

Supporting information

Pore engineering of Fe-N-C electrocatalyst to enhance the performance for oxygen reduction reaction by adding g-C₃N₄ into polyaniline and cyanamide as precursor

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Experimental Section:

Synthetic procedures:

Synthesis of g-C₃N₄: 10 g of melamine and 10 g of cyanuric acid (98%) were dispersed into 800 ml of ethanol. The solution was stirred for 1 hour and dispersed by ultrasonic for another 4 hours. After centrifugation and drying, the samples were heated at the temperature with heating rate of 3 °C/min per minute to 550 °C in the quartz tube. The furnace was kept at 550 °C for 6h to obtain g-C₃N₄.

Synthesis of Fe-N-C-(PANI+CM+g-C₃N₄) and Fe-N-C-(PANI), Fe-N-C-(PANI+CM) as reference samples: 3 ml of Aniline (ANI) oligomer and 8.0 g Cyanamide (CM) were first added into 420 ml 1M HCl solution. Then, 80 ml of FeCl₃ solution (5 g anhydrous FeCl₃ dissolved in 80 ml 1M HCl) was added, followed by adding (NH₄)₂S₄O₈ solution (7.5 g dissolved in 22.5 g water). After stirring for 48 h, g-C₃N₄ solution (0.5g as prepared g-C₃N₄ dispersed in 100 ml water for 2h with ultrasound) was added. After stirring for another 2h, the mixture was poured into a heating plate, then evaporated and dried at 90 °C, then finally put into the quartz tube. The specimen were kept at 350 °C under N₂ atmosphere for 2h, and then polymerized at 900 °C for 1 hour (heating rate of 3 °C /min). The as prepared product was taken out and washed with 0.5M H₂SO₄ to remove the residue iron nanoparticles and/or metal oxide. After drying at vacuum, the secondary heat treatment was conducted at 900 °C for 3h with a ramping rate of 3 °C/min under Ar atmosphere, the final product was obtained and denoted as Fe-N-C-(PANI+CM+g-C₃N₄). For comparison, the reference sample Fe-N-C-(PANI) were obtained by the polymerization and pyrolysis of only Aniline oligomer under the similar

condition, and the reference sample Fe-N-C-(PANI+CM) were obtained by pyrolysis of Aniline and Cyanamide.

Physical Characterization of Materials:

X-ray diffraction (XRD) measurements were performed with a Miniflex600 diffractometer using a Cu K α ($\lambda = 1.5405 \text{ \AA}$) radiation source. Raman spectra were taken on a LabRAM HR spectrometer with 532 nm wavelength incident laser light. Scanning electron microscopy (SEM) characterization were taken on field emission scanning electron microscope (FESEM ZEISS SIGMA500). Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), high-annular dark-field scanning transmission electron microscopy (STEM) and element mapping analysis were taken on FEI Tecnai G2 F30 electron microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed with an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo, America). The pore structures of the samples were analyzed by using an Autosorb-iQ2 (Quantachrome Instruments) physical absorber.

Electrochemical measurements:

Rotating Disk Electrode tests. All electrocatalytic measurements were performed in a three-electrode cell using a rotating disk electrode (RDE, PINE Research Instrumentation) of 5.0 mm in diameter with an electrochemical workstation (CHI 760D, Shanghai Chenhua, China) in 0.1M KOH electrolyte. A platinum wire and Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. All potentials in this study are referenced to reversible hydrogen electrode (RHE), $E_{(RHE)} = E_{(Ag/AgCl)} + 0.059\text{pH} + 0.197$. The catalyst ink is prepared by dispersing the catalyst (5 mg) in solution (1 mL) containing isopropanol (0.95 mL) and 5 wt% Nafion solution (50 μL), followed by ultrasonication for 30 min. Then, a certain volume of catalyst ink was pipetted onto the GC surface to give a 0.38 mg cm^{-2} loading for all samples. The loading of commercial Pt/C (20 wt%, Johnson Matthey) was $20 \text{ ug}_{Pt} \text{ cm}^{-2}$. Prior to testing, the electrolyte was saturated with oxygen by bubbling O_2 and a flow of O_2 was maintained over the electrolyte during the measurements. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) curves of the catalyst under N_2 -saturated alkaline electrolyte were also measured. The scan rate of LSV was 10 mV s^{-1} and the rotating speed was varied from 500 to 2500 rpm. For the ORR on a RDE, the electron transfer numbers can be calculated with Koutecky-Levich equations:

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

where J is the measured current density; and JK are the kinetic and JL diffusion-limiting current densities, respectively; ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear rotation speed).

