A computational study on the effect of local curvature on the adsorption of oxygen on single-walled carbon nanotubes

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Abstract

We investigated the effect of local curvature on the adsorption of oxygen on single-walled carbon nanotubes based on density functional theory calculations with van der Waals corrections. The results showed that as the curvature increases, the interaction of the nanotubes with oxygen increases as well. An oxygen atom was strongly chemisorbed on the bridge site of the nanotubes accompanied by a significant transfer of charge from the surface to the oxygen atom. Larger curvature enhanced both the adsorption energy and charge transfer due to the greater strain on the carbon atoms that led to a better interaction with oxygen. The oxygen molecule was physisorbed on the nanotubes with the interaction arising mostly from the long-range van der Waals interactions. The adsorption energy was also enhanced by greater curvature. The results

were compared with the flat graphene sheet to confirm the effects of surface curvature.

1. Introduction

Carbon-based nanomaterials such as fullerenes, graphene, and carbon nanotubes (CNTs) have attracted much attention for their fascinating properties that open possibilities for many applications. In particular, single-walled carbon nanotubes (SWCNTs) have been considered for nanoscale electronic, spintronic, and biomedical applications [1], as well as in fuel cell technology [2-4], and as electrochemical and biosensors [5-7]. They can also be decorated and modified to tailor to specific applications: i.e. metal-filled SWCNTs with modified electronic and magnetic properties [8-13]. Hydrogen fuel cells have been the subject of interest in the search for alternative sources of energy. One of these fuel cells is the proton exchange membrane fuel cell (PEMFC), which utilizes the energy from the electrochemical reaction of hydrogen and oxygen. The splitting of the hydrogen molecule at the anode is relatively easy by using a platinum catalyst, but separating the stronger oxygen molecule at the cathode is more difficult, thus causing significant energy losses [14]. PEMFC catalysts are normally supported by carbon-support materials such as carbon black (Vulcan XC-72). However, carbon black is known to undergo chemical oxidation to surface oxides and eventually to CO₂ at the cathode of the PEMFC [15]. Another study found that Pt accelerates the corrosion rate of carbon black [16]. There is a need to use alternative more stable carbon support, such as carbon material with more graphitic component (e.g. carbon nanotubes) [17].

The interaction of SWCNTs with oxygen has been widely studied for fundamental and

practical purposes. Exposure of SWCNTs to oxygen has been found to dramatically influence its electrical resistance, thermoelectric power, and local density of states (LDOS) [18]. Experiments have shown that oxygen adsorption can induce a significant increase in the emission current of CNT field emitters [19]. Also, oxygen adsorption induces p-type doping in CNT-based field effect transistors [20]. Moreover, the purification of synthesized CNTs could also be done through oxidation at elevated temperatures where the ambient oxygen reacts with the strained C-C bonds [21-22]. All of these previous studies suggest that oxygen is highly reactive with CNTs. However, the group of Barberio [23] found that there is no indication of oxygen adsorption for pristine and clean nanotubes. They exposed the SWCNTs to 1×10^{-6} Torr molecular oxygen at room temperature and found no evidence of interaction and mentioned that the strong sp^2 bonding of the graphitic ring structure may somehow prevent oxygen attachment to the SWCNT surface. Thus, a better understanding of the interaction between oxygen and CNTs is still needed.

In this study, we investigated further on the interaction of oxygen with SWCNTs through looking at the possible effects of the nanotube size, in particular its surface curvature, as it has been shown in previous theoretical and experimental work that the reactivity of gases on CNTs and other carbon-based materials can be enhanced due to the effects of surface curvature. [24-29] First principles calculations were employed to investigate the adsorption energies and stable structures for oxygen adsorption on SWCNTs with varying diameters and electrical properties, as well as graphene. Furthermore, insights on the effect of surface curvature were pursued by looking at the differences in the charge distributions. The results we obtained will be useful in

designing potential catalysts for oxygen reduction in the PEMFC.

