

## Supporting Information

### **Atomically Dispersed Fe-N<sub>x</sub> Active Sites within Hierarchical Mesoporous Carbon as Efficient Electrocatalysts for Oxygen Reduction Reaction**

Wenling Gu<sup>‡</sup>, Maochun Wu<sup>‡</sup>, Jing Sun, Jianbo Xu,<sup>\*</sup> Tianshou Zhao<sup>\*</sup>

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

\*Corresponding Authors: Prof. Jianbo Xu, and Prof. Tianshou Zhao; Emails: [mejianbo@ust.hk](mailto:mejianbo@ust.hk) and [metzhao@ust.hk](mailto:metzhao@ust.hk)

<sup>‡</sup>These authors contributed equally to this work.

## Experimental Section

**Chemicals and reagents.** Cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), iron (III) chloride ( $\text{FeCl}_3$ , 99.99%), oleylamine (OAm > 70%), commercial Pt/C catalyst (20 wt%) and dopamine are purchased from Sigma-Aldrich. Absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), methanol ( $\text{CH}_3\text{OH}$ ), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), potassium hydroxide (KOH), potassium thiocyanate (KSCN), sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) and disodium phosphate dodecahydrate ( $\text{Na}_2\text{HPO}_4$ ) were obtained from Beijing Chemical Reagent (Beijing, China). All the solvents and chemical reagents are used without further treatment. The aqueous solutions of 0.1 M KOH (pH = 13), 0.1 M PBS (pH = 7.4) and 0.5 M  $\text{H}_2\text{SO}_4$  (pH = 0.25) were prepared with Millipore Milli-Q (18.2 M $\Omega$  cm) deionized water.

**Morphology and structure characterizations.** The morphologies of the samples were tested by the scanning electron microscope (SEM, XL30 ESEM FEG SEM), TEM images were collected on a JEM-2100F microscopy. X-ray photoelectron spectroscopy (XPS) measurement was acquired from an ESCALAB-MKII X-ray photoelectron spectroscopy (VG Scientific, UK). Powder X-ray diffraction (XRD) was conducted by a D8 ADVANCE (Germany) coupled with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Raman spectra were performed on a Renishaw 2000 model confocal microscopy Raman spectrometer (Renishaw Ltd., Gloucestershire, U. K.). The Brunauer-Emmett-Teller (BET) surface area and pore volumes were measured from 77 K  $\text{N}_2$  sorption isotherms on ASAP 2020 equipment. X-ray Absorption Spectroscopy (XAS) experiments on Fe K-edge were carried out in transmission mode at Beamline 20-BM-B of the APS. The X-ray absorption fine structure spectra (Fe K-edge) were collected at a 1W1B station in Beijing Synchrotron Radiation Facility (BSRF). The storage rings of BSRF was operated at 2.5 GeV with a maximum current of 250 mA. Using Si(111) double-crystal monochromator, the data collection were carried out in transmission mode using ionization chamber. All spectra were collected in ambient conditions. XAFS Analysis and Results. The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software

packages. The k<sup>3</sup>-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k<sup>3</sup>-weighted  $\chi(k)$  data of Fe K-edge were Fourier transformed to real (R) space using a Hanning window ( $dk=1.0 \text{ \AA}^{-1}$ ) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of IFEFFIT software packages.

**Preparation of Co template.** 180 mg  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in 60 mL oleylamine by ultrasonication for 1 h to get a uniform solution. Then the mixture was transferred to a poly-tetrafluoroethylene reaction kettle, which was sealed and heated at 250 °C for 1.5 h. When the kettle cooling to room temperature, the colloidal products were collected by centrifugation and washed by hexane/ethanol (v:v, 4:1) mixture and ethanol, respectively, and then dispersed in 30 mL ethanol for further experiment.

**Preparation of FeNGC-T catalysts.** The Fe-N-doped hierarchically porous carbon materials (FeNGC-T) were prepared *via in situ* etching and polymerization followed by pyrolysis. Considering the lower reduction potentials of  $\text{Co}^{2+}/\text{Co}$  than that of  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{FeCl}_3$  was used as both oxidizing and etching agent. In the first, the etching agent was made with 1 g of  $\text{FeCl}_3$  dissolved into 10 mL ethanol. Another 0.15 g dopamine was added into the pristine template solution, and the mixtures were shaken for 5 h to disperse dopamine on the outer surface of the Co template. Then, an excessive amount of  $\text{FeCl}_3$  was gradually added into the prepared solution and stirred for 24 h, which would realize the polymerization of dopamine and the etching of Co template simultaneously. After the solvent was evaporated under reduced pressure, the materials were pyrolyzed at 800 °C for 2 h under the atmosphere of  $\text{N}_2$  to afford the final catalysts of FeNGC-T. Before electrochemical measurement, the samples were washed with dilute  $\text{H}_2\text{SO}_4$  (0.5 M) for 12 h to remove the inactive species.

