Supporting Information

Hierarchical Porous Carbon Doped with

Iron/Nitrogen/Sulfur for Efficient

Oxygen Reduction Reaction

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1. Experimental Section

The number of electrons transferred (n) during the ORR was calculated based on Koutecky-Levich (K-L) equations as follows:[1]

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

$$B = 0.62nFC_0D^{2/3}v^{-1/6} \qquad (2)$$

Where J is the current density obtained from the experiment, J_L and J_K are the diffusion-limiting current density and kinetic current density, ω is the angular velocity of the RDE, F is Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 in 0.1 M KOH (1.2×10^{-3} mol L^{-1}), D is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} cm^2 s^{-1}), v is the viscosity of the electrolyte (0.01 cm^2 s^{-1}).[2]

The following equations were used to calculate the hydrogen peroxide yields and the number of electrons transferred (n)[3]:

$$H_2O_2(\%) = 200\frac{I_r/N}{I_r/N + I_d} \qquad (3)$$

$$n = 4\frac{I_d}{I_r/N + I_d} \qquad (4)$$

Where N is current collection efficiency of the Pt ring (0.37), I_d is the disk current, and I_r is the ring current.

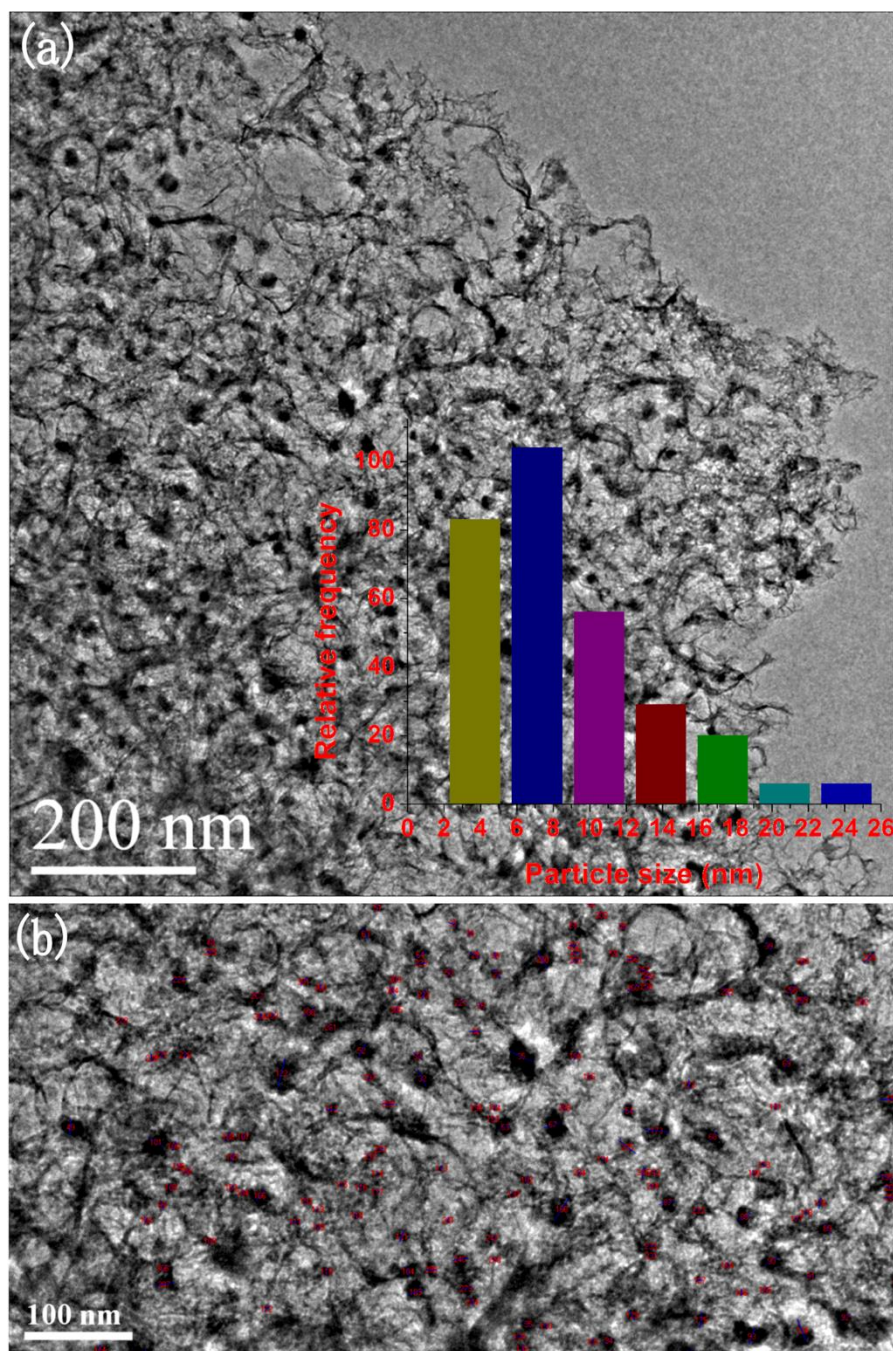## 2. Figures and Tables

Figure S1. (a) TEM image and particle sizes distribution histogram on FeNS/PC; (b) TEM magnified image during sizes measurement. The particles size distribution histogram was performed by measuring 305 iron nanoparticles.
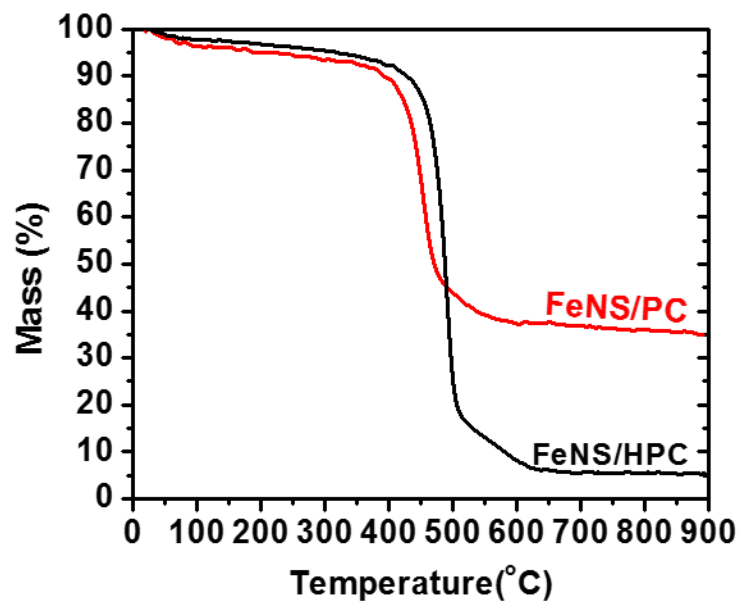
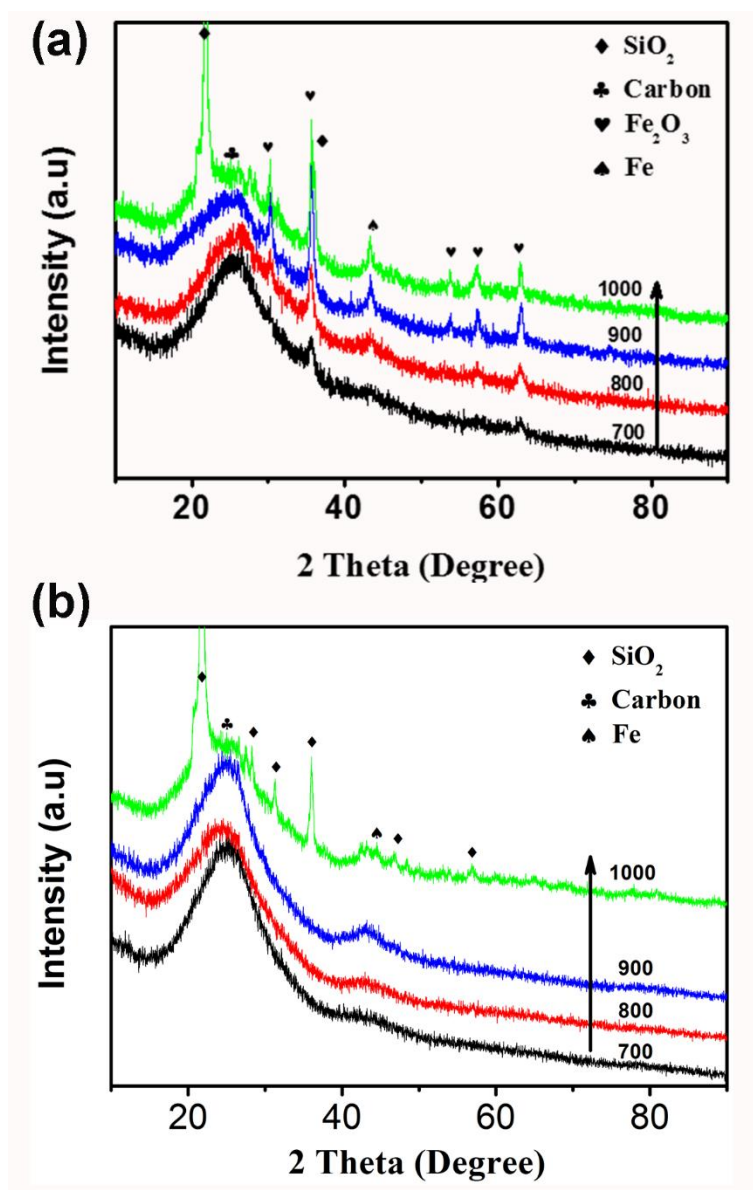**Figure S2.** TGA curves of FeNS/PC and FeNS/HPC.

