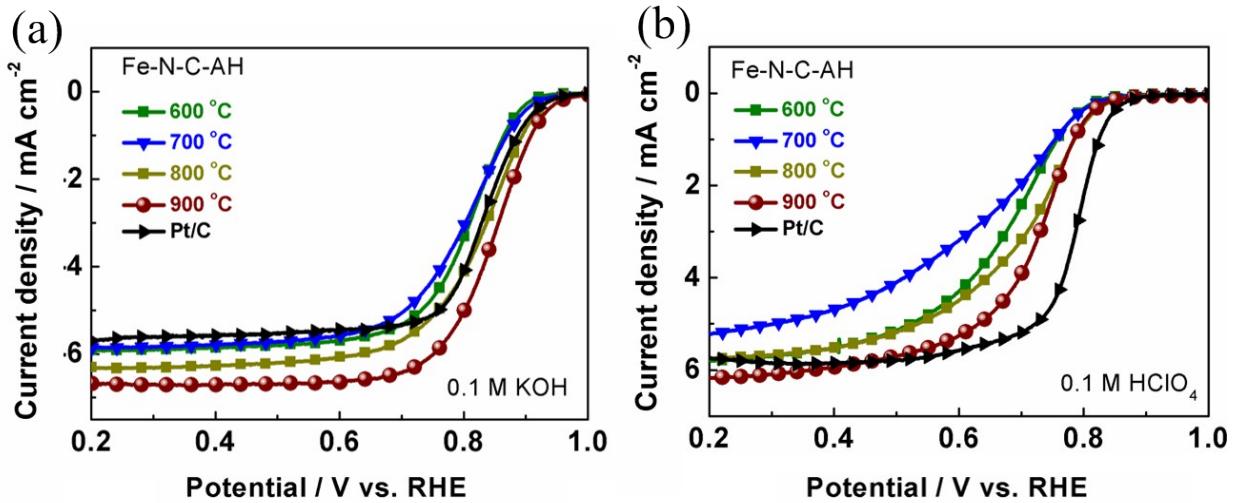


## Supporting Information

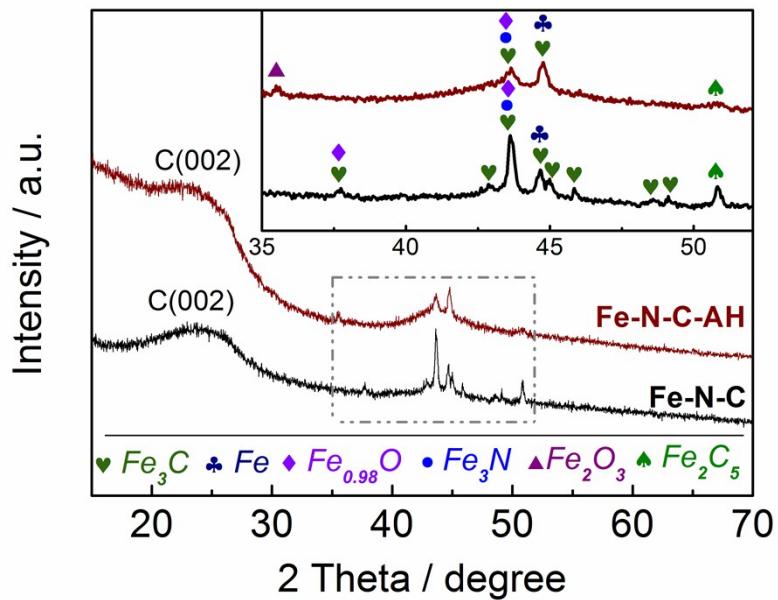
### **Out-plane Fe<sup>II</sup>-N<sub>4</sub> moiety modified Fe-N co-doped porous carbons as high-performance electrocatalysts for oxygen reduction reaction**

Zhongjie Qian, Zhaowen Hu, Zhengping Zhang, Zhilin Li, Meiling Dou\*, Feng Wang\*

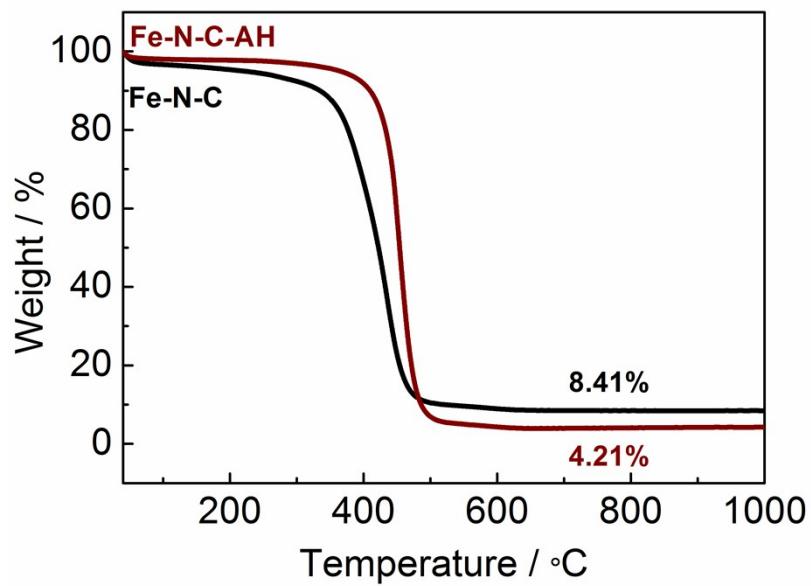
State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, P R China