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

$$J_k = nFKC_0$$

where n represents the transferred electron number; F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$); C_0 is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$); D_0 is the diffusion coefficient of O_2 in 0.1 M KOH electrolyte ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); ν is the kinematics viscosity for electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and k is the electron-transferred rate constant.

Zn-air battery assembly

The air electrodes used for liquid Zn-air batteries consisted of carbon paper (CP) with a gas diffusion layer (GDL), and a catalyst layer (CL). The CL was made by loading the catalyst ink onto the GDL by drop-casting, with a loading of 2.0 mg cm^{-2} for all catalysts. The catalyst ink was prepared as described for the electrochemical experiments. Electrochemical reactors with a total volume of 28 mL were constructed to test the liquid Zn-air batteries. A polished zinc plate (0.6 mm thickness) was used as the anode. 6 M KOH and 0.2 M $\text{Zn}(\text{CH}_3\text{COO})_2$ were used as electrolyte.

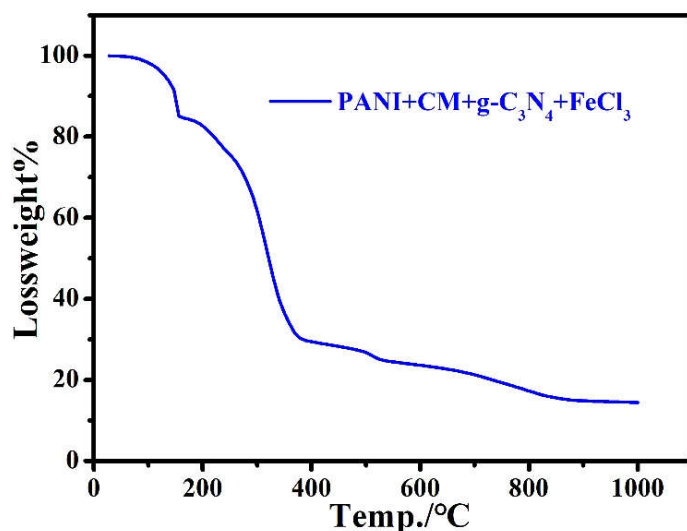


Figure S1 TGA graph of the PANI+CM+g-C₃N₄+FeCl₃ obtained by heat treatment at 1000 °C (N_2 flow: 30 mL min^{-1} , heating rate: 3 °C min^{-1})

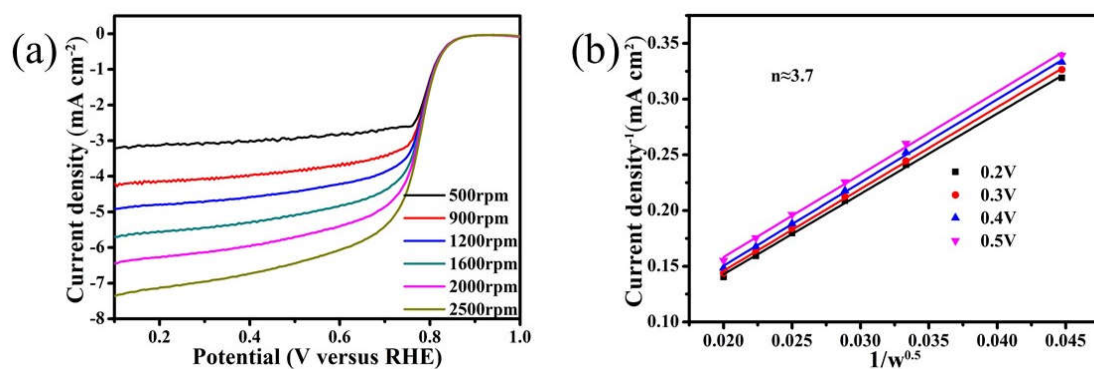


Figure S2 (a) LSV curves of Fe-N-C-(PANI+CM+g-C₃N₄) sample at different rotating rates in O₂-saturated 0.1M HClO₄ solution at room temperature ; (b) Corresponding K-L plots at different potentials for LSV curves and electron transfer number.