Figure S3. XRD patterns of FeNS/PC-x00 before acid leaching (a) and FeNS/HPC -x00, (x00=700, 800, 900 and 1000) after acid leaching (b).

The existence of SiO_2 after NaOH washing is due to the high stability of SiO_2 after high temperature at 1000 °C. The residual Fe peaks after acid leaching is attributed to the graphitic carbon encapsulated Fe nanoparticles, which are also verified in the HRTEM images in the manuscript.
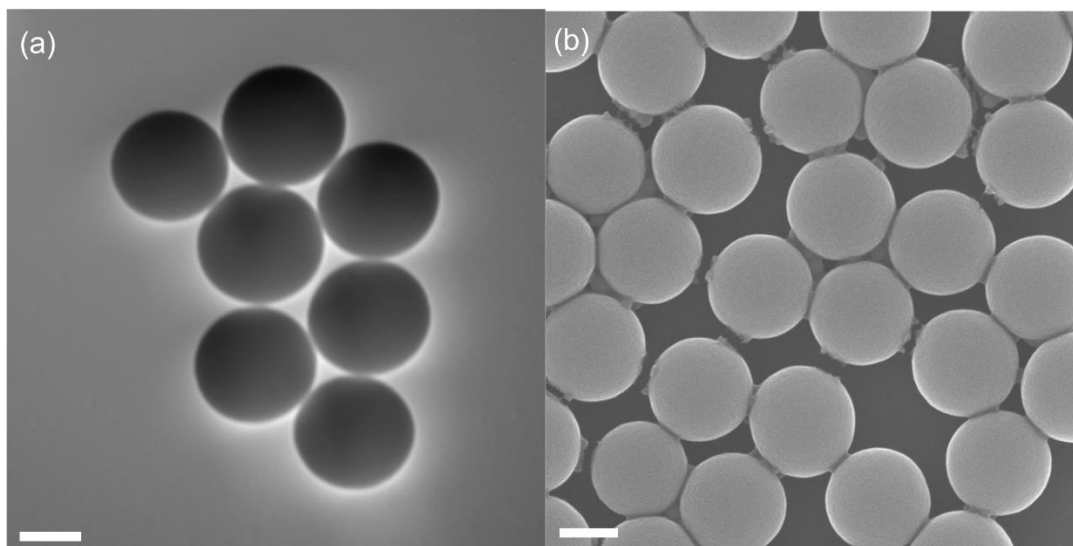
Figure S4. (a) TEM and (b) SEM images of the employed silica. The length of scale bar is 50 nm.
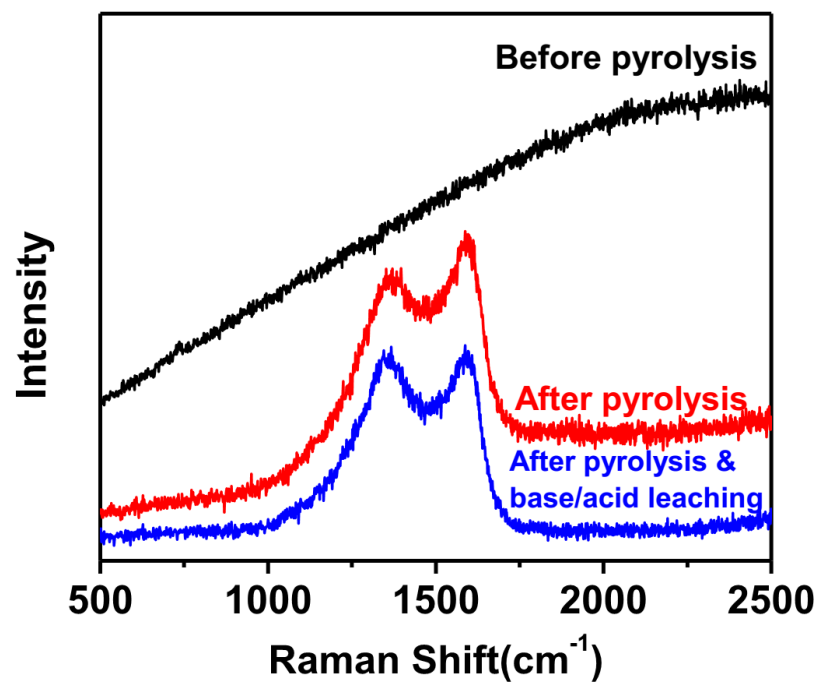
Figure S5. The Raman spectra of sample before pyrolysis, after pyrolysis and base & acid leaching.
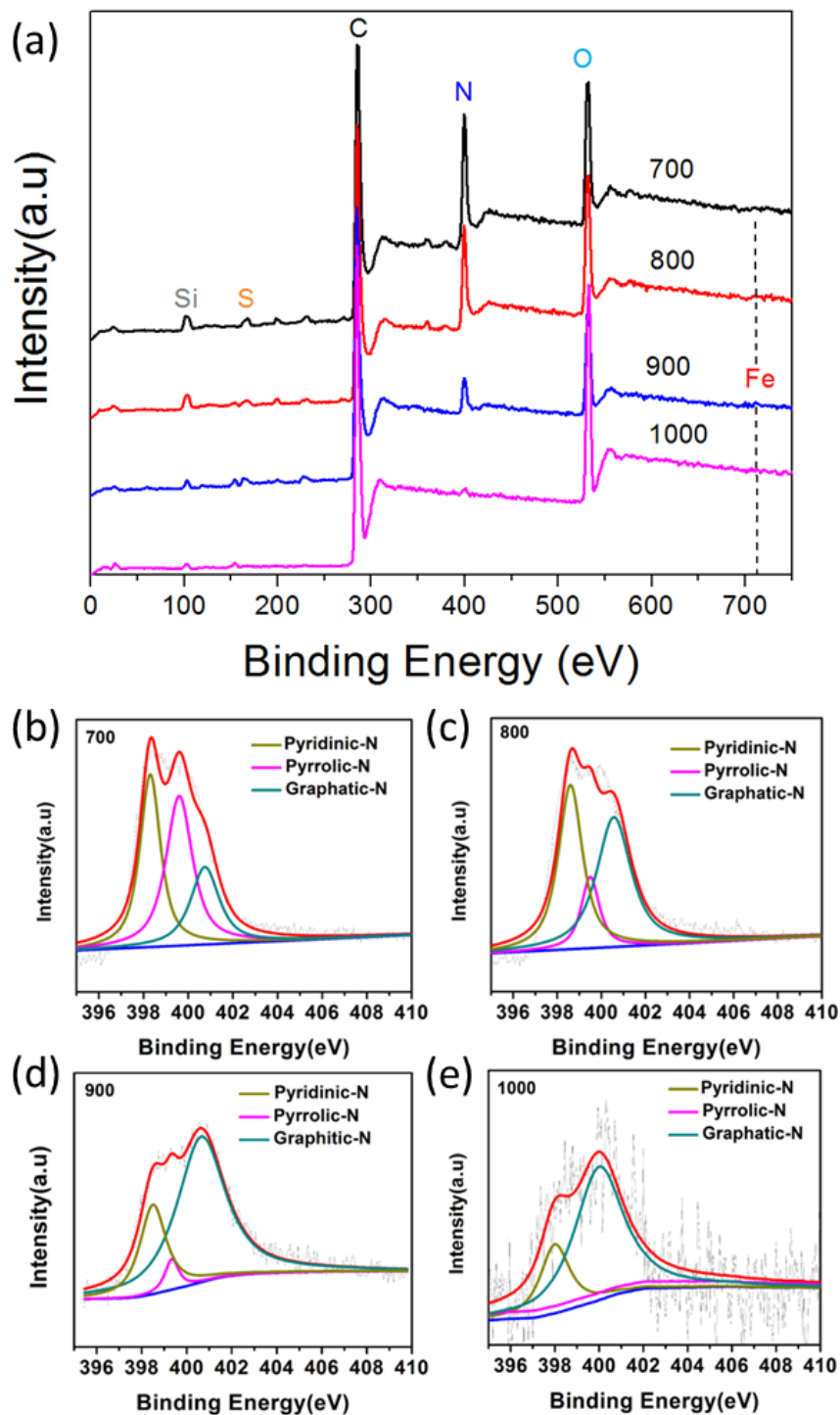
