Molecular hydrogen and oxygen interactions with armchair Si nanotubes

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1 Introduction

Adsorptions of atoms and molecules in fine pores have been recognized to have fundamental interest in both applied and fundamental research, because of the reduced dimensionality, and technological importance, for many reasons, including separation of mixtures, hydrogen storage [1–3], etc. In particular, there has been considerable interest in evaluating the capability of nanotubes as a hydrogen-storage material for clean energy sources [4–6]. The US Department of Energy (DOE) has set up an objective of developing and verifying on-board hydrogen storage systems having a storage capacity of 5.5 wt% by 2015 [7] and, thus, the hydrogen storage capacity of single walled nanostructures has become extremely important. A number of publications are devoted to the experimental and theoretical study of gas adsorption on different adsorbent structures [8–11]. Dillon et al. [12] have reported that carbon nanotubes (CNTs) can be used for hydrogen storage and measured the H₂ adsorption capacity of single-walled carbon nanotubes (SWCNT) and the gravimetric storage capacity ranging between 5–10 wt%. Darkrim and Levesque [13] studied the influence of the distance between the nearest neighbors SWNT’s on adsorption using the Lennard-Jones potential. A detailed study [14] on hydrogen adsorption and storage in SWNTs and multi-walled nanotubes using density-functional-based tight-binding calculations has shown that many hydrogen atoms can be stored in the interior and adsorbed to the outer wall of carbon nanotubes, and that the hydrogen storage capacity is limited by the repulsive interactions between H₂ molecules and also those with carbon atoms. In 2000, the storage capacities of silicon carbide nanotubes were reported to be 7% [15]. Mukherjee and Ray [16] have investigated, in detail, the feasibilities of using silicon carbide (SiC) nanotubes as hydrogen storage media. The relatively promising results led to the development of many works on adsorption of hydrogen in nanotubes by molecular simulations and by experiments. Notwithstanding the simulations and experiments, there are no existing adsorbents that satisfy the DOE target to date. Hence, there is still a need to develop highly efficient adsorbents that are specifically designed for hydrogen storage. Silicon nanotubes have been intensively studied in anticipation of their application in novel nanoscale materials and device structures, as well as for their fundamental physics [17–23]. Our previous studies have shown that atomic hydrogen and oxygen can be chemisorbed by armchair SiNTs [24]. In this report, we consider the case of molecular hydrogen and oxygen adsorptions in silicon nanotubes.

Upon exposure to gaseous molecules, the electrical resistance of a semiconducting SWNT is found to
dramatically increase or decrease. We note that the electronic properties of single-walled carbon nanotubes (SWCNTs) can be appreciably altered by the presence of other adsorbed molecules [25]. This has important ramifications for device applications involving SWNTs, and it has led to considerable interest in the possible use of SWNTs as the basis of chemical sensors [26]. Oxygen, in particular, has been found to influence electronic properties of SWNTs, with the electrical resistance, the thermoelectric power, and the local density of states all depending on oxygen exposure [27]. More strikingly, it has been reported that small-gap semiconducting nanotubes can be made metallic upon exposure to a small amount of oxygen. The increased electrical conductivity induced by oxygen adsorption has been attributed to an increase in the local density of states and a shrinking of the band gap of the nanotube. Zhao et al. [28] have reported that the incorporation of oxygen atoms as silicon monoxides in (8, 0) single-walled zigzag silicon nanotube stabilizes the nanotube and can tailor the electronic structure from semiconducting to metallic. Whether the electronic parameters and geometry of the SiNTs will be changed by small concentration of molecular oxygen or even influence the adsorption of hydrogen is our concern in this study.

We note, here, that although multi-walled nanotubes (MWNTs) have been synthesized and investigated first, there are very few ab initio studies on MWNTs compared to single-walled nanotubes (SWNTs), partly because of the complexity of MWNTs compared to SWNTs and the associated significant increase in computational cost. The first logical step towards the study of adsorption on MWNTs would obviously be adsorption on SWNTs. Also, the structure of MWSiNTs is a matter of some critical debate and one of the underlying problems is that it strongly depends on the method of preparation. Though MWSiNTs are useful because they are stabilized by a large number of layers and available in relatively large quantities, SWSiNTs are more ideal for understanding electronic structure, adsorption, and transport phenomena. They are very important in nanoscopic applications because of their quasi-one-dimensional structure as also nanoscale diameters and they are not affected by inter-layer interactions. In this work, we have thus concentrated on the molecular adsorption on armchair SWSiNTs. In the following, we first present the computational method, followed by discussions of results and conclusions.