2. Computational Details

We used first principles calculations based on density functional theory (DFT) [30-31]. Generalized Gradient Approximation (GGA) based on the Perdew-Burke-Ernzerhof (PBE) functional [32-34] was used as implemented in the Vienna Ab Initio Simulation Package (VASP) code. The projector-augmented wave (PAW) was adopted to represent the core electrons. [35] The plane wave basis set was used and the cut off energy was set to 550 eV to achieve higher accuracy. The k-point sampling of the one dimensional Brillouin zone for the SWCNTs was obtained using 35 Monkhorst-Pack k-points [36] along the nanotube axis, while a 9 x 9 x 1 grid was obtained for graphene. All calculations were spin polarized and were done until the energy of the systems converge to 0.01 eV/A. The VESTA software was used for visualization of the atomic structures [37]. In this study, the atomic and molecular adsorptions of oxygen were both investigated. Four different chiralities of SWCNTs were considered: (3,3), (5,0), (5,5) and (8,0) SWCNTs to provide not only an equal representation of armchair and zigzag SWCNTs but also have two pairs of nanotubes with the roughly the same diameters but different electronic properties. The diameters of the SWCNTs considered are rather small as compared to typical SWCNT samples commercially available in order to reduce computational cost. However, ultra-small SWCNTs with diameters of about 4 Å have been observed experimentally [38-39]. Thus the smallest SWCNTs considered in this study have diameters of about 4 Å. The unit cell parameters of the SWCNTs are shown in Table 1. The unit cell size for the armchair SWCNTs (3,3) and (5,5) were

doubled to minimize the difference of the relative concentration of oxygen on the SWCNTs. A vacuum distance of roughly 20 Å between neighboring SWCNTs was used to eliminate the effect of periodicity within the intertube distances. Van der Waals interactions were taken into account using the method by Grimme [40] as implemented in the VASP code. An initial magnetic moment of 2.0 μB was used for the oxygen atoms.

Table 1. Unit cell parameters for the SWCNTs considered in this study.

Chirality	Number of C atoms	Tube length (in Å)	Tube diameter, d (in Å)	Curvature radius (in Å)	Electronic Property
(3,3)	24	4.98	4.07	2.04	Metallic
(5,0)	20	4.26	3.92	2.32	Semi-conducting
(5,5)	40	4.91	6.78	3.39	Metallic
(8,0)	32	4.24	6.27	3.71	Semi-conducting

To analyze the effect of surface curvature, we considered the local curvature radius, R' , of the SWCNTs based on the C-C bond involved in the adsorption process. For the case of armchair SWCNTs, the C-C bond is along the circumferential axis, i.e. perpendicular to the tube axis, and thus, R' is simply equal to the tube radius. This is because the cross section of the tube along the C-C bond is round. On the other hand, for the case of zigzag SWCNTs, R' is larger than the tube radius since the cross section along the C-C bonds is ellipsoidal. We calculated R' along the C-C bond using the equation [41]:

$$R' = \frac{R}{\cos^2(\pi/6 - \theta)},$$

where R is the radius of the SWCNT and θ is the chiral angle, as shown in Fig. 1.

Figure 1. Schematic representation of the cross-section of a nanotube with radius R to show the local curvature radius, R' , along the C-C bond inclined by angle θ .

The adsorption of atomic oxygen was investigated by placing the oxygen adatom on the bridge site between the C-C bonds, as shown in the unit cells for the SWCNTs in Fig. 2. On the other hand, the molecular adsorption of oxygen was examined by placing the oxygen molecule on the same bridge sites as in Fig. 2. Two orientations of the O_2 molecule were analyzed as shown in Fig. 3: parallel and perpendicular to the C-C bond axis. A potential energy scan (PES) was conducted for varying values of the O-O bond length, r , and the distance of the O_2 molecule from the surface, z . The configuration with the minimum energy was fully-relaxed in order to obtain the adsorption energy and optimized geometry. The adsorption energy of the system, E_{ads} , is defined as

$$E_{ads} = E_{sys} - E_{iso},$$

where E_{sys} is the total energy of the system and E_{iso} is the sum of the energies of the isolated SWCNT and oxygen.

Figure 2. The unit cells of (a) (3,3) SWCNT, (b) (5,0) SWCNT, (c) (5,5) SWCNT, and (d) (8,0) SWCNT. Grey spheres indicate carbon atoms while the yellow circles show the bridge adsorption sites.

(a)

(b)

Figure 3. Schematic representation of the potential energy scan (PES) analysis for the molecular adsorption of oxygen on a (5,5) SWCNT for the oxygen molecule (a) parallel and (b) perpendicular to the C-C bond on the bridge site. The bond length, r , and the distance of the molecule from the bridge site, z , were varied. Grey spheres represent carbon atoms while red spheres represent oxygen atoms.

