Electronic Supplementary Information

Tuning the Fe-N₄ sites by introducing Bi-O bond in a Fe-N-C system

for promoting oxygen reduction reaction

Huihui Jin,^{a,b#} Jiawei Zhu,^{b,c#} Ruohan Yu,^b Wenqiang Li,^d Pengxia Ji,^b Lvhan Liang,^b

Bingshuai Liu,^b Chenxi Hu,^b Daping He^{a,b*} and Shichun Mu^{b,c*}

^a Hubei Engineering Research Center of RF-Microwave Technology and Application,

Wuhan University of Technology, Wuhan 430070, China.

^b State Key Laboratory of Advanced Technology for Materials Synthesis and

Processing,

Wuhan University of Technology, Wuhan 430070, China

^c Foshan Xianhu Laboratory,

Foshan 528200, China

^d Henan Key Laboratory of Function-Oriented Porous Materials, College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471934, China

E-mail: hedaping@whut.edu.cn, msc@whut.edu.cn

Experimental details

Materials

The chemical reagents purchased in the experiment were used without additional purification. Polyvinyl alcohol and 2-methylimidazole were from Aladdin reagent

company, commercial Pt/C producer was JM company, and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. The resistivity of the deionized water used was 18.25 M Ω cm.

Morphology and Structure Characterization

Characterization instruments used in the experiments included scanning electron microscopy (SEM, Zeiss Ultra Plus), transmission electron microscopy (TEM, Talos F2000s), X-ray diffraction (XRD, D8 Advance), RENISHAW Raman microscope (Raman, Invia), X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) and fully automatic specific surface area and porosity analyzer (ASAP 2020M). The Mössbauer measurements were performed at room temperature (or xx K) using a conventional spectrometer (Germany, Wissel MS-500) in transmission geometry with constant acceleration mode. A 57Co(Rh) source with activity of 25 mCi was used. The velocity calibration was done with a room temperature α -Fe absorber. The spectra were fitted by the software Recoil using Lorentzian Multiplet Analysis. The ESR spectra of Fe were tested on a JESFA200 spectrometer, and the changes in the g factor were analyzed to illustrate the changes in the electronic structure of the material before and after Bi doping.

Electrochemical Measurements

All electrochemical tests were performed on CHI 760E electrochemical workstation. The oxygen reduction test is based on three-electrode working model including a counter electrode, a reference electrode and a working electrode. The counter electrode is a platinum wire or a platinum black electrode, the reference electrode is a calibrated Ag/AgCl electrode (used in 0.1 M KOH) or saturated calomel electrode (SCE, used in 0.5 M H₂SO₄), the potential under them can be converted to reversible hydrogen potential by the Nernst equation, and the working electrode is a glassy carbon electrode coated with catalyst ink (20 μ L for as-prepared catalyst, 10 μ L for commercial Pt/C). The preparation of catalyst ink was as follow: 5 mg of as-prepared catalyst or 3 mg of commercial Pt/C was dispersed in a mixed solution consisting of 900 μ L of isopropanol, 100 μ L of deionized water and 20 μ L of Nafion (5%), and sonicated for 20 min to the ink state. All oxygen reduction tests were performed in N₂/O₂ saturated electrolytes, Cyclic voltammetry (CV) was measured at the scan rate of 50 mV s⁻¹, Linear sweep voltammetry (LSV) was measured at 1600 rpm at the scan rate of 10 mV s⁻¹.

In RDE testing, the electron transfer number (n) was calculated on the basis of Koutecky-Levich equation according to the LSV curve:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}$$

$$B = 0.62 n F C_0 D^{2/3} v^{-1/6}$$

Where j is the measured current density, j_K is the kinetic current density, j_L is the limiting current density, ω is the angular velocity of the electrode rotation, n is the electron transfer number, F is the Faraday constant (96485 C mol⁻¹), C₀ is the bulk concentration of O₂ (1.2 × 10⁻⁶ mol cm⁻³ for 0.1 M KOH, 1.1 × 10⁻⁶ mol cm⁻³ for 0.5 M H₂SO₄), D is the diffusion coefficient of O₂ (1.9 × 10⁻⁵ cm² s⁻¹ in 0.1 M KOH, 1.8 × 10⁻⁵

cm² s⁻¹ in 0.5 M H₂SO₄), and v is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹ for both 0.1 M KOH and 0.5 M H₂SO₄ solution).

