

## Electronic Supplementary Information

### **FeN<sub>x</sub> and γ-Fe<sub>2</sub>O<sub>3</sub> co-functionalized hollow graphitic carbon nanofibers for efficient oxygen reduction in an alkaline medium**

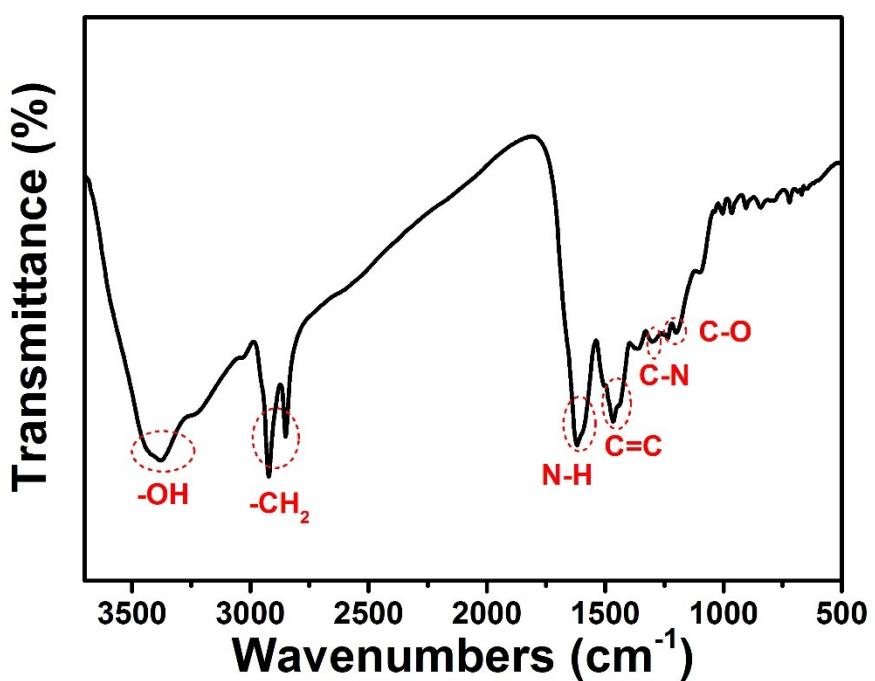
Qiang Yu,<sup>a</sup> Sitian Lian,<sup>a</sup> Jiantao Li,<sup>a</sup> Ruohan Yu,<sup>a,b</sup> Shibo Xi,<sup>c</sup> Jinsong Wu,<sup>b</sup> Dongyuan Zhao,<sup>a</sup> Liqiang Mai<sup>a</sup> and Liang Zhou \*<sup>a</sup>

<sup>a</sup> State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P. R. China

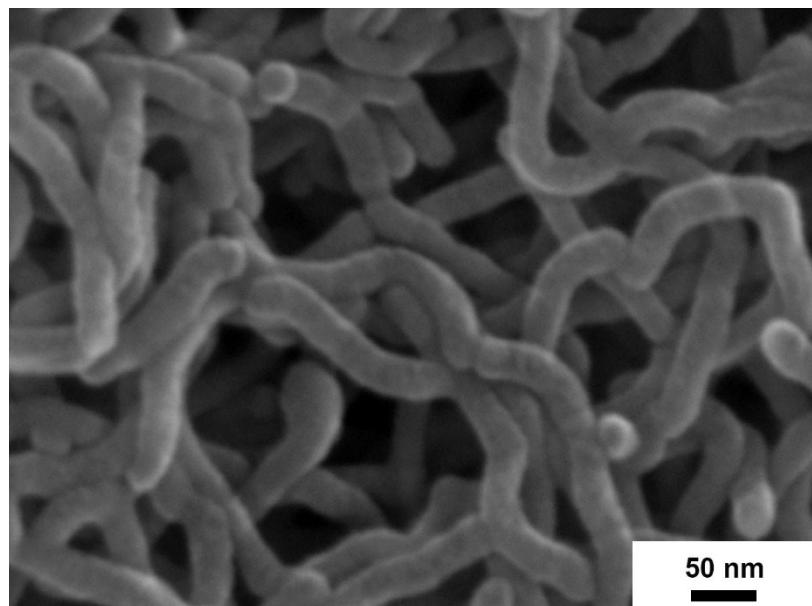
<sup>b</sup> Nanostructure Research Centre, Wuhan University of Technology, Wuhan 430070, P. R. China

