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## **Supplementary Information**

## N,P co-coordinated Fe species embedded in carbon hollow spheres for oxygen electrocatalysis

Xiaofeng Zhu,<sup>a</sup> Xin Tan,<sup>b</sup> Kuang-Hsu Wu,<sup>a</sup> Chao-Lung Chiang,<sup>c</sup> Yu-Chang Lin,<sup>c,d</sup> Yan-Gu Lin,<sup>c</sup> Da-Wei Wang,<sup>a</sup> Sean Smith,<sup>b</sup> Xunyu Lu,<sup>\*a</sup> and Rose Amal<sup>\*a</sup>

<sup>*a.*</sup> Particles and Catalysis Research Group, School of Chemical Engineering, University of New South Wales, Sydney, NSW 2052, Australia.

<sup>b.</sup> Department of Applied Mathematics, Research School of Physics and Engineering, Australian National University, Canberra, ACT 2601, Australia.

<sup>c.</sup> Material Science Group, Scientific Research Division, National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.

<sup>d</sup> Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan.

\* Correspondence to: R. Amal (r.amal@unsw.edu.au); X. Lu (xunyu.lu@unsw.edu.au)

## **Details of Simulation and Electrochemical Tests**

*Computational methods*: The spin-polarized DFT calculations were performed using the VASP program<sup>S1</sup> using a plane-wave basis set and a projector augmented wave method (PAW) for the treatment of core electrons.<sup>S2</sup> The generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA–PBE)<sup>S3</sup> was used in all the calculations. For the expansion of wavefunctions over the plane-wave basis set, a converged cutoff was set to 500 eV. Self-consistent-field (SCF) calculations were performed with an electronic structure iteration of  $1 \times 10^{-5}$  eV on the total energy, and the atomic positions were optimized until the forces were below 0.005 eV/Å during structural optimization.

In order to simulate the FeNPC electrocatalyst, a Fe-N<sub>4</sub> site with -O-P(OH)<sub>3</sub> group was embedded in a periodic 5×5 graphene support (50 carbon sites) with lattice parameters a=b=12.3 Å. The vacuum spacing was set to more than 18 Å along the surface normal to avoid the interactions between images. The k-space integration was sampled using a 2×2×1 Monkhorst-Pack grid.<sup>S4</sup> The charge states of Fe activation center are determined using the Bader charge analysis.<sup>S5</sup>

The ORR pathways on FeNPC electrocatalyst were calculated in detail according to electrochemical framework developed by Nørskov and his co-workers.<sup>S6-S8</sup> For ORR, the four-electron reaction mechanism follows several elementary steps:

$O_2(g) + * \rightarrow O_2^*$	(S1)
$0_{2}^{*} + H^{+} + e^{-} \rightarrow 00H^{*}$	(S2)
$00H^* + H^+ + e^- \rightarrow 0^* + H_2O(l)$	(S3)
$0^* + H^+ + e^- \rightarrow 0H^*$	(S4)
$OH^* + H^+ + e^- \rightarrow H_2O(l) + *$	(85)

where the \* represents the active site on the electrocatalyst surface, (l) and (g) refer to liquid and gas phases, respectively, and  $OOH^*$ ,  $O^*$  and  $OH^*$  are adsorbed intermediates.

The binding energies of  $OOH^*$ ,  $O^*$  and  $OH^*$  were obtained by DFT calculations as follows, <sup>S6-S8</sup>

$$\Delta E_{OOH^*} = E(OOH^*) - E(*) - (2E_{H_2O} - 3/2E_{H_2})$$
(S6)  
$$\Delta E_{O^*} = E(O^*) - E(*) - (E_{H_2O} - E_{H_2})$$
(S7)  
$$\Delta E_{OH^*} = E(OH^*) - E(*) - (E_{H_2O} - 1/2E_{H_2})$$
(S8)

in which, E(\*),  $E(OOH^*)$ ,  $E(O^*)$ , and  $E(OH^*)$  are the ground state energies of a clean surface and surfaces adsorbed with  $OOH^*$ ,  $O^*$ , and  $OH^*$ , respectively.  ${}^{E_{H_2O}}$  and  ${}^{E_{H_2}}$  are the calculated DFT energies of H<sub>2</sub>O and H<sub>2</sub> molecules in the gas phase. If we considered the zero point energy (ZPE) and entropy correction, the free energies of adsorption,  $\Delta G_{ads}$ , can be transformed from DFT binding energies,  $\Delta E_{ads}$ , as follows:

$$\Delta G_{ads} = \Delta E_{ads} + \Delta ZPE - T\Delta S + eU \tag{S9}$$

where  $\Delta E_{ads}$  is the binding energy of adsorption species  $OOH^*$ ,  $O^*$ , and  $OH^*$ .  $\Delta ZPE$ ,  $\Delta S$ , U and e are the ZPE changes, entropy changes, applied potential at the electrode, and charge transferred. The entropy and ZPE corrections in determining the adsorption free energy were calculated using DFT calculations of the vibriational frequencies and standard tables for gas phase molecules,<sup>S9</sup> which are summarized in the Table S1.

**Table S1.** Contribution to the free energies of adsorbed intermediates and non-adsorbed gas-phase

 molecules from ZPE correction and entropy contribution, respectively.

Species	ZPE (eV)	TS (eV)
H <sub>2</sub> O	0.57	0.67
$H_2$	0.27	0.41
OOH*	0.43	0.17
O*	0.07	0.06
OH*	0.35	0.10

Using the adsorption free energies obtained from (S9) and (S6)-(S8), the reaction free energies of ORR reactions (S1)-(S5) can be calculated as:

$$\Delta G_1 = \Delta G_{OOH^*} - 4.92 \tag{S10}$$

$$\Delta G_2 = \Delta G_{0^*} - \Delta G_{00H^*} \tag{S11}$$

$$\Delta G_3 = \Delta G_{OH^*} - \Delta G_{O^*}$$
(S12)  
$$\Delta G_4 = -\Delta G_{OH^*}$$
(S13)

Thus, for the ORR reactions, the onset potential,  $U_{RHE}^{onset}$ , and the over-potential,  $\eta^{ORR}$ , can be expressed as: <sup>S6-S8</sup>

$$U_{RHE}^{onset} = -\max \{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}$$
(S14)  
$$\eta^{ORR} = 1.23 V - U_{RHE}^{onset}/e$$
(S15)

The DFT simulations of the MnNPC, CoNPC and NiNPC were carried out using the same model and aforementioned procedures.

*Electrocatalytic Measurement of the Catalysts*: Electrochemical experiments of the catalysts were performed in a three-electrode or two-electrode system using a potentiostat (CHI760E Instruments, Shanghai Chenhua Instrument Corp.). All electrochemical measurements were performed in a standard three-electrode system at room temperature. Saturated calomel electrode (SCE) and Platinum (Pt) wire were used as reference and counter electrode, respectively. The obtained potentials were converted to potentials versus reversible hydrogen electrode (RHE). A round disk electrode (RDE, diameter: 5.0 mm) and round ring-disk electrode (RRDE, outer diameter: 7.0 mm, inner diameter: 5.0 mm, ring: Pt) were utilized as the working electrode. The catalysts were drop-cast onto the disk (glassy carbon) for estimating ORR performance. Prior to test, both RDE and RRDE were polished with alumina

suspension on polishing pad. The graphite rob was used as counter electrode when the tests were carried out in acidic solution.

The samples were prepared into homogeneous inks by blending 5 mg catalysts with 1000  $\mu$ L ethanol solution (ethanol : DI water = 1:1  $\nu/\nu$ ) and 25  $\mu$ L Nafion resin solution (5 wt.%) under ultrasonication. Then, the as-prepared ink was pipetted onto the disk of RDE/RRDE and dried naturally. The Pt/C electrode (20 wt.%, Premetek) was also prepared via the same method. The ORR activity tests were carried out in O<sub>2</sub>-saturated electrolytes at a scan rate of 5 mV/s, while the cyclic voltammogram (CV) was evaluated in N<sub>2</sub>- and O<sub>2</sub>-saturated electrolytes at a scan rate of 50 mV/s. Based on the data, the kinetic process of ORR was investigated via Koutecky-Levich (K-L) plot using K-L equation as follows:

$$j^{-1} = j_{K}^{-1} + j_{L}^{-1} = j^{-1} + (\beta \omega^{1/2})^{-1}$$
(S16)  
$$\beta = 0.2nFC_{0}D_{0}^{2/3}v^{-1/6}$$
(S17)