In RDDE testing, $H_2O_2\%$ yield and n were calculated by the following equation:

$$n = \frac{4I_d}{I_d + \frac{I_r}{N}}$$
$$H_2 O_2 \% = 200 \times \frac{\frac{I_r}{N}}{\frac{I_r}{N} + I_d}$$

Where the I_d is the disk current, I_r is the ring current, N=0.37

Computational Calculation Section

The calculations were conducted with the CASTEP package in Materials Studio of Accelrys Inc.¹ The calculation models (FeN4 and FeN4-BiO) were built based on the graphene nanoribbons. A vacuum space as large as 15 Å was used along the c direction to avoid periodic interactions. Electron exchange-correlation was described with the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).² A cutoff energy of 400 eV for plane-wave basis set was applied, and a 2×2×1 Monkhorst Pack k-point (MPk) grid was employed to integrate the Brillouin zone. The convergence tolerance quality of geometry optimization was set as: 1.0×10-5 eV/atom for energy, 0.05 eV/Å for maximum force and 0.002 Å for maximum displacement. The adsorption energies of various intermediates in ORR were explored to assess the theoretical activity.

ORR reaction pathway in alkaline media was listed as follows:

$$O_2(g) + H_2O(I) + * + e^- \to OOH^* + OH^-$$
 (1)

$$OOH^* + e^- \to O^* + OH^- \tag{2}$$

$$O^* + H_2O(I) + e^- \to OH^* + OH^- \tag{3}$$

$$OH^* + e^- \to * + OH^- \tag{4}$$

The adsorption free energies of OH*, O* and OOH* were calculated based on:

$$\Delta EOH^* = E(OH^*) - E(^*) - [E(H_2O) - 1/2 E(H_2)]$$
(5)

$$\Delta EO^* = E(O^*) - E(^*) - [E(H_2O) - E(H_2)]$$
(6)

$$\Delta EOOH^* = E(OOH^*) - E(^*) - [2 \ E(H_2O) - 3/2 \ E(H_2)]$$
(7)

The zero-point energy (ZPE) and entropy corrections were also considered to convert \triangle EDFT ads(binding energy) into \triangle Gads (adsorption free energy) through the following equation. Here we use 0.06, 0.37 and 0.44 eV for O*, OH* and OOH* as proposed by Li et al.³

$$\Delta G_{ads} = \Delta EDFT \, ads + \Delta ZPE - T\Delta S \tag{8}$$

Then, the reaction free energy $\triangle G$ of each step was calculated as follows:

$$\Delta G_1 = \Delta G_{OOH^*} - 4.92 \ eV + eU - k_b T \ln(a_{H^*}) \tag{9}$$

$$\Delta G_2 = \Delta G_{O^*} - \Delta G_{OOH^*} + eU - k_b T ln(a_{H^*})$$
(10)

$$\Delta G_3 = \Delta G_{OH^*} - \Delta G_{O^*} + eU - k_b T ln(a_{H^*})$$
(11)

$$\Delta G_4 = -\Delta G_{OH^*} + eU - k_b T ln(a_{H^*})$$
(12)

The U is the potential against the normal hydrogen electrode (NHE), and the theoretical overpotential can be obtained according to:

$$\eta_{ORR} = max \left[\Delta G_{1}, \Delta G_{2}, \Delta G_{3}, \Delta G_{4} \right] / e + 1.23 V \tag{13}$$

References:

1 G. Kresse, J. Furthmüller, Phys. Rev. B, **1996**, 54, 11169-11186.

2 J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett, **1996**, 77, 3865.

3 Y. Yao, S. Hu, W. Chen, Z. Huang, W. Wei, T. Yao, R. Liu, K. Zang, X. Wang, G. Wu, W. Yuan, T. Yuan, B. Zhu, W. Liu, Z. Li, D. He, Z. Xue, Y. Wang, Z. Zheng, J. Dong, C. Chang, Y. Chen, X. Hong, J. Luo, S. Wei, W. Li, P. Strasser, Y. Wu, Y. Li, Nat. Catal. **2019**, 2, 304-313.

Supplementary Figures and Tables



Fig. S1 XRD patterns of precursors



Fig. S2 SEM images of Fe/Bi-RNC (a) low-resolution, (b) high-resolution



Fig. S3 TEM image of Fe/Bi-RNC



Fig. S4 XRD patterns of Fe-RNC and Fe/Bi-RNC



Fig. S5 Raman spectra of NC, Fe-RNC and Fe/Bi-RNC



Fig. S6 FTIR spectra of Fe-RNC and Fe/Bi-RNC



Fig. S7 N1s XPS spectra of (a) NC, (b) RNC, (c) Fe-RNC and (d) Fe/Bi-RNC



Fig. S8 N types content summary



Fig. S9 Onset potential and half-wave potential of different catalysts under O_{2} -



saturated 0.1 M KOH electrolytes

Fig. S10 LSV curves of (a) Fe-RNC series samples prepared with different amount of iron salts and (b) Fe/Bi-RNC series samples prepared with different amount of bismuth salts under O_2 -saturated 0.1 M KOH



Fig. S11 The ORR path evaluation of Fe/Bi-RNC in 0.1 M KOH (a) LSV curves of Fe/Bi-

