

Supporting information

Porous Polyaniline-derived FeN_xC/C Catalysts with High Activity and Stability towards Oxygen Reduction Reaction using Ferric Chloride both as Oxidants and Iron Sources

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Reference

S1

Experimental

Catalyst Syntheses

Aniline monomer was distilled under reduced pressure at below 4°C. Carbon nanospheres (CNS, i.e., Vulcan XC-72 with ca. 40nm in diameter and 230 m² g⁻¹ in surface area) with rich micropores was treated in an aqueous HCl solution for 24 h to remove the potential metal impurities. HCl (as the dopant acid), ferric chloride (FeCl₃·6H₂O) (as the oxidant), and other reagent were used as-received without further treated. The solution was prepared using ultra pure water obtained from a Lab. ultra pure water filter system with a resistivity ≥18MΩ cm⁻¹.

0.5g CNS as supports was first ultrasonically dispersed in 0.5 M HCl solution. 3 mL aniline was dissolved to form uniform solution under magnetic stirring in the ice-bath (0–5°C) for 30 min. FeCl₃·6H₂O (2.4 mol·L⁻¹) solution was added drop-wise to the above suspension and kept stirring in the ice-bath (0–5°C) for 16 h, and the molar ratio of FeCl₃·6H₂O to aniline is 8:1. The suspension containing carbon, polymer and transition metal was filtered by water pump. The product was dried in vacuum at 60°C for 24 h. Subsequent heat-treatment was performed at 900°C for 1 h at a heating rate of 30°C/min in an ammonia atmosphere, and then the sample was cooled under the same atmosphere from 900 °C to 60 °C. As a comparison, another sample heat-treatment was performed at 900°C for 1 h at a heating rate of 3°C min⁻¹, and the other conditions unchanged. The pyrolyzed sample was then pre-leached in 0.5 M H₂SO₄ at 80°C for 10 h to remove unstable and inactive species from the catalyst,

followed by thoroughly washed in de-ionized water and absolute ethyl alcohol, and then dried at 80°C under vacuum. Finally, the product was heat-treated again at 900°C for 3 h in nitrogen atmosphere to obtain the FeN_xC/C catalyst.

Physical and Chemical Characterizations

The phase of the catalyst was analyzed using D/Max-RB X-ray Powder Diffractometer (XRD) with Cu-Kα radiation, and the XRD patterns were recorded between 10° and 80° and a powder diffraction file database was used to assign the diffractograms. The morphology and structure of the sample were further analyzed using JSM-7100F field emission scanning electron microscope (SEM) and JEM-2100F high-resolution transmission electron microscopy (TEM). Nitrogen adsorption-desorption isotherms were recorded at 78 K with a Micromeritics ASAP 2020 Brunauer Emmett Teller (BET) analyzer. The electronic structure of surfaces for the catalyst was performed using VG-Multi-lab2000 X-ray photoelectron spectroscopy (XPS). Raman spectroscopy was carried out on a Renishaw using the Ar ion laser with an excitation wavelength of 514.5 nm.

Electrochemical characterizations

ORR activity of the catalyst was evaluated on an electrochemical workstation (Autolab PGSTAT 30 potentiostat, Eco Chemie B.V, Holland) at room temperature using a three-electrode electrochemical cell. To prepare the working electrode, a homogeneous catalyst ink was made by mixture of 8.0 mg catalyst, 50 μL Nafion ionomer solution (5 wt%, DuPont) and 0.95 mL ultra pure water. The 20 μL of the

catalyst ink was spread onto the surface of a glassy carbon (GC) disk electrode of geometric area 0.20 cm^2 with a micrometer pipette to form a catalyst layer, followed by drying under an infrared bulb. For the prepared catalysts, the loading was 0.8 mg cm^{-2} ,¹ and for the commercial Pt/C catalyst, the Pt loading was $20 \mu\text{g Pt cm}^{-2}$.

All the electrochemical properties of the catalysts were measured using a conventional three compartment electro-chemical cell in 0.1M HClO_4 aqueous solution. A Pt gauze and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The SCE reference electrode was calibrated against the reversible hydrogen electrode (RHE). The working electrode was constructed with a GC disk electrode coated with the catalyst layer. The ORR activity was carried out using rotating disk electrode (RDE) technique by linear sweep voltammetry (LSV) in the potential range of 0.2 to 1.1 V (vs. RHE) with a scan rate of 5mV s^{-1} in an O_2 -saturated 0.1M HClO_4 solution. The cyclic voltammetry curves (CV) was collected in the potential range of 0 to 1 V (vs. RHE) with a scan rate of 50 mV s^{-1} in an O_2 -saturated 0.1M HClO_4 solution. In this paper, all the potentials were normalized to the reversible hydrogen electrode, all current densities were normalized to the geometric surface area of the disk electrode and all the electrochemical experiments were carried out at room temperature and ambient pressure. ORR stability of the catalyst was investigated by continuous potential cycling in O_2 -saturated 0.1 M HClO_4 between 0 to 1 V (vs. RHE) with the scan rate at 0.10 V s^{-1} . After continuous cycles, the ORR steady-state polarization measurement was conducted in O_2 -saturated 0.1 M HClO_4 electrolyte with scanning rates of 5 mV s^{-1}

and rotation rate at 1600 rpm.

