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# Theoretical investigation of the ORR on boron–silicon nanotubes (B–SiNTs) as acceptable catalysts in fuel cells

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Here, the potential of boron doped silicon nanotubes (7, 0) as ORR catalysts is examined. Acceptable paths for the ORR on studied catalysts are examined through DFT. The optimum mechanism of the ORR on the surface of B<sub>2</sub>–SiNT (7, 0) is shown. The ORR on the surface of B<sub>2</sub>–SiNTs (7, 0) can continue through LH and ER mechanisms. The calculated beginning voltage for the ORR on B<sub>2</sub>–SiNTs (7, 0) is 0.37 V and it is smaller than the beginning voltage (0.45 V) for platinum-based catalysts. In the acidic solution the beginning voltage for the oxygen reduction process can be evaluated to be 0.97 V, which corresponds to 0.37 V as a minimum overvoltage for the ORR. The B<sub>2</sub>–SiNTs (7, 0) are suggested as an ORR catalyst in acidic environments.

## 1. Introduction

Fuel cells as energy machines are important due to their low contamination and great efficiency. The ORR rate in electrodes of cells is slow, therefore the ORR can be evaluated as a significant reason to increase the full cell efficiency.<sup>1–4</sup> Platinum-compounds have been used as catalysis in the ORR but platinum-compounds have low ability to endure CO.<sup>5–9</sup>

The potential of various compounds was investigated to find and propose effective catalysts for the ORR. Nanostructures and doped nanostructures with high ability for CO endurance can be used as suitable replacements for platinum-compounds.<sup>10–15</sup> The B-nanostructures are acceptable catalysts for the ORR in alkaline conditions and mechanisms of action of B-doped nanostructures in acidic position are not clear.<sup>16–23</sup>

The nanostructures due to their electrical conductivity and thermal conductivity can be used to product the transistors and non-volatile memory devices.<sup>24–28</sup> The electrical conductivity of doped carbon/silicon nanotubes indicated that the adoption of carbon/silicon nanotubes (with various atoms such as B, N, O and some metals) increased their electrical conductivity, significantly. These findings improved the application of carbon/silicon nanotubes in nano-electronic devices and novel catalyst to ORR.<sup>29–38</sup> Results demonstrated that the adoption of carbon/silicon nanotubes increased their electrical conductivity and enhanced the ORR efficiency.<sup>39–48</sup>

Wang *et al.*<sup>49</sup> demonstrated that boron-doped graphene nano-ribbons are suitable catalyst to ORR catalyst. Xiao *et al.*<sup>50</sup> proved

that the layered silicon–carbon nano sheets represented the high activity in ORR without CO poisoning. Xia and Zhang *et al.*<sup>51,52</sup> investigated the mechanisms of ORR of fuel cells in acidic environment on graphene cathodes. Stevenson *et al.*<sup>53</sup> proved in ORR the O<sub>2</sub> in a 2-electron path is reduced to form OOH on carbon nanotubes. Hu and Xiong *et al.*<sup>54,55</sup> confirmed that nitrogen and boron-doped nanostructures as ORR catalysts have low price, great durability and excellent potential. Zhao and Wei *et al.*<sup>56,57</sup> confirmed the doping of carbon nanotubes have vital roles on performance of ORR. Ferrighi *et al.*<sup>58</sup> demonstrated that boron atoms of nano-sheets increase the reactions of oxygen with graphene.

In current study, ORR on B-doped silicon nanotube (7, 0) as acceptable catalysts is examined to find possible mechanisms to ORR on B<sub>2</sub>–SiNT (7, 0) and to suggest high activity nano-catalysts to ORR.

## 2. Computational details

In this study the silicon nanotube (length and diameter are 1 and 0.475 nm) is modeled and their open elements are saturated with hydrogen atoms to elude border effects. The geometries of nanotubes and studied molecules (such as OOH, OH, H<sub>2</sub>O and CO) are optimized by M06-2X/6-311G+ (2d, 2p) in GAMESS package.<sup>59–72</sup> The consistent field is investigated by 10<sup>–6</sup> Hartree as convergence value. Vibrational frequencies of nanotubes and molecules by M06-2X/6-311G+ (2d, 2p) are calculated.

In the density functional, M06 functionals are extremely parameterized proximate exchange functionals theory and they are supported on generalized gradient approximation (meta-GGA). These functionals are used for traditional quantum chemistry, solid-state physics calculations and thermodynamic values of reactions.<sup>73–82</sup> M06-2X as the most accurate functional

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of Minnesota functional is a Global hybrid functional with 54% HF exchange and it is the ascendancy constructor within the 06 functionals for thermochemistry, kinetics and various chemical interactions.<sup>73–82</sup> The M06-2X functional as hybrid meta exchange–correlation functionals present 32 empirically improved factors within the exchange–correlation functional.<sup>83–87</sup>

The energy and Gibbs free energy ( $G = E_0 + \text{ZPE} + \Delta H + RT - TS$ ) values of nanotubes are calculated. The  $E_0$  and ZPE are electronic energy and zero-point energy and  $T$  is 298.15 K.<sup>59–72</sup> Adoption energy ( $E_{\text{doped}}$ ) and Gibbs free energy adoption ( $G_{\text{doped}}$ ) of B atoms in SiNT (7, 0) are calculated:

$$E_{\text{doped}} = E(\text{B-SiNT}) - E(\text{SiNT}) - E(\text{B}) \quad (1)$$

$$G_{\text{doped}} = G(\text{B-SiNT}) - G(\text{SiNT}) - G(\text{B}) \quad (2)$$

$$E_{\text{doped}} = E(\text{B}_2\text{-SiNT}) - E(\text{SiNT}) - 2E(\text{B}) \quad (3)$$

$$G_{\text{doped}} = G(\text{B}_2\text{-SiNT}) - G(\text{SiNT}) - 2G(\text{B}) \quad (4)$$

$E(\text{B-SiNT (7, 0)})$  and  $E(\text{B}_2\text{-SiNT (7, 0)})$  are energies of B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0).

