



Supporting Information

Super-Dispersed Fe–N Sites Embedded into Porous Graphitic Carbon for ORR: Size, Composition, and Activity Control

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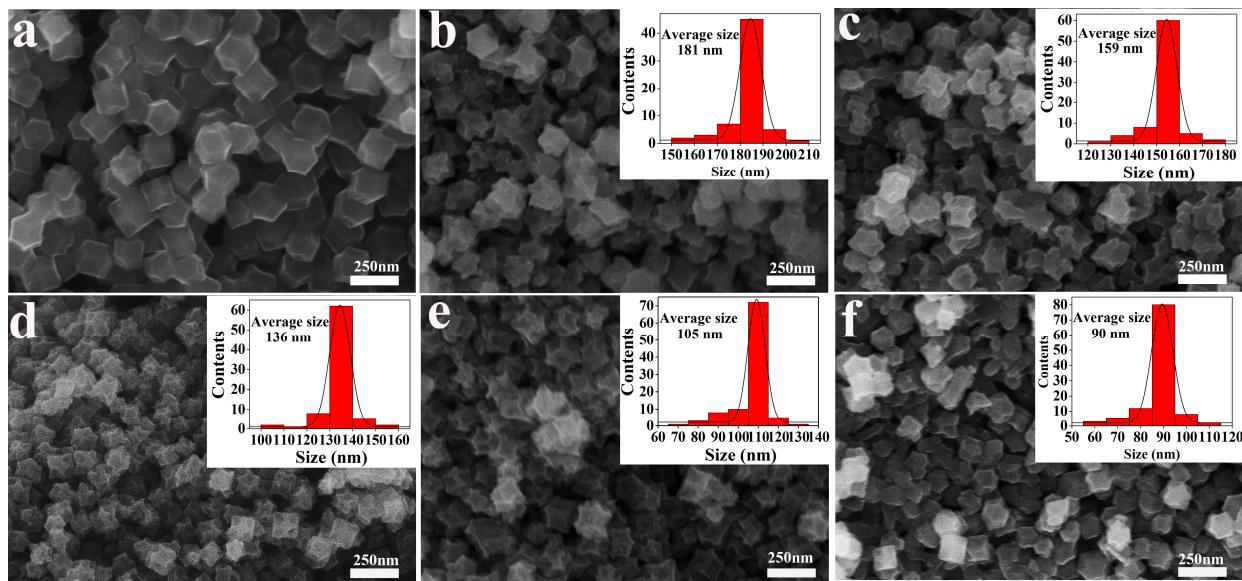


Figure S1. (a) SEM image of Fe-ZIF-0.05 precursor and (b–f) SEM images of Fe-N/C-0.05-600, Fe-N/C-0.05-700, Fe-N/C-0.05-800, Fe-N/C-0.05-900 and Fe-N/C-0.05-1000. The illustration shows the particle size distribution.

