Supporting Information

(B, N)-doped 3D porous graphene-CNT synthesized by chemical vapor deposition as a bi-functional catalyst for ORR and HER

Pingping Gao\textsuperscript{a,b}, Min Sun\textsuperscript{b}, Xiaobo Wu\textsuperscript{a,b,*}, Shuzhu Zhou\textsuperscript{a}, Xiaoting Deng\textsuperscript{b}, Zhiyong Xie\textsuperscript{b,*}, Li Xiao\textsuperscript{a}, Lihui Jiang\textsuperscript{c}, and Qizhong Huang\textsuperscript{b}

a) State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, P.R.China.
b) College of Metallurgy and materials Engineering, Hunan University of Technology, Zhuzhou, Hunan 412000, P.R. China
c) College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P.R.China.
E-mail:xzy507@csu.edu.cn; qzhuang@csu.edu.cn; wuxiaobo176@126.com Fax: +86-731-88877671; Tel: +86-731-88877671

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1.1 Experiments

3D graphene was synthesized by the method of CVD. The Preparation of 3D B-N-G-CNT hybrid materials as following: firstly, The 3D graphene foam was immersed into H$_3$BO$_3$ (0.1M) and Ni(NO$_3$)$_2$·6H$_2$O (0.01M) mixed solution and impregnated for 3h, washed and dried at 50°C subsequently. Secondly, the sample was heated to 800°C and maintained for 1h under NH$_3$/C$_3$H$_6$ (NH$_3$/C$_3$H$_6$=80:200 s.c.c.m). Finally, the sample was put into the HCl to completely dissolve the nickel. For comparison, 3D N-B-G ((N, B)-doped 3D porous graphene) was also prepared by the same procedure without carbon source gas in the second step of CVD process.

1.2 The SEM images of 3D B-N-G

![Fig. S1 the SEM images of 3DN-B-G](image_url)

1.3 The SEM images of 3D B-N-G-CNT
Fig. S2 the SEM images of 3D B-N-G-CNT

Fig. S3 the SEM images of 3D B-N-G-CNT-2
1.6 Volmer reaction

Volmer reaction [1]:

\[ \text{H}_2\text{O}^+ + e^- + M \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O} \]  \hspace{1cm} (\text{公式1.1})

Where \( M \) is an active site/catalyst; \( \text{H}_{\text{ads}} \): an adsorbed H intermediate.
1.7 Comparison of the durability performance of various electrocatalysts

Table S1. Comparison of the durability performance of various electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolysis test</th>
<th>Electrolyte</th>
<th>decay</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D B-N-G-CNT</td>
<td>ORR</td>
<td>0.1M KOH</td>
<td>1.2%(25000s)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>HER</td>
<td>0.1M H₂SO₄</td>
<td>Overpotential negative shift0.15mV(35 00cycles)</td>
<td></td>
</tr>
<tr>
<td>3D CNF-carbon sheets</td>
<td>ORR</td>
<td>0.1M KOH</td>
<td>≈2%(25000s)</td>
<td>Angew.Chem.Int. Ed. 2014,53, 6905-6909</td>
</tr>
<tr>
<td>3D B,N-doped graphene</td>
<td>ORR</td>
<td>0.1M KOH</td>
<td>≈5%(20000s)</td>
<td>Phys.Chem.Chem,Phys.,2013,15,12220-12226</td>
</tr>
<tr>
<td>Fe-N-graphene</td>
<td>ORR</td>
<td>0.1M HClO₄</td>
<td>10.3%(22500s)</td>
<td>J.Mater.Chem.A 2014,2,3231-3236</td>
</tr>
<tr>
<td>MoS₂-graphene</td>
<td>ORR</td>
<td>0.1M KOH</td>
<td>≈8%(10000s)</td>
<td>J.Mater.Chem.A 2015,3,7616-7622</td>
</tr>
<tr>
<td>g-C₃N₄-graphene</td>
<td>ORR</td>
<td>0.1M KOH</td>
<td>16.5%(21600s)</td>
<td>Nanoscale, 2015, 7(7):3035-3042.</td>
</tr>
<tr>
<td>B-N-graphene</td>
<td>ORR</td>
<td>0.1M KOH</td>
<td>≈3%(25000s)</td>
<td>Angew.Chem.Int. Ed.2013,125,3192-3198</td>
</tr>
<tr>
<td>Cobalt phosphide nanoparticles</td>
<td>HER</td>
<td>0.5M H₂SO₄</td>
<td>Overpotential negative shift5mv(400cycles)</td>
<td>Angew. Chem. Int. Ed. 2014, 53, 5427-5430</td>
</tr>
</tbody>
</table>