<sup>c</sup> Institute of Chemical and Engineering Sciences, A\*STAR (Agency for Science, Technology and Research), Singapore 627833, Singapore

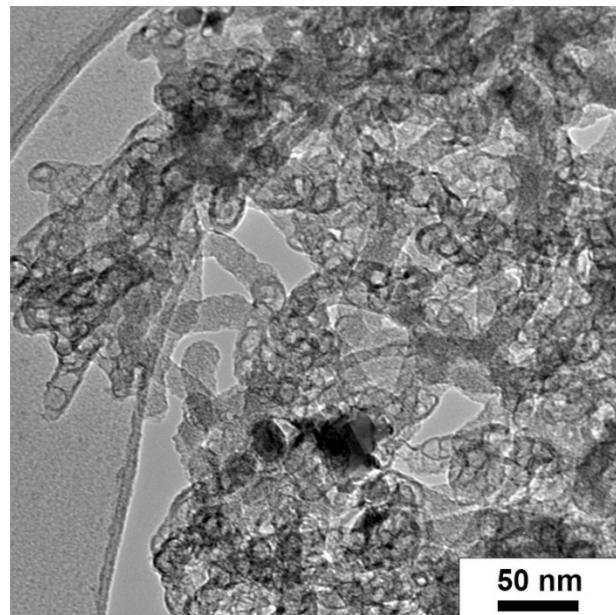
E-mail: liangzhou@whut.edu.cn



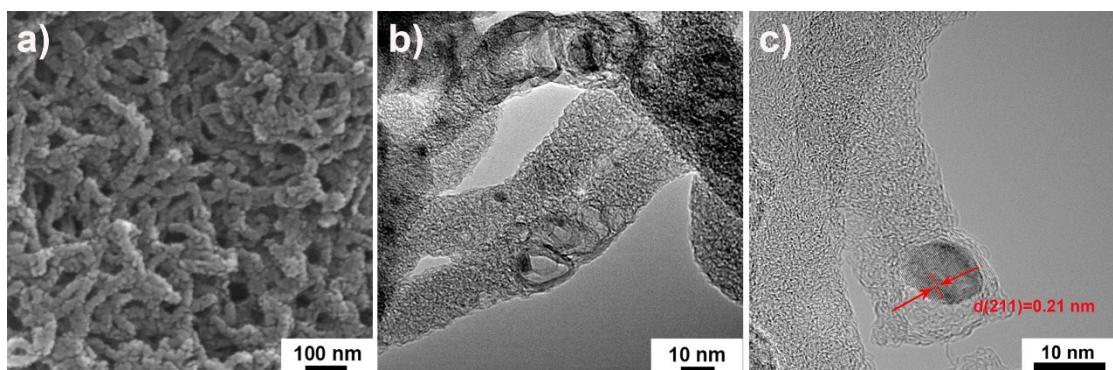
**Fig. S1** FTIR spectrum of RNFs.