For comparison, the catalysts of FeNGC with the absence of template and N-doped graphite carbon (NGC) were both provided. The catalyst of FeNGC was prepared by

the pyrolysis of FeCl<sub>3</sub> oxidized polymerization of dopamine under the same conditions as FeNGC-T.

**Electrocatalytic activity measurements:** Before each experiment, the working electrode should be polished with 0.3 μm and 0.05 μm alumina slurries and washed with deionized water and absolute ethanol to get a mirror finish. And the catalyst ink was prepared as follows: 4 mg catalyst sample was added into 1 mL of mixture solution which contained 20:1:0.075 (v:v:v) of water, absolute ethanol, and Nafion (5.0 wt %). Then the solution was sonicated for 30 min to obtain a 4 mg/mL catalyst. Before the experiments of CVs and amperometric i-t, 6 μL catalyst ink was dropped onto a glassy carbon electrode (GCE: 3.0 mm in diameter) with a loading amount of 0.34 mg/cm<sup>2</sup> and dried under an infrared lamp. The linear sweep voltammetry (LSV) measurements were measured by using RRDE or RDE techniques to evaluate the ORR electrocatalytic activity of different samples. Additionally, the 20% E-TEK Pt/C catalyst was also prepared in the same way and dropped with a loading amount of 25 μg Pt/cm<sup>2</sup> for a comparison.

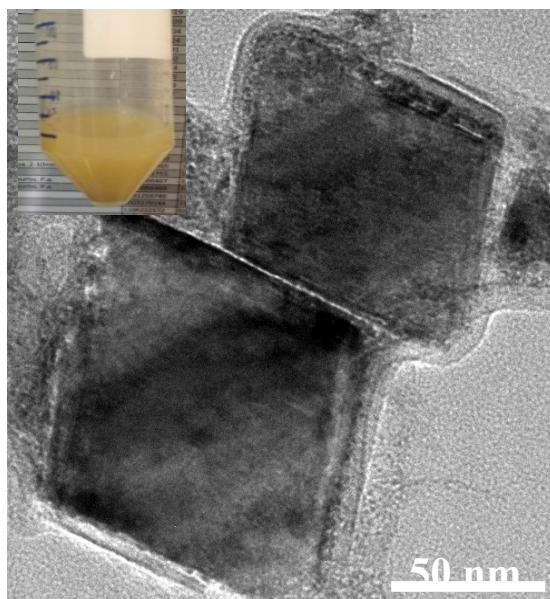
Before each experiment, the electrolyte was bubbled by purging high-purity N<sub>2</sub> gas for at least 30 min in order to remove the dissolved oxygen. And the modified working electrode should be electrochemically treated and cleaned by CV sweeping (potential scan from 1.1 V to 0 V (vs. RHE) ) with a scan rate of 100 mV s<sup>-1</sup> in a N<sub>2</sub>-saturated electrolyte until a reproducible curve appeared. Meanwhile, the contrastive CV curves in N<sub>2</sub>-saturated or O<sub>2</sub>-saturated were offered by CV sweeping with a scan rate of 50 mV s<sup>-1</sup> after purging N<sub>2</sub> or O<sub>2</sub> at least for 30 min. The amperometric i-t curves were obtained by sweeping the FeNGC-T, or 20% E-TEK Pt/C (Pt/C) catalyst modified electrode with 50000 s at the potential of 0.614 V (vs. RHE) ) in O<sub>2</sub>-saturated 0.1 M KOH, 0.1M PBS, and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

The RDE measurements were conducted in an O<sub>2</sub>-saturated 0.1 M KOH or 0.1 M PBS or 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte by a negative-direction sweeping potential with a scan rate of 5 mV s<sup>-1</sup> under different electrode rotation rates. The electron transfer also can be estimated according to the Koutecky–Levich equations:

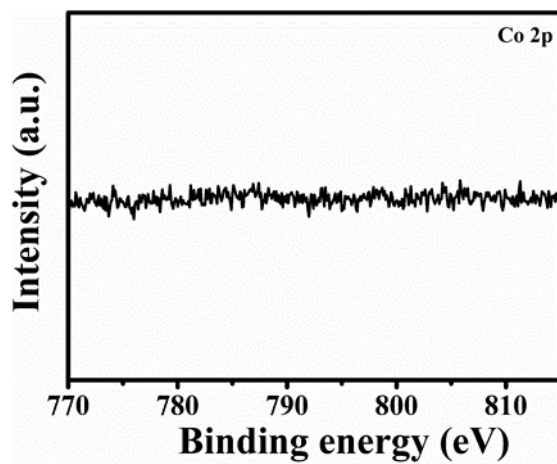
$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}}$$