Energy adsorption ( $\Delta E_{\text{ad}}$ ) and Gibbs free energy adsorption ( $\Delta G_{\text{ad}}$ ) of molecules (such as OOH, OH, H<sub>2</sub>O and CO) on surfaces of studied nanotubes (SiNT, B-SiNT, B-B-SiNT and B<sub>2</sub>-SiNT) are calculated:

$$\Delta E_{\text{ad}} = E(\text{molecule-nanotube}) - E(\text{nanotube}) - E(\text{molecule}) \quad (5)$$

$$\Delta G_{\text{ad}} = G(\text{molecule-nanotube}) - G(\text{nanotube}) - G(\text{molecule}) \quad (6)$$

$E(\text{molecule-nanotube})$  and  $G(\text{molecule-nanotube})$  are  $E$  and  $G$  of molecules-nanotubes.  $G(\text{nanotube})$  and  $G(\text{molecule})$  are  $G$  of nanotubes and molecules.  $E(\text{nanotube})$  and  $G(\text{molecule})$  are energy and  $G$  of nanotubes and molecules. Natural bond orbital charges ( $q$ ) and gap energy ( $E_{\text{HLG}}$ ) complexes are calculated<sup>59–72</sup> and transition state, reaction energy ( $\Delta E_{\text{r}}$ ) and activation barrier energy ( $\Delta E_{\text{a}}$ ) are examined by LST/QST method and M06-2X.<sup>64</sup>

Activation energy ( $\Delta E_{\text{a}} = E_{\text{TS}} - E_{\text{IS}}$ ) is difference of energy between transition ( $E_{\text{TS}}$ ) and initial ( $E_{\text{IS}}$ ) studied complexes. In this study, the reaction energy ( $\Delta E_{\text{a}} = E_{\text{FS}} - E_{\text{IS}}$ ) is difference of energy between final ( $E_{\text{FS}}$ ) and initial ( $E_{\text{IS}}$ ) studied complexes.<sup>88–95</sup> The  $\Delta G$  of ORR on B<sub>2</sub>-SiNT (7, 0) in according to standard hydrogen electrode was evaluated through  $\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + \Delta G_{\text{U}} + \Delta G_{\text{pH}}$  (obtained data were reported in Fig. 5).<sup>96–104</sup>  $\Delta G_{\text{pH}}$  ( $\Delta G_{\text{pH}} = kT \ln 10 \times \text{pH}$ ) is modification of proton Gibbs free energy and  $\Delta G_{\text{U}} = -neU$ . The  $n$ ,  $e$  and  $U$  are electrons, first charge and electrode potential. The  $U$  is requested potential and overvoltage is  $\eta = U_0 - U$ .<sup>49–58</sup> Conductor like screening method is used to estimate water environment (dielectric constant is 78.54).<sup>59–72</sup>

### 3. Results and discussion

#### 3.1. Molecule adsorptions on nanotube

In this section, the B adoption of SiNT (7, 0) were investigated and then interactions of B-SiNT (7, 0) structures with O<sub>2</sub>, OOH,

OH, H<sub>2</sub>O and CO molecules were investigated. The one Si atom of the SiNT (7, 0) was replaced with one B atom and the B-SiNT (7, 0) was produced (Fig. 1). Also the two Si atoms of the SiNT (7, 0) in two difference positions were replaced with two B atoms and B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) structures were produced (Fig. 1). Structures of SiNT, B-SiNT, B-B-SiNT, B<sub>2</sub>-SiNT, O<sub>2</sub>, OH, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> and CO are presented in Fig. 1. The adoption energy ( $E_{\text{doped}}$ ), adoption free Gibbs energy ( $G_{\text{doped}}$ ) and bond lengths of B-Si of B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) were reported in Fig. 1. In the B-SiNT (7, 0) the B atom was connected with three neighboring silicon atoms and the  $E_{\text{doped}}$  and  $G_{\text{doped}}$  were  $-2.18$  and  $-2.10$  eV and average of bonds of B-Si in B-SiNT (7, 0) is  $1.95$  Å. In the B-B-SiNT (7, 0) the B atoms are connected with four neighboring silicon atoms and the  $E_{\text{doped}}$  and  $G_{\text{doped}}$  are  $-2.23$  and  $-2.14$  eV and average of bonds of B-Si in B-B-SiNT (7, 0) is  $1.93$  Å. In the B<sub>2</sub>-SiNT (7, 0) the B atoms are connected with six neighboring silicon atoms and the  $E_{\text{doped}}$  and  $G_{\text{doped}}$  values are  $-2.28$  and  $-2.17$  eV and average of bonds of B-Si in B<sub>2</sub>-SiNT (7, 0) are  $1.92$  Å.

The  $q$  and  $E_{\text{HLG}}$  of SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) are stated in Table 1.  $E_{\text{HLG}}$  of SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) are  $1.84$ ,  $1.75$ ,  $1.68$  and  $1.64$  eV. The  $q$  of B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) are  $0.58$ ,  $0.69$  and  $0.73|e|$ . The  $|E_{\text{doped}}|$ ,  $|G_{\text{doped}}|$  and  $q$  values of B<sub>2</sub>-SiNT (7, 0) are higher than B-SiNT (7, 0) and B-B-SiNT (7, 0). Results showed that the  $E_{\text{HLG}}$  value of B<sub>2</sub>-SiNT (7, 0) is lower than corresponding values on surfaces of B-SiNT (7, 0) and B-B-SiNT (7, 0). Therefore, it can be concluded that the B<sub>2</sub>-SiNT (7, 0) is the most stable than B-SiNT (7, 0) and B-B-SiNT (7, 0) from thermodynamic view point. The B atoms in B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) structures are advantageous to adsorption of O<sub>2</sub> molecule and these B atoms are active positions of B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) as catalyst for ORR. Therefore, B atoms are essential location to adsorption of O<sub>2</sub> molecule and B atoms can be considered as initiator of first ORR step.

Therefore, O<sub>2</sub> adsorption on SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) were investigated. The possible positions of SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) to O<sub>2</sub> adsorption including top position B atom and bridge positions of B-Si, B-B and Si-Si bonds were examined in Fig. 2. The B-O, O-O and Si-O in SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) with O<sub>2</sub> are presented in Fig. 2 (2a–2l structures). The  $\Delta E_{\text{ad}}$  and  $\Delta G_{\text{ad}}$  of O<sub>2</sub> on SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) are displayed in Table 2.  $|\Delta G_{\text{ad}}|$  of O<sub>2</sub> on B-SiNT, B-B-SiNT and B<sub>2</sub>-SiNT are greater than SiNT (7, 0). The  $|\Delta E_{\text{ad}}|$  and  $|\Delta G_{\text{ad}}|$  of O<sub>2</sub> on B<sub>2</sub>-SiNT (7, 0) are greater than B-SiNT (7, 0), B-B-SiNT (7, 0). The bridge position of B-B in B<sub>2</sub>-SiNT (7, 0) is stable than top position B in B<sub>2</sub>-SiNT (7, 0) to O<sub>2</sub> adsorption.