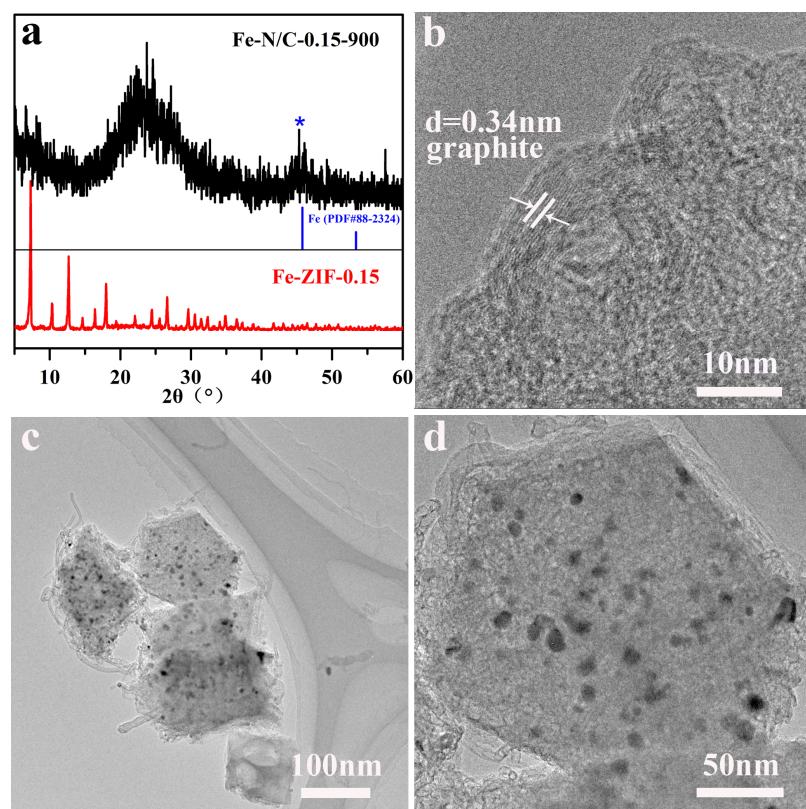


Figure S2. (a) XRD and (b–d) TEM images of Fe-N/C-0.15-900

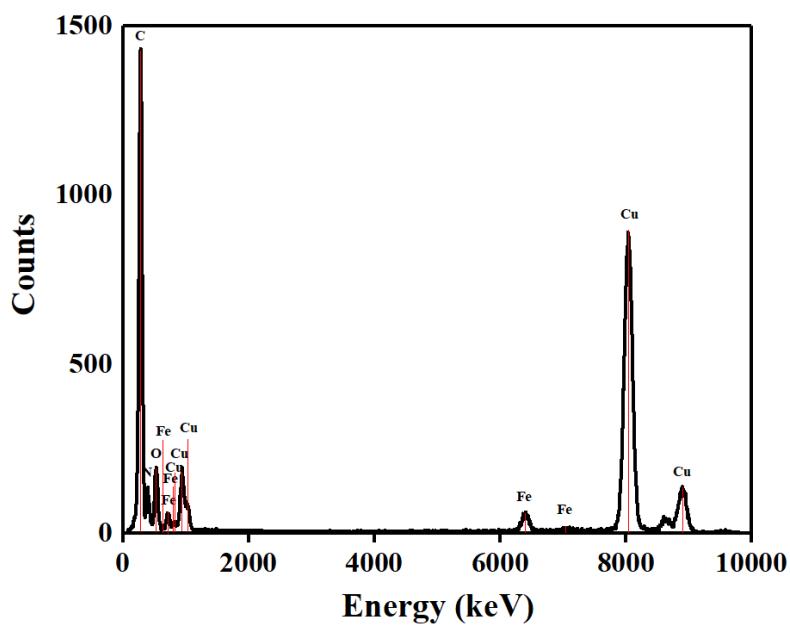


Figure S3. The sum spectrum of the maps for Fe-N/C-0.05-900

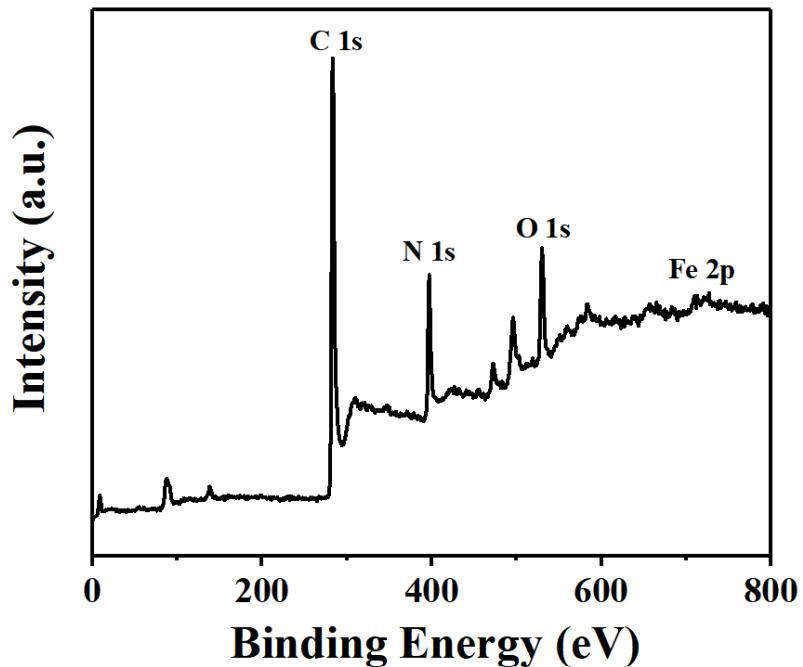


Figure S4. The full spectrum of Fe-N/C-0.05-900

Table S1. The element atomic contents of Fe, C, N and O in Fe-N/C-0.05-900 by XPS measurement

Sample	Element atomic ration (%)			
	Fe	C	N	O
Fe-N-C-0.05-900	1.20	87.76	7.34	3.70

Table S2. The comparison of ORR activity between our work and the references

Catalyst	E_{onset} (mV)	$E_{1/2}$ (mV)	J_{lim} (mA cm ⁻²)	Tafel Slope (mV/dec)	Electrolyte	Refs.
Fe-N/C-0.05-900	99	88.5	4.8	52	0.1 M KOH	In this work
Fe-N/C-155	100	85	6.0	--	0.1 M KOH	<i>J. Mater. Chem. A.</i> 2019 , <i>7</i> , 16508-16515. (Ref. 29 in paper)
FeNi0.25-NC	--	86	5.8	--	0.1M NaOH	<i>Appl. Surf. Sci.</i> 2021 , <i>538</i> , 148017. (Ref. 30 in paper)