2 Computational method

Two standard methods in computational condensed matter physics are based on Hartree-Fork (HF) theory and density functional theory (DFT) in the local density approximation or in the generalized gradient approximation. Both methods have their advantages and disadvantages [29–36]. For example, DFT within the local spin density approximation calculations underestimate the band gaps of semiconductors. The discontinuity of exchange-correlation Kohn-Sham potential results in this discrepancy between theoretical and experimental band gaps [37,38]. On the other hand, hybrid density functional theory incorporating a mixture of HF exchange and DFT exchange-correlation has proved to be an efficient method for many systems. We note here that, though different DFT functionals may produce slightly different quantitatively but not qualitatively different results, studies on semiconducting materials have shown that, hybrid functionals, in particular, B3LYP is one of the most efficient and computationally inexpensive among all DFT functionals available for calculation of electronic and structural properties of the semiconducting materials. Hybrid functionals are in general found to be efficient in reproducing the band gaps of semiconductors and insulators [39,40] by treating the exchange part of the interactions better. Studies show that B3LYP has successfully predicted a wide range of material properties [41–47]. We have carried out here, first-principles calculations on molecular adsorption on SWNT using hybrid density functional theory. In particular, we have used B3LYP [48–50] (Becke’s 3-parameter and the Lee-Yang-Parr exchange-correlation hybrid functional) and the 3-21G* basis set as implemented in the GAUSSIAN 09 suite of programs for full geometry optimizations without any symmetry constraints of the nanotube structures [51]. All computations reported here have been performed using the supercomputing facilities of the University of Texas at Arlington.

Our approach for construction of the nanotubes is based on single-walled carbon nanotubes. Here, we have used finite cluster approach with dangling bonds terminated by hydrogen atoms to simulate the effect of infinite nanotubes. The easiest way to visualize how nanotubes are built is to start with graphite-like sheet of silicon. Then a single-walled nanotube (SWNT) is constructed by wrapping one single layer of the graphite-like sheet to form a cylindrical shape. The structure of such nanotubes can be described in terms of chirality and length. Chirality and diameter are specified in terms of the magnitude of the components of chiral vector. The chiral vector $C_h$ which maps an atom from the left hand border onto an atom on the right border is an integer multiple of the two basis vectors $a_1$ and $a_2$, i.e., $C_h = na_1 + ma_2$ with integers $n$ and $m$. Thus, the geometry of any nanotube can be described by the integer pair $(n, m)$ which determines the chiral vector. Depending upon how the sheet is rolled we have three types of tubes. For armchair $m = n$, for zigzag $m = 0$ and for chiral nanotubes $m \neq n$.

In our previous work [24], we have presented the binding energies per atom, the highest-occupied-molecular-orbital to lowest-unoccupied-molecular-orbital (HOMOLUMO) or the “band gap”, and other electronic structure properties for armchair SWSiNTs from (4, 4) to (12, 12). Both the binding energy per atom and the gap tend to saturate from (6, 6). Thus, the Si (6, 6) nanotube was chosen as the adsorbent since any larger armchair nanotube is not expected to provide any more insight into the chemistry and physics of the adsorption process and the computational cost obviously rises significantly with the size of the nanotube.
molecule, one being perpendicular and the other being parallel to the tube axis. For both perpendicular and parallel adsorptions, the hydrogen molecule could be placed outside or inside of the nanotube initially. We first investigated the molecular adsorption from outside of the nanotube. When the hydrogen molecule approached the SiNT from outside the nanotube, after optimization we note that for all of the four initial sites of perpendicular adsorption, the optimized structure of the nanotube and the hydrogen molecule has a H-H distance of 0.75 Å. Since in our calculation, the optimized H₂ distance without the nanotube was also 0.75 Å (the experimental bond length is 0.74 Å), it is reasonable to assume that the molecule did not dissociate and, in fact, maintained the original diatomic linear structure. In addition, for all four different initial sites, after optimization the hydrogen molecule moved to on-top site. For example, when the hydrogen molecule was placed in normal bridge site initially perpendicular to the tube axis (Fig. 2), after optimization the hydrogen molecule moved to the on-top site. However, in the case of parallel adsorption, the hydrogen molecule moved to various sites, still holding a molecular form. But the most stable site is still the on-top site. However, the hydrogen molecule changed its orientation from parallel to perpendicular to the tube axis. For example, in Figure 2, the hydrogen molecule was placed initially in an on-top site with the hydrogen molecule parallel to the tube axis, after optimization, the hydrogen molecule is still in an on-top site but realigns itself perpendicular to the tube axis. Hydrogen molecules, most likely orient themselves perpendicular to the tubes if adsorbed in on-top site.

