 nm) of 17 mW power.

Electrochemical measurement

All the electrochemical measurements were conducted on a CHI 660 electrochemical station (CH Instruments, Inc.) with a conventional three-electrode system. In a typical electrochemical measurement, a total of 5 mg of catalysts was dispersed by sonication in a mixture of 480 µL isopropanol (J&K Scientific LTD.) and 20 µL of Nafion aqueous solution (5 wt.%, DuPont) for 30 min. 12 µL of the above suspension was slightly dropped onto a glassy carbon rotating disk electrode (RDE, 5 mm diameter) or rotating ring-disk electrode (RRDE, 4.93 mm inner diameter and 5.38 mm outer diameter) in two times and air dried naturally, fixed with a total loading mass of about 0.6 mg/cm². The electrolyte was 0.1 M KOH aqueous solution, and the reference and counter electrodes were saturated calomel electrode (SCE) and Pt wire, respectively. The electrolyte was saturated with O₂ before the experiment, and O₂ was continuously supplied during the experimental operation. All potential values reported in this study were converted to the reversible hydrogen electrode (RHE) scale, according to the equation: $E_{RHE} = E_{SCE} + 0.0591 \text{pH} + 0.242$. For the stability test, the working electrode ran at -0.7 V vs SCE for 50,000 s in O₂-saturated 0.1M KOH with a rotation rate of 1600 rpm. For comparison, commercial Pt/C (20 wt.% Pt) powder purchased from was tested under the same conditions, with a loading mass of 0.25 mg cm⁻². Linear sweep voltammetry (LSV) was measured by RDE/RRDE technique the with the scan rate of 10 mV/s at various rotating speeds from 400 to 2400 rpm.

The electron transfer number involved in ORR on the carbon catalysts was calculated using the Koutechy-Levich equation:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{(B\omega^{-1/2})}$$
$$B = 0.62nFC_0 D_0^{2/3} V^{-1/6}$$

where *J* corresponds to the current density obtained from the measurement, J_K and J_L are the kinetic and limiting current densities, respectively, ω is the angular velocity of the disk (from 400 to 2400 rpm in the reaction), *n* is the total electron transfer number during oxygen reduction, *F* is the Faraday constant (96485 C mol⁻¹), C_0 (1.2 × 10⁻⁶ mol/cm³ in 0.1 M KOH) is the bulk concentration of O₂, D_0 (1.9 × 10⁻⁵ cm²/s in 0.1 M KOH) represents the diffusion coefficient of O₂, and *V* (0.01 cm²/s in 0.1 M KOH) corresponds to the kinematic viscosity of the electrolyte.

The hydrogen peroxide yield $[H_2O_2 (\%)]$ and the electron transfer number (*n*) were obtained from the two equations shown below:

$$H_2O_2(\%) = 200 \times (I_R/N)/(I_R/N+I_D)$$

 $n = 4 \times I_D/(I_R/N+I_D)$

Where I_D corresponds to the disk current, I_R is the ring current, and N represents the ring collection efficiency (N = 0.4).

Section 2. Characterization and electrochemical performances of corresponding materials



Figure S1. SEM images of Fe,N-PCNs-900 catalyst.



Figure S2. SEM images of Fe,N-PCNs-500 sample without acid washing.



Figure S3. The XRD pattern of Fe,N-PCNs-500 sample without and with acid washing.



Figure S4. The high-resolution N 1s spectra of Fe,N-PCNs catalysts prepared at different temperatures.



Figure S5. The full scan XPS spectra of Fe,N-PCNs catalysts prepared at different temperatures.



Figure S6. The high-resolution Fe 2p spectra of Fe,N-PCNs catalysts prepared at different temperatures.



Figure S7. The nitrogen adsorption-desorption isotherm (a) and the pore size distribution (b) curve of Fe,N-PCNs-900 catalyst.



Figure S8. RRDE voltammograms of the ORR on Fe,N-PCN-900 (a) and commercial 20% Pt/C catalyst (b) at 1600 rpm in O_2 -saturated 0.1 M KOH. Ring potential: 1.5 V vs. RHE.



Figure S9. The dependence of electron transfer number n (a) on the potential and the H_2O_2 generation (b) for the Fe,N-PCN-900 catalyst calculated from the corresponding RRDE data.



Figure S10. I-t plots (normalized to the initial current) of Fe,N-PCNs-900 and Pt/C catalysts at -0.7 V vs SCE, performed at the rotation speed of 1600 rpm.



Figure S11. SEM images of Fe,N-PCNs-900 catalyst after durability testing.



Figure S12. LSVs of the Fe,N-PCNs-900 catalyst in O₂-saturated 0.1M KOH without and with 3M CH₃OH.

Section 3. Supplementary Table

| Table S1. Performance comparison between I | Fe,N-PCNs-900 and | d other previously i | reported |
|--|-------------------------|----------------------|----------|
| ORR electrocatalysts. | | | |
| Flectrocatalyst | $F_{1,n}(\mathbf{V})$ # | Electrolyte ^ | Ref |

| | Electrocatalyst | $E_{1/2}(V)$ # | Electrolyte ^ | Ref. |
|----------|--|----------------|---------------|-----------|
| Fe-based | Fe,N-PCNs-900 | 0.87 | 0.1 M KOH | This work |
| | Fe-Nx/C | 0.837 | 0.1 M KOH | 1 |
| | Fe-N-doped hollow C | 0.85 | 0.1 M KOH | 2 |
| | Fe ₃ C-Fe-N-CNFs | 0.81 | 0.1 M KOH | 3 |
| | Fe@N-C-nanoshell | 0.83 | 0.1 M KOH | 4 |
| | Fe ₃ C- graphene nanoribbons | 0.78 | 0.1 M KOH | 5 |
| | Fe/Fe ₂ N/Fe ₃ C-N-C box | 0.85 | 0.1 M KOH | 6 |
| Others | Co-N-porous C nanotubes | 0.82 | 0.1 M KOH | 7 |
| | Co ₃ O ₄ /N-rGO | 0.79 | 0.1 M KOH | 8 |
| | NiFe/N-C sheets | 0.7 | 0.1 M KOH | 9 |
| | Co-CoO/N-rGO | 0.78 | 0.1 M KOH | 10 |

[#] $E_{1/2}$ is the half-wave potential of ORR. All the potentials are *versus* the RHE. ^ All electrocatalysts tested in O₂-saturated 0.1 M KOH solution.

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