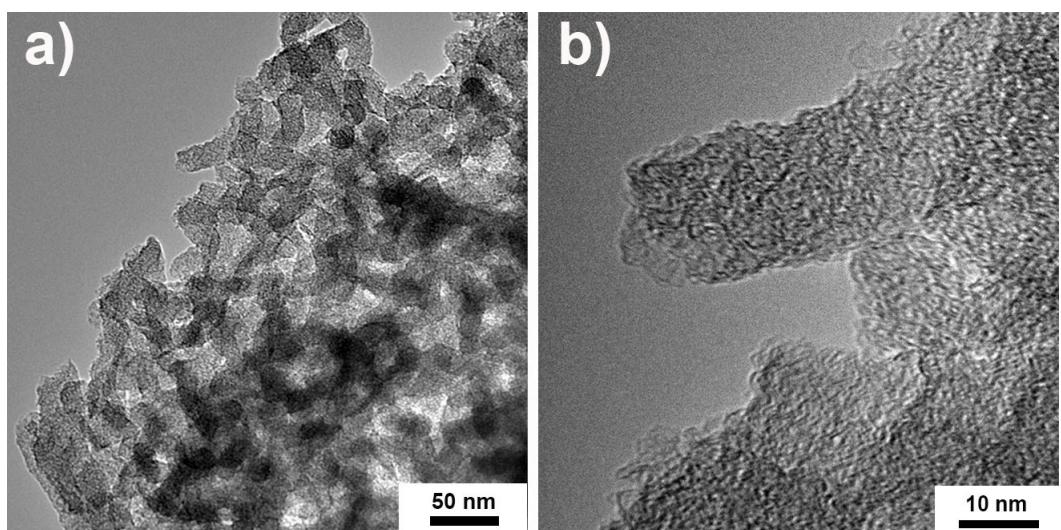
**Fig. S2** High magnification SEM image of RNFs.



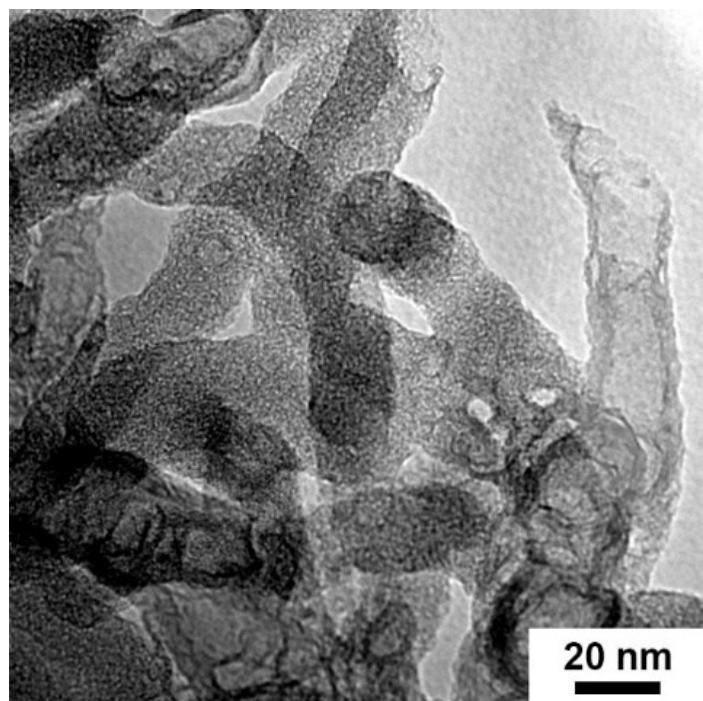
**Fig. S3** Low magnification TEM image of  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs.



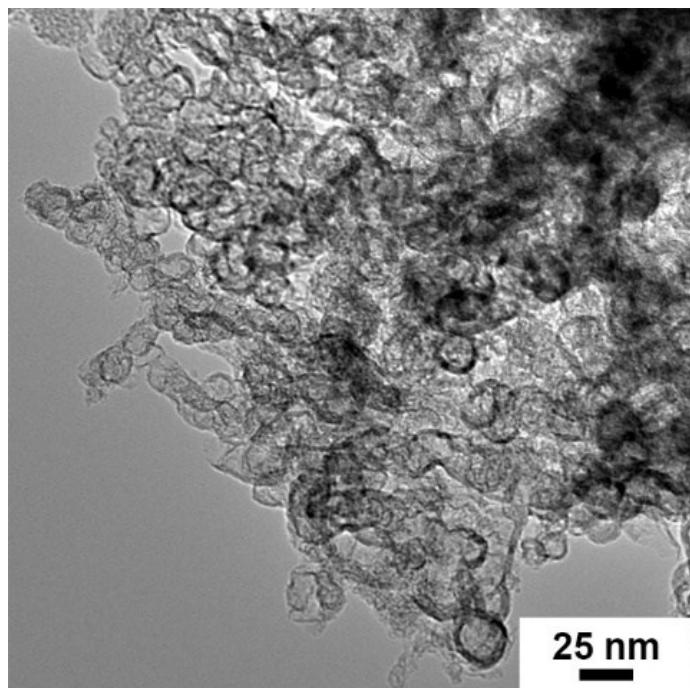
**Fig. S4** SEM (a), TEM (b), and HRTEM (c) images of  $\text{FeN}_x/\text{Fe}_3\text{C}$ -CNFs.