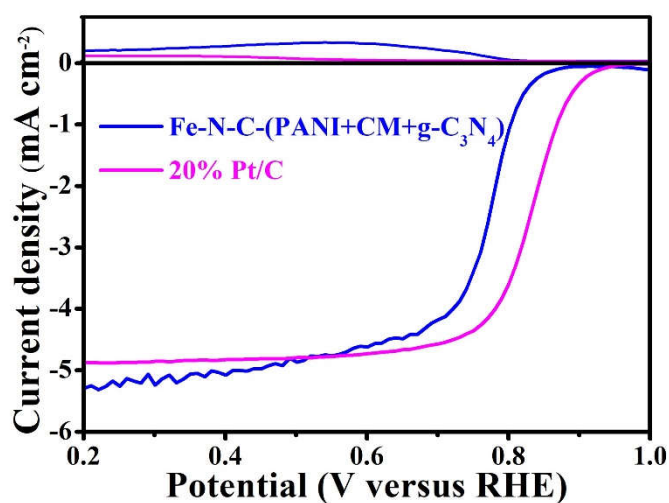


Figure S3 LSV curves (both disc and ring current densities) of Fe-N-C-(PANI+CM+g-C₃N₄) and 20% Pt/C in O₂-saturated 0.1M HClO₄ at a scan rate of 10 mV s⁻¹ and a rotating speed of 1600 rpm.

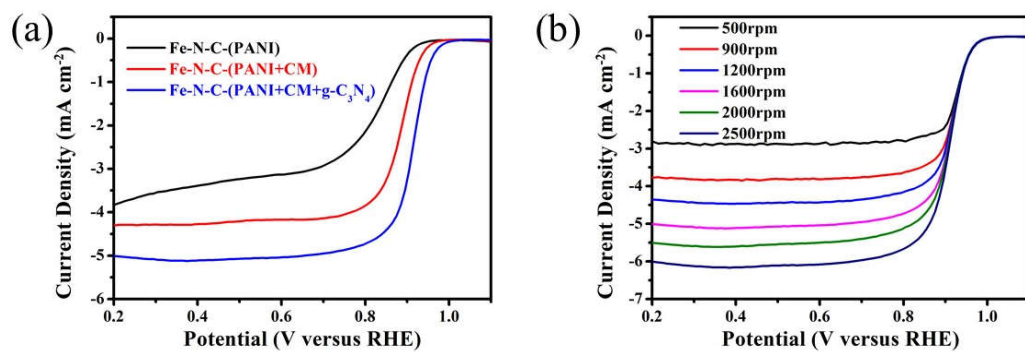


Figure S4 (a) ORR polarization curves tested from RDE Fe-N-C-(PANI+CM+g-C₃N₄), Fe-N-C-(PANI+CM), and Fe-N-C-(PANI) in an O₂-saturated 0.1 M KOH solution; (b) LSV curves of Fe-N-C-(PANI+CM+g-C₃N₄) sample at different rotating rates in O₂-saturated 0.1M KOH solution at room temperature.

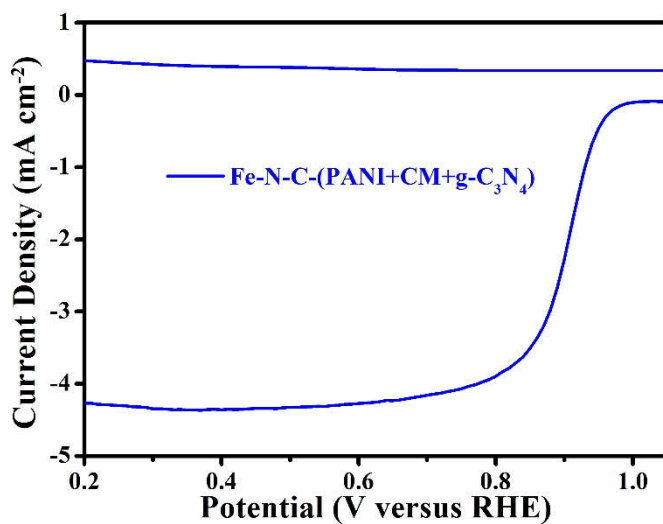


Figure S5 LSV curves (both disc and ring current densities) of Fe-N-C-(PANI+CM+g-C₃N₄) in O₂-saturated 0.1M KOH at a scan rate of 10 mV s⁻¹ and a rotating speed of 1600 rpm.