Wang, Xiao and Xia *et al.*<sup>49–51</sup> calculated the O<sub>2</sub> adsorption on surfaces of boron-doped graphene nanoribbon, silicon-carbon nano sheets and B and N doped-graphene by theoretical methods, respectively (results reported in Table 4). The  $\Delta E_{\text{ad}}$  of O<sub>2</sub> on B-doped graphene, silicon-carbon nano-sheets and N-doped graphene are  $-0.62$ ,  $-0.53$  and  $-0.60$  eV. Therefore  $\Delta E_{\text{ad}}$  value ( $-0.61$  eV) of O<sub>2</sub> on B<sub>2</sub>-SiNT (7, 0) in present study is



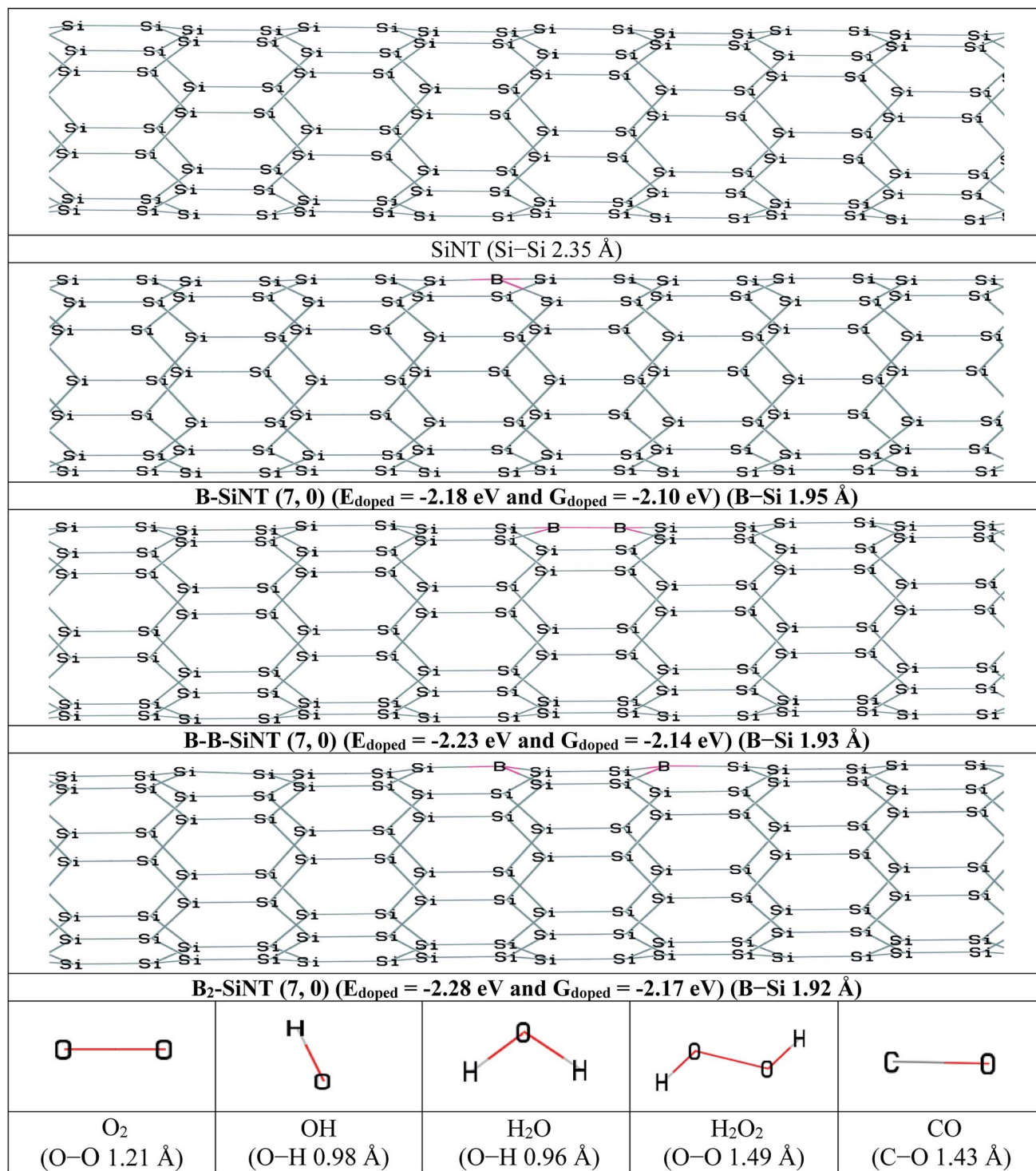


Fig. 1 The initial structures of SiNT, B-SiNT, B-B-SiNT and B<sub>2</sub>-SiNT and O<sub>2</sub>, OH, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> and CO molecules.

similar to corresponding values of O<sub>2</sub> on various nanostructures were calculated in previous theoretical works.<sup>49–51</sup>

The charge transfer ( $q$ ) and HOMO-LUMO band gap ( $E_{\text{HLG}}$ ) of the complexes of SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) with O<sub>2</sub> molecule are displayed in Table 1. The  $E_{\text{HLG}}$  values of O<sub>2</sub> adsorption on B-SiNT (7, 0), B-B-SiNT (7,

0) and B<sub>2</sub>-SiNT (7, 0) are lower than SiNT (7, 0). The  $E_{\text{HLG}}$  values of O<sub>2</sub> adsorption on B<sub>2</sub>-SiNT (7, 0) are lower than B-SiNT (7, 0), B-B-SiNT (7, 0). The bridge position of B-B in B<sub>2</sub>-SiNT (7, 0) has higher  $q$  and lower  $E_{\text{HLG}}$  than top position B in B<sub>2</sub>-SiNT (7, 0) to O<sub>2</sub> adsorption. Complex of B<sub>2</sub>-SiNT (7, 0) with O<sub>2</sub> molecule (**2d** structure) is the most stable than other complexes of B-SiNT (7,





Table 1 Charge transfer ( $q$ ) (in  $|e|$ ) and HOMO–LUMO band gap ( $E_{\text{HLG}}$ ) (in eV) of studied complexes