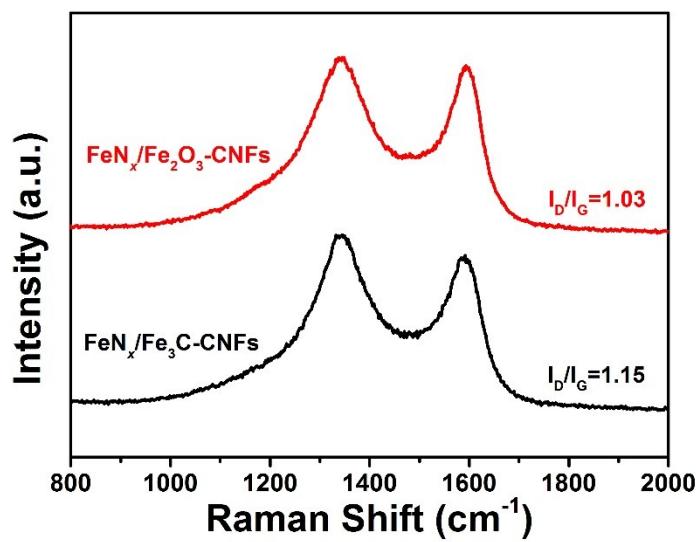
**Fig. S5** TEM (a, b) images of N-doped CNFs.



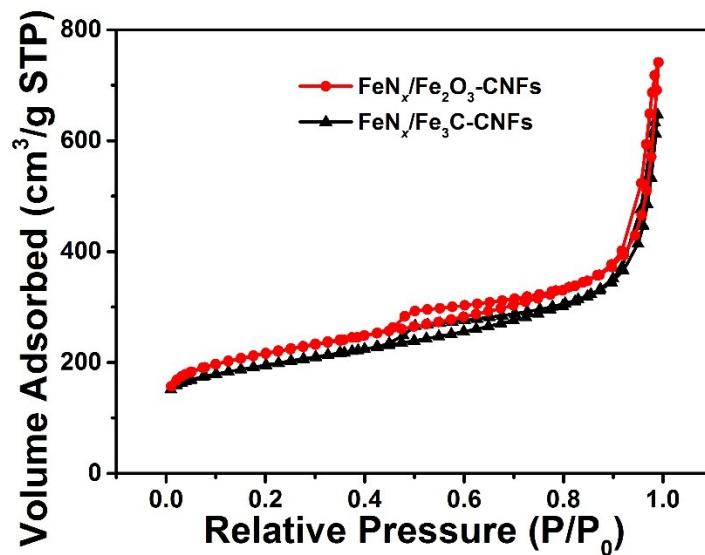
**Fig. S6** TEM image of  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs-700.



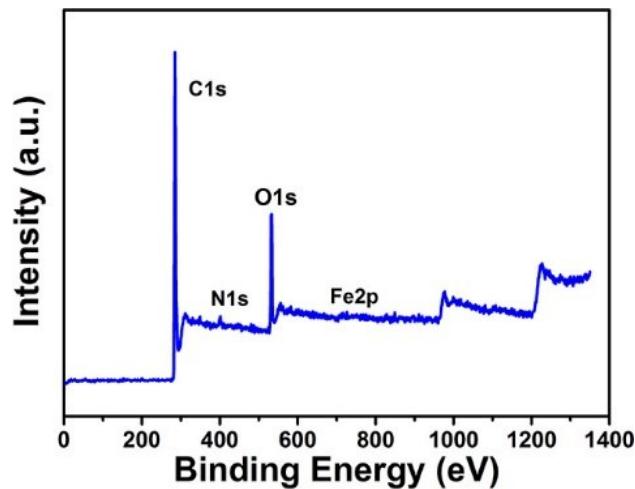
**Fig. S7** TEM image of  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs-900.



