Electronic Supplementary Information (ESI)

Controllable Synthesis of Porous Iron-Nitrogen-Carbon Nanofibers with Enhanced Oxygen Reduction Electrocatalysis in Acidic Medium

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1. Experimental Details

Synthesis of porous Fe-N-C nanofibers: The precursor solution for electrospinning was combined by PAN (M_w = 150,000, Aldrich), $Fe(NO_3)_3$•$9H_2O$ (AR, ≥98.5 %, Sinopharm Chemical Reagent Ltd.), Si nanoparticles (50 nm in diameter) and *N,N*-dimethylformaimde (DMF, AR, ≥99.5 %, Sinopharm Chemical Reagent Ltd.), which were used without further purification. The weight ratio of Si NPs and PAN (Si/PAN) was set from 0 to 2.5, with a step of 0.5. The mixture was then electrospun PAN nanofibers with Si nanoparticles. Subsequently, the as-electrospun nanofibers was transferred into a porcelain boat and heated in a furnace under a industrial-like process.[20,21] The samples was stabilized from room temperature to 260 °C in air with a slow rate of 2 °C/min, incubated for another 30 min, and carbonized in argon at 800 °C for two hours. The Si nanoparticles were removed using 3 mol/L KOH solution at room temperature for 72 hours, washed with deionized water by three times, and then dried at 60 °C to yield the final produce. KOH is less harmful to environment than HF for etching Si.[25] The final samples were named as FeNC-00, PFeNC05, PFeNC10, PFeNC15, PFeNC20 and PFeNC25, where the last two

numbers were equal to 10 times weight ratio of Si NPs and PAN (Si/PAN). Sample named FeNC was the one without adding Si nanoparticles and the etching process.

Structural and compositional characterizations: The thermal gravimetric analysis (TGA) and derivative TGA (DTG) of FeNC-Si00 was performed on a TGA-Q5000 IR thermogravimetric analyzer (TA instruments, USA) using a heat rate of 10 °C/min in nitrogen atmosphere. The Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) spectra were taken by Nicolet Avatar 360 FT-IR E.S.P. and ESCALAB 250XI spectrometer, respectively. The scanning electron microscopy (SEM) images were obtained by JOEL JSM-6301F equipped with an energy dispersive X-ray spectrometer (EDX). TECNAI G^2 20 was used to acquire the (TEM) images of all samples.

Electrochemical characterizations: The ORR performances of the catalysts were measured in an acidic medium (0.1 mol/L oxygen-saturated $HClO_4$ solution) on an electrochemical workstation (CHI660C) at room temperature by using a rotation disk electrode (RDE). The loadings of catalysts on the working electrode were uniformly 0.141 mg/cm^2. The reference electrode was used Hg/Hg_2SO_4 (saturated K_2SO_4), and all the potential data were corrected to be versus reversible hydrogen electrode (RHE). The rotation speed of the working electrode was 1600 revolutions per minute (rpm). Before recording, at least 20 cycles of cyclic voltammetry (CV) were done to stabilize the curves.

2. TEM images of sampels before etching.

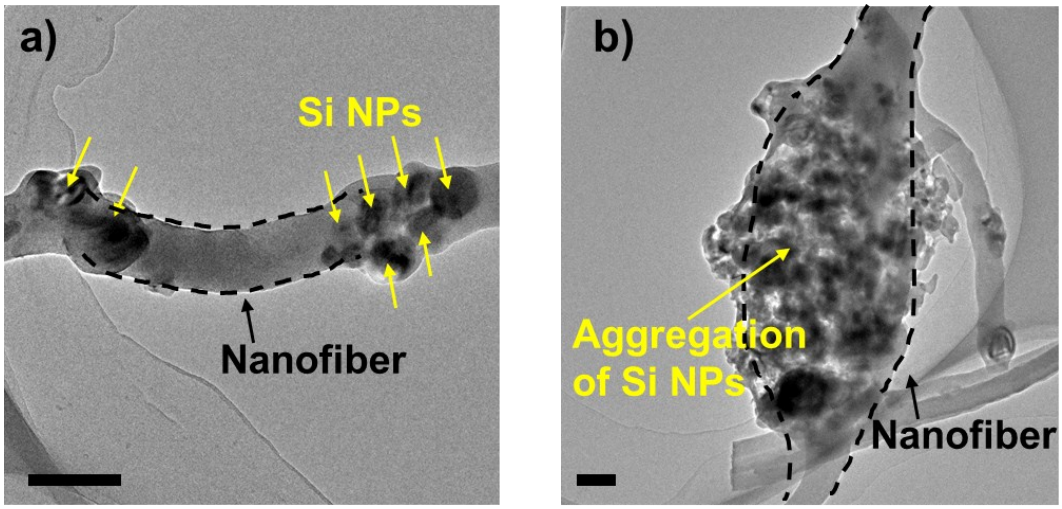

Figure S1. TEM images of PFeNC05 (a) and PFeNC15 (b) before etching Si NPs. The black dashed lines indicate the boundaries of nanofibers. The yellow arrows point Si NPs. The scale bars are all 200 nm.