Complex	$q$	$E_{\text{HLG}}$	Complex	$q$	$E_{\text{HLG}}$	Complex	$q$	$E_{\text{HLG}}$	Complex	$q$	$E_{\text{HLG}}$
<i>SiNT</i>	—	1.84	<i>B–SiNT</i>	0.58	1.75	<i>B–B–SiNT</i>	0.69	1.68	<i>B<sub>2</sub>–SiNT</i>	0.73	1.64
<i>2a</i>	0.36	1.69	<i>2b</i>	0.47	1.61	<i>2c</i>	0.59	1.52	<i>2d</i>	0.64	1.48
<i>2e</i>	0.29	1.75	<i>2f</i>	0.39	1.68	<i>2g</i>	0.51	1.59	<i>2h</i>	0.58	1.55
<i>2i</i>	0.32	1.72	<i>2j</i>	0.43	1.64	<i>2k</i>	0.54	1.56	<i>2l</i>	0.61	1.52
<i>2m</i>	0.49	1.35	<i>2n</i>	0.62	1.23	<i>2o</i>	0.73	1.17	<i>2p</i>	0.82	1.14
<i>3a</i>	0.41	1.54	<i>3b</i>	0.51	1.45	<i>3c</i>	0.65	1.38	<i>3d</i>	0.73	1.25
<i>3e</i>	0.59	1.14	<i>3f</i>	0.81	1.05	<i>3g</i>	0.84	0.99	<i>3h</i>	0.91	0.95
<i>3m</i>	0.11	1.80	<i>3n</i>	0.14	1.70	<i>3o</i>	0.19	1.62	<i>3p</i>	0.21	1.60
<i>3q</i>	0.08	1.82	<i>3r</i>	0.12	1.72	<i>3s</i>	0.15	1.64	<i>3t</i>	0.18	1.63

0) and B–B–SiNT (7, 0) with O<sub>2</sub> molecule from thermodynamic view point. It can be concluded that O<sub>2</sub> adsorbed on B<sub>2</sub>–SiNT (7, 0) in figure **2d** significantly and there are suitable interactions

between the O<sub>2</sub> molecule and B<sub>2</sub>–SiNT (7, 0) and the adsorption of O<sub>2</sub> molecules on studied surfaces are chemical adsorption processes.

	SiNT (7, 0)	B–SiNT (7, 0)	B–B–SiNT (7, 0)	B <sub>2</sub> –SiNT (7, 0)
<b>O<sub>2</sub></b>				
<b>Bond Length</b>	<b>2a</b> (Si–O 1.96 Å) (O–O 1.58 Å)	<b>2b</b> (B–O 1.96 Å) (O–O 1.41 Å)	<b>2c</b> (B–O 1.96 Å) (O–O 1.37 Å)	<b>2d</b> (B–O 1.67 Å) (O–O 1.32 Å)
<b>O<sub>2</sub></b>				
<b>Bond length</b>	<b>2e</b> (Si–O 1.99 Å) (O–O 1.56 Å)	<b>2f</b> (Si–O 1.97 Å) (O–O 1.56 Å)	<b>2g</b> (Si–O 1.95 Å) (O–O 1.56 Å)	<b>2h</b> (B–O 1.54 Å) (Si–O 1.96 Å)
<b>O<sub>2</sub></b>				
<b>Bond length</b>	<b>2i</b> (Si–O 1.99 Å) (O–O 1.59 Å)	<b>2j</b> (B–O 1.59 Å) (O–O 1.49 Å)	<b>2k</b> (B–O 1.58 Å) (O–O 1.46 Å)	<b>2l</b> (B–O 1.56 Å) (O–O 1.44 Å)
<b>OH</b>				
<b>Bond length</b>	<b>2m</b> (Si–O 1.93 Å)	<b>2n</b> (B–O 1.56 Å)	<b>2o</b> (B–O 1.53 Å)	<b>2p</b> (B–O 1.51 Å)

Fig. 2 Complexes of the SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B<sub>2</sub>–SiNT (7, 0) with O<sub>2</sub> and OH molecules.

Table 2 The  $\Delta E_{\text{ad}}$  (in eV) and  $\Delta G_{\text{ad}}$  (in eV) values of studied complexes

Complex	$\Delta E_{\text{ad}}$	$\Delta G_{\text{ad}}$	Complex	$\Delta E_{\text{ad}}$	$\Delta G_{\text{ad}}$	Complex	$\Delta E_{\text{ad}}$	$\Delta G_{\text{ad}}$	Complex	$\Delta E_{\text{ad}}$	$\Delta G_{\text{ad}}$
<b>2a</b>	−0.41	−0.36	<b>2b</b>	−0.61	−0.54	<b>2c</b>	−0.84	−0.79	<b>2d</b>	−0.88	−0.81
<b>2e</b>	−0.39	−0.33	<b>2f</b>	−0.42	−0.38	<b>2g</b>	−0.55	−0.51	<b>2h</b>	−0.61	−0.55
<b>2i</b>	−0.27	−0.24	<b>2j</b>	−0.64	−0.61	<b>2k</b>	−0.69	−0.64	<b>2l</b>	−0.73	−0.68
<b>2m</b>	−2.07	−1.97	<b>2n</b>	−2.23	−2.15	<b>2o</b>	−2.31	−2.21	<b>2p</b>	−2.39	−2.28
<b>3a</b>	−0.87	−0.81	<b>3b</b>	−1.06	−0.99	<b>3c</b>	−1.11	−1.03	<b>3d</b>	−1.17	−1.12
<b>3e</b>	−3.11	−2.97	<b>3f</b>	−3.59	−3.45	<b>3g</b>	−3.67	−3.56	<b>3h</b>	−3.79	−3.67
<b>3i</b>	−2.24	−2.13	<b>3j</b>	−2.25	−2.15	<b>3k</b>	−2.27	−2.17	<b>3l</b>	−2.31	−2.21
<b>3m</b>	−0.15	−0.10	<b>3n</b>	−0.18	−0.13	<b>3o</b>	−0.20	−0.15	<b>3p</b>	−0.24	−0.19
<b>3q</b>	−0.09	−0.05	<b>3r</b>	−0.10	−0.07	<b>3s</b>	−0.11	−0.08	<b>3t</b>	−0.14	−0.12

In this study the interactions of important intermediates such as O, H, OOH, OH, H<sub>2</sub>O and CO molecules with SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) surfaces in process of ORR were investigated (Fig. 2 and 3). The bonds of Si-O of SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) with molecules are stated.  $E_{\text{HLG}}$ ,  $q$ ,  $\Delta E_{\text{ad}}$ ,  $\Delta G_{\text{ad}}$  of molecules on SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) are reported in Tables 1 and 2. OOH and OH intermediates can be adsorb on B site of B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0). The O intermediate has tendency to adsorb on B-Si and B-B bridge positions of B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0). It can be concluded that the complexes of B<sub>2</sub>-SiNT (7, 0) with O, H, OOH, OH and H<sub>2</sub>O molecules are stable than SiNT (7, 0), B-SiNT (7, 0) and B-B-SiNT (7, 0).