$$B = 0.2nF(D_0)^{2/3}\nu^{-1/6}C_0$$

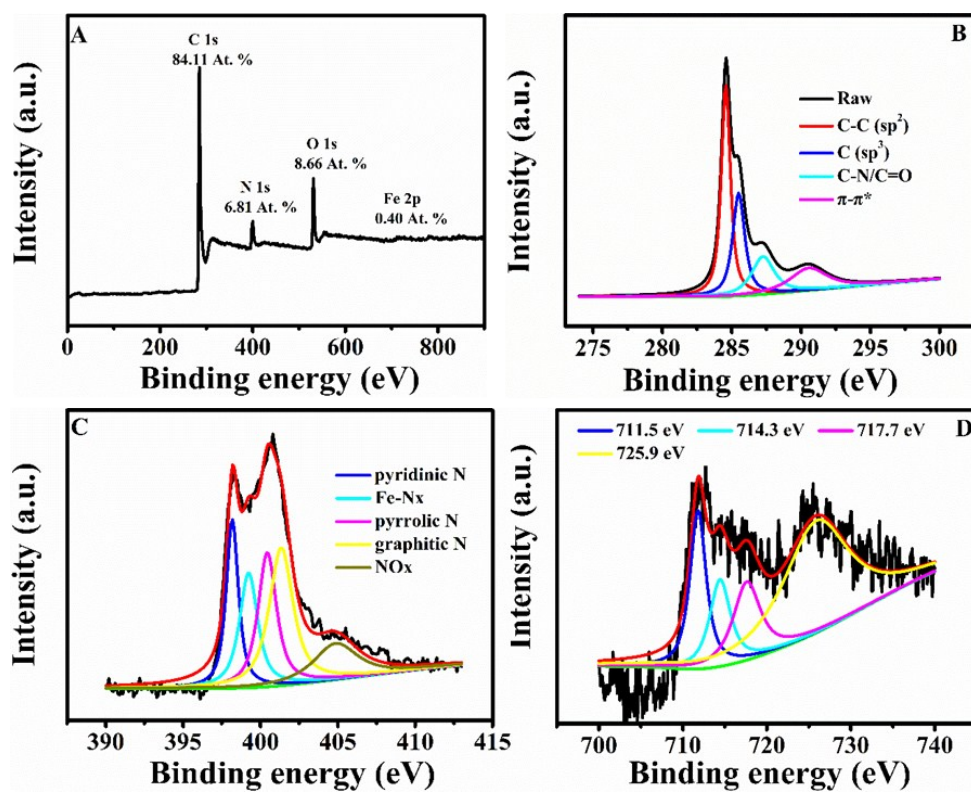
where  $j$  represents the current density,  $j_k$  is the kinetic-limiting current density,  $\omega$  is the electrode rotation rates,  $n$  means the transferred electron number,  $F$  is the Faraday constant of 96485 C/mol, and  $D_0$  is the diffusion coefficient of  $O_2$ ,  $\nu$  represents the kinematic viscosity of the electrolyte,  $C_0$  is the bulk concentration of  $O_2$ .



