Density functional study of oxygen adsorption on 4-Å carbon nanotubes

H. J. Liu,^{1,2} C. T. Chan,² Z. Y. Liu,¹ and J. Shi¹¹*Department of Physics, Wuhan University, Wuhan 430072, China*²*Department of Physics and Institute of Nano-Science and Technology, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China*

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Adsorptions of both oxygen atoms and oxygen molecules on 4 Å single-wall carbon nanotubes, which have been fabricated using a templating method recently, are studied by the plane-wave pseudopotential method. Our calculations will provide some useful information on the stability of such ultrasmall tubes under ambient environment. We found that the calculated oxygen binding energy shows strong chirality dependence. Different adsorption pictures of singlet O₂ can be used to select a single chirality from these ultrasmall-radius tubes.

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I. INTRODUCTION

In the past decade, carbon nanotubes have been intensively studied because of their interesting novel properties and great potential application in nanotechnology. A single-wall carbon nanotube (SWNT) can be viewed as a graphene sheet rolled into a cylinder so that the structure is quasi one dimensional and usually has a helical arrangement of carbon hexagons. Although theoretical calculations^{1,2} had shown that tubes with diameters of 4 Å are energetically stable, the existence of such small tubes was in dispute for a long time. Recently, ultrasmall-radius SWNT's have been successfully fabricated inside the confined environment of inert AlPO₄-5 zeolite (AFI) channels.³⁻⁶ These nanotubes are perfectly aligned with a diameter of about 4 Å. Their existence has now been supported by techniques including Raman, x-ray, and direct transmission electron microscopy (TEM) imaging.

There is currently growing interest in the interaction of carbon nanotubes with oxygen. Experimentally it has been shown that the electronic and transport properties of carbon nanotubes are extremely sensitive to oxygen exposure.⁷⁻⁹ One obvious application of such sensitivity is the construction of gas sensors built from SWNT's. On the theoretical side, many calculations and analyses with different levels of sophistication have been reported.¹⁰⁻²⁵ Some of these studies are focused on the physisorption of O₂ while others consider both physisorption and chemisorption. Various adsorption sites, both inside and outside of SWNT's are discussed and compared with each other and also with graphene. Although some conclusions are similar, there are also several controversial results about the oxygen binding energies and the equilibrium bonding distance between oxygen and tube, and whether the reaction is exothermic or endothermic.

To date, most of these works are focused on the zigzag and armchair SWNT's with relatively larger diameters—say, (8,0) and (6,6). To the best of our knowledge, there is no theoretical investigation of the oxygen adsorption of ultrasmall (~4 Å in diameter) SWNT's and, in particular, the effect of chirality, which is expected to be stronger in smaller-diameter tubes. There are actually three types of SWNT's with diameters of about 4 Å: namely, the zigzag (5,0), the armchair (3,3), and the chiral (4,2). Evidence from

the breathing modes measured using Raman and optical absorption measurements suggest that all of them are made using the zeolite template method.^{6,26,27} While these tubes are usually confined inside the zeolite template, the zeolite can be dissolved by acid to recover them as standalone entities. These tubes are expected to be more reactive than larger-diameter tubes due to their large curvature, and thus whether they are air stable is an issue that needs to be addressed. In this work, density functional theory (DFT) calculations are used to study the adsorption of oxygen on the outer surface of these 4 Å tubes. We will discuss the calculated atomic structure, binding energies, electronic structure, and chirality dependence. The results will also tell us whether these tubes are stable (and if so, how stable) when they are exposed in ambient conditions. We will consider adsorption of both O atoms and O₂ molecules in our discussions.

II. MODELS AND COMPUTATIONAL METHOD

The total energy calculations were performed using the plane-wave pseudopotential method²⁸⁻³⁰ with generalized gradient approximation (GGA) correction of the exchange-correlation energy,³¹ and the energy cutoff is set to 29.1 Ryd in the present work. For adsorption of O atom, we adopt a standard supercell geometry so that the tubes (together with the adsorbed O atoms) are aligned in a hexagonal array³² and the center-to-center distance between nearest tubes in the supercell is 16 Å. This large separation allows for negligible interaction between the tube and its periodic images, even when the oxygen atoms are attached to the tube surface. We also need to keep a reasonably large distance between the adsorbed O atoms along the tube axis. For the armchair (3,3), since the length of the primitive cell is relatively short, we use a double-primitive-cell configuration with a nominal formula of C₂₄O. For the zigzag (5,0) and chiral (4,2), we put one O atom in each primitive cell, giving nominal formulas of C₂₀O and C₅₆O, respectively. The initial distance between tube and O atom is set at about 1.2 Å. Unless indicated otherwise, spin polarization is considered in the calculations. For adsorption of O₂ molecule, the model is the same except that two O atoms are introduced with an initial bond length

of 1.2 Å. The Brillouin zones of the supercell is sampled with $1 \times 1 \times 20$ Monkhorst meshes for the case of (5,0) tube, and equivalent $\mathbf{k}$ -point sets are used for (3,3) and (4,2) tubes. Atomic positions are fully relaxed.