Figure S6. (a) XPS spectra of the samples FeNS/HPC prepared at 700, 800, 900 and 1000 °C. The corresponding high resolution N1s spectra of FeNS/HPC prepared at (b) 700°C, (c) 800°C, (d) 900°C and (e) 1000°C.
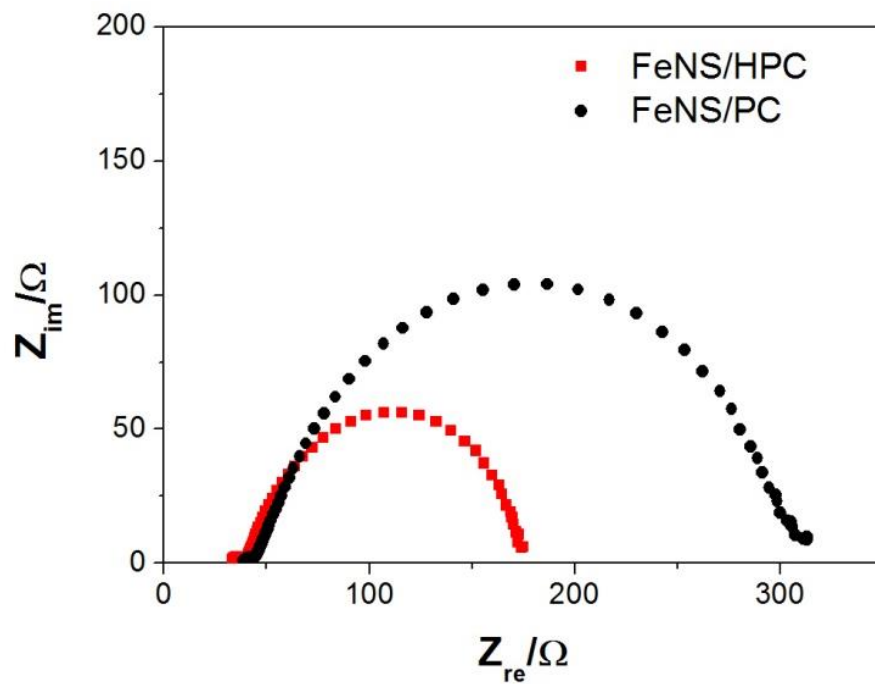
Figure S7. Electrochemical impedance spectra of FeNS/PC and FeNS/HPC. The EIS test was carried out at 0.86 V vs RHE with amplitude of 0.01 V from 100 KHz to 0.01Hz.