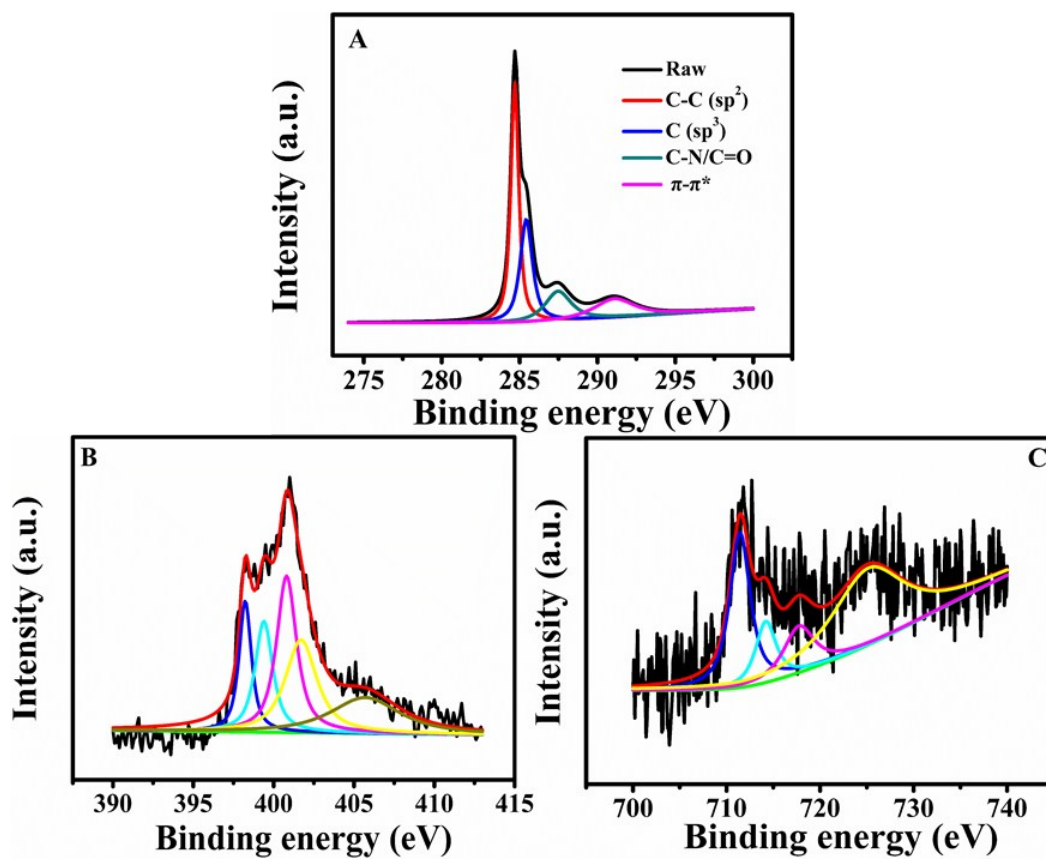
**Figure S1.** TEM image of the obtained Co template.



**Figure S2.** The Co 2p XPS spectra of FeNGC-T.

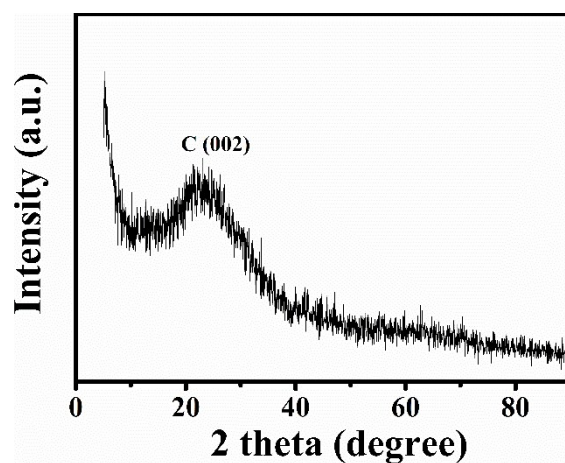


**Figure S3.** XPS survey spectra (A) of FeNGC-T; High-resolution C 1s spectra (B), N 1s spectra (C) and Fe 2p spectra (D) of the catalyst FeNGC-T.