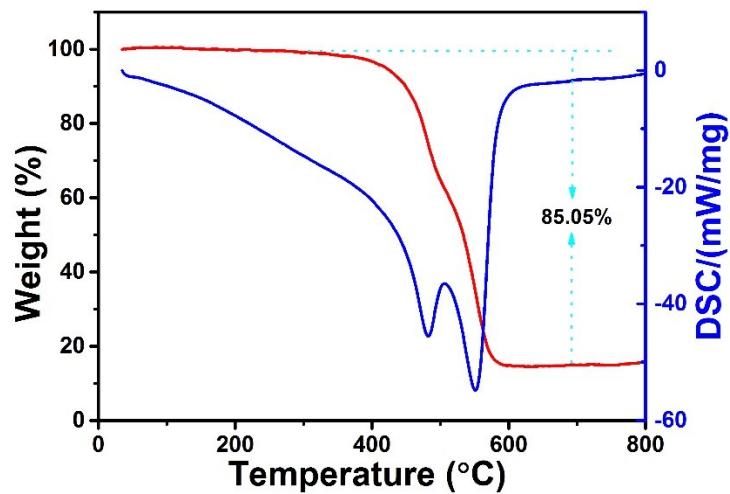
**Fig. S8** Raman spectra of  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs and  $\text{FeN}_x/\text{Fe}_3\text{C}$ -CNFs.



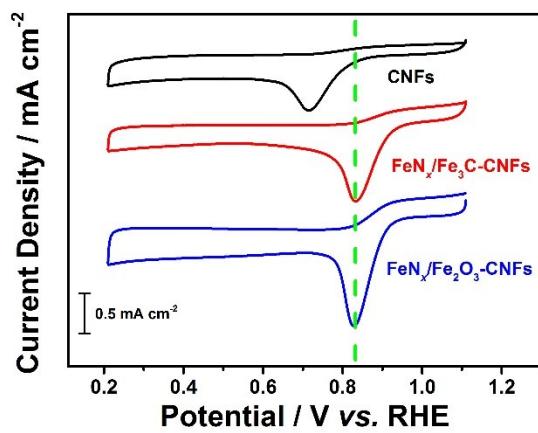
**Fig. S9**  $\text{N}_2$  adsorption/desorption isotherms of  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs and  $\text{FeN}_x/\text{Fe}_3\text{C}$ -CNFs.



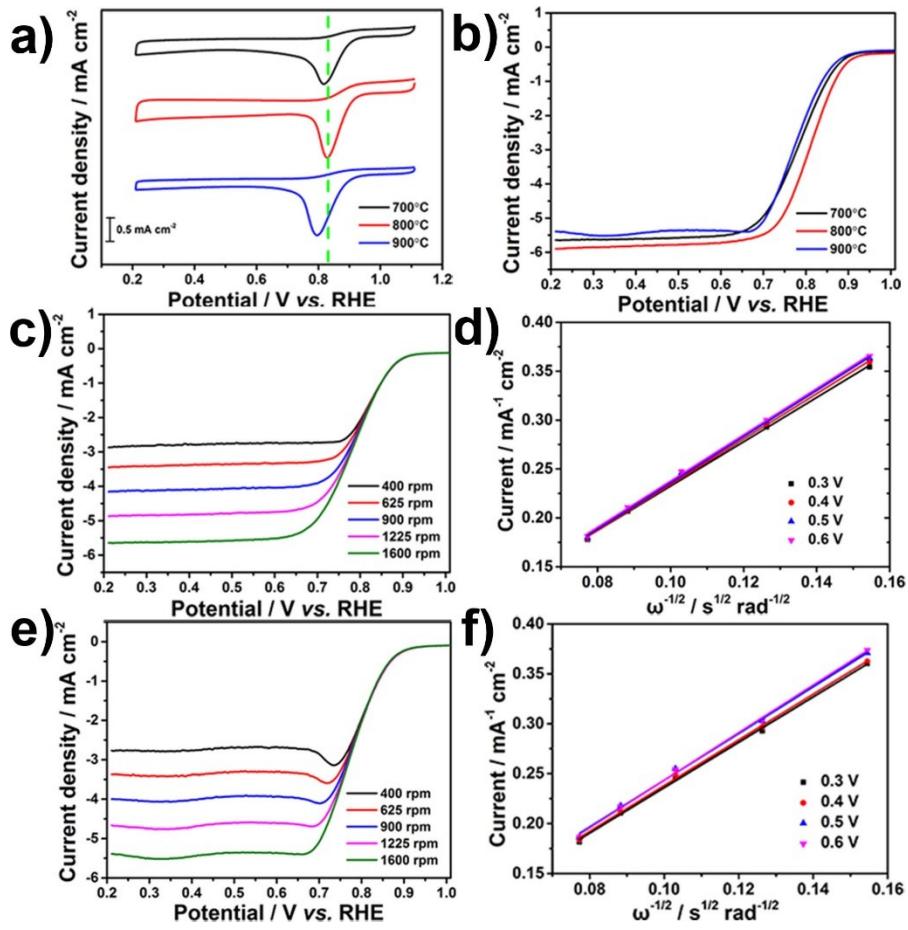
**Fig. S10** XPS survey spectrum of  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs.