RNC under different rotate speeds, (b) K-L plots under different potential



Fig. S12 Onset potential and half-wave potential of different catalysts under ${\rm O}_{2^{\text{-}}}$

saturated 0.5 M H_2SO_4 electrolytes



Fig. S13 Tafel plots of different catalysts under O₂-saturated 0.5 M H₂SO₄ electrolytes



Fig. S14 $H_2O_2\%$ and electron transfer number comparison between Fe/Bi-RNC and 20% Pt/C under O_2 -saturated 0.5 M H_2SO_4 electrolytes



Fig. S15 The ORR path evaluation of Fe/Bi-RNC in 0.5 M H₂SO₄ (a) LSV curves under

different rotate speeds, (b) K-L plots under different potential



Fig. S16 Stability testing of Fe/Bi-RNC and 20% Pt/C in O₂-saturated 0.5 M H₂SO₄



Fig. S17 Methanol tolerance testing of Fe/Bi-RNC and 20% Pt/C in O₂-saturated 0.5 M



Fig. S18 LSV curves of Fe/Bi-RNC before and after SCN- poisoning



Fig. S19 Theoretical models of a) Fe-N $_4$ and b) Fe-N $_4$ -BiO

 H_2SO_4



Fig. S20 Oxygen adsorption configuration upon a) Fe-N₄ and b) Fe-N₄-BiO



Fig. S21 Adsorption configuration of a) OOH*, b) O* and c) OH* on the Fe-N₄ model



Fig. S22 Adsorption configuration of a) OOH*, b) O* and c) OH* on the Fe-N₄-BiO model



Fig. S23 Adsorption configuration of a) OOH*, b) O* and c) OH* on the onefold BiO model



Fig. S24 ORR free energy diagram of the onefold BiO model

Table S1. The fitted Mössbauer parameter table and the corresponding assignment of Fe-RNC and Fe/Bi-RNC. The isomer shift (IS), quadrupole splitting (QS), hyperfine field (H) and the relative content of each substance are given.

| Sample | Component | IS | QS | Area | Assignments |
|-----------|----------------|-----------|-----------|----------|------------------------------------|
| | | (mm/s) | (mm/s) | (%) | (Iron Phase) |
| Fe-RNC | Doublet Site 1 | 0.451(25) | 0.88(60) | 55.1(81) | Fe(II)-N ₄ |
| | | | | | (low spin) |
| | Doublet Site 2 | 0.342(39) | 1.519(81) | 44.9(79) | Fe(II)-N ₄ |
| | | | | | (similar to [FePc]²-) |
| Fe/Bi-RNC | Doublet Site 1 | 0.392(56) | 0.98(28) | 45.1(78) | Fe(II)-N ₄ |
| | | | | | (low spin) |
| | Doublet Site 2 | 0.355(35) | 1.465(87) | 25.8(88) | Fe(II)-N ₄ |
| | | | | | (similar to [FePc] ²⁻) |
| | Doublet Site 3 | 0.186(78) | 0.78(18) | 29.1(80) | Ox-Fe(III)-N ₄ |

| Sample | Fe (wt %) | Bi (wt %) | |
|------------------------|-----------|-----------|---|
| Fe _L -RNC | 0.98 | | _ |
| Fe-RNC | 1.21 | | |
| Fe _M -RNC | 1.74 | | |
| FeBi _L -RNC | 1.14 | 0.069 | |
| FeBi-RNC | 1.22 | 0.095 | |
| FeBi _M -RNC | 1.17 | 0.123 | |
| | | | |

 Table S2 Element content of Fe-RNC series samples and Fe/Bi-RNC series samples from ICP

 results

| Catalyst | Electrolyte | E _{1/2} vs RHE | Reference |
|----------------|-------------|-------------------------|-----------|
| FexN/NC-7 | 0.1 M KOH | 0.885 | Ref 3 |
| Co-Fe/NC-700 | 0.1 M KOH | 0.854 | Ref 6 |
| Fe-N-C/HPC-NH3 | 0.1 M KOH | 0.803 | Ref 11 |
| Fe-NHHPC-900 | 0.1 M KOH | 0.86 | Ref 12 |
| DMP-DPD-Fe-900 | 0.1 M KOH | 0.85 | Ref 13 |
| Fe(Zn)-N-C | 0.1 M KOH | 0.83 | Ref 14 |
| M-Fe-NCNS | 0.1 M KOH | 0.88 | Ref 16 |
| Fe-N/P-C | 0.1 M KOH | 0.867 | Ref 18 |
| FeNGC-T | 0.1 M KOH | 0.88 | Ref 37 |
| N/Fe-CG | 0.1 M KOH | 0.86 | Ref 46 |
| Fe/Bi-RNC | 0.1 M KOH | 0.899 | This work |
| | | | |

Table S3. Comparison of half-wave potentials for ORR of non-noble metal catalysts systems

 from literature and this work in alkaline medium.