III. RESULTS AND DISCUSSIONS

We begin our investigation with single-O-atom adsorption on the outer surface of the 4 Å tubes. For tubes (5,0), (3,3), and (4,2), there are basically two distinct adsorption sites of single O atom on the outer surface of the tubes. One site (labeled as site I) is associated with the carbon-carbon bonds that are aligned “along” the tube axis, and the other (labeled as site II) is associated with the bonds that are wrapping “around” the tube circumference. Figure 1 is a ball-and-stick model of these two adsorption sites for tubes (5,0), (3,3), and (4,2), respectively. We note these are adsorption configurations before structural relaxations.

Upon relaxations of all six configurations, we observed the addition of two C-O bonds with obvious geometrical distortion caused by the adsorption of oxygen. However, such distortion is quite different between site I and site II. For example, the adsorption of oxygen atom on site I of zigzag (5,0) leads only to an increase of the underlying C-C distance (from 1.40 Å to 1.46 Å) and the C-C bond survives, leading to sp^3 hybridization for the two C atoms. However, the adsorption of oxygen atom on site II of (5,0) dramatically changes the tube’s geometry and the breaking of corresponding C-C bond is observed (C-C distance increases from 1.45 Å to 2.18 Å). Similar results are found for the armchair (3,3) and chiral (4,2), as well as those found in previous reports for other tubes.^{16,18,24} The difference between these two adsorption sites is due to curvature effect that weakens the carbon bonds that are wrapping around the circumference of the tube.^{16,27}

To examine the binding properties of these tubes, we have calculated the total energy of the tube+O, as well as the pristine tube and the spin-polarized O₂ molecule. The binding energy E_b is calculated using the expression

$$E_b = E(\text{tube} + \text{O}) - E(\text{tube}) - \frac{1}{2}E(\text{O}_2), \quad (1)$$

To minimize any artificial supercell effects, the total energy of O₂ is calculated in the same supercell as that used in the tube+O system. The bond length of spin-polarized O₂ we obtained is 1.24 Å, in good agreement with the experimental value of 1.21 Å. The calculated binding energies for different adsorption sites are summarized in Table I together with the corresponding structural parameters. This table contains some interesting features. First, all the calculated binding energies are negative. As defined by Eq. (1), this means that the adsorption of the O atom is exothermic for all the three tubes. The high-energy-gain is an indication of a chemisorption process. Second, for each tube, we find that site II always has a lower O binding energy (means more stable) than site I, which is consistent with the observation that $R_{\text{C-O}}(\text{II})$ is always smaller than $R_{\text{C-O}}(\text{I})$ for each tube and again can be attributed to the curvature effect. Third, the O binding energy

FIG. 1. (Color online) Ball-and-stick model (before relaxations) of a single O atom adsorbed on tube (5,0) at site I (top, left), tube (5,0) at site II (top, right), tube (3,3) at site I (middle, left), tube (3,3) at site II (middle, right), tube (4,2) at site I (bottom, left), and tube (4,2) at site II (bottom, right).

shows a strong chirality dependence with the order $E_b(5,0) < E_b(4,2) < E_b(3,3)$ on site I and reversed order on site II. Here a more negative number means stronger binding and higher stability. Furthermore, the energy difference between site I and site II is smallest for tube (5,0) and highest for tube (3,3), with tube (4,2) in between. All these findings agree well with those obtained from another density functional calculation.³³ We want to note that here chirality plays an important role. We see that although site I and site II have

TABLE I. Calculated binding energy (in eV) for one O atom adsorbed on tubes (5,0), (3,3), and (4,2): $E_b(\text{I})$ for O atom on site I and $E_b(\text{II})$ for site II. The corresponding structural parameters (in units of Å) are also listed: $R_{\text{C-C}}$ is the underlying C-C distance, and $R_{\text{C-O}}$ is the distance between O atom and its nearest C atom.