1.8 Calculation parameters

Based on the density functional theory and first-principles method, the ATK (Atomistix ToolKit) software have been used to simulate and calculate the total energy of the B-N-CNT, B-N-G and B-N-G-CNT structure before and after the adsorption of H, O atoms, thus the ORR and HER catalytic activity of these three structures are compared and analyzed. The generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation function are chosen, with a Single Zeta Polarized basis set for C, H atoms, and a Double Zeta Polarized basis set for O, B, N atoms. The mesh cutoff of atoms being 75 Hartree and the tolerance of total energy being 0.0001 eV. Periodic boundary conditions are used for all calculations, and Brillouin-zone k-point sampling are performed using a 1×5×5
Monkhorst-Pack (MP) grid, with a sampling density bigger than 11 points/Å. The LBFGS algorithm is used to optimize atomic position until the maximum force on a single atom converges to 0.05 eV/Å. And thanks to High Performance Computing Center of Central South University for providing computing software.

Calculation parameters:
exchange correlation: GGA.PBE
The k-point sampling of grid (MP grid): 1×5×5, sampling density>11 points per emmy
Basis Set:
C, H: SingleZetaPolarized
O, B, N: DoubleZetaPolarized
mesh cut-off energy: 75 Hartree
max forces convergence precision: 0.05eV/Å
Using LBFGS algorithm to optimize the geometric structure

Initial configuration
-B-O 1.68emmi:O can easy bonding with B atom
-N-H 0.96emmi: H can easy binding with N atom

The calculation results:
The energy of Isolated O atom: -427.80375 eV
The energy of Isolated H atom: -12.36145 eV
### Table S2: The characteristic of B-N-G adsorbs on O and H atoms

<table>
<thead>
<tr>
<th></th>
<th>Top view</th>
<th>Side view</th>
<th>energy</th>
<th>Binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-N-G</td>
<td><img src="image1.png" alt="Top view" /> <img src="image2.png" alt="Side view" /></td>
<td><img src="image2.png" alt="Side view" /></td>
<td>-28208.21696 eV</td>
<td>7.19423 eV</td>
</tr>
<tr>
<td>B-N-G-O</td>
<td><img src="image3.png" alt="Top view" /> <img src="image4.png" alt="Side view" /></td>
<td><img src="image4.png" alt="Side view" /></td>
<td>-28643.21494 eV</td>
<td>7.19423 eV</td>
</tr>
<tr>
<td>B-N-G-H</td>
<td><img src="image5.png" alt="Top view" /> <img src="image6.png" alt="Side view" /></td>
<td><img src="image6.png" alt="Side view" /></td>
<td>-28221.67789 eV</td>
<td>1.09948 eV</td>
</tr>
</tbody>
</table>
1.10 The characteristic of B-N-CNT adsorbson O and H atoms

Table S3 the characteristic of B-N-CNT adsorbson O and H atoms

<table>
<thead>
<tr>
<th></th>
<th>Top view</th>
<th>Side view</th>
<th>energy</th>
<th>Binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B-N-CNT</strong></td>
<td><img src="image1.png" alt="Top view" /></td>
<td><img src="image2.png" alt="Side view" /></td>
<td>-22541.70591 eV</td>
<td></td>
</tr>
<tr>
<td><strong>B-N-CNT-O</strong></td>
<td><img src="image3.png" alt="Top view" /></td>
<td><img src="image4.png" alt="Side view" /></td>
<td>-22975.68624 eV</td>
<td>6.17658 eV</td>
</tr>
<tr>
<td><strong>B-N-CNT-H</strong></td>
<td><img src="image5.png" alt="Top view" /></td>
<td><img src="image6.png" alt="Side view" /></td>
<td>-22555.86133 eV</td>
<td>1.79397 eV</td>
</tr>
</tbody>
</table>
The characteristic of B-N-G-CNT adsorption O and H atoms at the interface between graphene and CNT

