Supporting Information

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

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This PDF file includes:

1.1Experiments

3D grapheme 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_3BO_3 (0.1M) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.01M) mixed solution and impregnated for 3h, washed and dried at 50°C subsequently. Secondly, the sample was heated to 800°Cand maintained for 1h under NH_3/C_3H_6 (NH_3/C_3H_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 gasin the second step of CVD process

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

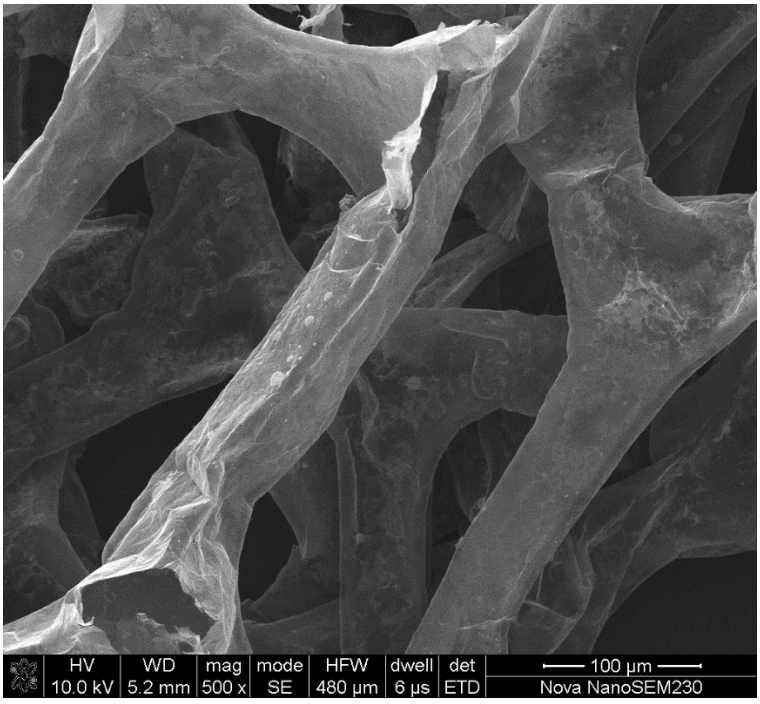


Fig. S1the SEM images of3DN-B-G

1.3The SEM images of 3D B-N-G-CNT

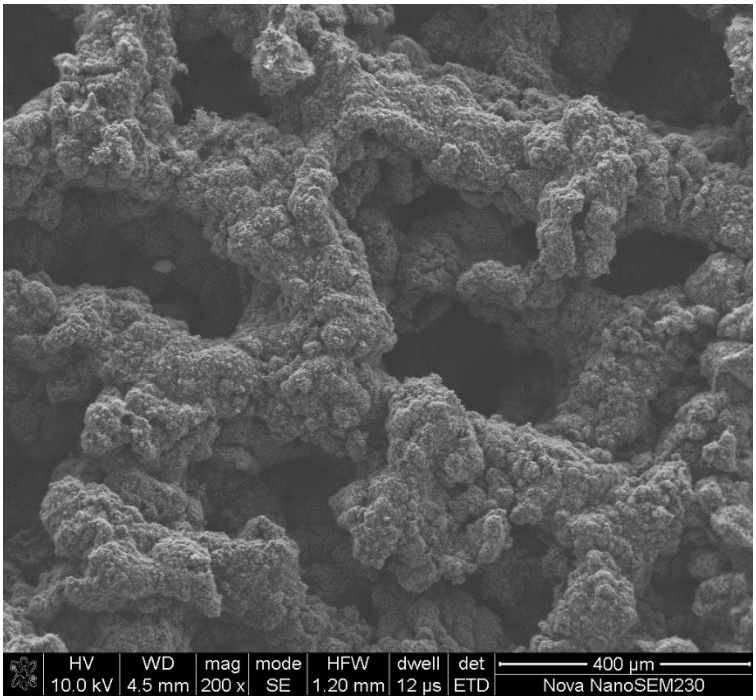


Fig. S2 the SEM images of3D B-N-G-CNT

1.4the SEM images of 3D B-N-G-CNT-2

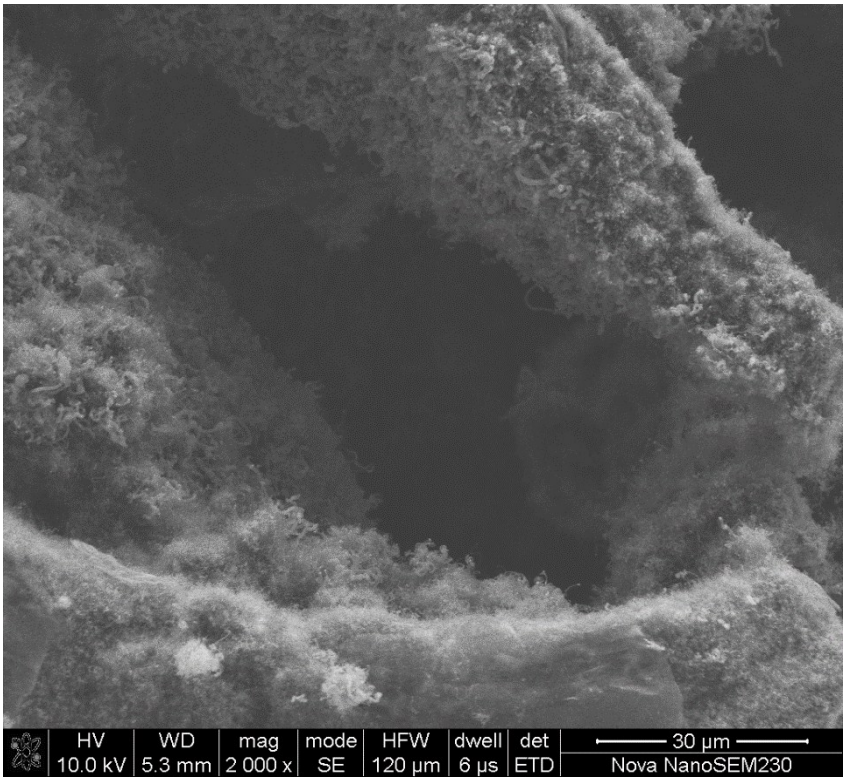


Fig. S3the SEM images of 3D B-N-G-CNT-2

1.5 Nitrogen adsorption curves for B-N-G and B-N-G-CNT

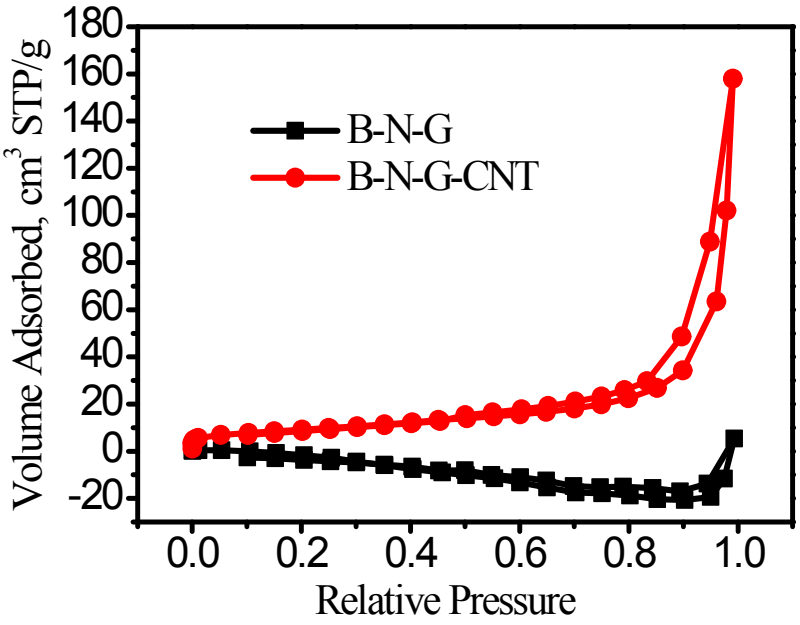


Fig. S4 Nitrogen adsorption curves for B-N-G and B-N-G-CNT

1.6Volmer reaction

Volmer reaction [1]:

$$H_3O^+ + e^- + M \rightarrow H_{ads} + H_2O \qquad \text{(公式1.1)}$$

Where M is an active site/catalyst; Hads: an adsorbed H intermediate.