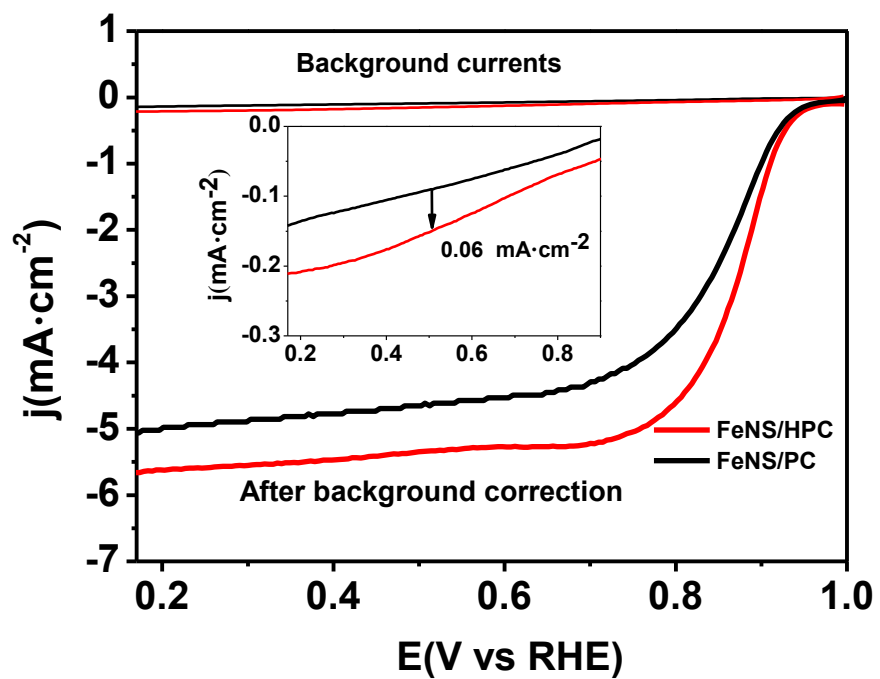
Figure S8. The comparison of background current and ORR current after background correction of FeNS/HPC and FeNS/PC. The background current is tested in Ar saturated 0.1 M KOH at scan rate of 5 mVs^{-1}.
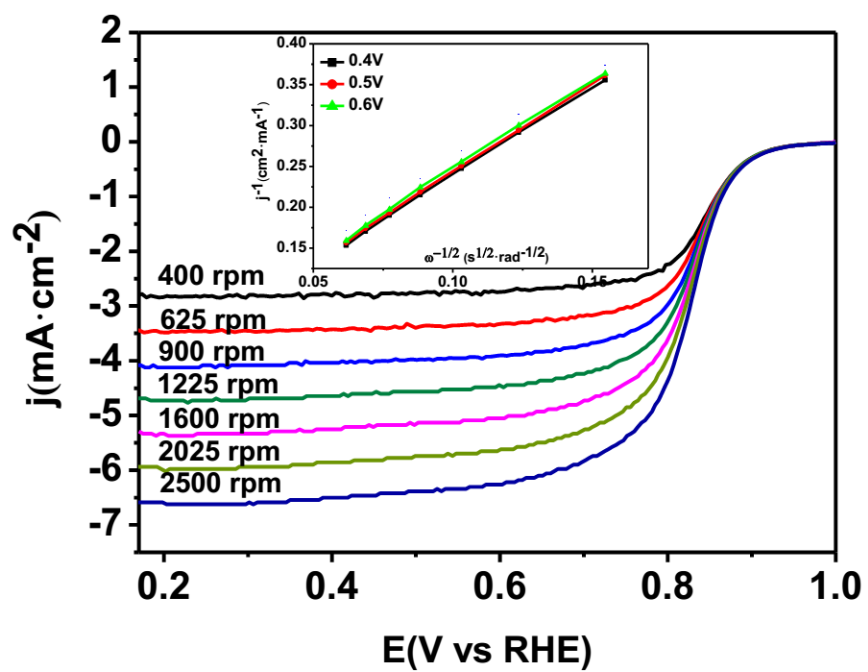
Figure S9. ORR LSV curves of commercial Pt/C at various rotation rates from 400 to 2500 rpm

