# MnO<sub>x</sub> Enhanced Atomically Dispersed Iron-Nitrogen-Carbon Catalyst for Oxygen Reduction Reaction

Shichao Ding,<sup>a,1</sup> Zhaoyuan Lyu,<sup>a,1</sup> Erik Sarnello,<sup>b</sup> Mingjie Xu,<sup>c</sup> Lingzhe Fang,<sup>b</sup> Hangyu Tian,<sup>a</sup> Sam Ellery Karcher,<sup>a</sup> Tao Li,<sup>b,d</sup> Xiaoqing Pan,<sup>c</sup> John McCloy,<sup>a</sup> Guodong Ding,<sup>e</sup> Qiang Zhang,<sup>e</sup> Qiurong Shi,<sup>a</sup> Dan Du,<sup>a</sup> Jin-Cheng Li,<sup>a,\*</sup> Xiao Zhang,<sup>f,\*</sup> Yuehe Lin,<sup>a,e,f,\*</sup>

a School of Mechanical and Materials Engineering, Washington State University, Pullman, WA, 99164, USA

b Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL, 60115, USA

c Irvine Materials Research Institute (IMRI); Department of Materials Science and Engineering, University of California, Irvine, CA, 92697, USA

d X-ray Science Division, Argonne National Laboratory, Lemont, IL, 60439, USA

e Department of Chemistry, Washington State University, Pullman, Washington 99164, United States

f. Voiland School of Chemical Engineering and Bioengineering, Washington State University

\* Corresponding Authors. E-mail: yuehe.lin@wsu.edu; jin-cheng.li@wsu.edu; x.zhang@wsu.edu <sup>1</sup> Shichao Ding and Zhaoyuan Lyu have contributed equally to this work.

# **Experimental section**

# Materials

Methyl orange (MO), hydrogen peroxide, 3,3',5,5'-tetramethylbenzidine, ophenylenediamine and Pyrrole (reagent grade, 98%) were purchased from Sigma-Aldrich, USA; Iron(iii) chloride (anhydrous, 98%) and horseradish peroxidase (300 units/mg) were provided by Thermo Fisher Scientific, USA; Potassium permanganate was supplied by Fisher Scientific, USA. All chemicals used without further purification.

## Fabrication of Mn-Fe-N-C SAC

Firstly, 500 mg of methyl orange (MO) was dissolved in DI water, then 5 g of  $FeCl_3$  was added under vigorous stirring to form an oxidized MO template. After stirring for 30 min, 1.5 mL

pyrrole was added to form the  $Fe^{3+}$  doped polypyrrole nanotube (Fe-PPy NT). Secondly, the obtained Fe-PPy NT was dispersed in KMnO<sub>4</sub> solution at room temperature to prepare MnO<sub>x</sub> coated PPy nanotube. Last, Mn-Fe-N-C SAC was obtained from the pyrolytic process at 900°C under nitrogen atmosphere and ammonia for 30 min, respectively. Then using 0.5 M H<sub>2</sub>SO<sub>4</sub> acid washing 4 h at 60°C.

#### **Catalyst characterization**

The materials were characterized using scanning electron microscopy (SEM, FEI Apreo VolumeScope) and transmission electron microscopy (TEM, Tecnai F20, 200 kV; Philips CM200 UT, 200 kV; JEOL ARM300F, 300 kV), X-ray photoelectron spectroscopy (XPS, ThermoFisher Thermo, Al Kα), and X-ray diffraction (XRD, Rigaku Miniflex 600, 40 kV). Nitrogen gas adsorptions were done using a Micromeritics ASAP 2020Plus at 77 K. Raman spectroscopy (Thermo Scientific DXR2xi) were measured with 455 nm excitation.

