Adsorption pathways of singlet O_2 on 4 Å carbon nanotubes

H. J. Liu^{1,2} and C. T. Chan²¹*Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China*²*Department of Physics and Institute of Nano-Science and Technology, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong*

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Using density functional calculations and the nudged elastic band method, we investigate the adsorption pathways of singlet O_2 on 4 Å single-wall carbon nanotubes, which have been recently fabricated using a templating method. We find that the reaction barriers for these ultrasmall-radius tubes are lower than those previously reported for larger-diameter tubes. Moreover, another chemisorbed product is identified for the (3,3) tube, and the reaction path is very different from those reported for larger armchair tubes.

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Carbon nanotubes have attracted a lot of attention from the science community due to their interesting novel properties and great application potentials.^{1–3} Among them, single-wall carbon nanotubes (SWNTs) are of particular importance and their quasi-one-dimensional character has been intensively investigated. However, the synthesis of SWNTs is challenging, especially for SNWTs with very small diameters. Recently, SWNTs with diameter of 4 Å have been successfully fabricated using a templating method,⁴ and the very small diameter of these tubes gives them unusual properties such as superconducting fluctuations,⁵ high Li storage capacity,⁶ and unusual optical properties,⁷ etc. Due to their small diameters, we have to go beyond the band-folding picture² to explain physical and chemical properties. In this Brief Report, density functional calculations are used to study the reaction of oxygen molecules with these 4 Å tubes, which are expected to be more reactive than tubes with larger radii. Although a large number of studies, both experimental^{8–10} and theoretical,^{11–25} have considered the interaction of carbon nanotubes with oxygen, most of these works are focused on the oxygen binding energies and adsorption configurations, and little is known about the reaction process between oxygen and nanotubes.

There is a recent theoretical study²⁶ on the interaction of O_2 with single-walled (8,0) and (6,6) tubes, and similar reaction paths were found for both of them. The overall process is exothermic, with an activation barrier of 0.61 eV for the (8,0) tube, and 0.87 eV for the (6,6) tube. We will show in this report that the energies are somewhat different for our 4 Å tubes, even for the same chirality. Moreover, another chemisorbed state is found for the armchair (3,3) tube, making the reaction picture quite different from previous results. As mentioned before, we will focus on the reaction pathways in our discussions.

Our total energy calculations were performed using the plane-wave pseudopotential method, as implemented in the Vienna *ab initio* simulation package (VASP).^{27–29} The exchange-correlation energy is in the form of the Perdew-Wang 91 functional,³⁰ and the cutoff energy is 396 eV for the plane-wave basis set. A standard hexagonal supercell is used to model the carbon nanotubes and the adsorbed oxygen. The closest distance between adjacent tubes in the supercell is set to 12 Å, which allows for negligible interaction between the

tube (together with the adsorbed oxygen) and its periodic image. The $\mathbf{k}$ points are sampled on a uniform grid along the tube axis, and atomic positions are fully relaxed. To calculate the energy barriers involved in the reaction process, we use the so-called nudged elastic band (NEB) method.^{31–33} The NEB is an efficient method for finding saddle points and minimum-energy paths (MEP) between a given initial and final state of a reaction. In our calculations, a number of intermediate images of the system (typically on the order of eight) are constructed along the reaction path, and each image finds the lowest energy while maintaining equal spacing to neighboring images. This constrained optimization is done by adding spring forces along the band between images and by projecting out the component of the forces due to the potential perpendicular to the band. To drive the highest-energy image exactly to the saddle point, the climbing image³⁴ is used after the regular NEB.