1.7Comparison of the durability performance of various electrocatalysts

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

Catalyst	Electrolysis test	electrolyte	decay	reference
3D B-N-G-CNT	ORR	0.1M KOH	1.2%(25000s)	This work
	HER	0.1MH_2SO_4	Overpotential negative shift0.15mV(3500cycles)	
3D CNF-carbon sheets	ORR	0.1M KOH	≈2%(25000s)	Angew.Chem.Int. Ed. 2014,53, 6905-6909
3D B,N-doped graphene	ORR	0.1M KOH	≈5%(20000s)	Phys.Chem.Chem,Phys.,2013,15,12220-12226
Fe-N-graphene	ORR	0.1M $HClO_4$	10.3%(22500s)	J.Mater.Chem.A 2014,2,3231-3236
MoS_2-graphene	ORR	0.1M KOH	≈8%(10000s)	J.Mater.Chem.A 2015,3,7616-7622
g-C_3N_4-garphene	ORR	0.1M KOH	16.5%(21600s)	Nanoscale, 2015, 7(7):3035-3042.
B-N-graphene	ORR	0.1M KOH	≈3%(25000s)	Angew.Chem.Int. Ed.2013,125,3192-3198
Cobalt phosphide nanoparticles	HER	0.5MH_2SO_4	Overpotential negative shift 5mv(400cycles)	Angew. Chem.Int. Ed. 2014, 53, 5427-5430

1.8Calculation 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-Pach (MP) grid, with a sampling density bigger than 11 points/Å-1. 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.

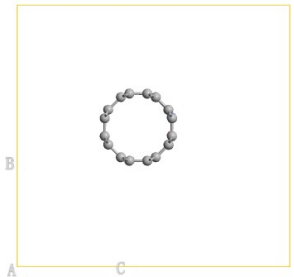
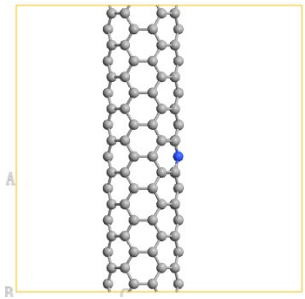
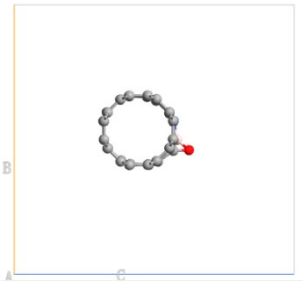
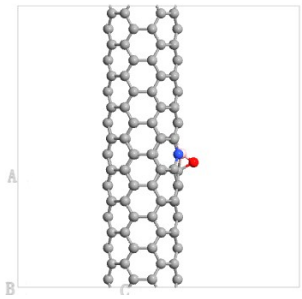
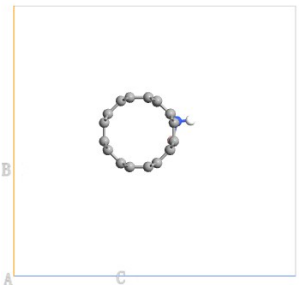
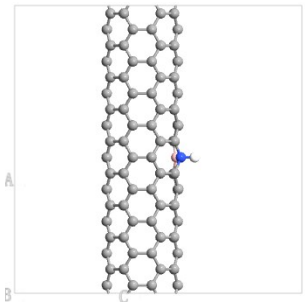
Calculation parameters：
exchange correlation：GGA.PBE
The k-point sampling of grid (MP grid)：1×5×5, sampling density>11 points per emmy
Basis Set：
C、H：SingleZetaPolarized
O、B、N：DoubleZetaPolarized
mesh cut-off energy：75 Hartree
max forces convergence precision：0.05eV/Å
Using LBFGS algorithm to optimize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

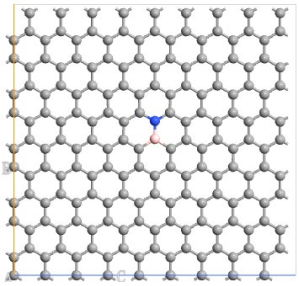
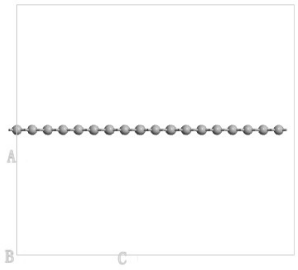
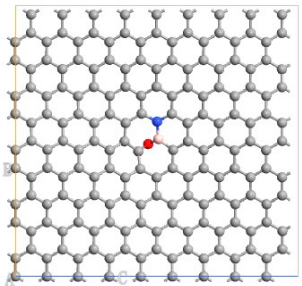
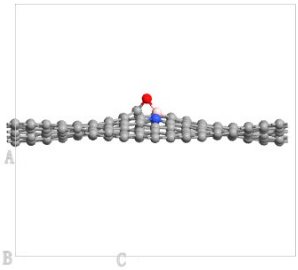
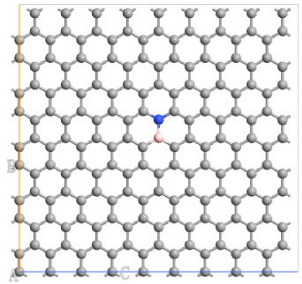
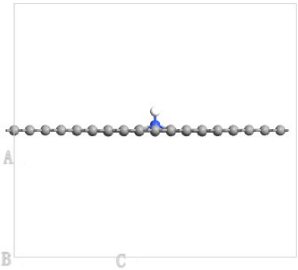
1.9The characteristic of B-N-G adsorbson O and H atoms