3. Results and Discussion

3.1. Adsorption of atomic oxygen

The adsorption of atomic oxygen on the bridge site was investigated to find out the effect of local surface curvature on the stability of an oxygen adatom on the SWCNT

surface. The stable structures for O atom on the SWCNTs are shown in Fig. 4 and the
 adsorption energies, O magnetization and some structural parameters are tabulated in
 Table 2. The results instantly reveal a straightforward relationship between the surface
 curvature and the adsorption energy; as the curvature increases (i.e. decreasing R'), the
 adsorption energy increases as well. The large energies indicate strong chemisorption of
 the O atom with a significant charge transfer from C to O, and that the charge transfer is
 enhanced by greater curvature. To confirm this, we analyzed the charge distribution by
 looking at the contour plots of the charge density on planes passing through the
 chemisorbed O atoms on the bridge sites, as shown in Fig. 5. We can see that the C-C
 bond is destroyed and that new C-O bonds have formed for the (3,3) SWCNT. This was
 not the case for the (5,0) SWCNT, as the C-C bond was still intact. Furthermore, there is
 a greater overlapping of charges between the oxygen and carbon atoms in the (3,3)
 SWCNT as compared with the (5,0) SWCNT. Though both have quite similar diameters,
 the one with the lower R' has more charge transfer. We can clearly see this from the
 Bader analysis of the charge distribution in Table 3. The energy of the anti-bonding π^*
 states increased for all cases, implying a depletion of anti-bonding states near the Fermi
 energy, which is consistent with the stable adsorption energies obtained. In effect, for
 the semiconducting cases, the HOMO-LUMO gap increased by about 3% after oxygen
 adsorption. Lastly, the singlet state with a net zero magnetic moment was found to be
 the ground state from the spin-polarized optimization, which explains the disappearance
 of the magnetization of the oxygen atom upon adsorption.

Figure 4. Optimized structures for the adsorption of oxygen on the bridge sites of (a) (3,3) SWCNT, (b) (5,0) SWCNT, (c) (5,5) SWCNT, and (d) (8,0) SWCNT. Grey spheres represent carbon atoms while red spheres represent oxygen atoms.

Table 2. Adsorption energy (E_A), magnetization, and geometric configuration data for oxygen atom adsorption. C_1 and C_2 indicate the two carbon atoms in the bridge site.

SWCNT	d (Å)	R' (Å)	E_A (eV)	Magnetization of O (μ_B)	Interatomic distances (Å)		
					O- C_1	O- C_2	C_1 - C_2
(3,3)	4.07	2.04	-6.91	0	1.41	1.41	2.14
(5,0)	3.92	2.32	-5.70	0	1.43	1.43	1.50
(5,5)	6.78	3.39	-5.52	0	1.40	1.40	2.17
(8,0)	6.27	3.71	-5.07	0	1.39	1.39	2.18

Figure 5. Charge density distribution for (a) (3,3) SWCNT and (b) (5,0) SWCNT. Grey spheres represent carbon atoms while red spheres represent oxygen atoms.

It is interesting to note that the C-C bond was not destroyed only for the case of (5,0) SWCNT. One reason for this could be due to the very small size of the SWCNT unit cell. The flattening of the nanotube can be seen in (5,0) case as the structure bulges out on the sides of the bridge site where the O atom is adsorbed. Thus we can see more interaction between the carbon atoms that limits the capacity of the receiving C atoms on the bridge site to interact with the oxygen. This also explains the lower charge transfer on the (5,0) case. These observations are consistent with previous studies, both theoretically [41] and experimentally [42-43], wherein the (5,0) SWCNT was found to be significantly more robust than the (3,3) and (4,2) SWCNTs, all three of which have similar diameters. So with the exception of the (5,0) SWCNT, a trend can be generalized that relates the charge transfer with the R' . As the curvature decreases, we see both a decrease in adsorption energy and charge transfer. In the case of the flat graphene surface, we obtained an adsorption energy of -4.51 eV, which is comparable

with the value obtained by the group of Ishii [43], and a charge transfer of 0.43 electrons from the surface to the oxygen atom. Thus the trend holds that the values we obtained for the adsorption energy and charge transfer approached that of the values for graphene as curvature decreases.

Table 3. Charge difference for the adsorption of O atom on the bridge site of SWCNTs. The values shown are in units of e as obtained from the analysis of the Bader Charge. Positive and negative values refer to the accumulation and depletion of charges respectively. C_1 and C_2 indicate the two carbon atoms in the bridge site.