There are three types of SWNT with diameters of 4 Å, and they are the zigzag (5,0), the armchair (3,3), and the chiral (4,2), and all of them are known to coexist inside the zeolite channels.^{4,35,36} The unit cell of each tube contains 20, 12, and 56 carbon atoms, respectively. With the limited computation resources available to us, we discuss the reaction of oxygen molecules with the (5,0) and (3,3) tubes in the present work. The ground state of O_2 is triplet, and singlet O_2 could be produced by photoexcitation, in either the $^1\Delta_g$ or $^1\Sigma_g^+$ state. However, we only consider the singlet $^1\Delta_g$ as it is much more reactive than the triplet state and is mainly responsible for the oxidation of carbon nanotubes.²⁶

For the (5,0) tube reacting with singlet O_2 , we previously found three chemisorbed products.³⁷ The one with the highest energy is the so-called cycloaddition of O_2 on top of the zigzag C—C bond (or “site II” using the same notation as in Ref. 37). The epoxy configuration has the lowest energy with the dissociation of O_2 and each O atom occupying site I. The product with energy in between is with O_2 chemisorbed on the bridge site (“site I” in Ref. 37), making a square ring with the underlying carbon atoms. The binding energies of these three chemisorbed products agree well with the trend observed before for a series of larger zigzag tubes, which found that the adsorption energy decreases as the diameter increases.³⁸ In addition to chemisorption, physisorption of O_2 occurs on both site I and site II. Figure 1 shows the NEB

FIG. 1. (Color online) The minimum-energy path from physisorption (site I) to chemisorption (site I) of singlet O₂ on tube (5,0). The average C—O distance is taken as reaction coordinate, and the energy of physisorbed product is set at zero.

calculated minimum-energy path from physisorption (site I) to chemisorption (site I), where eight images are chosen between them and the average C—O distance is taken as reaction coordinate. A ball-and-stick model of the chemisorbed product is also shown in the figure and the label “A” indicates the transition state. Relative to the physisorbed product, the chemisorbed product is 1.55 eV lower in energy. The activation barrier is only 0.30 eV, which means that the (5,0) tube can be easily oxidized in ambient environment. The reaction path is similar to those previously found for a larger zigzag tube (8,0), except that the energy barrier is quite a bit smaller than the reported value of 0.75 eV.^{26,39} This means that our 4 Å tube is more reactive than larger-diameter tubes.

The reaction path from physisorption (site II) to cycloaddition product is shown in Fig. 2. Relative to the physisorbed product, the cycloaddition structure is 0.87 eV more stable. As shown in Fig. 2, the activation barrier is also quite low with a value of 0.36 eV. The cycloaddition product could go another step to the more stable epoxy product, with an energy barrier of 0.48 eV. A similar reaction pathway was first shown in Ref. 26 for a larger tube (8,0). However, for our ultrasmall tube (5,0), the activation barriers are lower than

FIG. 2. (Color online) The minimum-energy path from physisorption (site II) to the cycloaddition and epoxy state of singlet O₂ on tube (5,0). The average C—O distance is taken as reaction coordinate, and the energy of physisorbed product is set at zero.

FIG. 3. (Color online) The minimum-energy path from physisorption to chemisorption of singlet O₂ on tube (3,3) at site II. The average C—O distance is taken as reaction coordinate, and the energy of physisorbed product is set at zero.

those found for (8,0) (the values are 0.61 and 0.54 eV, respectively), and again this means that the (5,0) tube is not stable when exposed to oxygen. We want to mention that once the epoxy structure is formed, the desorption barrier becomes 2.48 eV and that is quite high. It is thus difficult in the experiment to completely get rid of the adsorbed O₂.

We now move to the reaction of O₂ with the armchair (3,3). In addition to the physisorbed products, we previously reported three chemisorbed products. The one with relatively higher energy is cycloaddition of O₂ on top of a C—C bond that wraps along the tube axis (site I in Ref. 37). The second chemisorbed product, with two dissociated oxygen atoms wrapping around the tube circumference (site II), is much lower in energy. The epoxy product has the lowest energy, with the dissociated oxygen atoms each taking different site II. Figure 3 shows the calculated MEP from physisorption to chemisorption at site II. Relative to the physisorbed state, the chemisorbed product is much lower in energy, but the activation barrier is only 0.35 eV.