C-Fe(OH) ₃ @ZIF-1000	99	88	5.9	--	0.1 M KOH	<i>ACS Appl. Energy Mater.</i> 2019 , <i>2</i> , 3194-3203. (Ref. 31 in paper)
NC@CoF _e ,NeCNP	97	86.5	7.99@85mV	61	1.0 M KOH	<i>Int. J. Hydrol. Energy.</i> 2021 , <i>46</i> , 9341-9350. (Ref. 32 in paper)
Fe-N ₅ /C@G	88	83	5.5	--	0.1 M KOH	<i>New J. Chem.</i> 2021 , <i>45</i> , 13004-13014. (Ref. 1 in ESI)
HP S-doped Fe-N-C	99	91	4.47	56	1.0 M KOH	<i>Mater. Today Energy</i> 2021 , <i>19</i> , 100624 (Ref. 2 in ESI)
Fe-SAs/N-C	101	91	5.8	--	0.1 M KOH	<i>ACS Catal.</i> 2019 , <i>9</i> , 2158-2163. (Ref. 3 in ESI)
FeNPs@PANI/rGO	106.1	94.2	4.5	64	0.1 M KOH	<i>J.Power Sources.</i> 2020 , <i>451</i> , 227733. (Ref. 4 in ESI)

Fe/N/C-48–950–1	99	86	4.8	--	0.1 M KOH	<i>Electrochim. Acta</i> 2021 , 366, 137408. (Ref. 5 in ESI)
Fe-N/C	97.1	84.4	5.68	67	0.1 M KOH	<i>Int. J. Hydrot. Energy</i> 2019 , 44, 27379–27389. (Ref. 6 in ESI)
Fe-N/C	82	72	5.0	55.6	0.1 M KOH	<i>ACS Catal.</i> 2017 , 7, 1655–1663. (Ref. 7 in ESI)