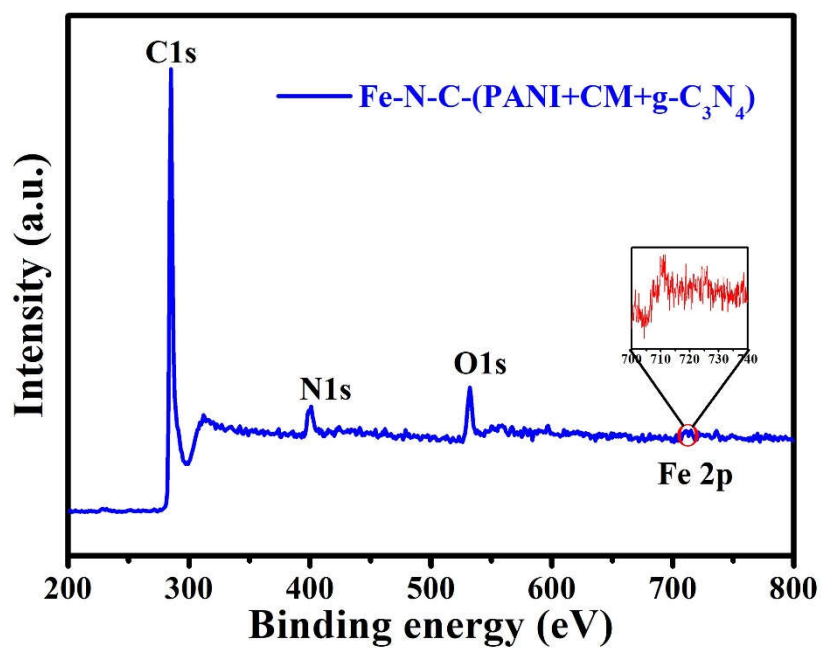


Figure S6 XPS survey spectrum of Fe-N-C-(PANI+CM+g-C₃N₄)

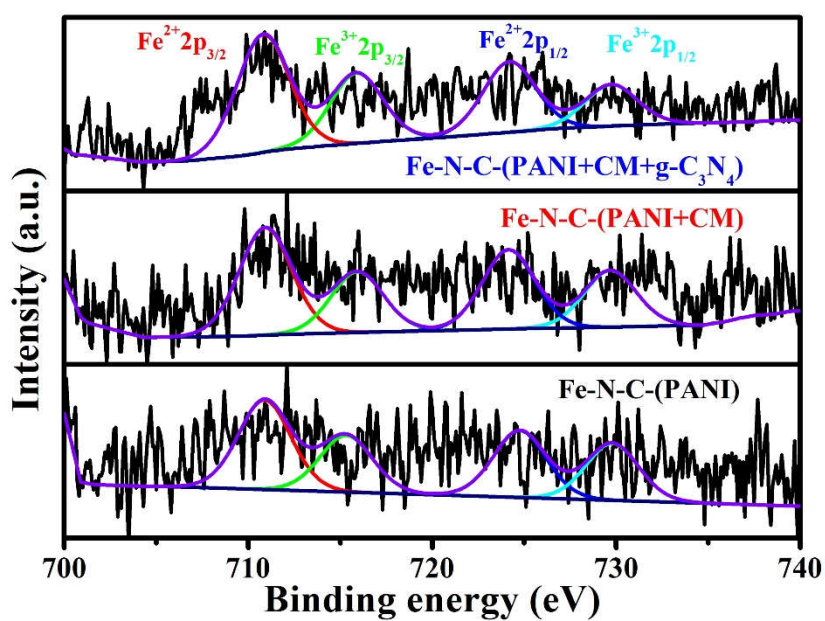


Figure S7 Fe 2p XPS spectra of Fe-N-C-(PANI), Fe-N-C-(PANI+CM) and Fe-N-C-(PANI+CM+g-C₃N₄).