where *j* was the measured current density,  $j_{\rm K}$  and  $j_{\rm L}$  were the kinetic and diffusion-limiting current densities,  $\omega$  was the rotation speed (rpm), F is the Faraday constant (96485 C/mol), *n* was the transferred electron numbers,  $C_0$  was the bulk concentration of O<sub>2</sub> in 0.1 M KOH (1.21 × 10<sup>-3</sup> mol/L) and 0.1 M HClO<sub>4</sub> (1.26 × 10<sup>-3</sup> mol/L),  $D_0$  was the diffusion coefficient of O<sub>2</sub> in 0.1 M KOH (1.9 × 10<sup>-5</sup> cm<sup>2</sup>/s) and 0.1 M HClO<sub>4</sub> (1.96 × 10<sup>-5</sup> cm<sup>2</sup>/s), and *v* was the kinematic viscosity (0.01 cm<sup>2</sup>/s).

To estimate the electrochemical surface area (ECSA), the CV was recorded in the non-faradaic region in the  $N_2$ -saturated electrolyte. The transferred electron numbers and the yield of hydrogen peroxide were determined by the RRDE tests, according to the following calculations:

$$H_2 O_2 \% = 200 \times \left(\frac{j_R}{N}\right) / \left(\frac{j_R}{N} + j_D\right)$$

$$n = 4 \times j_D / \left(\frac{j_R}{N} + j_D\right)$$
(S18)
(S19)

where  $j_R$  and  $j_D$  were the ring and disk current density, respectively, while the *N* was the collecting efficiency (*N*=0.37). *n* was the transferred electron number during the ORR.

To assess the stability of the catalysts, the ORR activity of the catalysts was measured after the ADT of 5000 cycles within the ORR-active region in the O<sub>2</sub>-saturated electrolytes. The OER performance of samples was estimated in 1 M KOH solution with a loading of 0.25 mg cm<sup>-2</sup> at a san rate of 5 mV s<sup>-1</sup> on rotating round disc electrode (RRDE) set-up. Simultaneously, Pt ring electrode is applied a potential of 0.47 V. The rotation speed was fixed as 1600 rpm. The aforementioned drop-casting method was used to prepare working electrodes.

*Estimation of Zn-air Batteries*: The air-cathode for rechargeable Zn–air battery was prepared by dropcasting the FeNPC catalysts (1.0 mg cm<sup>-2</sup>) onto a hydrophobic carbon paper (0.5 cm × 1.0 cm) and evaluated in a mixed electrolyte containing 6 M KOH and 0.2 M zinc acetate (ZnAc). A steady air flow rate was kept purging during the tests. The OCV, polarization profiles (LSV, 5 mV s<sup>-1</sup>) and galvanostatic cycling were recorded on the potentiostat at room temperature. The commercial Pt/C (20 wt%) with the same loading was also used as the catalyst in the air-electrode for Zn-air battery under identical conditions.

EXAFS data analysis and first-shell fitting were carried out using Athena and Artemis in Demeter Software Package. No phase-correction was applied for the presenting data. The coordination number (CN) was calculated by the product of N (degeneracy) and  $s_0^2$  amplitude as they are arithmetically inseparable and  $E_0$  was fixed at below 10 in absolute terms. An R-factor of < 0.02 has been satisfied in all fittings. The fitting and the corresponding analysis followed the standard procedures as recommended for IFEFFIT.



Figure S1. TEM images of the FeNPC without chemical leaching.



Figure S2. TEM images (a,b) and elemental mapping patterns (c) of the FeNC sample.



**Figure S3.** X-ray diffraction patterns of the catalysts with the standard XRD patterns for carbon and Fe<sub>2</sub>O<sub>3</sub>.



Figure S4. Raman spectra of the samples.



**Figure S5.** N<sub>2</sub> adsorption-desorption isotherms of the FeNPC and FeNC as well as and their pore size distributions (inset).

Samples	$S_{\rm BET} \left( {{m^{2}}/{g}}  ight)$	$V_{\rm pore}({\rm cm^{3/g}})$	$d_{\rm pore} ({\rm nm})$	Metal content (wt%)
FeNPC	1656	0.50	5.86	0.61
FeNPC-s	1379	0.47	4.98	7.02
FeNC	1945	0.61	5.47	0.66
CoNPC	2541	0.79	5.43	0.78
MnNPC	4253	1.29	4.94	0.43
NiNPC	1390	0.45	5.73	0.87

Table S2. Properties of the as-prepared samples.