As is well-known, silicon, in stable form, favors a sp³ configuration as opposed to a favored sp² configuration by carbon. In our study, the adsorbent is a bare Si (6, 6) nanotube with a smooth tube wall presenting a planar sp²-like structure. After adsorption of the hydrogen molecule, the surface of the nanotube becomes more puckered, indicating the possibility of the existence of sp³-like hybridization. To determine the possibility of any transition from sp² to sp³, we performed a natural bond orbital (NBO) analysis. The bare Si (6, 6) nanotube only has sp²-like bonds, which can be confirmed from the Gaussian NBO analysis [52]. The hybridization of silicon atoms on Si (6, 6) is around sp².01 on average. After adsorption of hydrogen molecule from outside of the nanotube, the hybridization of the silicon atoms increased to, on the average, to about around sp².41. It is evident that the transition from sp²-like to sp³-like hybridization among silicon atoms occurred after hydrogen adsorption. This tendency for sp²-sp³ hybridization upon H₂ adsorption is strong for Si (6, 6), because highly bent sp² bonding of the nanotube is favored for the transition to sp³-like bonding. It should be noted that although there is a tendency for the sp²-to-sp³ transition, we do not see pure sp³ hybridization of Si atoms on the tube. Figure 3 shows NBO plot of one Si atom on the Si (6, 6) nanotube after external adsorption of the hydrogen molecule with three σ bonds and one π bond again instead of four sp³-sp³ bonds. A careful examination of the structure of the nanotubes reveals that

3 Results and discussions

3.1 Adsorptions of hydrogen molecule

The study of single hydrogen molecule adsorption has been performed with two orientations for the hydrogen

\[
E_a = \begin{cases} 
[E (\text{SiNT}) + E (X_2)] - E (\text{SiNT} + X_2), & \text{if the molecule does not dissociate} \\
[E (\text{SiNT}) + 2E (X)] - E (\text{SiNT} + 2X)/2, & \text{if the molecule dissociates}
\end{cases}
\]

where \( E (\text{SiNT}) \) is the ground state total energy of the bare silicon nanotube, \( E (X_2) \) and \( E (X) \) are the ground state energies of the X molecule and atom, respectively, \( E (\text{SiNT} + X_2) \) and \( E (\text{SiNT} + 2X) \) are the total energies of the optimized clusters incorporating SiNT and the adsorbed molecule or atom. As mentioned before, all nanotubes are hydrogen terminated at two ends to saturate the dangling bonds and to simulate the effect of “infinite” tubes. The radial buckling was calculated by taking the standard deviation of the distance from the Si atoms to the tube axis.

We describe the interaction of molecules with SiNTs for (1) adsorption from outside of nanotube, (2) adsorption from inside of nanotube, (3) molecular axis perpendicular to the tube axis, (4) molecular axis parallel to the tube axis. To find the most stable configuration, several adsorption sites have been considered, depending on the position and orientation of molecular bond. The molecule can be located at the top of Si atom, the bridge of Si-Si bond (normal bridge site and the zigzag bridge site), and the center of the Si hexagon (hollow site) (Fig. 1).

The adsorption energy for each system was computed from:

\[
E_a = \begin{cases} 
[E (\text{SiNT}) + E (X_2)] - E (\text{SiNT} + X_2), & \text{if the molecule does not dissociate} \\
[E (\text{SiNT}) + 2E (X)] - E (\text{SiNT} + 2X)/2, & \text{if the molecule dissociates}
\end{cases}
\]
there are basically two kinds of local geometrical configurations for the Si atoms, one being pyramidal (the sum of the angles between one Si atom and other three Si atoms surrounding it is approximately 338°) and the other planar (approximately 355°) (Fig. 4). There is an alternation of these two kinds of structures throughout the nanotube, attributed to the existence of possible geometrical frustration effect [53]. The geometrical frustration is revealed in that a certain type of local order favored by physical interactions cannot propagate throughout space. However, in the case of Si nanotubes, the frustration effect resulted in the co-existence of two different local structures. In Figure 5, we note that the hexagonal ring in our study has a chair-like ring structure, with the “chair seat” flattened to some extent. This “flattened chair seat” effect could be more pronounced in silicon nanotubes with small diameters. As the number of atoms increases, the structure will gradually switch to that of the bulk at some point where a particular bond geometry that is characteristic of the extended solid is energetically preferred. It can be noted that there is an outward and inward local structural distortion along the radial direction, which is consistent with significant increase of the radial buckling from 0.039 Å to 0.26 Å. The large adsorption energy of hydrogen molecule on Si (6, 6) could also be mostly from the “frustration” of the local structure on the surface induced by the adsorption of hydrogen molecule.
Table 1. Adsorption energies in eV for different adsorption sites, the corresponding optimized distances from the adsorbed molecule to the nearest silicon atom in Å, HOMO-LUMO gaps in eV and radial buckling in Å.

| Initial site | Final site | $D_{H-Si}$ (Å) | $D_{H-H}$ (Å) | Adsorption energy (eV) | HOMO-LUMO gap (eV) | Radial buckling (Å) |
|--------------|------------|----------------|---------------|-----------------------|-------------------|-------------------|
| Normal B.    | On-top     | 3.31           | 0.75          | 3.71                  | 1.26              | 0.261             |
| Zigzag B.    | On-top     | 3.31           | 0.75          | 3.71                  | 1.26              | 0.261             |
| Hollow       | On-top     | 3.31           | 0.75          | 3.71                  | 1.26              | 0.261             |
| On-top       | On-top     | 3.31           | 0.75          | 3.71                  | 1.26              | 0.261             |

Table 2. Adsorption energies in eV for different adsorption sites, the corresponding optimized distances from the adsorbed molecule to the nearest silicon atom in Å, HOMO-LUMO gaps in eV and radial buckling in Å.

| Initial site | Final site | $D_{H-Si}$ (Å) | $D_{H-H}$ (Å) | Adsorption energy (eV) | HOMO-LUMO gap (eV) | Radial buckling (Å) |
|--------------|------------|----------------|---------------|-----------------------|-------------------|-------------------|
| Normal B.    | Normal B.  | 4.99           | 0.75          | 1.80                  | 0.37              | 0.247             |
| Zigzag B.    | Zigzag B.  | 3.97           | 0.75          | 2.50                  | 0.56              | 0.254             |
| Hollow       | Hollow     | 3.99           | 0.75          | 2.64                  | 0.96              | 0.341             |
| On-top       | On-top     | 3.67           | 0.75          | 3.69                  | 1.26              | 0.264             |

Fig. 5. Side and top views of “chair-like” hexagonal ring after molecular adsorption on Si (6, 6) nanotube (two yellow and two green Si atoms are overlapping each other so we only see one atom from side view).

As far as bond lengths are concerned, the bare Si (6, 6) nanotube before adsorption has an average bond length of 2.240 Å. After adsorption, the average bond length increased to 2.269 Å. The bond-length measurements showed that the frustration effect is mainly caused by the local strain because a change in bond lengths occurs only for Si-Si bonds. We also examined the HOMO-LUMO gaps (Tabs. 1 and 2) and the Mulliken charge distribution (Fig. 6) on the nanotubes. The bare Si (6, 6) nanotube has a HOMO-LUMO gap of 0.98 eV and the charges on Si atoms are all very close to zero which means the absence of any charge polarization. The HOMO-LUMO gap increased from 0.98 eV to 1.26 eV for the most stable on-top site after adsorption of hydrogen molecule and significant charge polarization was observed on the nanotubes. For parallel adsorption in Figure 2, after optimization the Mulliken charge is $-0.007e$ and $0.009e$ on the two hydrogen atoms. The hydrogen atom with Mulliken charge of $0.009e$ is closer to nanotube than the other. The nearest Si atom has a Mulliken charge of $-0.097e$. The hydrogen molecule is slightly polarized and attracted to the nanotube by the negatively charged Si atom. Each negatively charged Si atom is surrounded by three positively charged Si atoms and vice versa. The negatively charged Si atoms are displaced away from the surface forming the tip of the pyramid. The driving force for such surface reconstruction effect is the attempt of the surface to lower its energy. This effect is similar as the relaxation at the (100) surface of sodium chloride while the negative chloride ions are displaced away from the bulk and the positive sodium cations are displaced inwards [54]. Since the HOMO-LUMO gap gives an indirect estimate of the electrical conductivity of the nanotube, the increase of the gap upon adsorption of hydrogen molecule implies a possible decrease of the electrical conductivity.
Fig. 7. Perpendicular and parallel adsorptions of $\text{H}_2$ from inside of the nanotube.

