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 B2–SiNT (7, 0) is shown. The ORR on the surface of B2–SiNTs (7, 0) can continue through LH and ER mechanisms. The calculated beginning voltage for the ORR on B2–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 B2–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.1–4 Platinum-compounds have been used as catalysis in the ORR but platinum-compounds have low ability to endure CO.5–9

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.10–15

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.16–21

The nanostructures due to their electrical conductivity and thermal conductivity can be used to produce the transistors and non-volatile memory devices.24–28 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 catalysts to ORR.29–34 Results demonstrated that the adoption of carbon/silicon nanotubes increased their electrical conductivity and enhanced the ORR efficiency.39–48

Wang et al.42 demonstrated that boron-doped graphene nanoribbons are suitable catalyst for ORR catalyst. Xiao et al.50 proved that the layered silicon–carbon nano sheets represented the high activity in ORR without CO poisoning. Xia and Zhang et al.51,52 investigated the mechanisms of ORR of fuel cells in acidic environment on graphene cathodes. Stevenson et al.53 proved in ORR the O2 in a 2-electron path is reduced to form OOH on carbon nanotubes. Hu and Xiong et al.54,55 confirmed that nitrogen and boron-doped nanostructures as ORR catalysts have low price, great durability and excellent potential. Zhao and Wei et al.56,57 confirmed the doping of carbon nanotubes have vital roles on performance of ORR. Ferrighi et al.58 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 B2–SiNT (7, 0) and to suggest high activity nanocatalysts 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, H2O and CO) are optimized by M06-2X/6-311G+ (2d, 2p) in GAMESS package.59–72 The consistent field is investigated by 10−6 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.73–82 M06-2X as the most accurate functional
of Minnesota functional is a Global hybrid functional with 54% HF exchange and it is the ascendency constructor within the 06 functionals for thermochemistry, kinetics and various chemical interactions. The M06-2X functional as hybrid meta exchange–correlation functionals present 32 empirically improved factors within the exchange–correlation functional.

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

$$E_{\text{ad}} = E(\text{SiNT}) - E(\text{B-SiNT}) - E(\text{B})$$

$$G_{\text{ad}} = G(\text{SiNT}) - G(\text{B-SiNT}) - G(\text{B})$$

Energy adsorption ($\Delta E_{\text{ad}}$) and Gibbs free energy adsorption ($\Delta G_{\text{ad}}$) of molecules (such as OOH, OH, H$_2$O and CO) on surfaces of studied nanotubes (SiNT, B–SiNT, B–B–SiNT and B$_2$–SiNT) are calculated:

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

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

Activation energy ($\Delta E_a = E_{TS} - E_{IS}$) of difference of energy between transition ($E_{TS}$) and initial ($E_{IS}$) studied complexes. In this study, the reaction energy ($\Delta E = E_{FS} - E_{ES}$) is difference of energy between final ($E_{FS}$) and initial ($E_{IS}$) studied complexes. The $\Delta G$ of ORR on B$_2$–SiNT (7, 0) in according to standard hydrogen electrode was evaluated through $\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{\text{ph}}$ (obtained data were reported in Fig. 5).

The $\Delta G_{\text{ph}}$ ($kT\ln 10 \times pH$) is modification of proton Gibbs free energy and $\Delta G_U = -neU$. The $n$, $e$ and $U$ are electrons, first charge and electrode potential. The $U$ is requested potential and overvoltage is $\eta = U_0 - U$. Conductor like screening method is used to estimate water environment (dielectric constant is 78.54).