3. More TEM images of porous nanofiber sampels.

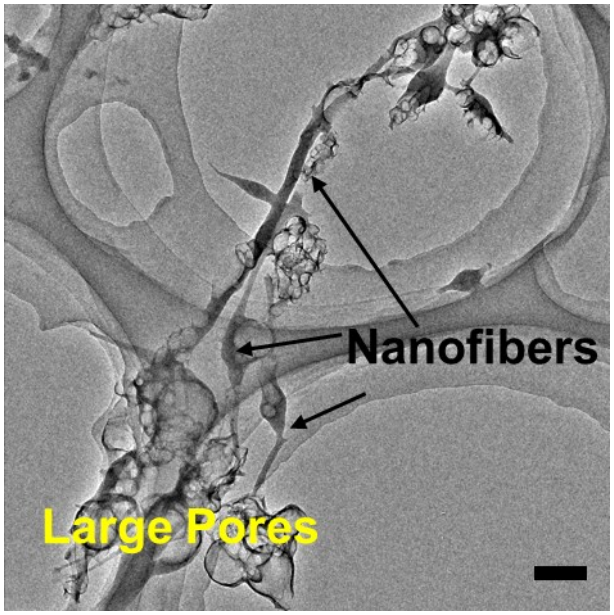

Figure S2. TEM image of PFeNC15. The black arrows indicate nanofibers, while there are also many large pores on the nanofibers. The scale bar is 200 nm.

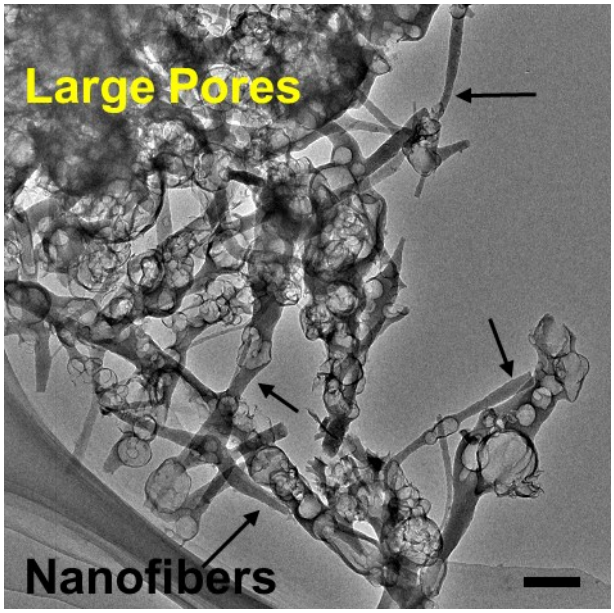

Figure S3. TEM image of PFeNC20. The black arrows indicate nanofibers, while there are many large pores on the nanofibers. The scale bar is 200 nm.