**Table 3.** Adsorption energies in eV for different adsorption sites, the corresponding optimized distances from the adsorbed molecule to the nearest silicon atom in Å, HOMO-LUMO gaps in eV and radial buckling in Å.

| Initial site | Final site | $D_{\text{H-Si}}$ (Å) | $D_{\text{H-H}}$ (Å) | Adsorption energy (eV) | HOMO-LUMO gap (eV) | Radial buckling (Å) |
|-------------|------------|---------------------|---------------------|-----------------------|--------------------|---------------------|
| Normal B.   | On-top     | 3.18                | 0.75                | 3.70                  | 1.26               | 0.261               |
| Zigzag B.   | On-top     | 3.44                | 0.75                | 2.11                  | 0.79               | 0.246               |
| Hollow      | On-top     | 3.27                | 0.75                | 2.66                  | 0.99               | 0.356               |
| On-top      | On-top     | 3.21                | 0.75                | 3.70                  | 1.26               | 0.261               |

**Table 4.** Adsorption energies in eV for different adsorption sites, the corresponding optimized distances from the adsorbed molecule to the nearest silicon atom in Å, HOMO-LUMO gaps in eV and radial buckling in Å.

| Initial site | Final site | $D_{\text{H-Si}}$ (Å) | $D_{\text{H-H}}$ (Å) | Adsorption energy (eV) | HOMO-LUMO gap (eV) | Radial buckling (Å) |
|-------------|------------|---------------------|---------------------|-----------------------|--------------------|---------------------|
| Normal B.   | Normal B.  | 4.83                | 0.75                | 2.65                  | 0.95               | 0.362               |
| Zigzag B.   | On-top     | 3.77                | 0.75                | 3.69                  | 1.26               | 0.261               |
| Hollow      | Hollow     | 3.65                | 0.75                | 2.70                  | 0.99               | 0.244               |
| On-top      | On-top     | 3.82                | 0.75                | 3.69                  | 1.26               | 0.264               |

The internal adsorption of hydrogen molecule showed similar trends as external adsorption. The parallel adsorption tends to be, in general, less favorable because after optimization the hydrogen molecule changed its orientation from parallel to perpendicular to the tube axis. In both perpendicular and parallel cases, the hydrogen molecule does not dissociate, with a bond length of 0.75 Å. In perpendicular adsorption, on-top site is the only preferred site whereas in the parallel adsorption on-top site is the most preferred site, in agreement with the most stable site for the external adsorption. Figure 7 shows a typical example of the hydrogen molecule placed initially in normal bridge site perpendicular to the tube axis and moving to the on-top site with the molecular axis perpendicular to the tube axis after optimization. Figure 7 also shows a similar example of the hydrogen molecule placed initially in zigzag bridge site parallel to the tube axis and moving to the on-top site perpendicular to the tube axis after optimization. However, for perpendicular adsorption, although the on-top site is the only preferred site the adsorption energies for the four different initial sites are not the same. It should be noted that, in general, as the distance between the hydrogen molecule and the nearest Si atom increases, the adsorption energy decreases as a result of weaker interaction (Tabs. 3 and 4). Similar to external adsorption, the HOMO-LUMO gap increases for the on-top site, accompanied also by increases in radial buckling and the average Si-Si bond length. NBO and geometrical analysis also yield similar results as for the external adsorption of hydrogen molecule (Fig. 8). There is $sp^2$-to-$sp^3$ transition occurring throughout the tube and also alternate pyramidal and planar configurations are observed throughout the nanotube. The stretch of Si-Si bond length was also observed for internal adsorption, resulting in effects similar to applications of mechanical stress [55]. In our study, the adsorption of the hydrogen molecule on the on-top site results in an increase of the band gap. This may be explained by the more $sp^3$ character contribution to the decrease of
the oxygen molecule dissociated into two atoms.