References

- [1]. Liu, F.; Yan, N.; Zhu, G.Q.; Liu, Z. G.; Ma, S.Q.; Xiang, G.L.; Wang, S.R.; Liu, X. J.; Wang, W. Fe–N–C single-atom catalysts with an axial structure prepared by a new design and synthesis method for ORR. *New J. Chem.* **2021**, 45, 13004–13014.
- [2]. Ma, J. J.; Li, J. S.; Wang, R.G.; Yang, Y. Y.; Yin, P. F.; Mao, J.; Ling, T.; Qiao, S. Z.; Hierarchical porous S-doped Fe-N-C electrocatalyst for high-power-density zinc-air battery. *Mater. Today Energy*. **2021**, 19, 100624.
- [3]. Yang, Z. k.; Wang, Y.; Zhu, M.Z.; Li, Z.J.; Chen, W.X.; Wei, W.C.; Yuan, T.W.; Qu, Y.T.; Xu, Q.; Zhao, C. M. Boosting oxygen reduction catalysis with Fe–N₄ Sites decorated porous carbons toward fuel cells. *ACS Catal.* **2019**, 9, 2158–2163.
- [4]. Mohammad S. A.; Halima B.; Young-Bae K.; Iron nanoparticles implanted metal-organic-frameworks based Fe–N–C catalysts for high-performance oxygen reduction reaction. *J. Power Sources*. **2020**, 451, 227733. 5.
- [5]. Huang, J.W.; Chen, Y. B.; Yang, J. M.; Zhu, H. B.; Yang, H. Boosting the oxygen reduction performance of MOF-5-derived Fe-N-C electrocatalysts via a dual strategy of cation-exchange and guest-encapsulation. *Electrochim. Acta* **2021**, 366, 137408.
- [6]. Zhang, X. K.; Huang, X.B.; Hu, W. H.; Huang, Y. M. A metal-organic framework-derived Fe-N-C electrocatalyst with highly dispersed Fe-N_x towards oxygen reduction reaction. *Int. J. Hydrot. Energy* **2019**, 44, 27379–27389.
- [7]. Lai, Q. X.; Zheng, L.R.; Liang, Y.Y.; He, J. P.; Zhao, J. X.; Chen, J. H. Metal-organic-framework-derived Fe-N/C electrocatalyst with five coordinated

Fe-N_x sites for advanced oxygen reduction in acid media. *ACS Catal.* **2017**, *7*, 1655-1663.