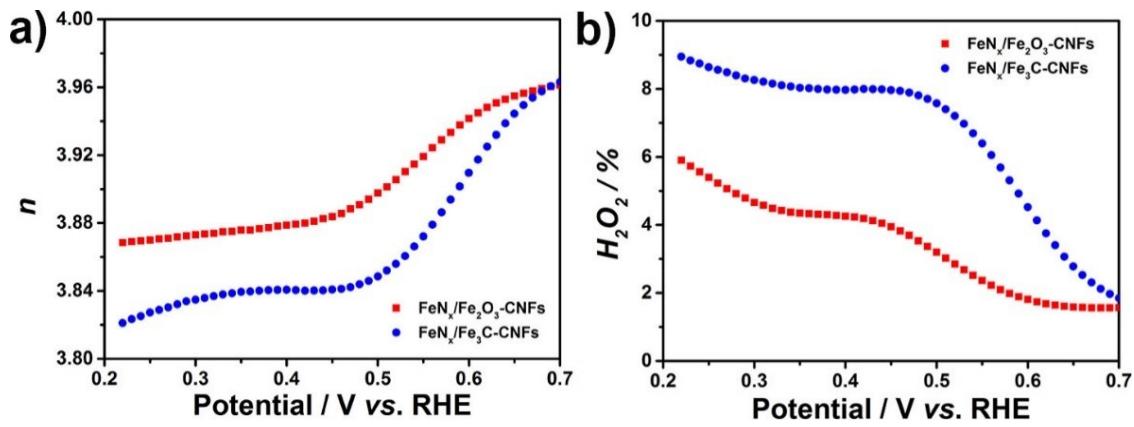
**Fig. S11** TG and DSC curves of  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs.



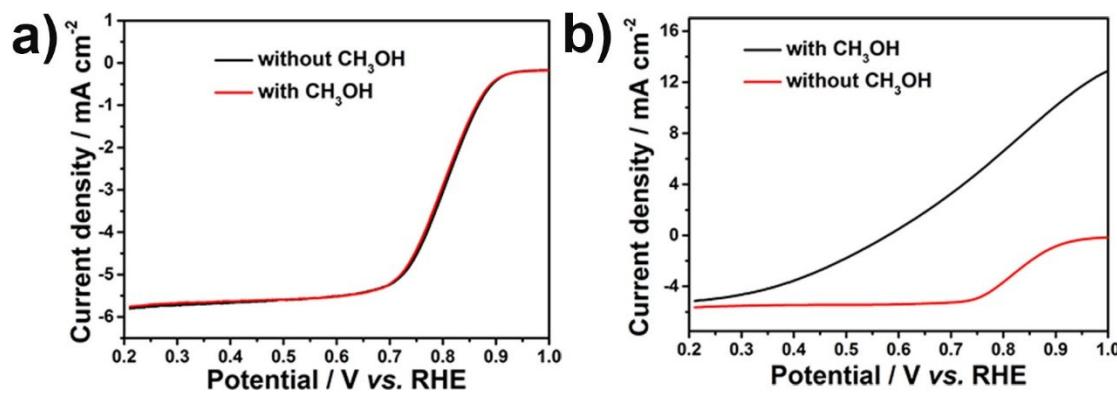
**Fig. S12** CV curves of CNFs,  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs, and  $\text{FeN}_x/\text{Fe}_3\text{C}$ -CNFs with a scan rate of  $5 \text{ mV s}^{-1}$ .