S2

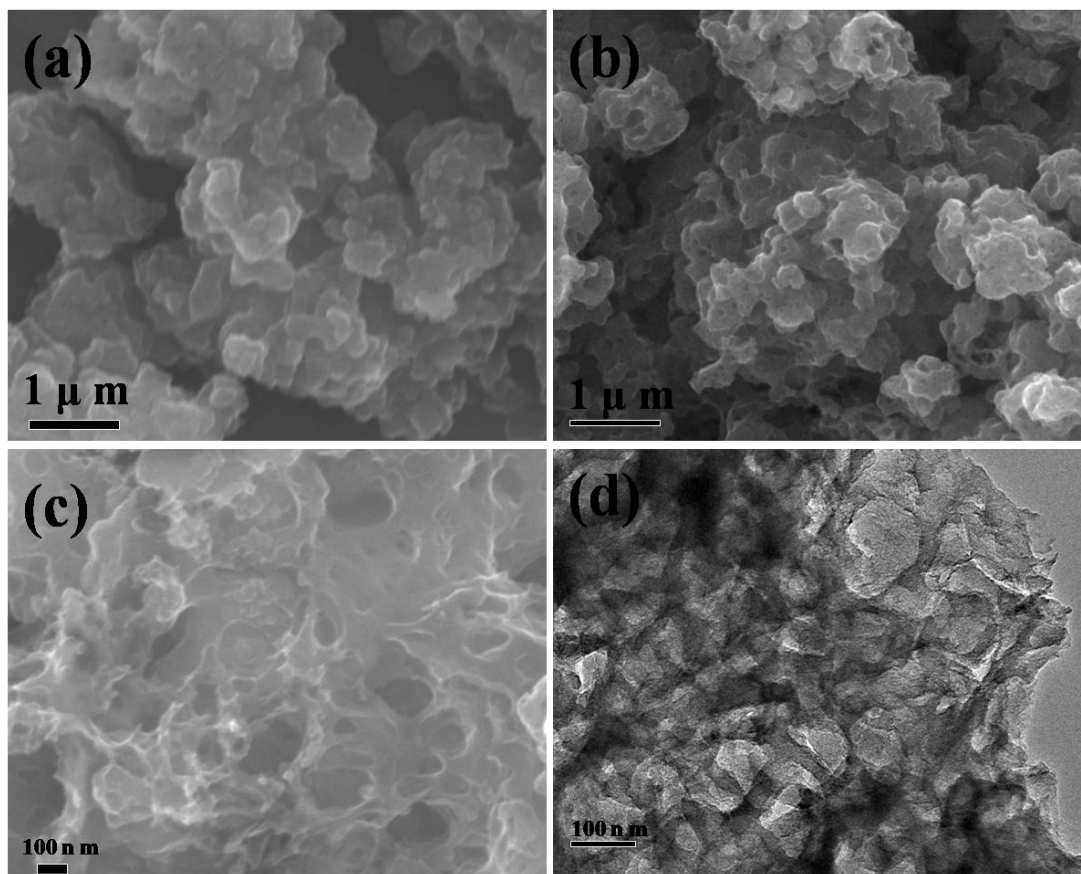


Fig. S1 SEM images of samples treated at different heating rates of (a) Fe_{N_x}C/C-S, (b) Fe_{N_x}C/C-F, the high levels of magnified (c) SEM and (d) TEM images of Fe_{N_x}C/C-F.

S3

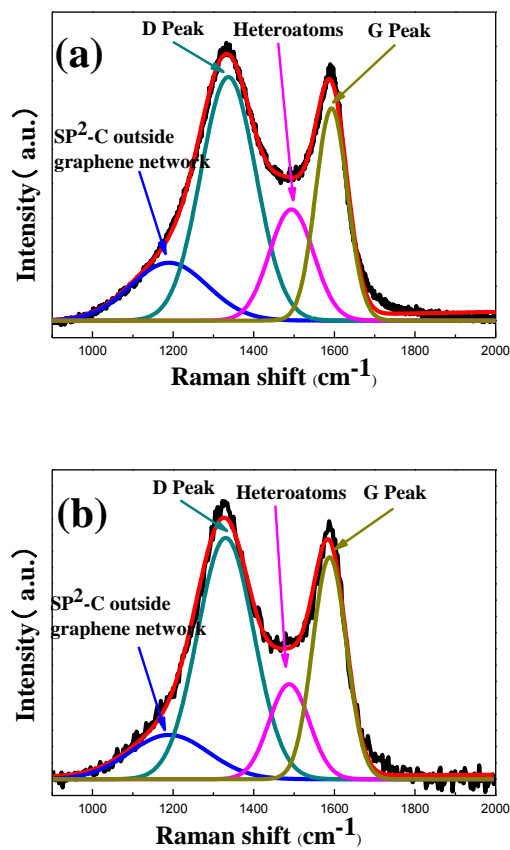


Fig. S2 Raman spectra of CNS, HT₁-acid.