Wang, Xiao and Xia *et al.*<sup>49–51</sup> calculated the O, OH and OOH adsorption on surfaces of boron-doped graphene nanoribbon, silicon-carbon nano sheets and B and N doped-graphene by theoretical methods, respectively (results reported in Table 4).  $\Delta E_{\text{ad}}$  of O on B-doped graphene, silicon-carbon nano-sheets and N-doped graphene were −3.74, −4.11 and −3.55 eV.  $\Delta E_{\text{ad}}$  of OH on boron-doped graphene, silicon-carbon nano-sheets and N-doped graphene were −2.38, −2.87 and −2.41 eV.  $\Delta E_{\text{ad}}$  of OOH on B-doped graphene, silicon-carbon nano-sheets and N-doped graphene are −1.12, −1.18 and −1.06 eV.  $\Delta E_{\text{ad}}$  values of O, OH and OOH (−1.17, −2.39 and −1.17 eV) on B<sub>2</sub>-SiNT (7, 0) in present study are similar to corresponding values of O, OH and OOH on various nano-structures were calculated in previous theoretical works.<sup>49–51</sup>

The H<sub>2</sub>O molecule favored to adsorb on above ring position of SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0)

and the average of  $\Delta E_{\text{ad}}$  and  $\Delta G_{\text{ad}}$  values are −0.19 and −0.14 eV. The average of  $q$  and  $E_{\text{HLG}}$  values for adsorption of H<sub>2</sub>O molecule on SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) surface is 0.16|e| and 1.68 eV. H<sub>2</sub>O molecule can be adsorbed on SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) surfaces as physical adsorption processes.

In process of ORR the CO can occupy the positions of catalysts and the performance of ORR is reduced and efficiency of catalyst decreases sharply. Previous works showed that reactions between CO molecule and surface of platinum nano-catalyst was powerful ( $\Delta E_{\text{ad}}$  is −1.90 eV) and CO poisoning was happen.<sup>20,66</sup> The average of  $\Delta E_{\text{ad}}$  and  $\Delta G_{\text{ad}}$  of CO on SiNT, B-SiNT, B-B-SiNT and B<sub>2</sub>-SiNT surfaces are −0.11 and −0.08 eV. The average of  $q$  and  $E_{\text{HLG}}$  values for adsorption of CO on SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) surface is 0.13|e| and 1.70 eV. The CO molecule can be adsorbed on SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) surfaces as physical adsorption processes. It can be concluded that B<sub>2</sub>-SiNT (7, 0) as acceptable catalyst can be endurance to CO poisoning and it can solve the major problem of platinum nano-catalysts.

Wang, Xiao and Xia *et al.*<sup>49–51</sup> calculated the H<sub>2</sub>O and CO adsorption on surfaces of boron-doped graphene nanoribbon, silicon-carbon nano sheets and B and N doped-graphene. The  $\Delta E_{\text{ad}}$  of H<sub>2</sub>O on surfaces of B-doped graphene, silicon-carbon nano-sheets and N-doped graphene were −0.24, −0.18 and −0.08 eV. The  $\Delta E_{\text{ad}}$  of CO on surfaces of B-doped graphene, silicon-carbon nano-sheets and N-doped graphene were −0.17, −0.07 and −0.12 eV. The  $\Delta E_{\text{ad}}$  of H<sub>2</sub>O and CO (−0.24 and −0.14 eV) on B<sub>2</sub>-SiNT (7, 0) in present study are similar to

Table 3 The  $\Delta E_{\text{a}}$  and  $\Delta E_{\text{r}}$  for ORR on B<sub>2</sub>-SiNT (7, 0)

Path	Studied reaction steps	$\Delta E_{\text{a}}$ (eV)	$\Delta E_{\text{r}}$ (eV)
1	$\text{O}_2 + \text{B}_2\text{-SiNT (7, 0)} \rightarrow \text{B}_2\text{-SiNT (7, 0)}^*\text{-O}_2$	—	−0.68
1	$\text{B}_2\text{-SiNT (7, 0)}^*\text{-O}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{B}_2\text{-SiNT (7, 0)}^*\text{-OOH}$	0.00	−1.07
1	$\text{B}_2\text{-SiNT (7, 0)}^*\text{-OOH} + \text{H}^+ + \text{e}^- \rightarrow \text{B}_2\text{-SiNT (7, 0)}^*\text{-O} + \text{H}_2\text{O}$	0.18	−2.75
1	$\text{B}_2\text{-SiNT (7, 0)}^*\text{-O} + \text{H}^+ + \text{e}^- \rightarrow \text{B}_2\text{-SiNT (7, 0)}^*\text{-OH}$	0.37	−1.57
1	$\text{B}_2\text{-SiNT (7, 0)}^*\text{-OH} + \text{H}^+ + \text{e}^- \rightarrow \text{B}_2\text{-SiNT (7, 0)}^* + \text{H}_2\text{O}$	0.07	−1.34
2	$\text{O}_2 + \text{B}_2\text{-SiNT (7, 0)} \rightarrow \text{B}_2\text{-SiNT (7, 0)}^*\text{-O}_2$	—	−0.68
2	$\text{B}_2\text{-SiNT (7, 0)}^*\text{-O}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{B}_2\text{-SiNT (7, 0)}^*\text{-OOH}$	0.00	−1.07
2	$\text{B}_2\text{-SiNT (7, 0)}^*\text{-OOH} + \text{H}^+ + \text{e}^- \rightarrow \text{B}_2\text{-SiNT (7, 0)}^*\text{-OH}$	0.24	−2.97
2	$\text{B}_2\text{-SiNT (7, 0)}^*\text{-OH} + \text{H}^+ + \text{e}^- \rightarrow \text{B}_2\text{-SiNT (7, 0)}^* + \text{H}_2\text{O}$	0.35	−1.20
2	$\text{B}_2\text{-SiNT (7, 0)}^*\text{-OH} + \text{H}^+ + \text{e}^- \rightarrow \text{B}_2\text{-SiNT (7, 0)}^* + \text{H}_2\text{O}$	0.07	−1.34