Table S4: The characteristic of B-N-G-CNT adsorption O and H atoms at the interface between graphene and CNT

<table>
<thead>
<tr>
<th></th>
<th>Top view</th>
<th>Side view</th>
<th>energy</th>
<th>Binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-N-G-CNT</td>
<td><img src="image1.png" alt="Top View" /></td>
<td><img src="image2.png" alt="Side View" /></td>
<td>-37076.79784 eV</td>
<td></td>
</tr>
<tr>
<td>B-N-G-CNT-O</td>
<td><img src="image1.png" alt="Top View" /></td>
<td><img src="image2.png" alt="Side View" /></td>
<td>-37510.01400 eV</td>
<td>5.41241</td>
</tr>
<tr>
<td>B-N-G-CNT-H</td>
<td><img src="image1.png" alt="Top View" /></td>
<td><img src="image2.png" alt="Side View" /></td>
<td>-37091.37993 eV</td>
<td>2.22064</td>
</tr>
</tbody>
</table>

When constructing the doped model, in order to compare the catalytic performance of the composite structure with the individual structure, considering that the position of the largest change in the local atomic structure of the G-CNT structure is at the interface between the CNT and the graphene, the B-N-G-CNT structure with BN pairs doping on the interface is used. Considering the structural stability of structures after adsorption, the adsorption site was selected as O adsorbed on B, and H atom adsorbed on N. The structure of the three structures adsorbing H and O after relaxation is shown in the figure below:
Eq. (1) gives the formula for the ORR and HER with HX as the intermediate product and X as the three catalyst: B-N-CNT, B-N-G, and B-N-G-CNT, while X being empty represents no catalyst. From left to right, Eq. (1) represents HER, and the reverse process from right to left is ORR.

\[
\begin{align*}
\text{H}_2\text{O} + \text{X} \rightarrow \text{HX} + \text{OH} & \rightarrow 0.5\text{O}_2 + \text{H}_2 + \text{X} \\
\end{align*}
\]

(1)

Eq. (2) gives the formula for the ORR and HER with OX as the intermediate product and X as the catalyst.

\[
\begin{align*}
\text{H}_2\text{O} + \text{X} \rightarrow \text{OX} + \text{H}_2 & \rightarrow 0.5\text{O}_2 + \text{H}_2 + \text{X} \\
\end{align*}
\]

(2)

With the energy of the intermediate minus the energy of the reactants as a reference value of the reaction barrier, sets the reference potential barrier of HER to \( \Delta E_1 \), and ORR to \( \Delta E_2 \), then the reference barrier corresponding to Eq. (1) is:

\[
\begin{align*}
\Delta E_1 &= E(\text{HX} + \text{OH}) - E(\text{H}_2\text{O} + \text{X}) \\
\Delta E_2 &= E(\text{OX} + \text{H}_2) - E(0.5\text{O}_2 + \text{H}_2 + \text{X}) \\
\end{align*}
\]

(3)

And the reference barrier corresponding to Eq. (2) is:
\[ \Delta E_1 = E(\text{OX} + \text{H}_2) - E(\text{H}_2\text{O} + \text{X}) \]

\[ \Delta E_2 = E(\text{OX} + \text{H}_2) - E(0.5\text{O}_2 + \text{H}_2 + \text{X}) \]

Equation (4)

Table S5: The reactants energy and the reference barrier corresponding to Eq. (1)