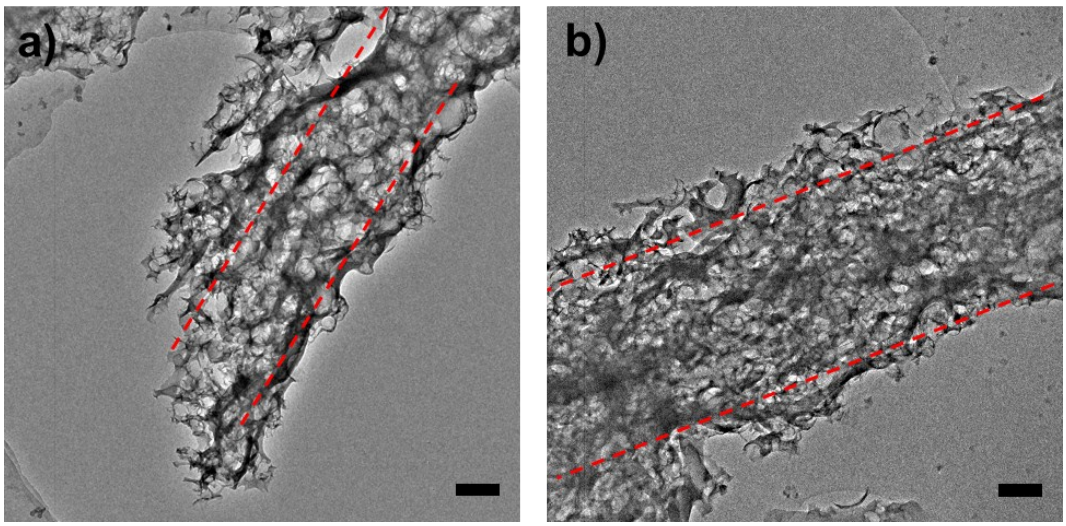

Figure S4. TEM images of PFeNC25. The red dashed lines indicate the boundary of porous nanofibers. The scale bars are all 200 nm.

4. Model of Si NPs aggregation.

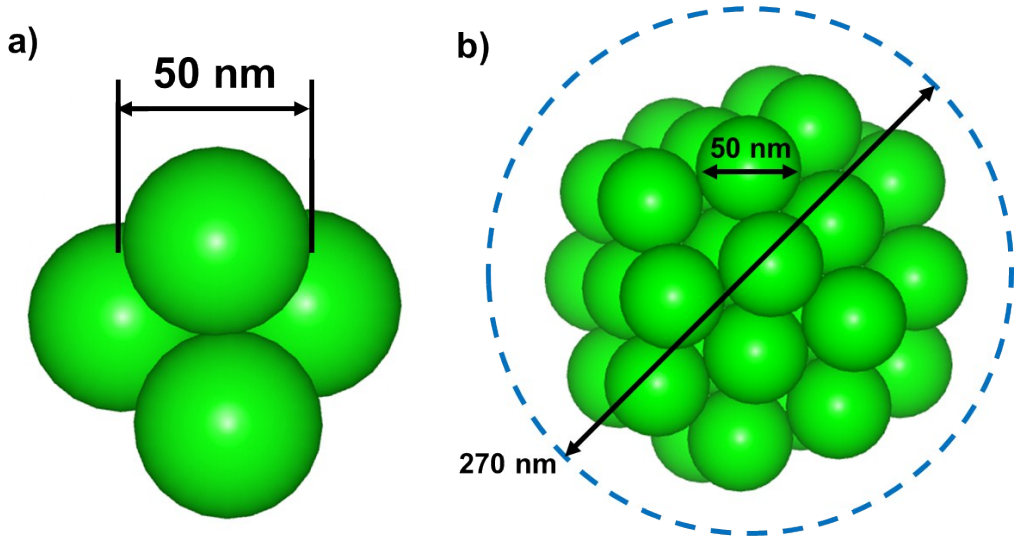

Figure S5. Model of Si NPs aggregation. (a) Close package model of four Si NPs with 50 nm in diameter. (b) Close package model of 38 Si NPs, which can be contained in sphere of 270 nm in diameter. The fill factor of close package can be calculated as $\varphi = \pi/(3\sqrt{2}) = 0.74$.