S4

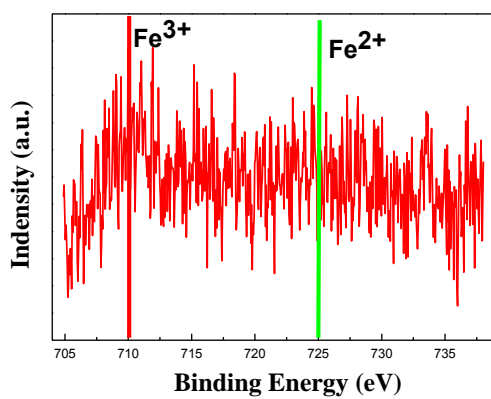


Fig. S3 XPS spectra of Fe.

S5

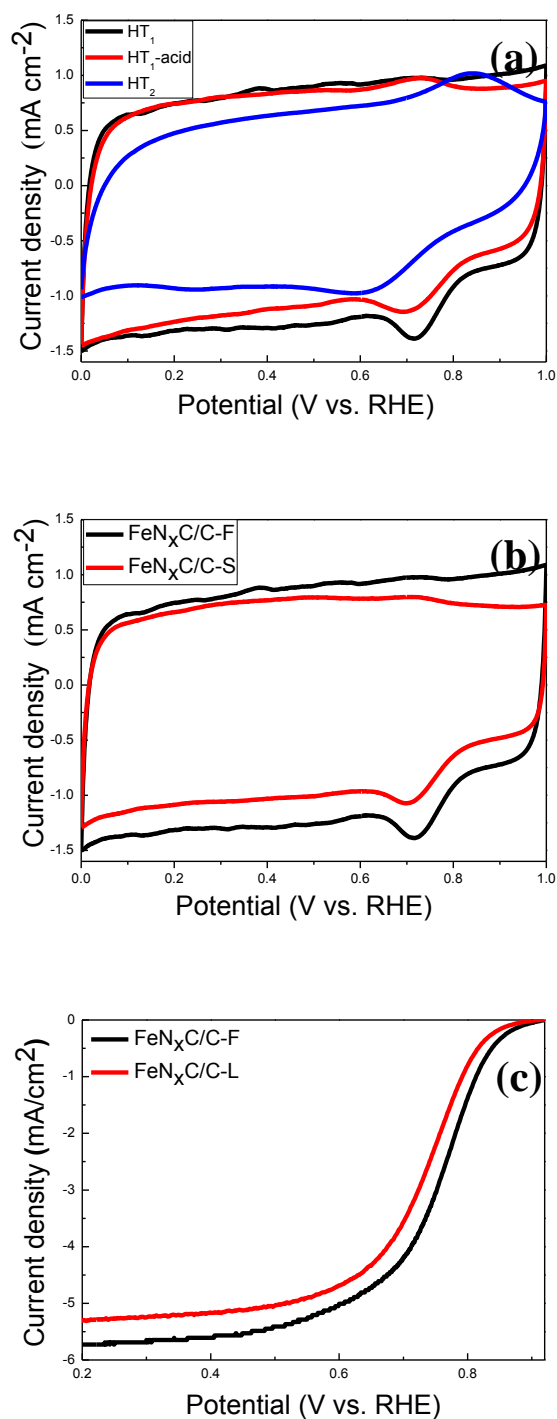


Fig. S4 (a) CV curves for Fe_{N_x}C/C-F at the different synthesis stages in O₂-saturated 0.1 M HClO₄, (b) CV and (c) LSV curves of Fe_{N_x}C/C-F and Fe_{N_x}C/C-S in O₂-saturated 0.1 M HClO₄, respectively.

S6

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

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

where J denotes the measured current density, J_K is the kinetic current density, J_L is the diffusion-limited current density, ω is the electrode rotation rate, F is the Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 ($1.26 \times 10^{-3} \text{ mol L}^{-1}$), D_0 is the diffusion coefficient of O_2 ($1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and ν is the kinetic viscosity of the electrolyte ($1.0 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$).