<table>
<thead>
<tr>
<th>X</th>
<th>E(H\text{H}_2\text{O})</th>
<th>E(X)</th>
<th>E(\text{OH})</th>
<th>E(\text{O}_2)</th>
<th>E(\text{H}_2)</th>
<th>E(\text{HX})</th>
<th>\Delta E_1</th>
<th>\Delta E_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without</td>
<td>-465.71</td>
<td>0.00</td>
<td>-846.66</td>
<td>-30.42</td>
<td>-12.36</td>
<td>6.72</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>B-N-CNT</td>
<td>-465.71</td>
<td>-28208.22</td>
<td>-846.66</td>
<td>-30.42</td>
<td>-28221.68</td>
<td>5.62</td>
<td>2.65</td>
<td></td>
</tr>
</tbody>
</table>

Table S6: The reactants energy and the reference barrier corresponding to Eq. (2)

<table>
<thead>
<tr>
<th>X</th>
<th>E(H\text{H}_2\text{O})</th>
<th>E(X)</th>
<th>E(\text{OH})</th>
<th>E(\text{O}_2)</th>
<th>E(\text{H}_2)</th>
<th>E(\text{OX})</th>
<th>\Delta E_1</th>
<th>\Delta E_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without</td>
<td>-465.71</td>
<td>0.00</td>
<td>-864.66</td>
<td>-30.42</td>
<td>-427.80</td>
<td>7.49</td>
<td>4.52</td>
<td></td>
</tr>
<tr>
<td>B-N-CNT</td>
<td>-465.71</td>
<td>-28208.22</td>
<td>-864.66</td>
<td>-30.42</td>
<td>-28643.21</td>
<td>0.30</td>
<td>-2.67</td>
<td></td>
</tr>
<tr>
<td>B-N-G</td>
<td>-465.71</td>
<td>-22541.71</td>
<td>-864.66</td>
<td>-30.42</td>
<td>-22975.69</td>
<td>1.32</td>
<td>-1.65</td>
<td></td>
</tr>
<tr>
<td>B-N-G-CNT</td>
<td>-465.71</td>
<td>-37077.12</td>
<td>-864.66</td>
<td>-30.42</td>
<td>-37510.67</td>
<td>1.78</td>
<td>-1.18</td>
<td></td>
</tr>
</tbody>
</table>

Fig. S6: Schematic diagram of reaction path and reference barrier

Tables S5 and S6 give the reactants energy and the reference barrier corresponding to Eq. (1) and (2), respectively. From the standpoint of energy alone, investigating the HER reference barrier \( \Delta E_1 \) and the ORR reference potential \( \Delta E_2 \), the lowest energy is the \( \Delta E_2 \) corresponding to Eq. (2) with B-N-CNT as catalyst and OX as the intermediate product, which is -2.67 eV. However, it does not mean that the catalytic performance of B-N-CNT is the best, because the real barrier and the reference barrier which given by Eq. (2) may be different. Between the \( \text{H}_2\text{O} + \text{X} \) to \( \text{OX} + \text{H}_2 \), there will inevitably appear O-H bond recombination, that is, an intermediate product such as HX or H atom may occur, and the corresponding reference barrier can be referred to the \( \Delta E_1 \) of Eq. (1). Therefore, to evaluate the catalytic performance, the reference barrier given by Eq. (1) is more valuable and more representative of the real reaction barrier.
It can be seen from Table S5 that compared with no catalyst, using B-N-CNT, B-N-G, or B-N-G-CNT as catalyst can reduce both the HER and ORR reference barrier, with the reduced reference barrier heights being 1.10, 1.79, 2.40 eV, respectively. The B-N-G-CNT has the largest reduction barrier, also the best HER and ORR catalytic performance, which is consistent with our experimental results. The N atoms in B-N-G-CNT show the best activity, which may be related to the non-six-membered ring structure appearing at the interface between the CNT and the graphene. Considering both theoretical and experimental data, we believe that it is the intermediate product formed by the doped N atoms and the H atoms involved in the reaction that effectively reduces the reaction energy barrier and enhances the catalytic activity. Therefore, it is predicted that an appropriate increase in the doping ratio of N atoms in the experiment should help to enhance the catalytic activity.

References