5. Characterization of FeNC sample.

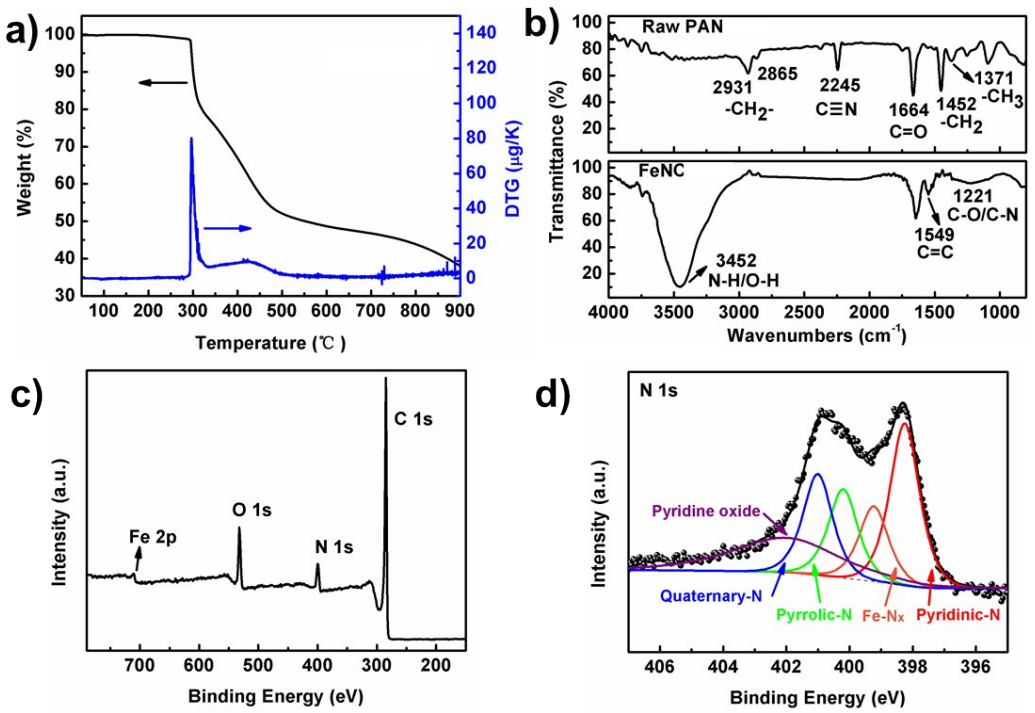

Figure S6. Characterization of FeNC sample. (a) TGA and DTG results of raw PAN nanofiber. Because there was abrupt mass loss at about 300 °C, we chose 260 °C as the temperature of incubation. PAN can be converted to carbon structure after treatment at 800 °C. (b) FTIR spectrum of raw PAN nanofibers (up) and FeNC nanofibers (down), indexing wavenumbers and corresponding chemical bonds of each peak. (c) Survey XPS spectrum of FeNC sample. (d) N 1s peak of XPS spectrum, which has been separated into five single peaks of pyridine oxide, quaternary N, pyrrolic N, Fe-N_x and pyridinic N.[27]

6. Element contents of PFeNC05 samples before and after etching.

Table R1. Element contents of PFeNC05 sample before and after etching by XPS.

State	Si (at %)	C (at %)	N (at %)	O (at %)	Fe (at %)
Before Etching	4.09	69.89	12.46	13.18	0.37
After Etching	0.12	78.39	11.55	9.68	0.25

7. Measurement of specific surface area (SSA).

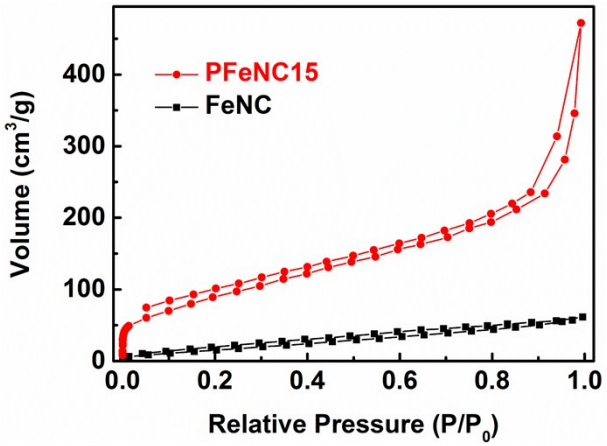

Figure S7. Nitrogen adsorption/desorption isotherms of FeNC and PFeNC15 samples. Quadrasorb SI-MP was employed to measure nitrogen absorption curves, which were used to calculate SSA of each sample by the Brunauer-Emmett-Teller (BET) theory. SSA of FeNC and PFeNC15 were 67.25 and 234.4 m^2/g, respectively. There was 3.5-times enhancement of SSA after creating the porous structure. The measured values were higher than the calculated SSA values (11.76 m^2/g in FeNC and 116.7 m^2/g in PFeNC15) in Fig. 3 of the main text. The disparities of them could be caused by micropores on the surface of nanofibers.

8. Normalized Activity by calculated SSA.

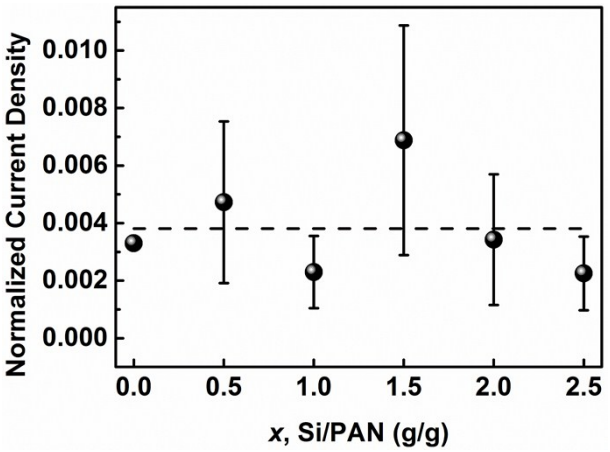

Figure S8. Dependence of normalized current density by calculated SSA on weight ratio of Si NPs and PAN (Si/PAN). The data are generated from Fig. 3 in main text. All normalized values were near the average value of 0.038.