# Tunable and convenient synthesis of highly dispersed Fe-$N_x$ catalysts from graphene-supported Zn-Fe-ZIF for efficient oxygen reduction in acids

Limeng Yang[a,*], Zhigang Shao[b,]

a. School of Textile Science and Engineering, Xi'an Polytechnic University, 19 Jinhua Road, Xi'an 710048, China

b. Dalian National Laboratories for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

† E-mail: yanglmxpu@163.com

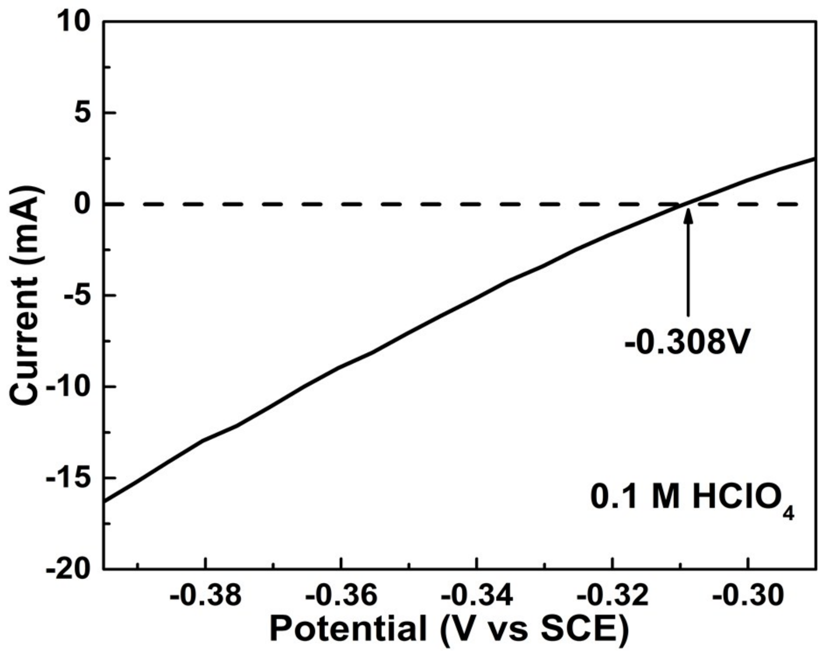


**Figure S1.** LSV curves collected at room temperature in $H_2$-saturated 0.1 M $HClO_4$ aqueous solution with a scan rate of 1 $mV \cdot s^{-1}$. The experiment was performed in a $H_2$-saturated electrolyte with platinum wire as working electrode. The thermodynamic equilibrium potential for $H^+/H_2$ reaction was determined at zero current.

**Table S1.** The BET surface area and pore volume of different samples

| Catalysts | BET surface area ($m^2\ g^{-1}$) | Micropore area ($m^2\ g^{-1}$) | Total Pore volume (cc $g^{-1}$) |
|---|---|---|---|
| C-rGO-ZIF-1* | 460 | 211 | 1.32 |
| C-rGO-ZIF-2* | 650 | 175 | 2.03 |
| C-rGO-ZIF-3* | 493 | 309 | 1.33 |

**Table S2.** Relative contents of different elements in as-synthesized catalysts.

| elements (at%) | C-rGO-ZIF-1* | C-rGO-ZIF-2* | C-rGO-ZIF-3* | Zn-Fe-ZIF-3 | C-Zn-Fe-ZIF-3 |
|---|---|---|---|---|---|
| C 1s | 92.86 | 93.17 | 92.64 | 61.39 | 91.0 |
| Fe 2p | 0.37 | 0.40 | 0.38 | — | 0.23 |
| N 1s | 2.87 | 3.47 | 3.34 | 20.79 | 3.07 |
| O 1s | 3.90 | 2.95 | 3.64 | 5.23 | 5.30 |
| Zn 2p | — | — | — | 12.59 | 0.39 |

**Table S3.** Percentage of different N species in each catalyst.

| Types of N (at%) | C-rGO-ZIF-1* | C-rGO-ZIF-2* | C-rGO-ZIF-3* |
|---|---|---|---|
| Pyridinic N | 13.1 | 12.8 | 9.9 |
| Fe-N | 19.3 | 22.0 | 20.3 |
| Pyrrollic N | 4.9 | 5.2 | 5.2 |
| Graphitic N | 46.0 | 47.1 | 44.5 |
| Oxidized N | 16.7 | 12.9 | 20.8 |
| Pyridinic + Graphitic N | 59.1 | 59.9 | 54.4 |