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$_2$, OOH, OH, H$_2$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) were produced (Fig. 1). Also the two Si atoms of the SiNT (7, 0) in two different positions were replaced with two B atoms and B–B–SiNT (7, 0) and B$_2$–SiNT (7, 0) structures were produced (Fig. 1). Structures of SiNT, B–SiNT, B–B–SiNT, B$_2$–SiNT, O$_2$, OH, H$_2$O, H$_2$O$_2$, CO are presented in Fig. 1. The adoption energy ($E_{\text{ad}}$), adoption free Gibbs energy ($G_{\text{ad}}$) and bond lengths of B–Si of B–SiNT (7, 0), B–B–SiNT (7, 0) and B$_2$–SiNT (7, 0) were reported in Fig. 1. In the B–B–SiNT (7, 0) the B atom was connected with three neighboring silicon atoms and the $E_{\text{ad}}$ and $G_{\text{ad}}$ 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 $E_{\text{ad}}$ and $G_{\text{ad}}$ were $-2.23$ and $-2.14$ eV and average of bonds of B–Si in B–B–SiNT (7, 0) is 1.93 Å. In the B$_2$–SiNT (7, 0) the B atoms are connected with six neighboring silicon atoms and the $E_{\text{ad}}$ and $G_{\text{ad}}$ values are $-2.28$ and $-2.17$ eV and average of bonds of B–Si in B$_2$–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$_2$–SiNT (7, 0) are stated in Table 1. $E_{\text{HLG}}$ of SiNT (7, 0), B–SiNT (7, 0) and B–B–SiNT (7, 0) are 1.74, 1.85, 1.68 and 1.64 eV. The $q$ of SiNT (7, 0), B–SiNT (7, 0) and B–B–SiNT (7, 0) are 0.58, 0.69 and 0.73 e. The $E_{\text{ad}}$, $E_{\text{ad}}$ and $q$ values of B–SiNT (7, 0) are greater than SiNT (7, 0) and B–B–SiNT (7, 0). Results showed that the $E_{\text{HLG}}$ value of B$_2$–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$_2$–SiNT (7, 0) is the most stable than 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$_2$–SiNT (7, 0) structures are advantageous to adsorption of O$_2$ molecule and these B atoms are active positions of B–SiNT (7, 0), B–B–SiNT (7, 0) and B$_2$–SiNT (7, 0) as catalyst for ORR. Therefore, B atoms are essential location to adsorption of O$_2$ molecule and B atoms can be considered as initiator of first OERR step.

Therefore, O$_2$ adsorption on SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B$_2$–SiNT (7, 0) were investigated. The possible positions of SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B$_2$–SiNT (7, 0) to O$_2$ 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$_2$–SiNT (7, 0) with O$_2$ are presented in Fig. 2 (2a–2f structures). The $\Delta E_{\text{ad}}$ and $\Delta G_{\text{ad}}$ of O$_2$ on SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B$_2$–SiNT (7, 0) are displayed in Table 2. $\Delta G_{\text{ad}}$ of O$_2$ on B–SiNT, B–B–SiNT and B$_2$–SiNT are greater than SiNT (7, 0). The $\Delta E_{\text{ad}}$ and $\Delta G_{\text{ad}}$ of O$_2$ on B–SiNT (7, 0) are greater than B–SiNT (7, 0), B–B–SiNT (7, 0). The bridge position of B–B in B$_2$–SiNT (7, 0) is stable than top position B in B$_2$–SiNT (7, 0) to O$_2$ adsorption.

Wang, Xiao and Xia et al. calculated the O$_2$ 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$_2$ 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$_2$ on B$_2$–SiNT (7, 0) in present study is...
similar to corresponding values of O$_2$ on various nanostructures were calculated in previous theoretical works.

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$_2$–SiNT (7, 0) with O$_2$ molecule are displayed in Table 1. The $E_{\text{HLG}}$ values of O$_2$ adsorption on B–SiNT (7, 0), B–B–SiNT (7, 0) and B$_2$–SiNT (7, 0) are lower than SiNT (7, 0). The $E_{\text{HLG}}$ values of O$_2$ adsorption on B$_2$–SiNT (7, 0) are lower than B–SiNT (7, 0), B–B–SiNT (7, 0). The bridge position of B–B in B$_2$–SiNT (7, 0) has higher $q$ and lower $E_{\text{HLG}}$ than top position B in B$_2$–SiNT (7, 0) to O$_2$ adsorption. Complex of B$_2$–SiNT (7, 0) with O$_2$ molecule (2$d$ structure) is the most stable than other complexes of B–SiNT (7, 0), B–B–SiNT (7, 0) and B$_2$–SiNT (7, 0) with O$_2$ molecule.

Fig. 1  The initial structures of SiNT, B–SiNT, B–B–SiNT and B$_2$–SiNT and O$_2$, OH, H$_2$O, H$_2$O$_2$ and CO molecules.
0) and B–B–SiNT (7, 0) with O₂ molecule from thermodynamic view point. It can be concluded that O₂ adsorbed on B₂–SiNT (7, 0) in figure 2d significantly and there are suitable interactions between the O₂ molecule and B₂–SiNT (7, 0) and the adsorption of O₂ molecules on studied surfaces are chemical adsorption processes.