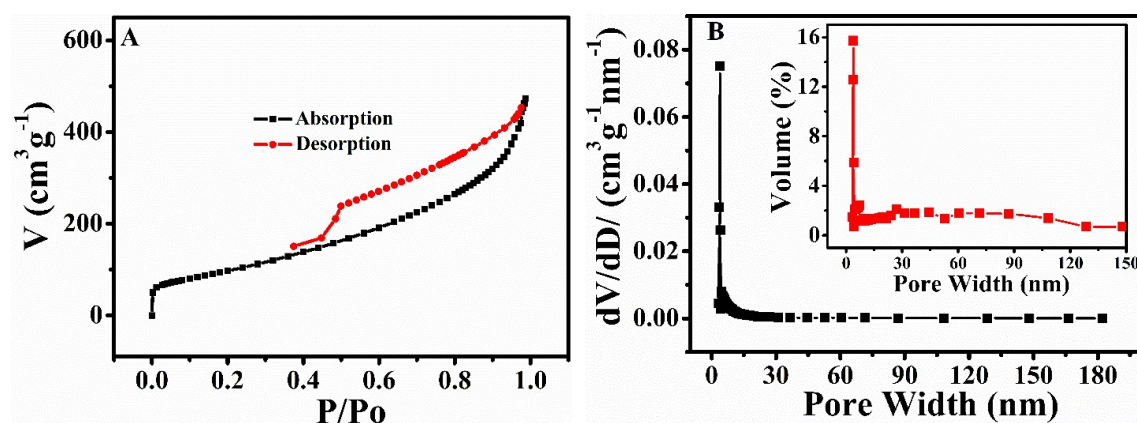


**Figure S4.** High-resolution C 1s XPS spectra (A), N 1s XPS spectra (B), Fe 2p XPS spectra (C) of the FeNGC.

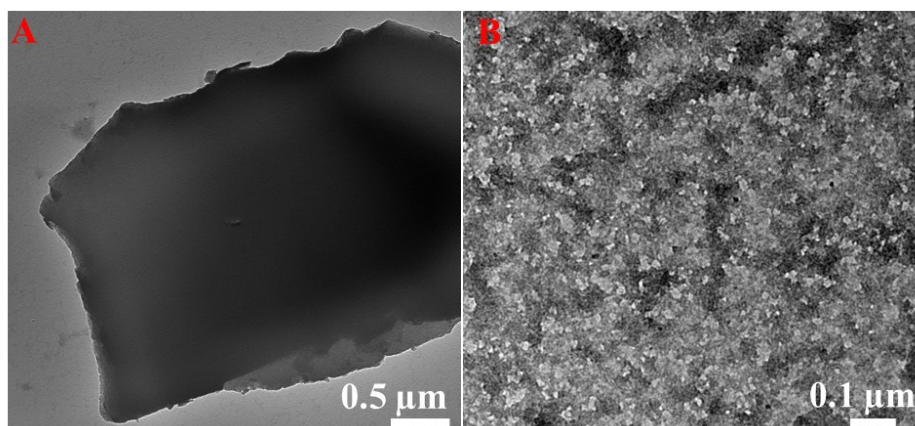




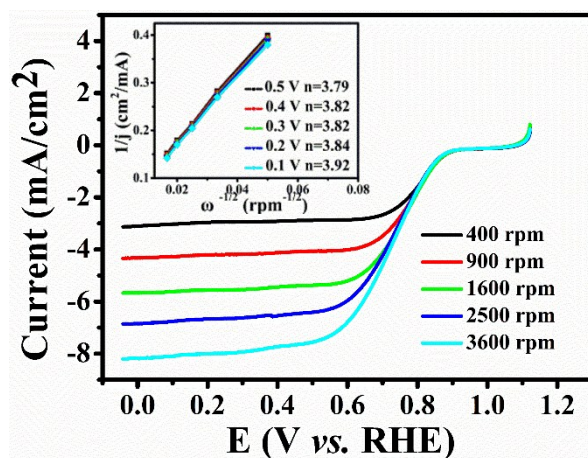
**Figure S5.** XRD pattern of the obtained FeNGC-T catalyst.



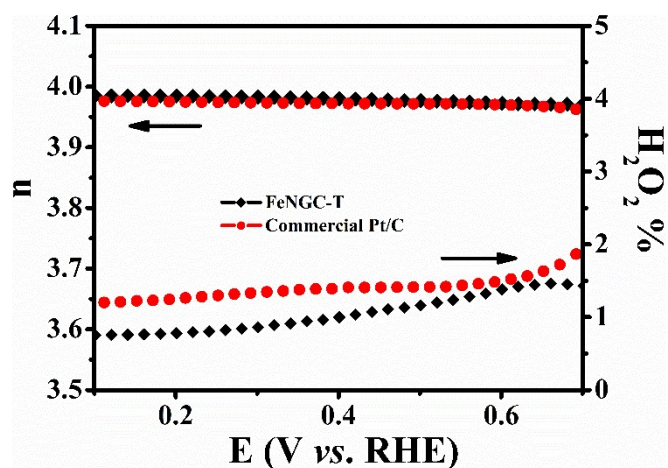
**Figure S6.** The N<sub>2</sub> adsorption-desorption isotherm (A) and BJH pore distributions (B) of the FeNGC.



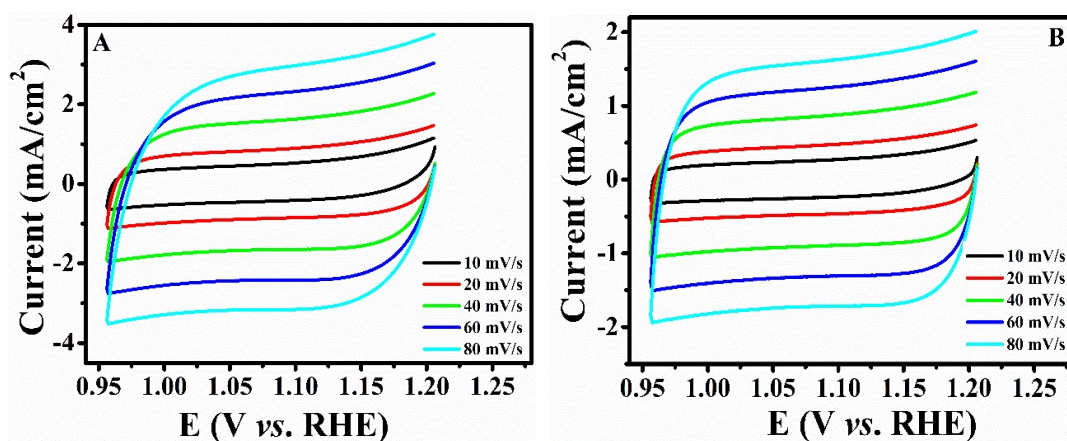
**Figure S7.** The TEM images of precursors of FeNGC (A) and FeNGC-T (B).