The X-ray absorption spectroscopy measurements at the Fe K-edge (7,112 eV) were performed at the Advanced Photon Source (APS) on the bending-magnet beamline 12-BM and 20-BM. A Fe metal foil was used to calibrate the X-ray beam energy and was simultaneously measured with each sample. The radiation was monochromatized by a Si (111) double-crystal monochromator. The harmonic rejection was accomplished with a Harmonic rejection mirror. All single-atom sample spectra were collected in fluorescence mode by vortex four-element silicon drift detector, and the standards (including the foil) have been measured in transmission mode. XAS data reduction and analysis were processed by Athena software. For wavelet transform analysis, the  $\chi(k)$  exported from Athena was input to the Hama Fortran code. The parameters were set as follows: k weight, 3; R range, 1-4 Å; k range, 0-10 Å<sup>-1</sup>.

#### **Electrochemical measurements**

2.5 mg as-prepared catalysts were ultrasonically dispersed in a mixture that consists of 990  $\mu$ L ethanol and 10  $\mu$ L 1 wt% Nafion solution to form a concentration of 2.5 mg/ml catalyst ink. A certain volume of catalyst ink was coated onto the surface of the working electrode with the loading of 0.6 mg/cm<sup>2</sup>. Pt/C (20 wt%, Alfa Aesar) with a "standard" loading (0.1 mg/cm<sup>2</sup>) was used as a benchmark. The electrochemical measurements were

performed using a standard three-electrode cell by CHI700E electrochemical workstation (CH Instruments). A graphite rod and calomel electrode (SCE) filled with saturated KCl aqueous solution were served as the counter electrode and reference electrode, respectively. All potential values refer to that of a reversible hydrogen electrode (RHE).

RDE and RRDE measurements were performed in  $O_2$ -saturated 0.1 M HClO<sub>4</sub>. The scan rate was 5 mV/s. RRDE Polarization curves were collected at a disk rotation rate of 1600 rpm. The potential of the ring was set at 1.3 V in 0.1 M HClO<sub>4</sub>. The collection efficiency of the RRDE (N) was 0.37. The peroxide yield (H<sub>2</sub>O<sub>2</sub>%) and the electron transfer number (n) were calculated as follows:

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

where Id is the disk current and Ir is the ring current.

The turn-over frequency (TOF) is estimated:

$$TOF = \frac{j_k \times N_e}{W_{Fe} \times C_{cat} \times N_A / M_{Fe}}$$

Where  $j_k$  is the kinetic current density (mA cm<sup>-2</sup>) at 0.8V,  $N_e$  is electron number per Coulomb 6.24×10<sup>18</sup>,  $W_{Fe}$  is the metal content in the catalyst,  $C_{cat}$  is the catalyst loading on the electrode,  $N_A$  is Avogadro constant 6.022×10<sup>23</sup>,  $M_{Fe}$  is the molar mass of Fe 55.85 g · mol<sup>-1</sup>.

All LSV tests were measured at a rotating speed range from 1000 to 2200 rpm at the scan rate of 10 mV/s. Kouteckey-Levich (K-L) plots to present the linear relation between  $j^{-1}$  and  $\omega^{-1/2}$  were obtained based on the following equations:

$$j^{-1} = j_{\mathcal{L}}^{-1} + j_{\mathcal{K}}^{-1} = B^{-1}\omega^{-1/2} + j_{\mathcal{K}}^{-1}$$

$$B=0.62nFC_0D_0^{2/3}\upsilon^{1/6}$$

## $j_{K}=j^{*}j_{L}/(j_{L}-j)$

where *j* means the measured current density,  $j_L$  is the diffusion-limiting current density,  $j_K$  corresponded to the kinetic current density,  $\omega$  is the rotation rate (rpm), and n is the number

of electron transfers.  $B^{-1}$  means the slope of K-L plots, F is the Faraday constant (96485 C/mol), C<sub>0</sub> is the bulk concentration of O<sub>2</sub> (1.2 ×10<sup>-3</sup> mol/L in 0.1 M HClO<sub>4</sub>), D<sub>0</sub> is the diffusion coefficient of O<sub>2</sub> (1.93×10<sup>-5</sup> cm<sup>2</sup>/S in 0.1 M HClO<sub>4</sub>), and v is the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup>/S in 0.1 M HClO<sub>4</sub>).