**Table S4.** Percentage of different N species in each catalyst.

| Fitting parameters | $H_0$(T) | $\delta_{iso}$ (mm $s^{-1}$) | $\Delta E_Q$ (mm $s^{-1}$) | Relative area (%) | Assignment |
|---|---|---|---|---|---|
| Sextet | 33.1 | 0.02 | -0.05 | 21.7 | α-Fe |
| Doublet-1 | - | 0.20 | 3.64 | 23.7 | low-spin state $Fe^{II}$-$N_4$ |
| Doublet-2 | - | 0.42 | 1.39 | 42.2 | moderate spin-state $Fe^{II}$-$N_{4/2+2}$[1] |
| Singlet | - | -0.10 | - | 12.5 | γ-Fe |

**Tab. S5** ORR performance of NPMCs tested in acidic medium

| Catalysts | Electrocatalyst loading ($mg/cm^2$) | Half-wave potential (V vs. RHE) | Onset potential (V vs. RHE) | Reference |
|---|---|---|---|---|
| Fe SAs/N-C | 0.25 | 0.80 | 0.90 | ACS. Catal. 2019, 9, 2158. [2] |
| PMF-800 | 1.2 | 0.62 | 0.89 | J. Am. Chem. Soc. 2015, 137, 1436. [3] |
| Fe-N/MPC2 | 0.6 | 0.72 | 0.82 | Appl. Catal. B-Environ. 2017, 205, 637. [4] |
| WC@C/N/CA-850 | 0.4 | 0.50 | 0.76 | Electrochim Acta. 2017, 236, 154. [5] |
| CoN-CNS | 0.4 | 0.64 | 0.86 | J. Power Sources. 2017, 346, 80. [6] |
| Fe3C@C-900 | 0.6 | 0.68 | 0.80 | Carbon 2017, 116, 606. [7] |
| Py-FCC/C-50 | 1.3 | 0.70 | 0.82 | J. Mater. Chem. A. 2017, 5, 9279. [8] |
| Cr/N/C-950 | 0.6 | 0.77 | 0.82 | Angew. Chem. Int. Ed. 2019, 58, 12469. [9] |
| C-PANI-MIL-2 | 0.4 | 0.67 | 0.86 | Chemelectrochem. 2018, 5, 3731. [10] |
| **C-rGO-ZIF-2*** | **0.4** | **0.77** | **0.89** | **This work** |

**Tab. S6** ORR performance of NPMCs tested in PEMFCs
(all of the cell temperature is 80 °C)

| Catalysts | Electrocat- -alyst loading ($mg/cm^2$) | Maximum power densities ($mW/cm^2$) | $H_2/O_2$ back pressure (MPa) | $H_2/O_2$ flow rate (sccm) | MEA area ($cm^2$) | Reference |
|---|---|---|---|---|---|---|
| TPI@Z8(SiO2)-650-C | 2.7 | 750 | 0.2 | 300/400 | 5 | Nat. Catal. 2019, 2, 259. [11] |
| H-Fe-$N_x$-C | 2 | 710 | 0.2 | 100/200 | 5 | ACS Nano 2019, 13, 8087. [12] |
| Fe-N-C-Phen-PANI | 4 | 1060 | 0.14 | 300/400 | 5 | Adv. Mater. 2017, 29, 1604456. [13] |
| Fe/N/C-SCN | 4 | 1030 | 0.2 | 300/300 | 1 | Angew. Chem. Int. Ed. 2015, 54, 9907. [14] |
| Fe/N/CF | 3 | 900 | 0.15 | 300/400 | 5 | Proc. Natl. Acad. Sci. U. S. A 2015, 112, 10629. [15] |
| Zn (mIm)2TPIP | 2.2 | 620 | 0.1 | 400/400 | 5 | Adv. Mater. 2014, 26, 1093. [16] |
| Fe/PI-1000-III-$NH_3$ | 4 | 600 | 0.2 | 300/300 | 1 | J. Mater. Chem. A 2014, 2, 11561. [17] |
| (CM+PANI)-Fe-C | 4 | 940 | 0.1 | 200/200 | 5 | Science 2017, 357, 479. [18] |
| NC Phen Ar+$NH_3$ | 4 | 830 | 0.2 | 300/300 | 1.14 | Electrochim. Acta. 2015, 159, 184. [19] |
| **C-rGO-ZIF-2*** | **4** | **301** | **0.18** | 300/400 | **4** | **This work** |

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