In general, molecular chemisorptions of O$_2$ on the SiNT sidewall is stronger than H$_2$, as indicated by larger adsorption energies. The bond length measurement shows a significant charge transfer between two oxygen atoms and the neighboring silicon atoms due to the difference in the electronegativities between O and Si atoms (Fig. 10). The electronegativity of oxygen is larger than silicon and thus there is charge transfer from Si to O which can be confirmed from the figure. Although in three cases the oxygen atoms are all at the normal bridge and zigzag bridge sites, their adsorption energies, HOMO-LUMO gap, as well as distance between the two dissociated oxygen atoms differ from case to case. The oxygen molecule did not dissociate when we placed the molecule at the on-top site initially perpendicular to the tube axis.

The O-O distance is 1.58 Å indicating a slightly stretched O-O molecular bond, and the bond is parallel to the Si-Si bond bridge. The oxygen molecule and the neighboring Si atoms form a Si-O-O-Si structure (Fig. 10b), thus, giving rise to a charge-transfer complex (CT complex). In this charge-transfer complex, a fraction of electronic charge is transferred between the oxygen molecule and the single-walled SiNT. The resulting electrostatic attraction provides a stabilizing force for the complex. This nature of attraction in a charge-transfer complex is not a stable chemical bond and is much weaker than covalent bond. The total energy of this complex is higher than the three dissociative cases indicating this structure may be an intermediate or transition state.

### Table 5. Adsorption energies in eV for different adsorption sites, the corresponding optimized distances from the adsorbed molecule to the nearest silicon atom in Å, HOMO-LUMO gaps in eV and radial buckling in Å.

| Initial site | Final site | $D_{O-Si}$ (Å) | $D_{O-O}$ (Å) | Adsorption energy (eV) | HOMO-LUMO gap (eV) | Radial buckling (Å) |
|--------------|------------|----------------|----------------|------------------------|-------------------|-------------------|
| Normal B. NB + ZB 1.65/1.68 2.80 | 9.64 | 1.01 | 0.309 |
| Zigzag B. NB + ZB 1.71/1.72 3.53 | 9.26 | 1.00 | 0.278 |
| Hollow NB + ZB 1.71/1.72 3.69 | 9.27 | 0.95 | 0.292 |
| On-top Top + Top 1.74/1.74 1.58 | 5.18 | 0.87 | 0.340 |

Fig. 8. NBO plot of a Si atom on Si (6, 6) after internal adsorption of single hydrogen molecule: (a) the three $sp^2$-like bonding, (b, c) the π bond.
Table 6. Adsorption energies in eV for different adsorption sites, the corresponding optimized distances from the adsorbed molecule to the nearest silicon atom in Å, HOMO-LUMO gaps in eV and radial buckling in Å.

| Initial site | Final site | $D_{O-Si}$ (Å) | $D_{O-O}$ (Å) | Adsorption energy (eV) | HOMO-LUMO gap (eV) | Radial buckling (Å) |
|--------------|------------|----------------|----------------|-----------------------|-------------------|-------------------|
| Normal B.    | Top + Top  | 1.74/1.72      | 1.57           | 5.68                  | 1.02              | 0.308             |
| Zigzag B.    | Top + Top  | 1.74/1.74      | 1.58           | 5.19                  | 0.87              | 0.339             |
| Hollow       | NB + NB    | 1.65/1.64      | 3.68           | 9.57                  | 0.80              | 0.340             |
| On-top       | Top + Top  | 1.73/1.75      | 1.58           | 5.66                  | 1.02              | 0.298             |

Fig. 9. Perpendicular and parallel adsorptions of $O_2$ from outside of the nanotube.

Fig. 10. Local adsorption configurations and Mulliken charge of $O_2$ on the sidewall of SiNTs. (a) The external adsorption with both oxygen atoms on bridge sites and (b) the external adsorption with the oxygen molecule parallel to the bridge.

Fig. 11. NBO plot of a Si atom on Si (6, 6) after external adsorption of single oxygen molecule. (a) The three $sp^2$-$sp^2$ like bonding, (b, c) the $\pi$ bond. Red atoms are oxygen atoms.

effect are also observed on the nanotube. Figure 11 shows the NBO analysis for external oxygen adsorption.