	SiNT (7, 0)	B-SiNT (7, 0)	B-B-SiNT (7, 0)	B <sub>2</sub> -SiNT (7, 0)
OOH				
Bond length	<b>3a</b> (Si-O 1.95 Å) (O-O 1.54 Å)	<b>3b</b> (B-O 1.51 Å) (O-O 1.51 Å)	<b>3c</b> (B-O 1.49 Å) (O-O 1.49 Å)	<b>3d</b> (B-O 1.53 Å) (O-O 1.47 Å)
O				
Bond length	<b>3e</b> (Si-O 1.85 Å)	<b>3f</b> (Si-O 1.83 Å) (B-O 1.47 Å)	<b>3g</b> (B-O 1.45 Å)	<b>3h</b> (Si-O 1.81 Å) (B-O 1.43 Å)
H				
Bond length	<b>3i</b> (Si-H 1.66 Å)	<b>3j</b> (Si-H 1.64 Å)	<b>3k</b> (Si-H 1.63 Å)	<b>3l</b> (Si-H 1.64 Å)
H <sub>2</sub> O				
Distance	<b>3m</b> (distance 3.21 Å)	<b>3n</b> (distance 3.17 Å)	<b>3o</b> (distance 3.14 Å)	<b>3p</b> (distance 3.11 Å)
CO				
Distance	<b>3q</b> (distance 3.34 Å)	<b>3r</b> (3.27 Å)	<b>3s</b> (distance 3.25 Å)	<b>3t</b> (distance 3.22 Å)

Fig. 3 Complexes of the SiNT (7, 0), B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) with O and H atoms, OOH, H<sub>2</sub>O and CO molecules.

corresponding values of H<sub>2</sub>O and CO on various nanostructures were calculated in previous theoretical works.<sup>49–51</sup>

### 3.2. B<sub>2</sub>-SiNT (7, 0) as catalyst to ORR

Nano-catalysts processed the chemical reactions through the ER and LH paths. The paths for ORR *via* B<sub>2</sub>-SiNT (7, 0) as

acceptable catalyst through the LH and ER mechanisms were investigated. As start, O<sub>2</sub> adsorption is investigated *via* O<sub>2</sub> dissociation or hydrogenation of O<sub>2</sub> to create B<sub>2</sub>-SiNT (7, 0)-\*OOH. Firstly, the O<sub>2</sub> dissociation process can be defined as B<sub>2</sub>-SiNT (7, 0)-\*O<sub>2</sub> → \*O-B<sub>2</sub>-SiNT (7, 0)-\*O. The dissociated O atoms were elected to link on B-Si position and activation barrier energy is 0.96 eV (figures **2a** (IS), **2b** (TS) and **2c** (FS)).





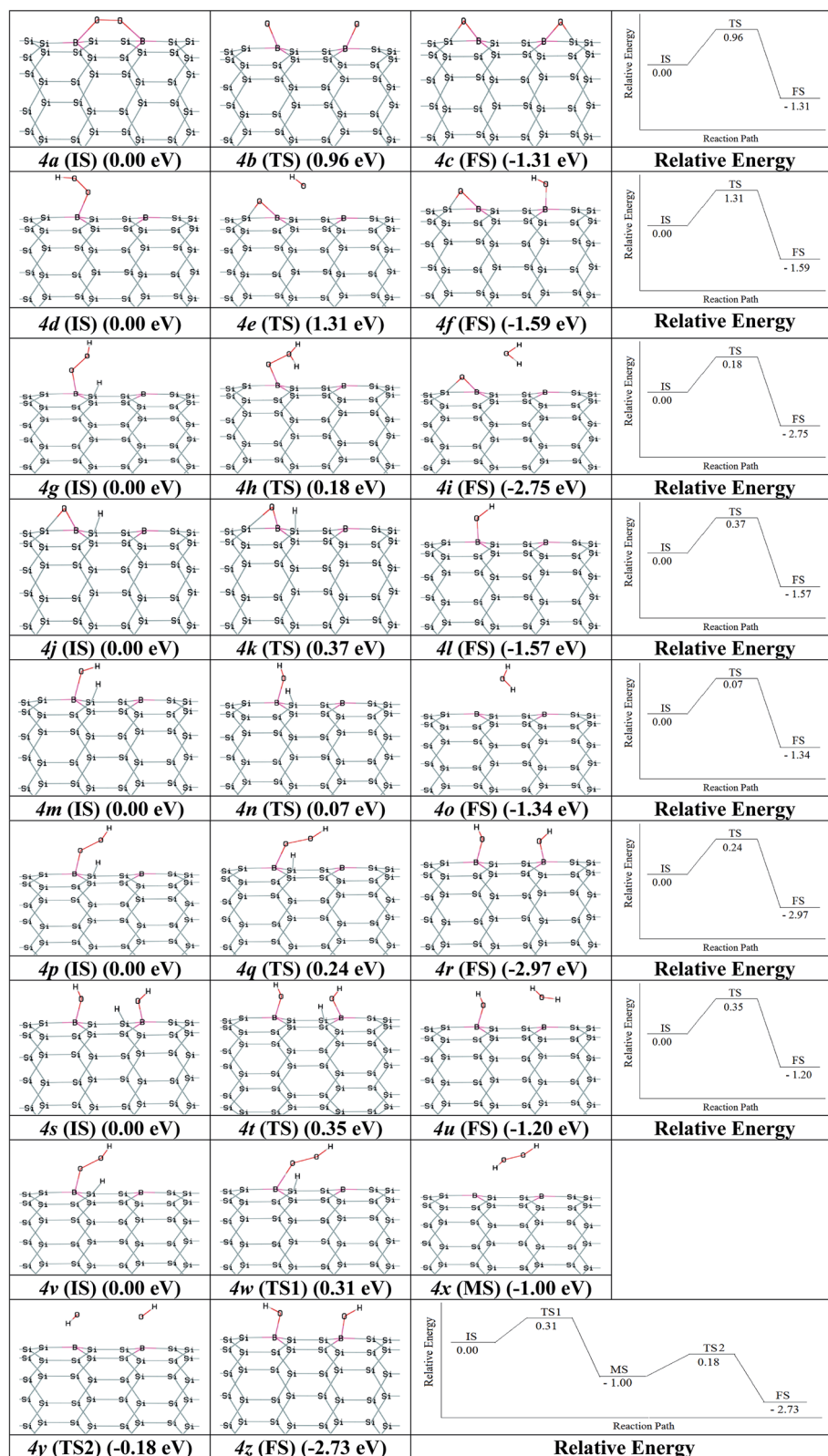


Fig. 4 The intermediates of ORR and relative energies: (1)  $\text{B}_2\text{-SiNT}(7, 0)\text{-}^*\text{O}_2 \rightarrow ^*\text{O-B}_2\text{-SiNT}(7, 0)\text{-}^*\text{O}$ ; (2)  $\text{B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OOH} \rightarrow ^*\text{O-B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OH}$ ; (3)  $\text{B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OOH} \rightarrow \text{B}_2\text{-SiNT}(7, 0)\text{-}^*\text{O} + \text{H}_2\text{O}$ ; (4)  $\text{B}_2\text{-SiNT}(7, 0)\text{-}^*\text{O} \rightarrow \text{B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OH}$ ; (5)  $\text{B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OH} \rightarrow \text{B}_2\text{-SiNT}(7, 0)\text{-}^* + \text{H}_2\text{O}$ ; (6)  $\text{B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OOH} \rightarrow ^*\text{OH-B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OH}$ ; (7)  $^*\text{OH-B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OH} \rightarrow ^*\text{OH-B}_2\text{-SiNT}(7, 0) + \text{H}_2\text{O}$ ; (8)  $\text{B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OOH} \rightarrow \text{B}_2\text{-SiNT}(7, 0) + \text{H}_2\text{O}_2 \rightarrow ^*\text{OH-B}_2\text{-SiNT}(7, 0)\text{-}^*\text{OH}$ .