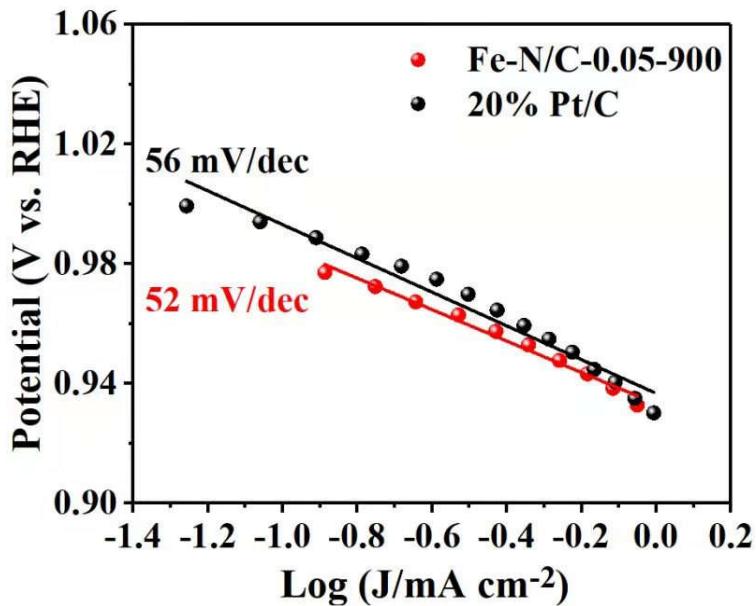


Figure S5. Tafel curves of Fe-N/C-0.05-900 and 20% Pt/C catalysts

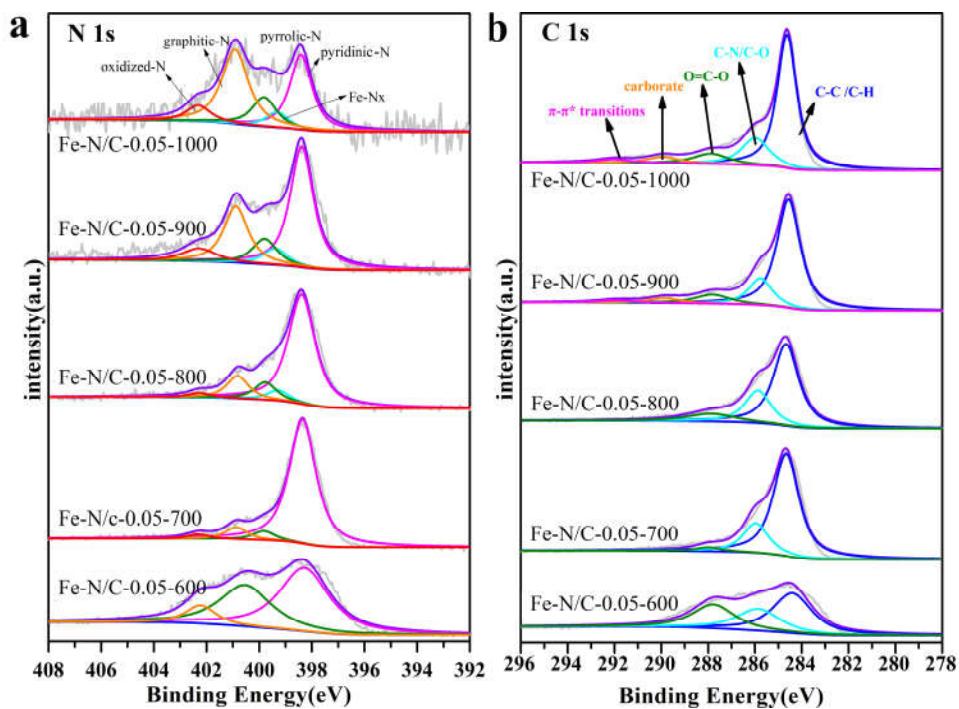


Figure S6. The evolution of XPS N 1s (a) and C 1s (b) spectra of the Fe-N/C catalysts with increasing heating temperature up to 1000 °C.

Table S3. The N elemental quantification determined by XPS analysis

Fe-N/C-	Fe-N/C-	Fe-N/C-	Fe-N/C-	Fe-N/C-
0.05	0.05	0.05	0.05	0.05
-600	-700	-800	-900	-1000
N at%	16.21	17.71	13.88	7.34
				3.69

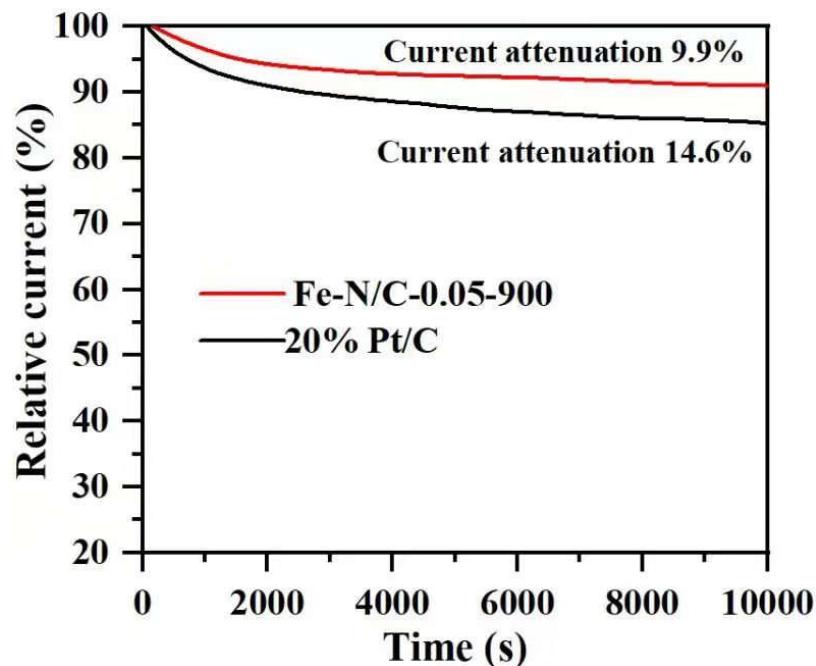


Figure S7. Chronoamperometric curves of Fe-N/C-0.05-900 and 20%Pt/C electrodes in O₂-saturated 0.1 M KOH at a rotating speed of 1600 rpm, the potential was controlled at 0.75 V for 10000 s.