Hybrid shells of N-doped carbon encapsulated by MnO nanoparticles towards oxygen reduction reaction electrocatalysts

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**Electrochemical Test**

To prepare the working electrode, 3.5 mg of catalyst mixed with 1.5 mg Cabot Vulcan XC-72 carbon (Vc-72) were dispersed in a solution containing 500 μL of mixed solution (2-propanol mixed with water (V$_{C3H8O}$:V$_{H2O}$=1:1) and 0.5 wt % Nafion solution). The suspension was ultrasonically dispersed to form a homogeneous ink. After that, the ink was pipetted onto the GC electrode and then was naturally drying to form a thin catalyst layer on the GC electrode.

The tests were conducted on a computer-controlled potentionstat/galvanostat workstation at room temperature. The supporting electrolyte was 0.1 mol L$^{-1}$ KOH aqueous solution, which was purged with N$_2$ or O$_2$ (purity 99.995%) for at least 30 min prior to testing and maintained under N$_2$ or O$_2$ atmosphere during the test. Cyclic voltammograms were recorded from 0.2 to -0.8 V *versus* Ag/AgCl in N$_2$- and O$_2$-saturated 0.1 mol L$^{-1}$ KOH electrolyte solutions with a scan rate of 20 mV s$^{-1}$. Rotating disk electrode (RDE) was performed in O$_2$-saturated 0.1 mol L$^{-1}$ KOH at 1600 rpm with a sweep rate of 5 mV s$^{-1}$. All potentials were reported with reference to the reversible hydrogen electrode (RHE) potential scale. In 0.1 mol L$^{-1}$ KOH solution, the potential of Ag/AgCl was calibrated as +0.965 V with respect to RHE.

Koutecky-Levich (K-L) plots was analyzed at various electrode potentials. The K–L plots show linear relationships between $j_k^{-1}$ and $\omega^{-1/2}$, the higher the slope is the smaller the number of electron transfer and the lower the oxygen reduction electric catalytic activity. The slopes of their best linear fit lines were used to calculate the
electron transfer number \( (n) \) according to the K-L equation:

\[
\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{\frac{\omega}{B} J_0^2} + \frac{1}{J_S}
\] (1)

\[
B = 0.62nFC_0(D_0)^{2/3}v^{-1/6}
\] (2)

\[
J_K = nFkC_0
\] (3)

where \( J \) is the measured current density, \( J_K \) and \( J_L \) are the kinetic- and diffusion-limiting current densities, \( \omega \) is the angular velocity, \( n \) represents the overall number of electrons transferred in oxygen reduction, \( F \) is the Faraday constant, \( C_0 \) is the bulk concentration of \( O_2 \), \( D_0 \) is the diffusion coefficient of \( O_2 \) in 0.1 mol L\(^{-1}\) KOH electrolyte, \( v \) is the kinematic viscosity of the electrolyte and \( k \) is the electron transfer rate constant.

The ring electrode can detect the intermediate product hydrogen peroxide produced by the ORR catalysts on the disk electrode, and the percent content of hydrogen peroxide \( (y_{\text{peroxide}}) \) is the ratio of the amount of hydrogen peroxide generated in the ORR total product. On account of the disk current \( (i_d) \) and ring current \( (i_r) \), the \( y_{\text{peroxide}} \) and electron transfer number \( (n) \) can be calculated based on the following equations:

\[
y_{\text{peroxide}} = \frac{200i_r}{(Ni_d + i_r)}
\] (4)

\[
n = 4Ni_d/(Ni_d + i_r)
\] (5)

where \( N \) is the current collection efficiency of RRDE. \( N \) was determined to be 0.37.
Fig. S1 (a) XRD patterns of PoPD, N-Carbon and MnO$_2$/PoPD/MnO$_2$ hybrid shells, (b) Raman spectra of N-Carbon, (c) XPS spectra and (d) XPS spectra of Mn 2p of MnO$_2$/PoPD/MnO$_2$ and MnO/N-Carbon/MnO hybrid shells.

Fig. S2 CV curves of N-Carbon(800), MnO/N-Carbon/MnO and Pt/C catalyst in 0.1 M KOH saturated with N$_2$ (black solid curves) or O$_2$ (red solid curves).
Fig. S3 LSV curves of (a) N-Carbon(800), (b) MnO/N-Carbon/MnO(700), (c) MnO/N-Carbon/MnO(800), (d) MnO/N-Carbon/MnO(900) and (e) Pt/C in O₂-saturated 0.1 M KOH with various rotating speeds.
Fig. S4 (a) The differential plots of $I$ versus $E$ constructed from the LSV curve. From the sharply increased slope of the plots, the onset potential indicative of the start of the ORR can be clearly seen. (b) K-L plots of MnO/N-Carbon/MnO(800) at 0.3-0.5 V. (c) The polarization curves of different catalysts and Pt/C recorded on disk (solid line) and the ring (dotted line). (d) Peroxide yield (solid line) and the electron transfer number (dotted line) of different catalysts and Pt/C at different potentials.
Fig. S5 (a) The stability tests for ORR of MnO/N-Carbon/MnO(800) and Pt/C in O$_2$-saturated 0.1 KOH. (b) Chronoamperometric curves of MnO/N-Carbon/MnO(800) and Pt/C maintained at 0.8 V in O$_2$-saturated 0.1 M KOH with 3 M methanol (the arrow indicates the addition of 3 M methanol into the electrochemical cell).

Fig. S6 Nyquist plots of N-Carbon(800) and MnO/ N-Carbon/MnO hybrid shell in 0.1 mol L$^{-1}$ KOH.
**Table S1** Comparison of the electrochemical performances of MnO/ N-Carbon/MnO(800) hybrid shells involved in ORR with reported results.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Morphology</th>
<th>$E_{\text{onset}}$ (V)</th>
<th>$I_s$ (mA cm$^{-2}$)</th>
<th>$n$</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>MnO</td>
<td>Nanorods</td>
<td>-</td>
<td>0.85</td>
<td>2.19</td>
<td>1</td>
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<tr>
<td>N/C-G-MnO</td>
<td>-</td>
<td>-</td>
<td>3.75</td>
<td>3.98</td>
<td>2</td>
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<tr>
<td>3D-N-RGO/MnO</td>
<td>Nanoparticles</td>
<td>0.83</td>
<td>1.62</td>
<td>3.03</td>
<td>3</td>
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<tr>
<td>MnO/RGO</td>
<td>Octahedral</td>
<td>-</td>
<td>4.72</td>
<td>3.85</td>
<td>4</td>
</tr>
<tr>
<td>GNS@MnO@N-doped carbon</td>
<td>Nanoparticles</td>
<td>0.98</td>
<td>5.10</td>
<td>3.08</td>
<td>5</td>
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<tr>
<td>MnO/NG-900</td>
<td>Nanoparticles</td>
<td>0.89</td>
<td>4.17</td>
<td>3.70</td>
<td>6</td>
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<tr>
<td>MnO/ N-Carbon /MnO(800)</td>
<td>Sandwich-like hybrid shells</td>
<td>0.91</td>
<td>6.01</td>
<td>3.93</td>
<td>this work</td>
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**References**