Table S2 the characteristic of B-N-G adsorbs on O and H atoms

	Top view	**Side view**	**energy**	**Binding energy**
B-N-G			**-28208.21696 eV**	
B-N-G-O			**-28643.21494 eV**	**7.19423 eV**
B-N-G-H			**-28221.67789 eV**	**1.09948 eV**

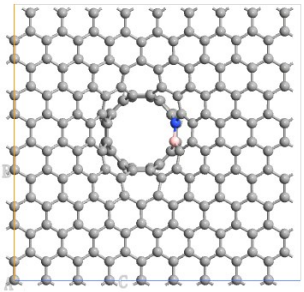
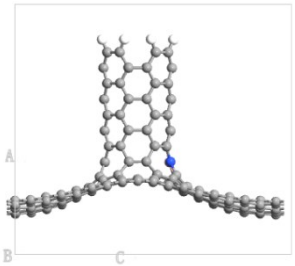
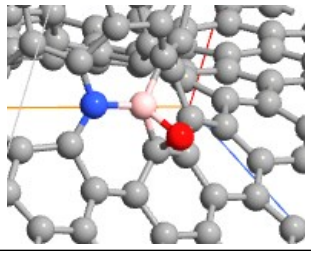
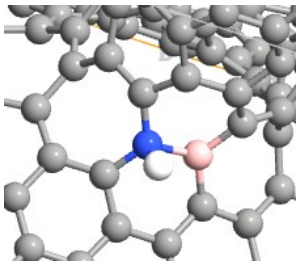
1.10 The characteristic of B-N-CNT adsorbson Oand H atoms

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

	Top view	**Side view**	**energy**	**Binding energy**
B-N-CNT			**-22541.70591 eV**	
B-N-CNT-O			**-22975.68624 eV**	**6.17658 eV**
B-N-CNT-H			**-22555.86133 eV**	**1.79397 eV**

1.11The characteristic of B-N-G-CNT adsorbson O and H atoms at the interface between grapheme and CNT

Table S4 the characteristic of B-N-G-CNT adsorbson O and H atoms at the interface between grapheme and CNT

	Top view	**Side view**	**energy**	**Binding energy**
B-N-G-CNT			**-37076.79784 eV**	
B-N-G-CNT-O			**-37510.01400 eV**	5.41241
B-N-G-CNT-H			**-37091.37993 eV**	2.22064

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:

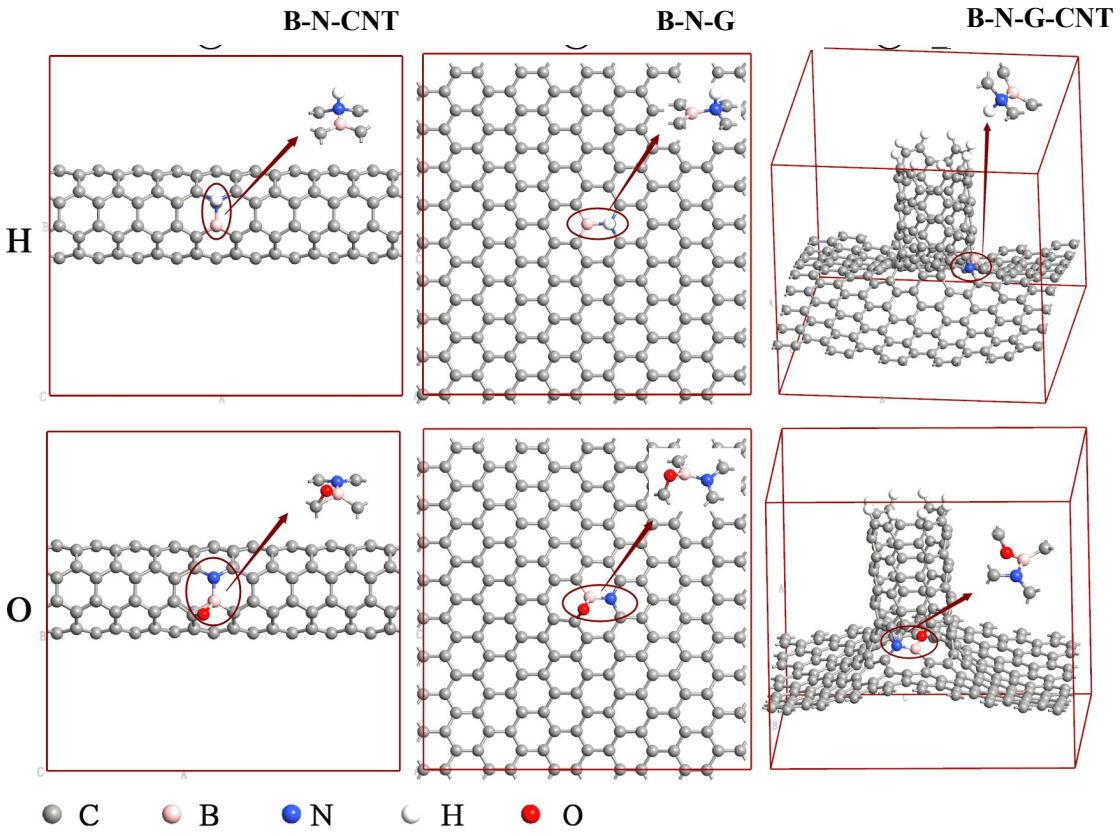


Fig. S5 the structure diagram of B-N-CNT, B-N-G and B-N-G-CNT adsorbing H and O atoms, respectively

$$H_2O+X \rightarrow HX+OH \rightarrow 0.5O_2+H_2+X \tag{1}$$

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.

$$H_2O+X \rightarrow OX+H_2 \rightarrow 0.5O_2+H_2+X \tag{2}$$

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

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 ΔE_1, and ORR to ΔE_2, then the reference barrier corresponding to Eq. (1) is:

$$\Delta E_1 = E(HX+OH) - E(H_2O+X) \tag{3}$$
$$\Delta E_2 = E(HX+OH) - E(0.5O_2+H_2+X)$$

And the reference barrier corresponding to Eq. (2) is:

$$\Delta E_1 = E(\mathrm{OX+H_2}) - E(\mathrm{H_2O+X}) \quad (4)$$
$$\Delta E_2 = E(\mathrm{OX+H_2}) - E(0.5\mathrm{O_2+H_2+X})$$

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

X	E(H_20)	E(X)	E(OH)	E(O_2)	E(H_2)	E(HX)	ΔE_1	ΔE_2
Without	-465.71	0.00	-446.63	-864.66	-30.42	-12.36	6.72	3.75
B-N-CNT	-465.71	-28208.22	-446.63	-864.66	-30.42	-28221.68	5.62	2.65
B-N-G	-465.71	-22541.71	-446.63	-864.66	-30.42	-22555.86	4.93	1.96
B-N-G-CNT	-465.71	-37077.12	-446.63	-864.66	-30.42	-37091.88	4.32	1.35

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

X	E(H_20)	E(X)	E(O_2)	E(H_2)	E(OX)	ΔE_1	ΔE_2
Without	-465.71	0.00	-864.66	-30.42	-427.80	7.49	4.52
B-N-CNT	-465.71	-28208.22	-864.66	-30.42	-28643.21	0.30	-2.67
B-N-G	-465.71	-22541.71	-864.66	-30.42	-22975.69	1.32	-1.65
B-N-G-CNT	-465.71	-37077.12	-864.66	-30.42	-37510.63	1.78	-1.18

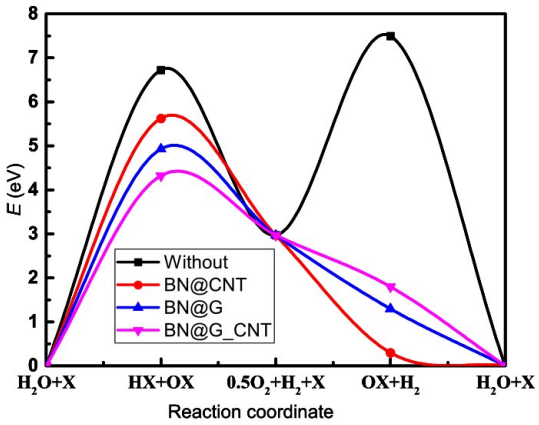


Fig. S6 schematic diagram of reaction path and reference barrier

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 ΔE_1 and the ORR reference potential ΔE_2, the lowest energy is the ΔE_2corresponding 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 H_2O+X to OX+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 ΔE_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

[1] B.E. Conway, B.V. Tilak, Interfacial processes involving electrocatalytic evolution and oxidation of H_2, and the role of chemisorbed H, Electrochimica Acta 47(22) (2002) 3571-3594.