Tube	$E_b(\text{I})$	$E_b(\text{II})$	$R_{\text{C-C}}(\text{I})$	$R_{\text{C-O}}(\text{I})$	$R_{\text{C-C}}(\text{II})$	$R_{\text{C-O}}(\text{II})$
(5,0)	-0.94	-1.06	1.46	1.45	2.18	1.39
(4,2)	-0.38	-1.77	1.48	1.47	2.13	1.41
(3,3)	-0.10	-1.97	1.49	1.48	2.14	1.41

quite different geometrical configurations upon oxygen adsorption, the binding energy difference for zigzag (5,0) is quite small, while that of (3,3) is large and this is correlated with the chiral angle. Such similarity of the oxygen binding energy between site I and site II is also observed for larger-diameter zigzag tubes.^{16,24}

The sensitivity of the electronic properties of SWNT's upon exposure to oxygen has attracted a lot of interest, one reason being its potential application in chemical sensors. It is shown that oxygen adsorption may change semiconducting SWNT into metallic.⁷ In Fig. 2, we present the calculated energy band structures near the Fermi level for these 4 Å tubes with a single O atom adsorbed on different sites. For comparison, the band structures of pristine tubes with the same supercell are also shown. A denser mesh of 50 **k** points along the Γ X direction is used for such calculations. From these figures, we find that there are indeed dramatic changes of the band structure when the O atom is adsorbed. Also, the band structure of tube with O on site I is quite different from that on site II. We want to emphasize that the electronic structure depends on the coverage and the adsorption pattern of oxygen.¹⁶ For the present configuration, we found that (4,2) remains semiconducting upon oxygen adsorption and there is no significant change of the calculated energy gap. For tube (5,0), there is a decrease of the density of states (DOS) at the Fermi level for both site I and site II. It is worth mentioning that for tube (3,3) with the O atom adsorbed on site II, the Fermi level is located slightly below two rather flat bands near the X point; as a consequence, the DOS at the Fermi level is very high [0.34 states/eV/(C atom)] compared with that of the pristine tube [0.06 states/eV/(C atom)].

We now move to the adsorption of O₂ molecule on the outer surface of these 4 Å nanotubes. Our aim is to investigate whether these tubes are stable in ambient conditions. Here we only consider the singlet O₂ (¹ Δ_g) since it is much more reactive than the triplet state (³ Σ_g^-) and is mainly responsible for the oxidation.¹³ The singlet state is treated as a closed-shell system and modeled by using a spin-restricted DFT calculation. The excitation energy from the ³ Σ_g^- state to the ¹ Δ_g state we obtained is 1.02 eV, in reasonably good agreement with the experimental value of 0.98 eV. As in the case of single-oxygen-atom adsorption considered in the previous section, initial orientations of O₂ on both site I and site II are chosen, and we will consider both physisorption and chemisorption for the present calculations. We note that the numbers quoted for physisorption below should be taken as qualitative, since density functional calculations with the

GGA are not quantitatively accurate for such weak interactions, although a more sophisticated methodology would be very difficult for such complex systems.

We first focus on the zigzag (5,0). We find that physisorption of O₂ occurs on both site I and site II, but the binding is very weak and at the margin of the accuracy of DFT calculations (Table II). This is consistent with the fact that the O-O distance in the physisorbed product is very close to the bond length in the free O₂ molecule and that the tube's geometry is almost unchanged. We want to mention that singlet O₂ physisorbs on site I at a distance of 3.43 Å with a binding energy of about -0.08 eV. This energy value is considerably smaller than those found in previous theoretical studies for bigger tubes.^{10,34} We believe that this discrepancy is mainly due to the use of the local density approximation (LDA) in previous calculations while we use the GGA. The LDA is known to overestimate binding energies. The equilibrium O₂-tube distance by our GGA calculations is also larger than the LDA value of 2.7 Å. Our results agree well with those obtained for O₂ physisorbed on the bridged site of (8,0), where the GGA was used in the calculations.²⁰ It should be emphasized that none of the standard DFT studies, including our own, could properly treat the long-range dispersion interactions involved in the physisorption of O₂. We expect that a proper treatment of such dispersion interactions could give an improved predication of the binding energies for O₂ physisorbed on the tube surface. As for chemisorption, we find a quite different picture. The O₂ molecule binds strongly on both sites. In the case of site I, two C-O bonds are formed, making a "square" ring as shown in Fig. 3(a). The tube's geometry is significantly modified due to strong interaction between the O₂ molecule and the tube. The O₂ molecule bond (parallel to the tube axis) is not broken, although the O-O distance is larger than that of the free O₂ molecule. This is also the case of site II except that the O-O bond is not parallel to the underlying C-C bond, as shown in Fig. 3(b). Such adsorption of singlet O₂ is known as cyclo-addition. Besides these two chemisorbed products, we find a more stable epoxy structure with the dissociation of O₂ molecule and each O atom taking site I [Fig. 3(c)]. The calculated binding energy for epoxy is -3.06 eV relative to singlet O₂.