## **Colorimetric experiment**

The 3,3',5,5'-tetramethylbenzidine (TMB) and o-phenylenediamine (OPD) were used as substrates for the colorimetric reaction of prepared samples. Specifically, same concentration Mn-Fe-N-C SAC and Fe-N-C SAC were dissolved, respectively. TMB and OPD were dissolved in DMSO to 10 mg mL<sup>-1</sup> and then 100 mL of the solution were added to the above solutions, respectively. The obtained mixtures were incubated in dark at 37°C for 5 min. All absorption spectra were performed by Tecan Safire2 Multi-Mode Microplate Reader.



Figure S1 SEM of Fe-PPy NT.



Figure S2 TEM of Fe-N-C SAC.



**Figure S3** High-resolution C 1s spectra of (a) Mn-Fe-N-C SAC and (b) Fe-N-C SAC. The high-resolution C 1s peak of Mn-Fe-N-C SAC and Fe-N-C SAC were deconvoluted into C-sp<sup>2</sup> (284.3 eV), C-sp<sup>3</sup> (284.9 eV), C-N (286.0 eV), C-O (286.4 eV), and C=O (288.8 eV).<sup>[1, 2]</sup>



Figure S4 XPS spectrum of Mn-Fe-N-C SAC and Fe-N-C SAC.



Figure S5 STEM dark-filed image and elemental maps of Fe-N-C SAC.



**Figure S6** High-resolution N 1s spectra of Mn-Fe-N-C SAC and Fe-N-C SAC, respectively. The spectrum of N 1s could be fitted into four peaks around ~398 eV, ~400 eV, ~401 eV and ~402 eV, which corresponding to pyridinic N, pyrrolic N, graphitic N and oxidized N, respectively.<sup>[3, 4]</sup>



Figure S7 Corresponding EDS linear scan profiles of Fe and Mn in Mn-Fe-N-C SAC.



**Figure S8** High-resolution Fe 2p spectra of (a) Mn-Fe-N-C SAC and (b) Fe-N-C SAC, respectively. For Fe 2p, four peaks around ~709 eV, ~713 eV, ~718.9 eV, ~720 eV and ~727 eV were assigned to Fe<sup>2+</sup>  $2p_{2/3}$ , Fe<sup>3+</sup>  $2p_{2/3}$ , Fe<sup>2+</sup>  $2p_{1/2}$  and Fe<sup>3+</sup>  $2p_{1/2}$  on the basis of binding energies, respectively.<sup>[5-7]</sup>



Figure S9 Corresponding EXAFS fitting curve of Mn-Fe-N-C SAC in k space.

**Table S1**. Structural parameters of samples obtained by fitting the EXAFS data. Parameters include average coordination number (N), path distance (R), R-space range for fitting (R-Range: 1-3), Debye-Waller factor ( $\sigma^2$ ), and the R-Factor of the fitting. An amplitude reduction factor ( $S_0^2$ ) of 0.794 was obtained by fitting the Fe foil.

Sample	Scattering pair	Ν	R(Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	R factor
Fe foil	Fe-Fe	8	2.46	0.005	- 0.009
	Fe-Fe	6	2.84	0.005	
Mn-Fe-N-C SAC	Fe-N	2.04	1.93	0.004	
	Fe-O	0.56	2.06	0.005	0.024
	Fe-Mn	1.09	2.54	0.003	



Figure S10 ORR polarization curves of Mn-Fe-N-C SAC that under different temperature process.



Figure S11 The RDE polarization curve for Pt/C under 0.1 M HClO<sub>4</sub>.