Figure S6.  $N_2$  adsorption-desorption isotherms and the corresponding TEM images of the (a-c) NiNPC, (d-f) CoNPC and (g-i) MnNPC sample.



Figure S7. High-resolution XPS spectra for Fe 2p (a) and O 1s (b) of the FeNC and FeNPC samples.

Samples	N (at%)			
~ F	Pyridinic N	Graphitic N	Oxidized N	Sum
FeNC	0.72	1.32	0.2	2.24
FeNPC	0.8	1.39	0.24	2.43

**Table S3.** The corresponding N concentrations of the FeNC and FeNPC.



Figure S8. The XANES spectra at Fe L-edge of the FeNC and FeNPC samples in a magnified region.



Figure S9. The high-resolution P 2p XPS spectra of the FePC.



Scheme S1. Proposed structure for the O<sub>2</sub>-FeN<sub>5</sub> active site of the FeNC.



Scheme S2. Diagram of ORR process over the  $O_2$ -Fe $N_4P_1$  active site in the alkaline solution.



**Figure S10.** The calculated transferred electron numbers (*n*) and  $H_2O_2$  yield of the commercial Pt/C (a) and FeNPC (b) at the potential range of 0.30–0.50 V (vs. RHE), based on their disk and ring current density (Figure 3b). The loading of the catalysts was 0.25 mg/cm<sup>-2</sup>. All the LSV curves were recorded in 0.1 M O<sub>2</sub>-saturated KOH electrolyte with a scan rate of 5 mV/s at a rotation speed of 1600 rpm.



**Figure S11.** (a) CV of the FeNPC sample. (b) ORR activity and the corresponding durability of the commercial Pt/C (loading:  $0.1 \text{ mg cm}^{-2}$ ) and FeNPC (loading:  $0.5 \text{ mg cm}^{-2}$ ). All curves were obtained in  $0.1 \text{ M O}_2$ -saturated HClO<sub>4</sub> at a rotation speed of 1600 rpm.



Figure S12. Kinetical analysis of the FeNPC catalyst towards cathodic ORR in (a,c) alkaline and (b,d) acid.



**Figure S13.** The TEM images (a) and XRD pattern (b) of the FeNPC-s with the standard XRD patterns for Fe<sub>2</sub>O<sub>3</sub> and metallic Fe.



Figure S14. The ORR performance of the FeNPC-s in  $O_2$ -saturated (a) 0.1 M KOH and (b) 0.1 M HClO<sub>4</sub>.



**Figure S15.** The measurement of electro-chemical surface area (ECSA) of the FeNPC-s (a,d), FeNPC (b,e) and FeNC (c,f) samples.



Figure S16. KSCN poisoning tests of the FeNPC in  $O_2$ -saturated (a) 0.1 M KOH and (b) 0.1 M HClO<sub>4</sub>.



Figure S17. ORR performance of the transition metals NPC samples in O<sub>2</sub>-saturated HClO<sub>4</sub> solution.



Figure S18. OER performance of NiNPC, CoNPC and MnNPC samples in 1 M KOH electrolyte.



**Figure S19.** (a) "Eumelanin" process of the dopamine.<sup>S10</sup> (b) The possible structure of Fe-PDA complex.



**Figure S20.** ORR theoretical onset potential versus the free energies of OH\* ( $\Delta G_{OH*}$ ) on FeNPC, MnNPC, CoNPC and NiNPC catalysts. The values for Pyridine-N<sub>4</sub> and Pt (111) are shown with black solid triangles and the black dashed line, respectively.



**Figure S21.** Measurement of electro-chemical surface area (ECSA) of the CoNPC (a,c) and MnNPC (b,d) samples. All curves were obtained in 0.1 M KOH and the loadings of the catalysts were fixed to  $0.25 \text{ mg cm}^{-2}$ .



**Figure S22.** LSV of the FeNPC and FeNC samples in 1 M KOH with a rotation speed of 1600 rpm at a scan rate of 5 mV s<sup>-1</sup> under  $N_2$  purging. Pt ring electrode is applied a potential of 0.47 V.