Atom	Charge Difference			
	(3,3) SWCNT	(5,0) SWCNT	(5,5) SWCNT	(8,0) SWCNT
O	0.621	0.260	0.485	0.462
C_1	-0.289	-0.124	-0.238	-0.214
C_2	-0.295	-0.128	-0.239	-0.211

3.2. Molecular adsorption of oxygen

For the molecular adsorption of oxygen on the SWCNTs, a potential energy scan (PES) for different values of the oxygen molecule bond length, r and the distance of the oxygen molecule from the bridge site, z , for two configurations of the oxygen molecule was performed as shown in Fig. 3. At first, static calculations were done to find the values for r and z that correspond to the minimum energy. Using the minimum energy configuration from the PES, the system was optimized to obtain the final adsorption

energies and structural parameters for the molecular adsorption of oxygen on SWCNTs. The minimum energy was found at a distance between 3.0 Å and 3.5 Å for all cases. The adsorption energies and structural parameters from the optimized calculations are shown in Table 4. From the results, weak binding of the oxygen molecule with the SWCNTs are seen, with adsorption energies below -0.5 eV and are characteristic of physisorption. Most of the interaction between the oxygen molecule and the SWCNTs arise from the long-range van der Waals interactions. The adsorption energies obtained from calculations without the van der Waals correction were in the range of 15-25 meV, consistent with previous DFT studies [44-45]. Again, a trend of increasing adsorption energy for greater curvature is observed. Bader analysis of the charge distribution showed minimal charge transfer between the surface and the oxygen molecule and with distances of more than 3 Å apart, it is unlikely that the orbitals interact efficiently with each other. Furthermore, no changes were observed to the magnetization of the oxygen atoms.

Table 4. Adsorption energy (E_A) and geometric configuration data for oxygen molecule adsorption. O_1 and O_2 indicate the two oxygen atoms in the oxygen molecule.

SWCN	Diameter			Magnetization		Distances (Å)	
				(μ _B)			
T	(Å)	R' (Å)	E_A (eV)	O_1	O_2	r	z
(3,3)	4.07	2.04	-0.32	2	2	1.23	3.19
(5,0)	3.92	2.32	-0.27	2	2	1.23	3.32
(5,5)	6.78	3.39	-0.14	2	2	1.23	3.48
(8,0)	6.27	3.71	-0.13	2	2	1.23	3.37

Planar sp^2 bonding characteristic of graphene plays a significant role in SWCNTs since basically, SWCNTs are just graphene sheets rolled up into cylinders. However, due to the surface curvature in SWCNTs, the carbon atoms acquire sp^3 -like properties that weaken the binding of the carbon atoms along the circumferential axis as compared with the nanotube axis. C-C bonds along the nanotube axis are considered to have an infinite R' and are thus flat. Due to this weakening of the bonding between carbon atoms, curvature plays an important effect in the ability of the SWCNTs to interact with adsorbates as compared with the flat graphene sheet. In our case, greater curvature allowed the C-C bonds along the circumferential axis to weaken and thus allowed better interaction with oxygen. This is particularly evident in the adsorption of atomic oxygen and to a lesser extent, also to the adsorption of the oxygen molecule. The only exception is the (5,0) SWCNT, due to its robust structure. Thus, if we can design carbon materials in such a way that we can induce sp^3 -like properties, i.e. introducing sp^3 -inducing defects on graphene and SWCNTs, we can increase its reactivity. Furthermore, doped CNTs, such as Pt-decorated CNTs, have shown good catalytic properties for oxygen reduction while reducing the amount of Pt used. [46] Thus, utilizing the effect of surface curvature in doped-SWCNTs, the catalytic activity of these hybrid metal-SWCNTs can be enhanced and make them useful in many applications, such as for oxygen reduction in the PEMFC. Further theoretical studies are suggested.

4. Conclusions

We have analyzed the effect of local curvature on the adsorption of atomic and molecular oxygen on SWCNTs and graphene through the investigation of its adsorption

energetics, structural properties, and charge distributions using first principles calculations based on density functional theory (DFT). We found that the oxygen atom is strongly chemisorbed on the bridge site of the SWCNTs and that the adsorption energy is stronger for bridge sites with lesser local curvature radii (R'), i.e. greater curvature. The adsorption is accompanied by a large transfer of charge from the carbon atoms in the bridge site to the adsorbed oxygen atom, and is likewise enhanced by greater curvature of the bridge site. These trends hold true for all SWCNT cases studied with the exception of the (5,0) SWCNT. This is most likely due to its small size, and despite its great surface curvature, interaction between carbon atoms affected the adsorption of the oxygen atom. Comparisons with the atomic adsorption of oxygen on a graphene sheet confirmed the beneficiary effect of surface curvature on the adsorption energy and charge transfer. We also found that the oxygen molecule interacts weakly with SWCNTs and is characteristic of physisorption. The interaction is mainly due to van der Waals forces. Just like in the case of atomic oxygen, greater surface curvature also enhances the adsorption energy and charge transfer, albeit to a lesser extent. The oxygen molecule remains too far away from the SWCNT surface for any significant charge transfer or interaction of molecular orbitals to occur. Nonetheless, surface curvature still enhances the physisorption process of the oxygen molecule in SWCNTs as compared with graphene.

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