The reaction path from physisorption to cycloaddition of O₂ on (3,3) is given in Fig. 4. We see that the energy barrier is quite small with a value of 0.21 eV, which means that the tube (3,3) is even more reactive than the tube (5,0). This is also consistent with the fact that tube (3,3) has the largest curvature of the C—C bond on the tube wall among the three types of 4 Å tubes. We may expect that the cycloaddition product could go through another step to the epoxy state, as in the case previously reported for the large armchair tube (6,6).^{26,39} However, during our NEB calculations, we find another chemisorbed state between the cycloaddition and epoxy products. Figure 5 is a ball-and-stick model of this intermediate state. We see that the O₂ is dissociated and the underlying C—C bond is broken; the tube’s geometry is dramatically changed due to strong interaction between the tube and oxygen. There is a large distance (2.81 Å) between the two dissociated O atoms compared with the typical O₂ bond length of 1.24 Å. The underlying C—C distance also increases from the ideal value of 1.43 Å to 2.52 Å. The cross section of the tube becomes ellipselike and the deformation energy is about 0.29 eV/atom. Here, the deformation energy is defined as the energy difference between the ideal

FIG. 4. (Color online) The minimum-energy path from physisorption to the cycloaddition and epoxy state of singlet O_2 on tube (3,3). An intermediate chemisorbed state is found between them. The average C—O distance is taken as reaction coordinate, and the energy of physisorbed product is set at zero.

and deformed tube. Table I gives the structural parameters for this intermediate state (labeled as N). We see that the distance between the O atom and the nearest C atom is only 1.21 Å, which is characteristic of a C=O double bond. We also find that the O atom lies in the same plane with the nearby C atoms with sp^2 hybridization. The presence of a C=O double bond in tube (3,3) is also due to its largest curvature and will induce some changes in the electronic structure of the tube.⁴⁰ In Table I, we also summarize the structural parameters for those transition states involved in the reaction pathways (labeled as A, B, C, D, E, F, and G in Figs. 1–4).

In order to investigate the stability of this intermediate

FIG. 5. (Color online) Top and side views of the intermediate chemisorbed product of tube (3,3).

TABLE I. The calculated structural parameters for the chemisorbed product labeled N, and the transition states involved in the reaction pathways of singlet O_2 on tubes (5,0) and (3,3). Here, O—O is the distance between two adsorbed O atoms, C—O is the length of the C—O bond, and C—C is the underlying C—C distance.

State	C—C (Å)	C—O (Å)	O—O (Å)
N	2.52	1.21	2.81
A	1.47		1.30
B	1.66	1.40	1.95
C	1.53		1.33
D	1.54		1.38
E	1.58	1.35	3.16
F	1.57	1.37	2.18
G	1.50		1.34

state, we performed *ab initio* molecular dynamics (MD). The starting temperature is 300 K and a microcanonical ensemble has been used. The MD runs for 1 ps with a time step of 1 fs. Figure 6 shows the distance between one of the oxygen atoms and the underlying carbon atom in the whole MD running time. We see that there is only slight fluctuation around the C=O bond length of 1.21 Å. Also shown in the figure is the evolution of the nearest C—C bond distance, and the fluctuation is also very small around its equilibrium bond length of 1.51 Å. The results for other bond lengths are similar and not shown here. All these results indicate that the intermediate state between cycloaddition and epoxy product is rather stable. As shown in Fig. 4, this chemisorbed state is lower in energy than the cycloaddition state but higher than the epoxy state. The presence of the intermediate state makes the reaction path quite different from that reported before for the larger armchair tube (6,6). The energy barrier is 0.46 eV from the cycloaddition product to this intermediate state, and 1.87 eV from the intermediate state to the epoxy state. Since the latter is so high, the probability of reaching the epoxy

FIG. 6. Molecular dynamics results of the C—C and C—O distance for the intermediate chemisorbed product of tube (3,3).

configuration is small under ambient conditions, and the intermediate state will be the main oxidation product. More importantly, once reaching the intermediate state, the desorption barrier becomes 1.96 eV, which means that it will be difficult to completely clean the adsorbed oxygen when such a structure is present.

In summary, we have discussed the reaction pathways of singlet O_2 on 4 Å carbon nanotubes (5,0) and (3,3), using the plane-wave pseudopotential method and the nudged elastic band technique. We find that the activation barriers are lower than previously reported for larger-diameter tubes, which in-

dicates that the 4 Å tube is more reactive. The presence of an intermediate state in the (3,3) tube is identified, and this state makes the reaction picture quite different from those reported before.

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