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 | \(q\) | \(E_{\text{HLG}}\) |
|---------|------|----------------|---------|------|----------------|---------|------|----------------|
| SiNT    | —    | 1.84           | B–SiNT  | 0.58 | 1.75           | B–B–SiNT| 0.69 | 1.68           | B₂–SiNT| 0.73 | 1.64           |
| 2a      | 0.36 | 1.69           | 2b      | 0.47 | 1.61           | 2c      | 0.59 | 1.52           | 2d      | 0.64 | 1.48           |
| 2e      | 0.29 | 1.75           | 2f      | 0.39 | 1.68           | 2g      | 0.51 | 1.59           | 2h      | 0.58 | 1.55           |
| 2i      | 0.32 | 1.72           | 2j      | 0.43 | 1.64           | 2k      | 0.54 | 1.56           | 2l      | 0.61 | 1.52           |
| 2m      | 0.49 | 1.33           | 2n      | 0.62 | 1.23           | 2o      | 0.73 | 1.17           | 2p      | 0.82 | 1.14           |
| 3a      | 0.41 | 1.54           | 3b      | 0.51 | 1.45           | 3c      | 0.65 | 1.38           | 3d      | 0.73 | 1.25           |
| 3e      | 0.59 | 1.14           | 3f      | 0.81 | 1.05           | 3g      | 0.84 | 0.99           | 3h      | 0.91 | 0.95           |
| 3m      | 0.11 | 1.80           | 3n      | 0.14 | 1.70           | 3o      | 0.19 | 1.62           | 3p      | 0.21 | 1.60           |
| 3q      | 0.08 | 1.82           | 3r      | 0.12 | 1.72           | 3s      | 0.15 | 1.64           | 3t      | 0.18 | 1.63           |

Fig. 2 Complexes of the SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B₂–SiNT (7, 0) with O₂ and OH molecules.
Table 2  The ∆E_{ad} (in eV) and ∆G_{ad} (in eV) values of studied complexes

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

In this study the interactions of important intermediates such as O, H, OOH, OH, H2O and CO molecules with SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B2–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 B2–SiNT (7, 0) with molecules are stated. ∆E_{ad}, q, ∆G_{ad}, ∆G_{ad} of molecules on SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B2–SiNT (7, 0) are reported in Tables 1 and 2. OH, O and OOH intermediates can be adsorb on B site of B–SiNT (7, 0), B–B–SiNT (7, 0) and B2–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 B2–SiNT (7, 0). It can be concluded that the complexes of B–SiNT (7, 0) with O, H, OOH, OH and H2O molecules are stable than SiNT (7, 0), B–SiNT (7, 0) and B–B–SiNT (7, 0).

Wang, Xiao and Xia et al.43–51 calculated the OOH and OH 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). ∆E_{ad} of O on B-doped graphene, silicon-carbon nano-sheets and N-doped graphene were −3.74, −4.11 and −3.55 eV. ∆E_{ad} of OH on boron-doped graphene, silicon-carbon nano-sheets and N-doped graphene were −2.38, −2.87 and −2.41 eV. ∆E_{ad} of OOH on B-doped graphene, silicon-carbon nano-sheets and N-doped graphene are −1.12, −1.18 and −1.06 eV. ∆E_{ad} values of OOH, OH and OOH (−1.17, −2.39 and −1.17 eV) on B2–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.43–51

The H2O molecule favored to adsorb on above ring position of SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B2–SiNT (7, 0) and the average of ∆E_{ad} and ∆G_{ad} values are −0.19 and −0.14 eV. The average of q and E_{H2G} values for adsorption of H2O molecule on SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B2–SiNT (7, 0) surface is 0.16 [e] and 1.68 eV. H2O molecule can be adsorbed on SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B2–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 (ΔE_{ad} is −1.90 eV) and CO poisoning was happen.26,26 The average of ∆E_{ad} and ∆G_{ad} of CO on SiNT, B–SiNT, B–B–SiNT and B2–SiNT surfaces are −0.11 and −0.08 eV. The average of q and E_{H2G} values for adsorption of CO on SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B2–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 B2–SiNT (7, 0) surfaces as physical adsorption processes. It can be concluded that B2–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.43–51 calculated the H2O and CO adsorption on surfaces of boron-doped graphene nanoribbon, silicon–carbon nano-sheets and B and N doped-graphene. The ∆E_{ad} of H2O on surfaces of B-doped graphene, silicon–carbon nano-sheets and N-doped graphene were −0.24, −0.18 and −0.08 eV. The ∆E_{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 ∆E_{ad} of H2O and CO (−0.24 and −0.14 eV) on B2–SiNT (7, 0) in present study are similar to