Similar adsorption can be found on the outer surface of the armchair (3,3). Our results are summarized in Table III. The small energy values listed in the first two rows are characteristics of physisorption, and the corresponding O-O bond length is only slightly larger than that of a free O₂ molecule. There are also three chemisorbed products. The one with relatively higher binding energy is cyclo-addition of O₂ on top of site I, as shown in Fig. 4(a). The chemisorption of O₂

FIG. 2. Energy band structures of tubes adsorbed with one O atom for (5,0), (3,3), and (4,2), with nominal formulas $C_{20}O$, $C_{24}O$, and $C_{56}O$, respectively. The band structures of pristine tubes are also shown for comparison. Note that the supercell contains two primitive cells in the case of tube (3,3). The Fermi level is at 0 eV.

on site II has a much lower binding energy, and there is a dramatic change of the tube's geometry. As before, two C-O bonds are formed; however, one of the C-C bond is now

TABLE II. Calculated binding energy (in unit of eV) and O-O bond length (in units of Å) for singlet O_2 adsorbed on tube (5,0). The zero of the energy is defined as the total energy of a pristine tube plus a singlet O_2 .

Tube (5,0)	E_b	O-O
Physisorption (site I)	-0.08	1.249
Physisorption (site II)	-0.19	1.253
Chemisorption (site I)	-1.63	1.511
Chemisorption (cyclo)	-1.06	1.512
Chemisorption (epoxy)	-3.06	3.197

broken which means that the tube's structure will be destroyed upon such adsorption [Fig. 4(b)]. The epoxy structure, with each O atom occupying site II, has the lowest energy and the opening of C-C bond is also observed [Fig. 4(c)].

It should be mentioned that, using the nudged elastic band (NEB) method,³⁵⁻³⁷ we found that the energy barriers from physisorption to chemisorption are quite small for both tubes (5,0) and (3,3). The NEB calculations are carried out by constructing eight images of the system between the physisorbed and chemisorbed states, and all the carbon and oxygen atoms are allowed to relax. Details of the calculations will be reported elsewhere. The calculated energy barriers are, respectively, 0.21 eV for tube (3,3) in the cyclo configuration, 0.32 eV for tube (5,0) at site I, 0.35 eV for tube (5,0) in the cyclo configuration, and 0.37 eV for tube (3,3) at site II. Such small numbers mean that these small-diameter tubes

FIG. 3. (Color online) Top and side views of an O_2 molecule chemisorbed on tube (5,0): (a) site I, (b) cyclo-addition, and (c) epoxy structure.

FIG. 4. (Color online) Top and side views of an O_2 molecule chemisorbed on tube (3,3): (a) cyclo-addition, (b) site II, and (c) epoxy structure.

can be oxidized easily in ambient conditions. Our conclusion is quite different from those reported in the previous studies for relatively larger tubes,^{20,38} which claimed that chemisorption is unlikely to occur at room temperature because of a large energy barrier associated with it. On the other hand, chemisorbed O_2 can be driven away from the (5,0) tube by heating and restoring its tube geometry. This is, however, not the case for the (3,3) tube since the tube structure is destroyed during adsorption at site II. We know that there are

TABLE III. Calculated binding energy (in unit of eV) and O-O bond length (in units of Å) for singlet O_2 adsorbed on tube (3,3). The zero of the energy is defined as the total energy of a pristine tube plus a singlet O_2 .

Tube (3,3)	E_b	O-O
Physisorption (site I)	-0.21	1.261
Physisorption (site II)	-0.27	1.265
Chemisorption (site II)	-3.43	2.727
Chemisorption (cyclo)	-1.07	1.525
Chemisorption (epoxy)	-4.19	3.604

three possible chiralities inside the zeolite channels. The tube (4,2) can be removed in experiment by pumping away all the hydrocarbon radicals.³⁹ The different adsorption picture of (5,0) and (3,3) tubes we discussed above is thus served as a useful way to selectively destroy one type of tube, leaving behind a single chirality (zigzag) from these ultrasmall-diameter carbon nanotubes.

IV. SUMMARY

Using density functional method, we have studied the adsorption of both O atom and O_2 molecule on the outer surface of 4 Å SWNT's. Our calculations indicate that there is a marked dependence of O binding energy on the chirality of these 4 Å tubes. The electronic properties of carbon nanotubes can change dramatically upon oxygen exposure. The zigzag (5,0) can be selected out from these tubes according to their different adsorption behaviors of singlet O_2 .

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