When the oxygen molecule is adsorbed from inside of the nanotube, the molecule also dissociated into two atoms in most cases. For example, in perpendicular adsorption, the two oxygen atoms all moved to zigzag bridge sites (Fig. 12) with adsorption energy of 9.61 eV (Tab. 7) when we placed the oxygen molecule in zigzag bridge site initially. The dissociated oxygen atoms could also be adsorbed in two normal bridge sites with smaller adsorption energy. The radial buckling for the internal adsorption is larger than the external adsorption indicating there is greater surface deformation. This is reasonable because when the oxygen molecule is placed inside of nanotube it could interact with more silicon atoms. The interaction of the oxygen with more silicon atoms induces greater deformation. When the oxygen molecule was placed in on-top site initially it did not dissociate with slightly increased bond length of 1.56 Å. And the O-O bond is parallel to the Si-Si bond bridge.

In the case of parallel adsorption, the dissociated oxygen atoms moved to two normal bridge sites with an adsorption energy of 8.73 eV when the initial site is hollow site, or two zigzag bridge sites (Fig. 12) with an adsorption energy of 9.93 eV when the oxygen molecule was placed in on-top site initially (Tab. 8). When the oxygen molecule was placed in normal bridge or zigzag bridge site it did not dissociate and the oxygen molecule has a stretched...
Table 7. Adsorption energies in eV for different adsorption sites, the corresponding optimized distances from the adsorbed molecule to the nearest silicon atom in Å, HOMO-LUMO gaps in eV and radial buckling in Å.

| Initial site | Final site | \(D_{O-Si}\) (Å) | \(D_{O-O}\) (Å) | Adsorption energy (eV) | HOMO-LUMO gap (eV) | Radial buckling (Å) |
|-------------|------------|------------------|----------------|---------------------|-------------------|-------------------|
| Normal B.   | NB + NB    | 1.72/1.72        | 3.81           | 8.93                | 0.66              | 0.367             |
| Zigzag B.   | ZB + ZB    | 1.65/1.76        | 3.96           | 9.62                | 0.69              | 0.382             |
| Hollow      | ZB + ZB    | 1.7/1.72         | 3.26           | 9.00                | 0.97              | 0.383             |
| On-top      | Top + Top  | 1.71/1.73        | 1.56           | 5.60                | 0.79              | 0.398             |

Table 8. Adsorption energies in eV for different adsorption sites, the corresponding optimized distances from the adsorbed molecule to the nearest silicon atom in Å, HOMO-LUMO gaps in eV and radial buckling in Å.

| Initial site | Final site | \(D_{O-Si}\) (Å) | \(D_{O-O}\) (Å) | Adsorption energy (eV) | HOMO-LUMO gap (eV) | Radial buckling (Å) |
|-------------|------------|------------------|----------------|---------------------|-------------------|-------------------|
| Normal B.   | Top + Top  | 1.74/1.73        | 1.58           | 5.24                | 0.85              | 0.346             |
| Zigzag B.   | Top + Top  | 1.76/1.76        | 1.57           | 5.17                | 0.88              | 0.290             |
| Hollow      | NB + NB    | 1.73/1.72        | 3.69           | 8.73                | 0.61              | 0.287             |
| On-top      | ZB + ZB    | 1.64/1.72        | 2.77           | 9.93                | 1.23              | 0.311             |

Fig. 12. Perpendicular and parallel adsorptions of \(\text{O}_2\) from inside of the nanotube.

bond length. The oxygen molecule also forms a Si-O-O-Si structure with the neighboring silicon atoms accompanied by large charge transfer. We note that, the oxygen molecule is more likely to form the charge-transfer complex when it was placed parallel to the tube axis either for external or internal adsorption. This structure is also reported to have been observed in the initial stage of Si oxidation [56]. However, it is also reported that the Si-O-O-Si structure is energetically very unstable. In our study, the clusters with the Si-O-O-Si structure all have a higher energy than the clusters with dissociative oxygen atoms indicating a less stable structure of Si-O-O-Si. For example, the cluster with Si-O-O-Si structure in Figure 10b has a total energy about 4.53 eV higher than the cluster with dissociated \(\text{O}_2\) molecule in Figure 10a. Also the O-O bond length in Si-O-O-Si structure is 1.58 Å indicating a stretch of original \(\text{O}_2\) molecule bond length of 1.30 Å. In fact, studies have shown that an \(\text{O}_2\) molecule is not stable in Si lattice and only the dioxygen complex formed from two O atoms with a common Si neighbor can be stable in certain configuration [57]. Our calculation has confirmed the existence of the Si-O-O-Si less favorable peroxide structure because of the lower adsorption energy as indicated above. A possible dissociation mechanism could be as follows: first, some electron charge from the tube wall reaches the highly electronegative \(\text{O}_2\), then the double O=O bond of the physisorbed \(\text{O}_2\) changes to a weaker O-O bond forming peroxide structure with Si atoms. Then the single O-O bond is broken and the \(\text{O}_2\) molecule dissociates moving to bridge sites on SiNTs.