**Figure S23**. (a) *V–i* polarization and power density curves of commercial Pt/C-employed Zn-air battery. (b) Galvanostatic discharge–charge cycling profiles of Pt/C-based Zn-air battery at 3 mA cm<sup>-2</sup> with a cycling interval of 10 min.



**Figure S24.** (a) First derivatives of XANES for the FeNC and FeNPC at Fe K-edge. (b) Corresponding EXAFS fitting of the FeNC at *k* space. (c) Wavelet transform (WT) of the FeNC.

Table S4. Structural	l parameters of FeNC and FeNPC extracted from the EXAFS fitting
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Samples	Fitting parameters			
	CN	R (Å)	$\sigma^2 (10^{-3} \text{ Å}^2)$	R-factor
FeNC	6.077±0.448	2.035±0.109	0.00912	0 0114818
FeNPC	5.993±0.409	$1.967 \pm 0.098$	0.00883	0.0111010

CN is the coordination number; R is interatomic distance between centre Fe atom and first neighbour atoms;  $\sigma^2$  is Debye-Waller factor which aims to compensate thermal and static disorder in absorber-scatter distance; R-factor is used to evaluate the coincidence of fitting.



Figure S25. SEM images with low (a,c) and high magnification (b,d) of the FeNPC sample.



Figure S26. High resolution STEM images of the FeNPC catalyst.



Figure S27. The EDS spectrum of the FeNPC catalyst.

Samples	$S_{\rm BET}~({ m m^{2}/g})$	Catalysts Loading (mg cm <sup>-2</sup> )	Onset potential (V vs RHE) <sup>a)</sup>	Half-wave potential (V vs RHE) <sup>a)</sup>	Ref.
FeNPC	1656	0.25	1.03	0.88	This work
FeNPC-s	1379	0.25	1.02	0.86	This work
FeNC	1945	0.25	0.97	0.82	This work
FePC	1371	0.04	0.95	$\sim 0.78$	[S11]
Fe- and P-					
functionalized	612	Not	0.92	$\sim 0.72$	[S12]
graphene		provided			
Fe/P/C nanowire	420	0.46	0.004	0.017	[012]
networks	439	0.46	0.884	0.815	[813]
Co-P,N-CNT	512.2	0.10	0.981	0.811	[S14]
Fe©N-C-12	594.5	0.311	~ 0.93	~ 0.81	[S15]
Fe/N-CNT	331.45	$\sim 0.20$	~ 0.96	0.81	[S16]
FeGH-ArNH <sub>3</sub>	Not provided	0.30	0.94	0.85	[S17]
Fe,N-doped carbon	1189	0.60	0.98	0.85	[S18]
PNDC	188.1	0.40	0.81	~ 0.69	[S19]
N,P co-doped	1548	0.15	0.94	~ 0.83	[S20]
FexP/NPCS	837.05	0.16	0.918	0.832	[S21]
N.P-HPC	1516	0.80	0.924	0.81	[S22]
POMCs	1182	0.79	~ 0.91	~ 0.80	[S23]
P-doped carbon nanofibers	1417	~ 0.10	0.881	0.79	[824]
P-doped graphene	Not provided	0.05	~ 0.92	Not provided	[S25]
D dama d 1.'	<b>5</b> 0 <b>4</b>	Not	0.92	0.95	[00/]
P-doped graphite	384	provided	(at 0.1 mA cm <sup>-2</sup> )	0.85	[520]
Fe@C-FeNC-2	Not provided	0.7	~ 1.0	~ 0.87	[S27]
Cu-N@C-60	333.877	0.2986	~ 0.93	~ 0.80	[S28]

**Table S5.** Comparison of specific surface areas and ORR performance of the as-prepared catalysts

 with reported catalysts.

Fe-N-C/VA-CNT <sup>b)</sup>	504	0.6	0.97	0.73	[S29]
ISAS-Co/HNCS b)	Not provided	0.501	~ 0.89	0.773	[S30]
Fe-N-C derived					
from PANI +	1136.2	1	1.04	0.91	[S31]
DCDA					
Pt/C	Not measured	0.1	1.01	0.85	This work

<sup>a)</sup> The ORR data was obtained over the catalysts in 0.1 M  $O_2$ -saturated KOH solution at a rotation speed of 1600 rpm.<sup>b)</sup> The ORR results were obtained in 0.5 M  $H_2SO_4$ .

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