**Table 4** The  $\Delta E_{\text{ad}}$  (in eV) values of  $\text{O}_2$ , O, OH and OOH on B-doped graphene, silicon-carbon nano-sheets and N-doped graphene<sup>65–67</sup> and B-SiNT (7, 0), B-B-SiNT (7, 0) and B<sub>2</sub>-SiNT (7, 0) in this study

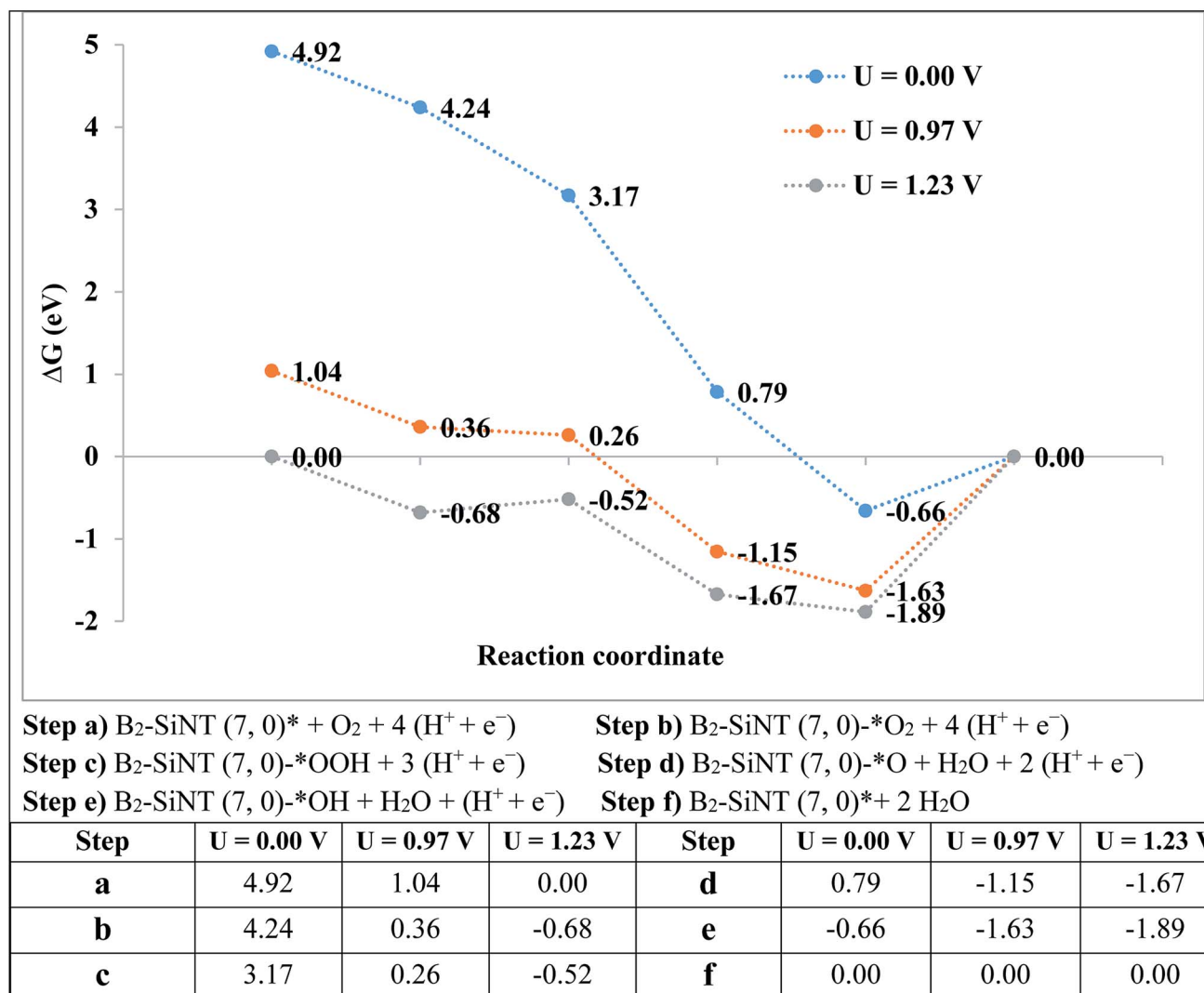
Catalysts/species	B-doped graphene <sup>49</sup>	Si-C nano-sheet <sup>50</sup>	N-doped graphene <sup>51</sup>	B-SiNT (7, 0)	B-B-SiNT (7, 0)	B <sub>2</sub> -SiNT (7, 0)
$\text{O}_2$	−0.62	−0.53	−0.60	−0.69	−0.84	−0.88
O	−3.74	−4.11	−3.55	−3.59	−3.67	−3.79
OH	−2.38	−2.87	−2.41	−2.23	−2.31	−2.39
OOH	−1.12	−1.18	−1.06	−1.06	−1.11	−1.17

Secondary, adsorbed  $\text{O}_2$  can interact *via* H atom to create B<sub>2</sub>-SiNT (7, 0)-\*OOH as follow: B<sub>2</sub>-SiNT (7, 0)-\* $\text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{B}_2\text{-SiNT (7, 0)-*OOH}$ , this process has no any activation barrier energy.

The OOH adsorption on of B<sub>2</sub>-SiNT (7, 0) has higher  $\Delta E_{\text{ad}}$  than  $\text{O}_2$  *ca.* 0.29 eV and also  $\text{O}_2$  dissociation on surface of B<sub>2</sub>-SiNT (7, 0) has high activation barrier energy. H atom is added into Si in B<sub>2</sub>-SiNT (7, 0)-\*OOH and H atom reacted *via* B<sub>2</sub>-SiNT

(7, 0)-\*OOH. Then the B<sub>2</sub>-SiNT (7, 0)-\*OOH dissociated to \*O-B<sub>2</sub>-SiNT (7, 0)-\*OH (figures 2d (IS), 2e (TS) and 2f (FS)), due to great activation barrier energy (1.31 eV) this process is impossible. The creation of B<sub>2</sub>-SiNT (7, 0)-\*OOH in ORR on B<sub>2</sub>-SiNT (7, 0) is suitable than dissociation of  $\text{O}_2$  molecule.