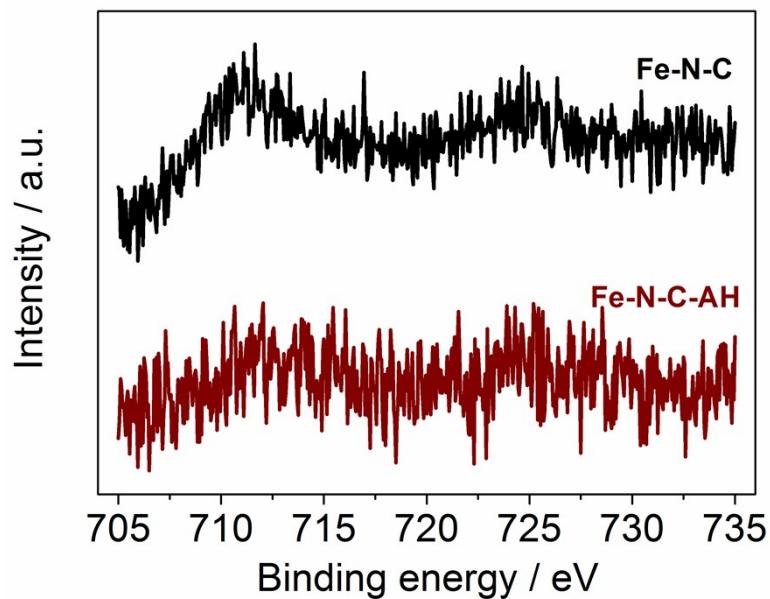
**Fig. S1.** LSV curves of Fe-N-C-AH electrocatalysts prepared with various pyrolysis and post-treatment temperatures profiled in O<sub>2</sub>-saturated (a) 0.1 M KOH and (b) 0.1 M HClO<sub>4</sub> (scan rate: 5 mV s<sup>-1</sup>, electrode rotation rate: 1600 rpm).



**Fig. S2.** XRD patterns of Fe-N-C and Fe-N-C-AH.



**Fig. S3.** TG profiles of Fe-N-C and Fe-N-C-AH.



**Fig. S4.** Fe 2p XPS spectra of Fe-N-C and Fe-N-C-AH.

**Table S1.** Pore characteristics of Fe-N-C and Fe-N-C-AH.

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$S_{\text{micro}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$S_{\text{micro}} / S_{\text{BET}} (\%)$	$V_{\text{pore}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{\text{micro}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{\text{micro}} / V_{\text{pore}} (\%)$
Fe-N-C	425.4	161.2	37.89	0.5454	0.069	12.65
Fe-N-C-AH	711.1	423.7	59.58	0.7289	0.182	24.96

**Table S2.** The content and configuration of N for Fe-N-C and Fe-N-C-AH.

Sample	N at. %	Relative content of different N species				
		Pyridinic N	Fe-N <sub>4</sub>	Pyrrolic N	Graphitic N	Oxidized N
Fe-N-C	2.21	32.30	22.15	25.55	10.92	9.08
Fe-N-C-AH	1.91	24.86	18.47	23.30	25.82	7.55

**Table S3.** Summary of the Mössbauer parameters for Fe-N-C and Fe-N-C-AH.

MS site	$\delta_{\text{iso}}^{\text{a}}$ / $\text{mm s}^{-1}$	$\Delta E_Q^{\text{b}}$	$\text{Fwhm}^{\text{c}}$ / $\text{mm s}^{-1}$	$H_0^{\text{d}}$ / T	Assignment
Sing	-0.05		0.43		Superparamagnetic iron
D1	0.31	0.983	0.58		Fe <sup>II</sup> -N <sub>4</sub> /C, low-spin
D2	0.21	1.19	0.58		Fe <sup>II</sup> -N <sub>4</sub> , mid-spin
Sext	0.17	-0.003	0.45	20.9	Iron carbide

<sup>a</sup> $\delta_{\text{iso}}$ : the isomer shift that related to the electric monopole interaction; <sup>b</sup> $\Delta E_Q$ : the quadrupole splitting that related to the electric quadrupole interaction; <sup>c</sup>Fwhm: the full-width at half maximum; <sup>d</sup> $H_0$ : the magnetic field.