When the oxygen molecule dissociates the two oxygen atoms prefer to be adsorbed in bridge sites – two normal bridge sites, or two zigzag bridge sites, or one normal bridge site and one zigzag bridge site. Highly reactive oxygen and silicon has a large difference in electronegativity (1.90 for silicon and 3.44 for oxygen) and, thus, it is comparatively easy to form Si-O-Si structure. The formation of the Si-O-Si has been observed on Si surface [58,59].
There are two types of Si-O-Si in our study of SiNTs. One type is that although the oxygen atom is interacting with both Si atoms, the two Si atoms also interact with each other. In the other case, the oxygen atom is breaking the Si-Si bond and bridging the two Si atoms. Hoshino [60] has studied adsorption of atomic and molecular oxygen on Si (111) surface. The Si-O-Si structure without the elimination of Si-Si bond is a transition state in his study and the bridging structure has a much lower potential energy. In silicon oxides, the Si-O-Si bond angles are not as rigid as the O-Si-O angles, which are close to the value of standard sp$^3$ hybridization (109.5°) and can vary widely in different phases. In Figure 10a, the oxygen atom with Mulliken charge –0.566e is breaking the Si-Si bond and forming a Si-O-Si chain structure, in which the Si-O bond length is 1.67 Å and 1.65 Å, respectively, and the O-Si-O angle is 137.6°. The oxygen atom with Mulliken charge of –0.491e is forming a Si-O-Si ring structure with two Si atoms, in which the Si-O bond length is 1.68 Å and 1.75 Å, the Si-Si bond length is 2.24 Å and the Si-O-Si angle is 81.2°. This is important in that it indicates in the Si-O-Si ring structure the Si-Si bond is a stable covalent bond and the other Si-O-Si bond formed by oxygen interstitially in silicon is very similar to that of SiO$_2$.

4 Conclusions

Internal and external molecular hydrogen and oxygen absorptions on a (6, 6) armchair silicon tube have been studied by full geometry and spin optimizations without any symmetry constraints with an all electron 3-21G* basis set and the B3LYP functional. The molecule was originally placed perpendicular or parallel to the tube axis. Hydrogen adsorption with the molecular axis aligned parallel to the surface of the nanotube is less favorable. Hydrogen molecule does not dissociate while oxygen molecule dissociates after optimization. The on-top site is the preferred site for hydrogen molecule with an adsorption energy of 3.71 eV and an optimized distance of 3.31 Å for external adsorption whereas the on-top site is the most preferred site with adsorption energy of 3.70 eV for internal adsorption and an optimized distance of around 3.2 Å. The adsorption of hydrogen in silicon nanotube which takes place near the surface would induce surface deformation and frustration. The deformation or the frustration is accompanied by the transition of the hybridization of Si atoms on SiNTs from sp$^2$ to sp$^3$. For oxygen, the molecule dissociates and the most preferred sites are the two bridge sites with an adsorption energy of 9.64 eV, the optimized distance being 1.65/1.68 Å when it is adsorbed from outside of the tube. When oxygen molecule is originally placed at on-top site it will hold as a molecule after adsorption with a slightly increased bond length. For the internal adsorption of oxygen, the molecule also dissociates in most cases and the zigzag bridge site is the most preferred site with an adsorption energy of 9.93 eV. The oxygen molecule could also be adsorbed parallel to the silicon bridge on the surface to form a Si-O-O-Si structure. But this structure is less stable than the dissociative adsorption. The oxygen molecule could also be adsorbed parallel to the silicon bridge on the surface to form a Si-O-O-Si structure. But this structure is less stable than the dissociative adsorption. After molecular adsorption for both hydrogen and oxygen, the buckling of the nanotubes increased.

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