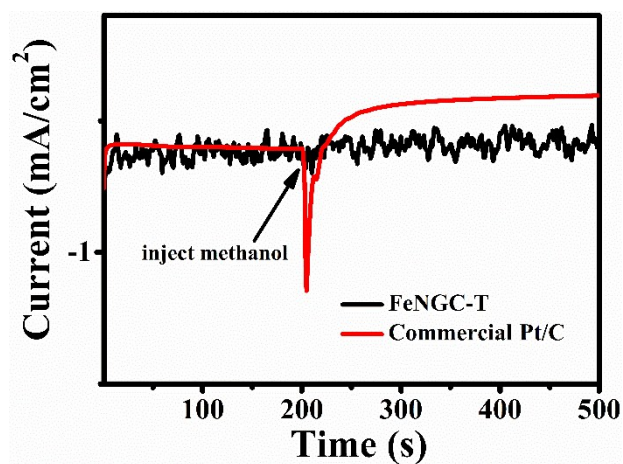
**Figure S8.** RDE curves of the FeNGC modified electrode at various rotation rates and the corresponding Koutecky–Levich plots (shown as inset).



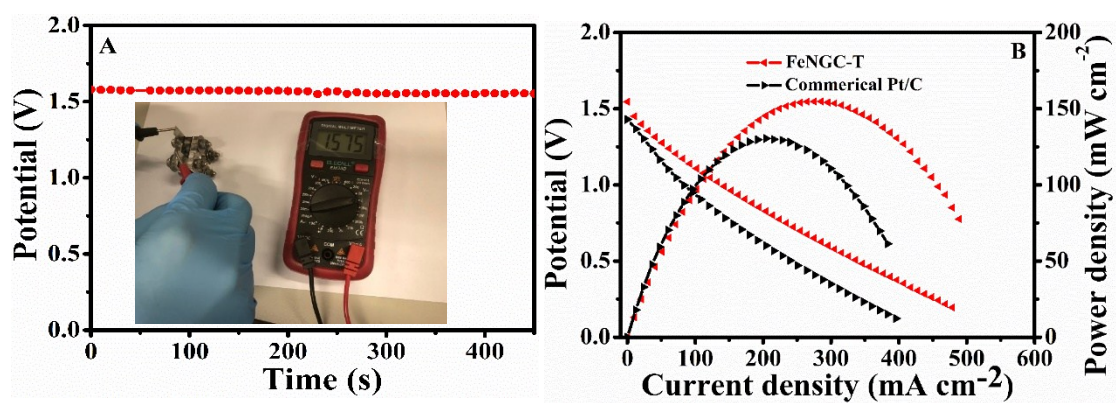
**Figure S9.** The electron transfer number and the  $\text{H}_2\text{O}_2$  percent of FeNGC-T and Pt/C catalysts during the ORR.



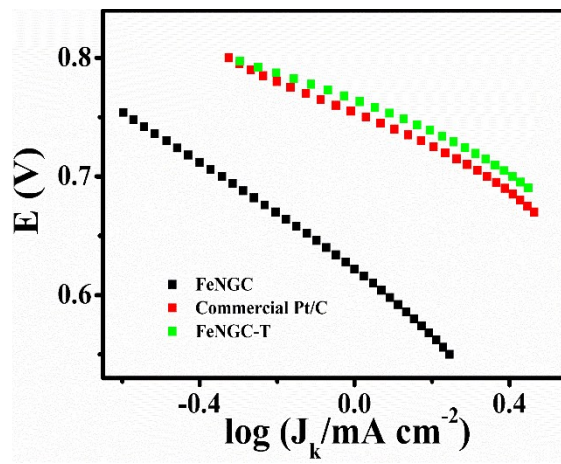
**Figure S10.** CV curves of FeNGC-T catalyst (A) and FeNGC (B) at different scan rates of 10, 20, 40, 60, 80, 100 mV/s.



**Figure S11.** Methanol tolerance measurement of FeNGC-T catalyst and commercial Pt/C in O<sub>2</sub>-saturated 0.1 M KOH.