Table 3  The ΔE_{ad} and ΔE_{ad} for ORR on B2–SiNT (7, 0)

| Path | Studied reaction steps | ∆E_{ad} (eV) | ∆E_{ad} (eV) |
|------|------------------------|--------------|--------------|
| 1    | O2 + B2–SiNT (7, 0) → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
| 1    | B2–SiNT (7, 0)→O2 + H2 + e− → B2–SiNT (7, 0) | −0.68        | −0.68        |
corresponding values of H$_2$O and CO on various nanostructures were calculated in previous theoretical works.$^{49-51}$

### 3.2. B$_2$–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$_2$–SiNT (7, 0) as acceptable catalyst through the LH and ER mechanisms were investigated. As start, O$_2$ adsorption is investigated via O$_2$ dissociation or hydrogenation of O$_2$ to create B$_2$–SiNT (7, 0)–*OOH. Firstly, the O$_2$ dissociation process can be defined as B$_2$–SiNT (7, 0)–*O$_2$ $\rightarrow$ *O–B$_2$–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)).

|       | SiNT (7, 0) | B-SiNT (7, 0) | B-B-SiNT (7, 0) | B$_2$–SiNT (7, 0) |
|-------|-------------|---------------|----------------|-------------------|
| OOH   | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) | ![Image](image4.png) |
| Bond length | $3a$ (Si–O 1.95 Å) (O–O 1.54 Å) | $3b$ (B–O 1.51 Å) (O–O 1.51 Å) | $3c$ (B–O 1.49 Å) (O–O 1.49 Å) | $3d$ (B–O 1.53 Å) (O–O 1.47 Å) |
| O     | ![Image](image5.png) | ![Image](image6.png) | ![Image](image7.png) | ![Image](image8.png) |
| Bond length | $3e$ (Si–O 1.85 Å) | $3f$ (Si–O 1.83 Å) (B–O 1.47 Å) | $3g$ (B–O 1.45 Å) | $3h$ (Si–O 1.81 Å) (B–O 1.43 Å) |
| H     | ![Image](image9.png) | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| Bond length | $3i$ (Si–H 1.66 Å) | $3j$ (Si–H 1.64 Å) | $3k$ (Si–H 1.63 Å) | $3l$ (Si–H 1.64 Å) |
| H$_2$O | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) | ![Image](image16.png) |
| Distance | $3m$ (distance 3.21 Å) | $3n$ (distance 3.17 Å) | $3o$ (distance 3.14 Å) | $3p$ (distance 3.11 Å) |
| CO    | ![Image](image17.png) | ![Image](image18.png) | ![Image](image19.png) | ![Image](image20.png) |
| Distance | $3q$ (distance 3.34 Å) | $3r$ (3.27 Å) | $3s$ (distance 3.25 Å) | $3t$ (distance 3.22 Å) |

Fig. 3 Complexes of the SiNT (7, 0), B–SiNT (7, 0), B–B–SiNT (7, 0) and B$_2$–SiNT (7, 0) with O and H atoms, OOH, H$_2$O and CO molecules.
Fig. 4 The intermediates of ORR and relative energies: (1) B$_2$–SiNT (7, 0)–*O$_2$ → *O–B$_2$–SiNT (7, 0)–*O; (2) B$_2$–SiNT (7, 0)–*OOH → *O–B$_2$–SiNT (7, 0)–*OH; (3) B$_2$–SiNT (7, 0)–*OOH → B$_2$–SiNT (7, 0)–*O + H$_2$O; (4) B$_2$–SiNT (7, 0)–*O → B$_2$–SiNT (7, 0)–*OH; (5) B$_2$–SiNT (7, 0)–*OH → B$_2$–SiNT (7, 0)–* + H$_2$O; (6) B$_2$–SiNT (7, 0)–*OOH → *OH–B$_2$–SiNT (7, 0)–*OH; (7) *OH–B$_2$–SiNT (7, 0)–*OH → *OH–B$_2$–SiNT (7, 0) + H$_2$O; (8) B$_2$–SiNT (7, 0)–*OOH → B$_2$–SiNT (7, 0) + H$_2$O$_2$ → *OH–B$_2$–SiNT (7, 0)–*OH.
Secondary, adsorbed O\textsubscript{2} can interact via H atom to create B\textsubscript{2}–SiNT (7, 0)–*OOH as follow: B\textsubscript{2}–SiNT (7, 0)–*O\textsubscript{2} + H\textsuperscript{+} + e\textsuperscript{−} → B\textsubscript{2}–SiNT (7, 0)–*OOH, this process has no any activation barrier energy.