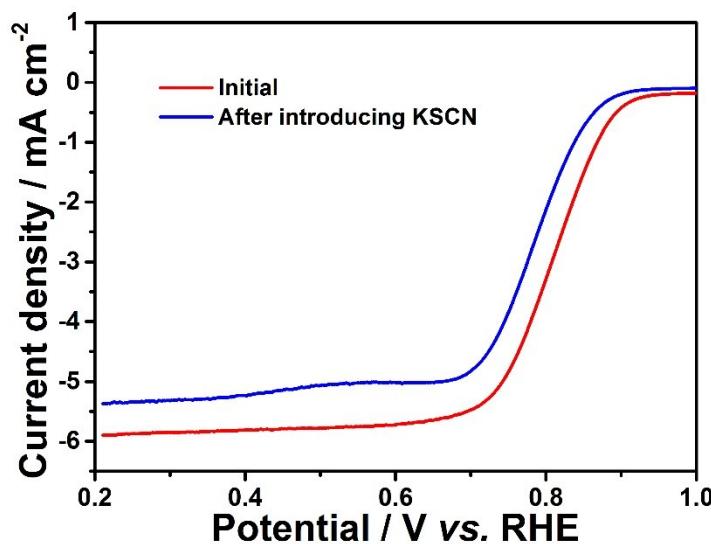
**Fig. S13** CV (a) and LSV (b) curves of FeN<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>-CNFs catalysts prepared at different activation temperatures; LSV curves (c) and the corresponding K-L plots (d) of FeN<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>-CNFs-700; LSV curves (e) and the corresponding K-L plots (f) of FeN<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>-CNFs-900.



**Fig. S14** Electron transfer number (a) and H<sub>2</sub>O<sub>2</sub> yields (b) of FeN<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>-CNFs and FeN<sub>x</sub>/Fe<sub>3</sub>C-CNFs at 0.2 – 0.7 V.



**Fig. S15** LSV curves of  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs (a) and Pt/C (b) with and without  $\text{CH}_3\text{OH}$ .



**Fig. S16** Effect of  $\text{SCN}^-$  on the catalytic activity of  $\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs.

**Table S1.** Textural properties of the samples.

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$S_{\text{t-Plot Micro}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$V_p$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{\text{t-Plot Micro}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )
$\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs - 700	679	299	1.43	0.15
$\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs - 800	712	308	1.15	0.16
$\text{FeN}_x/\text{Fe}_2\text{O}_3$ -CNFs - 900	1093	160	2.36	0.07
$\text{FeN}_x/\text{Fe}_3\text{C}$ -CNFs - 800	639	279	1.00	0.14
CNFs	408	308	0.34	0.15

**Table S2.** Summary of the Mössbauer site parameters to different iron species in FeN<sub>x</sub>/Fe<sub>2</sub>O<sub>3</sub>-CNFs catalysts.

Fe species	CS (mm s <sup>-1</sup> )	D (mm s <sup>-1</sup> )	A	W+ (mm s <sup>-1</sup> )	Content (%)
Doublet 1	0.86	2.01	15900	0.37	15.7%
Doublet 2	0.35	0.58	39400	0.35	39%
Sextet 1	0.31	0.04	28000	0.27	27.7
Sextet 2	1.05	-0.06	17700	0.60	17.5%