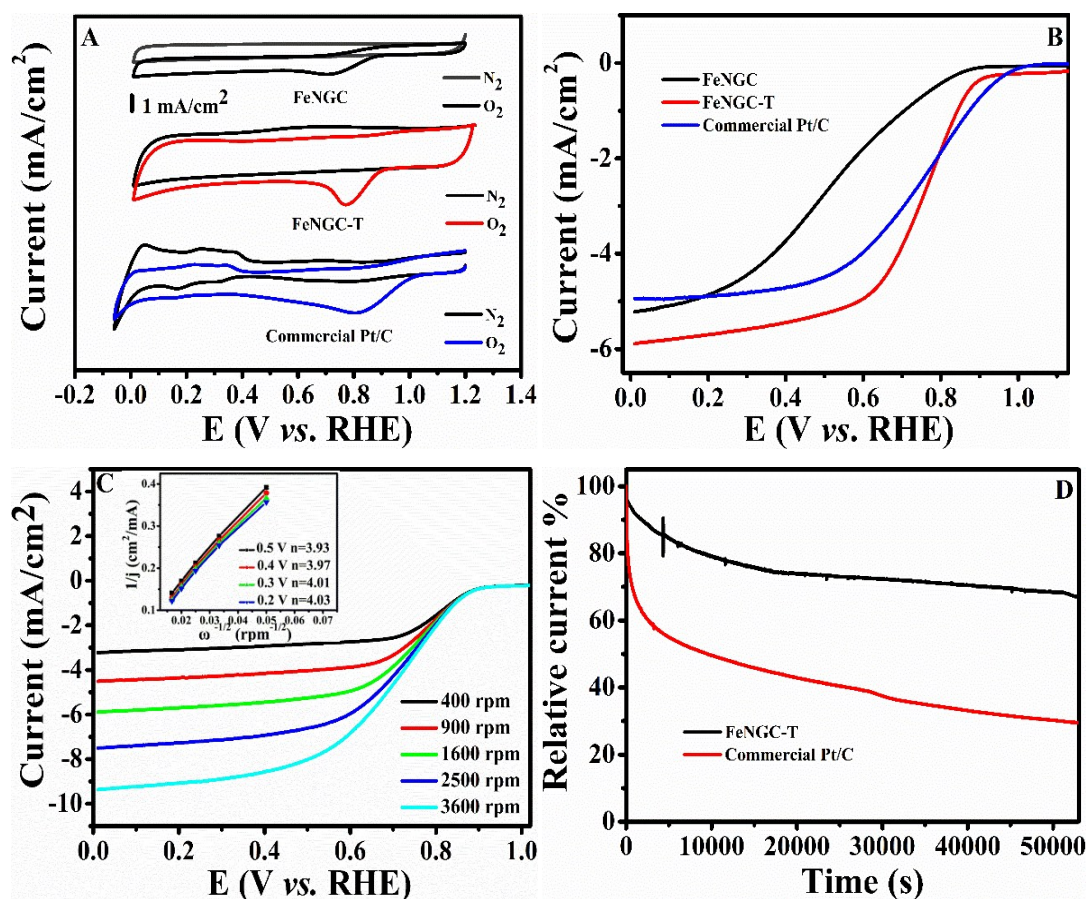


**Figure S12.** Open-circuit potential of FeNGC-T-based battery (A); Polarization and power density curves of Pt/C- and FeNGC-T-based batteries (B).



**Figure S13.** The Tafel plots of different materials in  $\text{O}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$ .





**Figure S14.** (A) CV curves of the FeNGC-T, FeNGC, and Pt/C in  $\text{N}_2$ -saturated and  $\text{O}_2$ -saturated  $0.1 \text{ M}$  PBS at a scan rate of  $50 \text{ mV s}^{-1}$ ; (B) LSV curves of various samples on a rotating disk electrode ( $1600 \text{ rpm}$ ) in  $\text{O}_2$ -saturated  $0.1 \text{ M}$  PBS at a scan rate of  $5 \text{ mV s}^{-1}$ ; (C) LSV of FeNGC-T at different rotating rates and (inset) the corresponding K-L plots at different potentials; (D) The amperometric  $i-t$  response to the FeNGC-T and Pt/C in  $\text{O}_2$  saturated  $0.1 \text{ M}$  PBS electrolyte.

**Table S1** The elements compositions of FeNGC and FeNGC-T.

Materials	Elements compositions(%) tested by XPS			
	C atom%	O atom%	N atom%	Fe atom%
FeNGC	90.92	5.48	3.43	0.17
FeNGC-T	84.11	8.66	6.81	0.40 (2.31 wt %)

**Table S2** The percent of C species of FeNGC and FeNGC-T.

Materials	C-C(sp <sup>2</sup> )/%	C(sp <sup>3</sup> )/%	sp <sup>3</sup> / sp <sup>2</sup>
FeNGC	0.403	0.2712	0.673
FeNGC-T	0.396	0.257	0.648