The OOH adsorption on of B\textsubscript{2}–SiNT (7, 0) has higher Δ\textit{E}_{ad} than O\textsubscript{2} ca. 0.29 eV and also O\textsubscript{2} dissociation on surface of B\textsubscript{2}–SiNT (7, 0) has high activation barrier energy. H atom is added into Si in B\textsubscript{2}–SiNT (7, 0)–*OOH and H atom reacted via B\textsubscript{2}–SiNT (7, 0)–*OOH. Then the B\textsubscript{2}–SiNT (7, 0)–*OOH dissociated to *O–B\textsubscript{2}–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\textsubscript{2}–SiNT (7, 0)–*OOH in ORR on B\textsubscript{2}–SiNT (7, 0) is suitable than dissociation of O\textsubscript{2} molecule.

The ORR is done through the B\textsubscript{2}–SiNT–*OOH intermediate as follows:

![Graph showing ORR values](image_url)

**Table 4** The Δ\textit{E}_{ad} (in eV) values of O\textsubscript{2}, O, OH and OOH on B-doped graphene, silicon–carbon nano-sheets and N-doped graphene and B\textsubscript{–}–SiNT (7, 0), B–B–SiNT (7, 0) and B\textsubscript{2}–SiNT (7, 0) in this study

| Catalysts/species | B-doped graphene | Si-C nano-sheet | N-doped graphene | B–SiNT (7, 0) | B–B–SiNT (7, 0) | B\textsubscript{2}–SiNT (7, 0) |
|------------------|------------------|----------------|------------------|--------------|----------------|----------------------|
| O\textsubscript{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                |

**Fig. 5** The \textit{G} values for ORR on B\textsubscript{2}–SiNT (7, 0).
Table 5  The onset-potential (in eV) values for the ORR performed on several catalysts$^{105-110}$

| Catalyst          | Onset potential | Catalyst          | Onset potential | Catalyst          | Onset potential |
|-------------------|-----------------|-------------------|-----------------|-------------------|-----------------|
| Pd/CNT$^{105}$    | 0.764           | Pd-Ni$^{107}$     | 1.105           | PdNi$^{109}$      | 1.040           |
| Pd/MWCNT$^{105}$  | 1.014           | PtCo/C$^{107}$    | 0.836           | Pd$^{109}$        | 0.901           |
| Pd-Ni(3:1)/C$^{106}$ | 1.005         | Pd-Fe/C$^{108}$   | 0.865           | Pd-Cu$^{110}$     | 1.001           |
| Pd$_x$Co/C$^{106}$ | 0.785          | Pd/C$^{110}$      | 0.920           | Pt/C$^{110}$      | 0.900           |

Investigated the onset-potential for the ORR performed on several catalysts$^{105-110}$ and results are stated in Table 5. The $G$ of ORR steps are stated in Fig. 5. The level of the final product ($B_2SiNT(7,0)$)$+2H_2O)$ 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 $B_2SiNT(7,0)$ 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 $B_2SiNT$ can be continued through LH and ER mechanisms. The rate-determining stage ($\Delta E_a = 0.35$ eV) for ORR on $B_2SiNT(7,0)$ surface is creation of $B_2SiNT(7,0)$--*OH structure. The calculated beginning voltage to ORR on surface of the $B_2SiNT(7,0)$ 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 $B_2SiNT(7,0)$ is suggested as catalyst to ORR with suitable efficacy.

Conflicts of interest

There are no conflicts to declare.

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