The ORR is done through the B<sub>2</sub>-SiNT-\*OOH intermediate as follows:



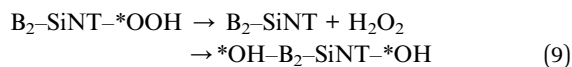
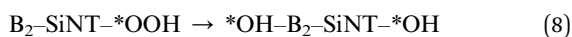
**Fig. 5** The G values for ORR on B<sub>2</sub>-SiNT (7, 0).





Table 5 The onset-potential (in eV) values for the ORR performed on several catalysts<sup>105–110</sup>

Catalyst	Onset potential	Catalyst	Onset potential	Catalyst	Onset potential
Pd/CNT <sup>105</sup>	0.764	Pd–Ni <sup>107</sup>	1.105	PdNi <sup>109</sup>	1.040
Pd/MWCNT <sup>105</sup>	1.014	PtCo/C <sup>107</sup>	0.836	Pd <sup>109</sup>	0.901
Pd–Ni(3 : 1)/C <sup>106</sup>	1.005	Pd–Fe/C <sup>108</sup>	0.865	Pd–Cu <sup>110</sup>	1.001
Pd <sub>2</sub> Co/C <sup>106</sup>	0.735	Pd/C <sup>108</sup>	0.920	Pt/C <sup>110</sup>	0.900



In path 1, B<sub>2</sub>-SiNT (7, 0)-\*OOH intermediate was decreased to H<sub>2</sub>O molecule and B<sub>2</sub>-SiNT (7, 0)-\*O (ΔE<sub>a</sub> = 0.18 eV). In this process, O–O is fragmented and the first H<sub>2</sub>O molecule is created (figures **2g** (IS), **2h** (TS) and **2i** (FS)). Then two hydrogenation stages were done and B<sub>2</sub>-SiNT (7, 0)-\*OH (figures **2j** (IS), **2k** (TS) and **2l** (FS)) and the second H<sub>2</sub>O molecule was created (figures **2m** (IS), **2n** (TS) and **2o** (FS)). The activation barrier energies of these two hydrogenation processes are 0.37 and 0.07 eV, respectively.

In path 2, H atom is linked to O and \*OH-B<sub>2</sub>-SiNT (7, 0)-\*OH is created and activation barrier energy is 0.24 eV (figures **2p** (IS), **2q** (TS) and **2r** (FS)). Then, \*OH-B<sub>2</sub>-SiNT (7, 0)-\*OH linked to H atom and the first H<sub>2</sub>O molecule is created and activation barrier energy of this stage is 0.35 eV (figures **2s** (IS), **2t** (TS) and **2u** (FS)). In the end stage of path 2, the B<sub>2</sub>-SiNT (7, 0)-\*OH is hydrogenated and in this step the second H<sub>2</sub>O molecule is separated.

In the path 3, the B<sub>2</sub>-SiNT (7, 0)-\*OOH is hydrogenated and the H<sub>2</sub>O<sub>2</sub> molecule and B<sub>2</sub>-SiNT (7, 0) catalyst are created and activation barrier is 0.31 eV (figures **2v** (IS), **2w** (TS1), **2x** (MS), **2y** (TS2) and **2z** (FS)). The H<sub>2</sub>O<sub>2</sub> molecule creation is a mediated state (MS) on surface of B<sub>2</sub>-SiNT (7, 0) and it cannot effect on potential of the B<sub>2</sub>-SiNT (7, 0), significantly. In next stage of path 3, separated H<sub>2</sub>O<sub>2</sub> dissociated into \*OH-B<sub>2</sub>-SiNT (7, 0)-\*OH structure and therefore H<sub>2</sub>O<sub>2</sub> dissociation has activation barrier energy about 0.82 eV. The ORR *via* path 3 continued *via* two hydrogenation stage as presented in path 1 in Fig. 4 (figures **4s** (IS), **4t** (TS) and **4u** (FS)) and path 2 in Fig. 4 (figures **4m** (IS), **4n** (TS) and **4o** (FS)).

The parameters of two acceptable paths about reduction of B<sub>2</sub>-SiNT (7, 0)-\*OOH structure are stated in Table 3. In path 1, rate-determining stage (ΔE<sub>a</sub> = 0.37 eV) on B<sub>2</sub>-SiNT (7, 0) surface is creation of B<sub>2</sub>-SiNT (7, 0)-\*OH. In path 2, creation of B<sub>2</sub>-SiNT (7, 0)-\*OH structure and H<sub>2</sub>O molecule is rate-determining stage (ΔE<sub>a</sub> = 0.35 eV). In path 2, creation of \*OH-B<sub>2</sub>-SiNT (7, 0)-\*OH has higher ΔE<sub>a</sub> than formation of B<sub>2</sub>-SiNT (7, 0)-\*O + H<sub>2</sub>O in path 1 *ca.* 0.06 eV and so path 1 can be considered as optimal pathway to ORR.

The over-potential of ORR on Pt-based compounds and graphene are 0.44 and 0.45 V.<sup>49–59</sup> The experimental researchers

investigated the onset-potential for the ORR performed on several catalysts<sup>105–110</sup> and results are stated in Table 5. The *G* of ORR steps are stated in Fig. 5. The level of the final produce (B<sub>2</sub>-SiNT (7, 0)-\* + 2H<sub>2</sub>O) is considered as reference step and ORR steps in *U* = 0 V is downhill. Reaction steps become downward that *U* is decreased to 0.97 V and beginning voltage for ORR is 0.97 V. The B<sub>2</sub>-SiNT (7, 0) is suggested as suitable ORR catalyst.

## 4. Conclusions

Performances of boron-silicon nanotube (7, 0) as novel catalyst to ORR are investigated. The ORR on surface of B<sub>2</sub>-SiNT can be continued through LH and ER mechanisms. The rate-determining stage (ΔE<sub>a</sub> = 0.35 eV) for ORR on B<sub>2</sub>-SiNT (7, 0) surface is creation of B<sub>2</sub>-SiNT (7, 0)-\*OH structure. The calculated beginning voltage to ORR on surface of the B<sub>2</sub>-SiNT (7, 0) is 0.37 V. In the acidic solution the beginning voltage to oxygen reduction process can be evaluated to 0.97 V. Results indicated that the B<sub>2</sub>-SiNT (7, 0) is suggested as catalyst to ORR with suitable efficiency.

## Conflicts of interest

There are no conflicts to declare.

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