Table S1. Elemental and species composition of FeNS/HPC

C^a (%)	O^a (%)	Si^a (%)	Fe^a (%)	N^a (%)			S^a (%)	
76.92	12.04	1.52	0.64	7.21			1.67	
				$N1^b$ (%)	$N2^b$ (%)	$N3^b$ (%)	$S1\&S2^c$ (%)	$S3^c$ (%)
				21	9	70	68	32

[a] These values refer to the atomic ratio obtained from XPS analysis. [b] These values were calculated based on their relative area of XPS peaks in terms of nitrogen species. [c] These values were calculated based on their relative area of XPS peaks in terms of sulfur species.

Table S2. Atomic percentage of different elements in the samples FeNS/HPC prepared at 700, 800, 900 and 1000 °C

T(℃)	C(%)	O(%)	N(%)	S(%)	Fe(%)	Si(%)
700	62.80	12.03	17.44	1.59	0.38	5.76
800	65.69	12.92	14.45	0.96	0.31	5.66
900	76.92	12.04	7.21	1.67	0.64	1.52
1000	76.48	20	1.66	-*	-*	1.86

* It represent that no sulfur or iron element is detected in corresponding catalyst

Table S3. Relative atomic percentage of nitrogen species on different FeNS/HPC$_{X00}$ materials

Materials	N-content (%)	Pyridinic-N (%)	Pyrrolic-N (%)	Graphitic-N (%)
N/S/Fe-HPC$_{-700}$	17.44	10.12	2.96	4.36
N/S/Fe-HPC$_{-800}$	14.45	6.79	2.02	5.63
N/S/Fe-HPC$_{-900}$	7.21	1.51	0.65	5.05
N/S/Fe-HPC$_{-1000}$	1.66	0.33	0.12	1.21

REFERENCES

1. Allen J. Bard and Larry R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, New York: Wiley, **2001.**

2. Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H., Co$_3$O$_4$ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. *Nat. Mater.***2011,** *10* (10), 780-786.

3. Paulus, U. A.; Schmidt, T. J.; Gasteiger, H. A.; Behm, R. J., Oxygen reduction on a high-surface area Pt/Vulcan carbon catalyst: a thin-film rotating ring-disk electrode study. *J. Electroanal. Chem.* **2001**, *495* (2), 134-145.