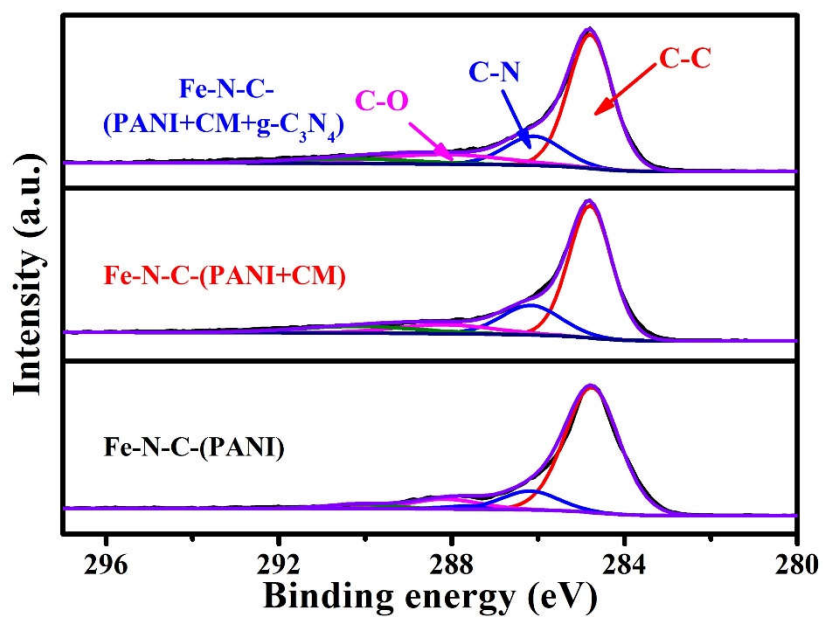


Figure S8 C1s XPS spectra of Fe-N-C-(PANI), Fe-N-C-(PANI+CM) and Fe-N-C-(PANI+CM+g-C₃N₄).

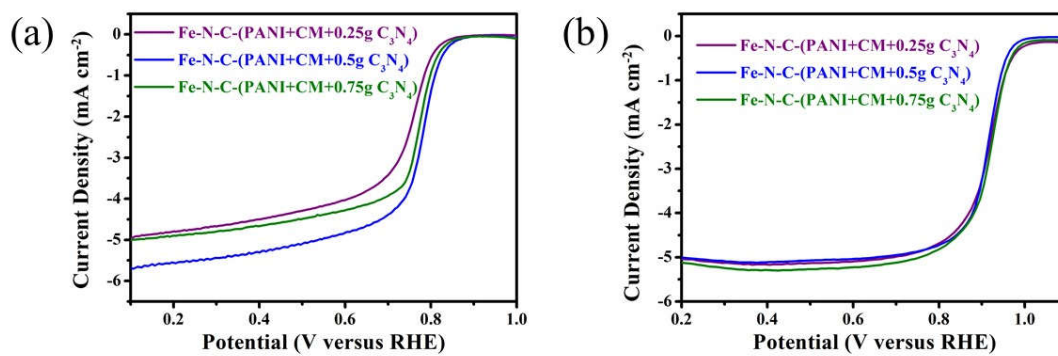


Figure S9. ORR polarization curves tested from RDE of Fe-N-C-(PANI+CM+g-C₃N₄) with different C₃N₄ ratio, in an O₂-saturated 0.1 M HClO₄ solution(a) and 0.1M KOH(b) with a rotation rate of 1600 rpm

Table S1

Samples	Electrolyte	E_{1/2}(V)	Reference
Fe-N-C- (PANI+CM+g-C₃N₄)	0.1M KOH	0.912	This Work
Fe-NC SAC	0.1M KOH	0.90	Nature Communications (2019)10:1278
Fe-NPC	0.1M KOH	0.89	Applied Catalysis B: Environmental 249 (2019) 306-315
Fe SAs/N-C	0.1M KOH	0.91	ACS Catal. 2019, 9, 2158-2163
C-FeZIF-1.44-950	0.1M KOH	0.864	Adv. Energy Mater. 2019, 9, 1802856
Fe-NSDC	0.1M KOH	0.84	Small 2019, 15, 1900307
Co@NHCC-800	0.1M KOH	0.837	Applied Catalysis B: Environmental 254 (2019) 55-65
Mn/Fe-HIB-MOF	0.1M KOH	0.833	Energy Environ Sci, 2019, 12, 727-738
Fe_{SA}-N-C	0.1M KOH	0.891	Angew. Chem. Int. Ed. 2018, 57, 8525-8529
SA-Fe-N-1.5-800	0.1M KOH	0.91	Adv. Energy Mater. 2018, 8, 1801226
Fe-N-C-900	0.1M KOH	0.905	Adv. Energy Mater. 2018, 1801956