Figure S12 (a) RDE polarization curves at various rotating speed for Fe-N-C SAC 0.1 M HClO<sub>4</sub>. (b) K-L plot of J<sup>-1</sup> versus  $\omega^{-1}$ .



Figure S13 Electron transfer numbers Mn-Fe-N-C SAC and Fe-N-C SAC.



Figure S14 Schematic illustration of Damjanovic model of ORR.



Figure S15 Chronoamperometric responses of Mn-Fe-N-C SAC and Fe-N-C SAC after adding methanol in the electrolyte.



Figure S16 Reaction between HRP, TMB and H<sub>2</sub>O<sub>2</sub>.



**Figure S17** Photographs showing the color change (yellow) of the electrolyte after reaction by the HRP detection under substrate of o-phenylenediamine (OPD). 1) OPD + Mn-Fe-N-C SAC reacted

electrolyte; 2) HRP + Mn-Fe-N-C SAC reacted electrolyte; 3) OPD + HRP + Mn-Fe-N-C SAC reacted electrolyte; 4) OPD + HRP + Fe-N-C SAC reacted electrolyte; 5) OPD + HRP + Pt/C reacted electrolyte.

Catalysts	$E_{1/2}(V)$	Ref.	
Mn-Fe-N-C SAC	0.799	This work	
Fe-N-C SAC	0.759	This work	
Fo N C corbon nonotubo	0.72	ACS Catalysis, 2018,	
re-n-C carbon nanotube	~0.75	8, 2824-2832	
		ACS Applied	
Fo N C optolyst	~0.78	Materials & Interfaces, 2019, 11,	
Te-IN-C catalyst			
		39820-39826.	
FaNC/PGO	0 752	Small Methods,	
Fene/Roo	0.752	2020, 4.6, 1900827.	
		Applied Catalysis B:	
Fe SA/NPCs	0.77	Environmental,	
	0.81	2020, 278, 119270.	
Fe SA/N-doped carbon		Nano Energy 2019,	
framework	0.01	61, 60-68.	
		Angewandte Chemie	
Fe/SNC catalyst	0.77	2017, 129.44, 13988-	
		13992.	
(CM + PANI)-Fe-C	0.80	Science.	
	0.00	2017;357:479-484	
	0.80	Advanced Science	
FeSA-G		2019;6:	
		1802066.	
	0.80	Proc Natl Acad Sci U	
SA-Fe/NG		SA.	
		2018;115:6626-6631.	
CNT@Fe_N_PC	0.82	NPG Asia Mater.	
	0.02	2018;10:e461.	

Table S2 Comparison of Mn-Fe-N-C SAC, Fe-N-C SAC, and related reported catalysts

### References

- [1] R. Li, Z. Wei, X. Gou, Acs Catalysis 2015, 5, 4133.
- [2] S. Yi, X. Qin, C. Liang, J. Li, R. Rajagopalan, Z. Zhang, J. Song, Y. Tang, F. Cheng, H. Wang, *Applied Catalysis B: Environmental* **2020**, *264*, 118537.
- [3] S. Chen, J. Bi, Y. Zhao, L. Yang, C. Zhang, Y. Ma, Q. Wu, X. Wang, Z. Hu, *Advanced materials* **2012**, *24*, 5593.
- [4] T. Sharifi, G. Hu, X. Jia, T. Wagberg, *ACS nano* **2012**, *6*, 8904.
- [5] L. Lin, Q. Zhu, A.-W. Xu, J Am Chem Soc 2014, 136, 11027.
- [6] Z. K. Yang, Z.-W. Zhao, K. Liang, X. Zhou, C.-C. Shen, Y.-N. Liu, X. Wang, A.-W. Xu, *Journal of Materials Chemistry A* **2016**, *4*, 19037.
- [7] Y.-L. Liu, X.-Y. Xu, C.-X. Shi, X.-W. Ye, P.-C. Sun, T.-H. Chen, *RSC advances* 2017, *7*, 8879.