CS: Center shift; D: Quadrupole splitting; A: Area; W+: Absorption line width

**Table S3.** Comparison of the ORR performance of non-precious metal catalyst in 0.1 M KOH at 1600 rpm.

Sample	Onset potential (V vs. RHE )	Half-wave potential (V vs. RHE)	J <sub>Limit</sub> @0.4 V (mA cm <sup>-2</sup> )	J <sub>Kinetic</sub> @0.9 V (mA cm <sup>-2</sup> )	Reference
FeN <sub>x</sub> /Fe <sub>2</sub> O <sub>3</sub> -CNFs	0.95	0.81	~6	0.50	This work
p-Fe-N-CNFs	0.91	0.82	5.05	/	1
PFA-Fe5-900-ALP	0.92	0.85	5.4	/	2
N-doped carbon tube	0.89	0.76	~4.9	~0.26	3
Fe-N/C-800	0.98	0.81	4.81	~0.32	4
Fe-N-CNFs	0.93	0.81	5.12	/	5
Co-N-doped Graphitic carbon	0.92	0.82	5.3	~0.32	6
FeCo/N-doped carbon aerogels	0.89	0.81	~6	~0.13	7
B-doped Fe-N <sub>x</sub> centers-enriched porous carbons	0.97	0.84	5.5	~0.93	8
MOG(Fe)/urea/CN Ts-700	0.92	0.72	5.37	~0.11	9
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /CNT	0.82	/	~4	/	10
Fe/N/S-PCNT	0.96	0.84	~5	~0.55	11
Graphene-like carbon nanosheets	0.86	0.77	4.8	/	12

1. B. C. Hu, Z. Y. Wu, S. Q. Chu, H. W. Zhu, H. W. Liang, J. Zhang and S. H. Yu, *Energy Environ. Sci.*, 2018, **11**, 2208-2215.

2. L. C. Pardo Pérez, N. R. Sahraie, J. Melke, P. Elsässer, D. Teschner, X. Huang, R. Krahnert, R. J. White, S. Enthaler, P. Strasser, and A. Fischer, *Adv. Funct. Mater.*, 2018, 1707551.
3. W. Wei, H. T. Ge, L. S. Huang, M. Kuang, A. M. Al-Enizi, L. J. Zhang and G. F. Zheng, *J. Mater. Chem. A*, 2017, **5**, 13634-13638.
4. W. H. Niu, L. G. Li, X. J. Liu, N. Wang, J. Liu, W.J. Zhou, Z. H. Tang, and S. W. Chen, *J. Am. Chem. Soc.*, 2015, **137**, 5555.
5. Z. Y. Wu, X. X. Xu, B. C. Hu, H. W. Liang, Y. Lin, *Angew. Chem. Int. Ed.*, 2015, **54**, 8179.
6. S. H. Liu, Z. Y. Wang, S. Zhou, F. J. Yu, M. Z. Yu, C. Y. Chiang, W. Z. Zhou, J. J. Zhao, and J. S. Qiu, *Adv. Mater.*, 2017, 1700874.
7. G. T. Fu, Y. Liu, Y. F. Chen, Y. W. Tang, J. B. Goodenough and J. M. Lee, *Nanoscale*, 2018, **10**, 19937-19944.
8. K. Yuan, S. Sfaelou, M. Qiu, D. Lützenkirchen-Hecht, X. D. Zhuang, Y. W. Chen, C. Yuan, X. L. Feng, and U. Scher, *ACS Energy Lett.*, 2018, **3**, 252-260.
9. H. Wang, X. C Cheng, F. X. Yin, B. H. Chen, T. Y. Fan, X. B. He, *Electrochim. Acta*, 2017, **232**, 114–122.
10. M. Sun, Y. Z. Dong, G. Zhang, J. H. Qu and J. H. Li, *J. Mater. Chem. A*, 2014, **2**, 13635.
11. Z. Tan, H. X. Li, Q. X. Feng, L. L. Jiang, H. Y. Pan, Z. Y. Huang, Q. Zhou, H. H. Zhou, S. Ma, Y. F. Kuang, *J. Mater. Chem. A*, 2019, **7**, 1607-1615.
12. C. Hu, Y. Zhou, R. Ma, Q. Liu and J. Wang, *J. Power Sources*, 2017, **345**, 120-130.