Highly Efficient Catalysis for Oxygen Reduction using Well-dispersed Iron Carbide Nanoparticles Embedded in the Multichannel Hollow Nanofibers

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Equations in Electrochemical characterization

The H$_2$O$_2$ yield and the number of electron transfer (n) were calculated with the following equations:

$$H_2O_2\% = \frac{200 \times I_r/N}{I_d + I_r/N}$$  \hspace{1cm} (1)

$$n = \frac{4I_d}{I_d + I_r/N}$$  \hspace{1cm} (2)

where $I_d$ is the disk current, $I_r$ is the ring current, and $N$ (0.37) is the collection efficiency of the rotating ring-disk electrode (RRDE).

Koutecky-Levich equations:

$$\frac{1}{J} = \frac{1}{J_l} + \frac{1}{J_k} = \frac{1}{B \omega^{0.5}} + \frac{1}{J_k}$$  \hspace{1cm} (3)

$$B = 0.62nFC_0(D_0)^{2/3}V^{-1/6}$$

where $J$ is the recorded current density, $J_k$ is the kinetic-limiting current density, $J_l$ is the diffusion-limiting current density, $\omega$ is the electrode rotating speed in rad s$^{-1}$, $F$ is the Faraday constant (96485 C mol$^{-1}$), $C_0$ is the bulk concentration of O$_2$ in 0.10 M KOH solution ($1.2 \times 10^{-6}$ mol cm$^{-3}$), $D_0$ is the diffusion coefficient of O$_2$ ($1.9 \times 10^{-5}$ cm$^2$ s$^{-1}$), and $V$ is the kinematic viscosity of 0.10 M KOH solution (0.01 cm$^2$ s$^{-1}$). The K-L plots ($\omega^{-1/2}$ vs $J^{-1}$) in O$_2$-saturated 0.1 M KOH can be derived from LSV curves at various rotation speeds and different potentials.
Calibrate to reversible hydrogen electrode (RHE)

In all measurements, we used Hg/HgO electrode as the reference electrode. It was calibrated with respect to RHE. The calibration was performed in the high purity H₂ saturated electrolyte with a Pt wire as the working electrode. CVs were run at a scan rate of 1 mV·s⁻¹, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions. In 0.1 M KOH, E (RHE) = E (Hg/HgO) + 0.879 V. All the potentials reported in this manuscript were against RHE.

**Figure S1.** (a) Calibration of the reference electrode against the RHE.
**Figure S2.** (a and b) SEM, (c) TEM images (d) XRD of Fe\textsubscript{3}C@SNFs.

**Figure S3.** (a) Nitrogen adsorption-desorption isotherms for the Fe\textsubscript{3}C@SNFs.
**Figure S4.** (a) XPS survey for the Fe$_3$C@MHNFs.

**Figure S5.** (a) LSV curves of Fe$_3$C@MHNFs at different rotating speeds, (b) the corresponding K-L plots.

**Figure S6.** SEM and TEM for (a) MHNFs, (b) Fe$_3$C-1@MHNFs, (c) Fe$_3$C@MHNFs, (d) Fe$_3$C-3@MHNFs.
Figure S7. (a) Polarization curves and (b) $E_{1/2}$ of the MHNFs, Fe$_3$C-1@MHNFs, Fe$_3$C@MHNFs and Fe$_3$C-3@MHNFs.

Figure S8. (a) Polarization curves of Fe$_3$C@MHNFs and A-Fe$_3$C@MHNFs; (b) TEM image of A-Fe$_3$C@MHNFs; (c) XPS survey, (d) N 1s XPS spectra of Fe$_3$C@MHNFs and A-Fe$_3$C@MHNFs.
Figure S9. (a) Raman; (b) CV curves; (c) Polarization curves; (d) $E_{1/2}$ of Fe$_3$C@MHNFs-800, Fe$_3$C@MHNFs and Fe$_3$C@MHNFs-1000.

Figure S10. (a) LSV curves of Fe$_3$C@MHNFs in 0.5 M H$_2$SO$_4$.

Figure S11. (a) XRD of the MHNFs.
Table S1. Comparison of the ORR activities of Fe₃C@MHNFs with the noble-metal-free catalysts literature-reported.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>$E_{1/2}$ (V vs. RHE)</th>
<th>Catalyst loading (mg cm⁻²)</th>
<th>References</th>
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<tbody>
<tr>
<td>Fe₃C@MHNFs</td>
<td>0.1 M KOH</td>
<td>0.90</td>
<td>0.20</td>
<td>This work</td>
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<tr>
<td>Fe-N/C-800</td>
<td>0.1 M KOH</td>
<td>0.80</td>
<td>0.10</td>
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<td>BCNFNHs</td>
<td>0.1 M KOH</td>
<td>0.86</td>
<td>1.20</td>
<td>2</td>
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<tr>
<td>Fe@C-FeNC</td>
<td>0.1 M KOH</td>
<td>0.89</td>
<td>0.70</td>
<td>3</td>
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<tr>
<td>C-FeZIF-900-0.84</td>
<td>0.1 M KOH</td>
<td>0.84</td>
<td>0.50</td>
<td>4</td>
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<tr>
<td>HP-Fe-N/CNFs</td>
<td>0.1 M KOH</td>
<td>0.81</td>
<td>0.25</td>
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<tr>
<td>Fe-NMP</td>
<td>0.1 M KOH</td>
<td>0.65</td>
<td>0.25</td>
<td>6</td>
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<tr>
<td>Fe/N/S-CNTs</td>
<td>0.1 M KOH</td>
<td>0.88</td>
<td>0.50</td>
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<tr>
<td>Fe14NDC-9</td>
<td>0.1 M KOH</td>
<td>0.88</td>
<td>0.25</td>
<td>8</td>
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Table S2. XPS of Fe₃C@MHNFs synthesized with ammoniation and A-Fe₃C@MHNFs synthesized without ammoniation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>C (at%)</th>
<th>N (at%)</th>
<th>O (at%)</th>
<th>Fe (at%)</th>
<th>pyridinic N (%)</th>
<th>pyrrolic N (%)</th>
<th>graphitic N (%)</th>
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<tr>
<td>Fe₃C@MHNFs</td>
<td>92.71</td>
<td>2.60</td>
<td>4.24</td>
<td>0.45</td>
<td>0.30</td>
<td>0.21</td>
<td>0.49</td>
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<td>A-Fe₃C@MHNFs</td>
<td>93.08</td>
<td>1.21</td>
<td>5.30</td>
<td>0.41</td>
<td>0.23</td>
<td>0.29</td>
<td>0.48</td>
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Reference