S7

The rotating ring-disk electrode (RRDE) measurements for the $\text{FeN}_x\text{C/C-F}$ was also performed with a three-electrode system in O_2 -saturated 0.1 M HClO_4 solution at a rotation rate of 1600 rpm . The H_2O_2 percentage released during ORR and the apparent electrons transferred numbers were calculated based on the following equations:²

$$n = 4I_D / (I_D + I_R / N) \quad (1)$$

$$\text{H}_2\text{O}_2 \% = 200I_R / (N \cdot I_D + I_R) \quad (2)$$

Represent the disk and ring currents respectively, and N is the current collection efficiency of the Pt ring, which was 0.25 in our system.

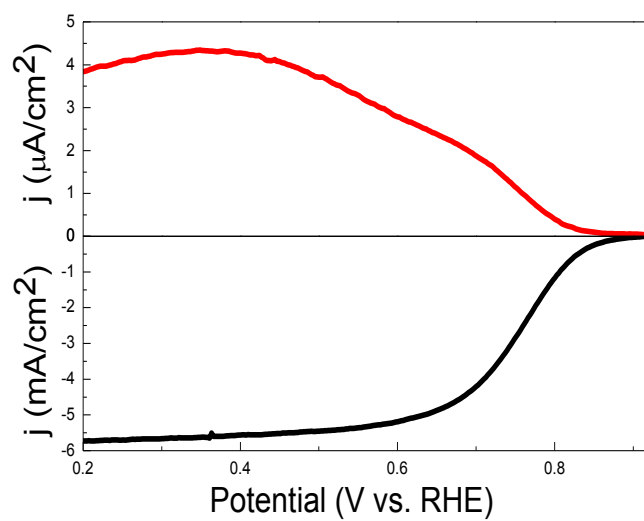


Fig. S5 RRDE test of the ORR for $\text{FeN}_x\text{C}/\text{C-F}$.

S8

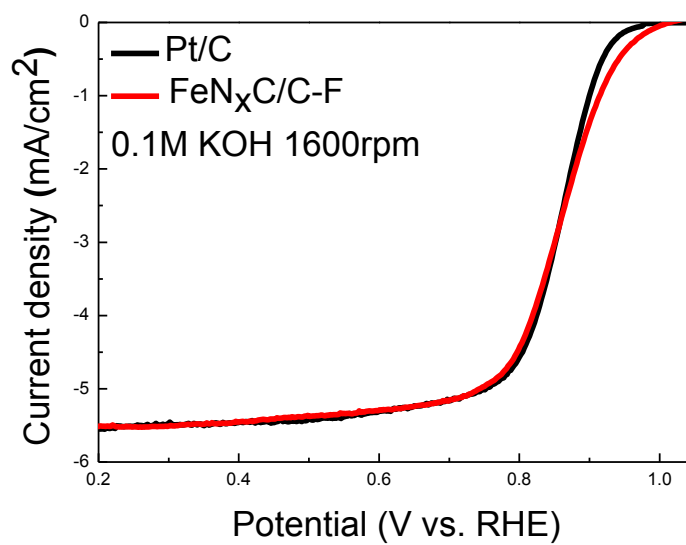


Fig. S6. ORR polarization curves for the $\text{FeN}_x\text{C}/\text{C-F}$ and Pt/C in O_2 -saturated 0.1 M KOH.

S9

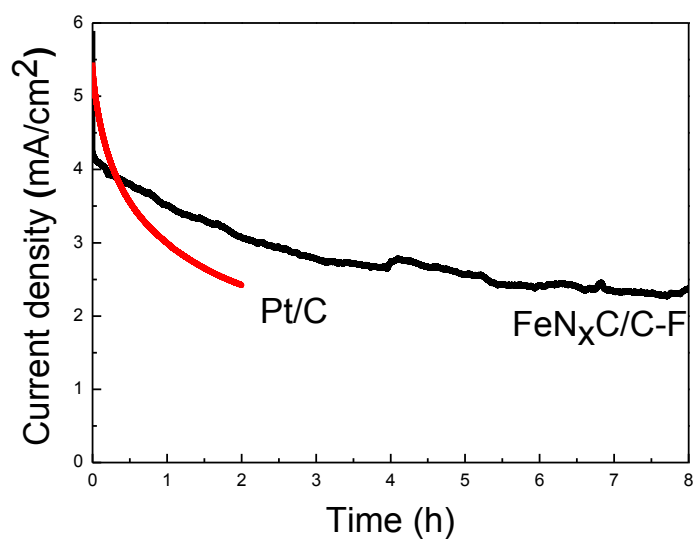


Fig. S7 Current vs time chronoamperometric response of the FeN_xC/C-F and Pt/C during a constant potential at 0.62 V at a rotation rate of 1600 rpm in O₂-saturated 0.1 M HClO₄.

Reference

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- 2 S. M. Zhang, H. Zhang, Q. Liu and S. L. Chen, *J. Mater. Chem. A*, 2013, **1(10)**, 3302-3308.