**Table S3.** EXAFS fitting parameters at the Fe K-edge for the FeNGC-T catalyst.

Sample	Shell	N <sup>a</sup>	R (Å) <sup>b</sup>	$\sigma^2$ (Å <sup>2</sup> ·10 <sup>3</sup> ) <sup>c</sup>	$\Delta E_0$ (eV) <sup>d</sup>	R factor (%)
FeNGC-T	Fe-N	3.1	1.99	11.1	-1.8	0.7
	Fe-C	5.4	2.61	12.0	-3.0	
	Fe-Fe	2.5	2.97	15.9	-4.4	

<sup>a</sup> N: coordination numbers; <sup>b</sup> R: bond distance; <sup>c</sup>  $\sigma^2$ : Debye-Waller factors; <sup>d</sup>  $\Delta E_0$ : the inner potential correction. R factor: goodness of fit.  $S_0^2$ , 0.77, was obtained from the experimental EXAFS fit of FePc reference by fixing CN as the known crystallographic value and was fixed to all the samples.

**Tables S4.** The ORR activity of different catalysts.

Catalysts	Electrolyte	$E_{\text{onset}}$ (V) vs. RHE	$E_{1/2}$ (V) vs. RHE	Electron transfer number (n)	Referen ce
<b>FeNGC-T</b>	<b>0.1 M KOH</b>	<b>0.99</b>	<b>0.85</b>	<b>3.96-4.03</b>	<b>This work</b>
	<b>0.1 M PBS</b>	<b>0.89</b>	<b>0.74</b>	<b>3.93-4.03</b>	
	<b>0.5 M H<sub>2</sub>SO<sub>4</sub></b>	<b>0.83</b>	<b>0.70</b>	<b>3.90-4.02</b>	
<b>NC900 (ZIF-8)</b>	<b>0.1 M KOH</b>	<b>0.83</b>	<b>0.68</b>	<b>3.3</b>	<b>1</b>
<b>Fe-P-C</b>	<b>0.1 M KOH</b>	<b>0.95</b>	—	<b>3.62</b>	<b>2</b>
	<b>0.1 M HClO<sub>4</sub></b>	<b>0.84</b>	<b>0.52</b>	<b>3.8</b>	
<b>N-doped Fe/Fe<sub>3</sub>C@C</b>	<b>0.1 M KOH</b>	<b>0.91</b>	<b>0.83</b>	<b>3.52-3.08</b>	<b>3</b>
<b>Co-O<sub>4</sub>-N</b>	<b>0.1 M KOH</b>	<b>0.88</b>	<b>0.81</b>	<b>3.75</b>	<b>4</b>
<b>Cu-CTF/CP</b>	<b>0.1 M PBS</b>	<b>0.81</b>	<b>0.59</b>	<b>3.75-3.95</b>	<b>5</b>
<b>Fe-N/C-800</b>	<b>0.1 M KOH</b>	<b>0.923</b>	<b>0.8</b>	<b>3.9</b>	<b>6</b>
	<b>0.1 M HClO<sub>4</sub></b>	<b>0.72</b>	<b>0.55</b>	<b>3.97</b>	
<b>CoS<sub>2</sub>/N,S-GO</b>	<b>0.1 M KOH</b>	<b>0.79</b>	—	<b>3.81</b>	<b>7</b>
<b>FeIM/ZIF-8</b>	<b>0.1 M HClO<sub>4</sub></b>	<b>0.915</b>	<b>0.755</b>	<b>3.70-3.81</b>	<b>8</b>



## Reference

1. A. Aijaz, N. Fujiwara, Q. Xu, *J. Am. Chem. Soc.* **2014**, *136*, 6790.
2. K. P. Singh, E. J. Bae, J. S. Yu, *J. Am. Chem. Soc.* **2015**, *137*, 3165.
3. Y. Hou, T. Huang, Z. Wen, S. Mao, S. Cui, J. Chen, *Adv. Energy Mater.* **2014**, *4*, 1400337.
4. J. Han, Y. J. Sa, Y. Shim, M. Choi, N. Park, S. H. Joo, S. Park, *Angew. Chem. Int. Ed.* **2015**, *54*, 12622.
5. K. Iwase, T. Yoshioka, S. J. Nakanishi, K. Hashimoto, K. Kamiya, *Angew. Chem. Int. Ed.* **2015**, *54*, 11068.
6. L. Lin, Q. Zhu, A. W. Xu, *J. Am. Chem. Soc.* **2014**, *136*, 11027.
7. T. Sun, Q. Wu, R. C. Che, Y. F. Bu, Y. F. Jiang, Y. Li, L. J. Yang, X. Z. Wang, Z. Hu, *ACS Catal.* **2015**, *5*, 1857.
8. D. Zhao, J. Shui, C. Chen, X. Chen, B. M. Repragle, D. Wang, D. Liu, *Chem. Sci.* **2012**, *3*, 3200.