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Interaction of Oxygen With Fe Nanowire-Filled Single-Walled Carbon Nanotubes

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Abstract

The interaction of oxygen with Fe nanowire-filled single-walled carbon nanotubes (SWCNT) was investigated using density functional theory calculations. The adsorption energies and stable structures on different adsorption sites on the Fe nanowire-filled SWCNT were obtained and compared with pristine SWCNT. The results show that the oxygen atom adsorbs strongly on a bridge site on the SWCNT surface in all cases, with weaker adsorption energies for the Fe nanowire-filled cases. Meanwhile, the molecular adsorption was enhanced by the presence of Fe while lowering the energy barrier required for dissociation. Thus, filling with Fe enhances the oxygen reduction capabilities of SWCNTs and makes them better catalysts for various applications such us in hydrogen fuel cells.

Key words: Carbon nanotubes; Fe nanowire; Oxygen adsorption; Density functional theory

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INTRODUCTION

Since their discovery in 1991 by Iijima, carbon nanotubes (CNTs) have received a great deal of attention due to their fascinating properties that open possibilities for many applications. Recent CNT research has focused mostly on device applications. In particular, single-walled carbon nanotubes (SWCNTs) have been considered for nanoscale electronic, spintronic, and biomedical applications (Ebbesen, 1997), as well as in fuel cell technology-as catalyst support and hydrogen storage material (Dicks, 2006; Lafuente et al., 2006; Girishkumar, Vinodgopal, & Kamat, 2004), and as electrochemical and biosensors (Zhao, Gan, & Zhuang, 2002; Wang, 2005; He & Dai, 2006). Several studies have been conducted on the interaction of CNTs with oxygen for both fundamental and practical reasons, since most of the possible applications of CNTs involve oxygen. Collins, Bradley, Ishigami, & Zettl (2000) found that exposure to ambient air or oxygen dramatically influences electrical resistance, thermoelectric power, and local density of states of SWCNTs. Experiments on CNT field emitters have shown that the adsorption of oxygen induces a significant increase in the emission current (Dean & Chalamala, 2000). Also, Kang, Park, Ko, Bae, & Park (2005) reported that oxygen adsorption on a CNT-based field effect transistor induces p-type doping in the CNT body. In addition, purification of synthesized CNTs from other undesired carbon-based nanoparticles could also be done through oxidation at high temperatures, where oxygen reacts with the strained C-C bonds (Ajayan et al., 1993; Ebbesen, Ajayan, Hiura, & Tanigaki, 1994). For the case of SWCNTs, Barberio et al found that there is no indication of oxygen adsorption for pristine and clean nanotubes (Barberio, Barone, Bonanno, & Xu, 2009).

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 (Xie et al., 2005). 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 CO_2 at the cathode of the PEMFC (Kangasniemi, Condit, & Jarvi, 2004). Another study found that Pt accelerates the corrosion rate of carbon black (Roen, Paik, & Jarvi, 2004). There is a need to use alternative more stable carbon support, such as carbon material with more graphitic component (e.g. carbon nanotubes) (Wang, Li, Chen, Waje, & Yan, 2006).

CNTs filled with ferromagnets demonstrate very high potential in providing modified electronic and magnetic properties, low dimensionality, and small volume that make them useful in various applications (Liu et al., 1998; Wong, Sheehan, & Lieber, 1997; Saito, 1997; Tans et al., 1997; Hu, Ouyang, Yang, & Lieber, 1999; Tans, Verschueren, & Dekker, 1998; Kasai et al., 2008). In particular, magnetic and electronic properties of Fe nanowire-filled SWCNTs (Fe-SWCNTs) were found to differ with varying diameters (Kisaku et al., 2005). In addition, the CNTs encapsulating the Fe nanowire transforms into an arch-like structure when the Fe nanowire is near a Ni (111) surface (David, Kishi, Kisaku, Nakanishi, & Kasai, 2006; David, Kasai, Moreno, & Kasai, 2008). Pt-decorated SWCNTs have been considered as catalyst material for oxygen reduction at the cathode of the PEMFC (Lafuente et al., 2006). However, platinum is a rare and expensive material and PEMFC research has focused on reducing or eliminating the use of platinum. In this paper, Fe-SWCNT is proposed as an alternative catalyst material. It is important to note however that hydrogen peroxide, which is a side product in the reduction of oxygen to water, has been found to selectively oxidize semiconducting SWCNTs. The presence of Fe was found to promote this oxidation (Miyata, Maniwa, & Kataura, 2006). Theoretical calculations have shown that this selective oxidation could possibly be applicable to semiconducting Fe-SWCNTs (Moreno, David, Kasai, Nakanishi, & Kasai, 2009).

For this study, we are looking at the possibility of Fe-SWCNT as an alternative to Pt-decorated SWCNT as catalyst material for oxygen reduction at the cathode of the PEMFC. The effect of oxygen adsorption on Fe-SWCNTs will be investigated through first principles calculations. In particular, the adsorption energies and stable structures will be evaluated for Fe-SWCNTs with different diameters and electronic properties. The effect of Fe filling will also be investigated by comparing the obtained results with the adsorption of oxygen on pristine SWCNT.

1. THEORETICAL MODEL AND METHODS

In this study, the atomic and molecular adsorptions of oxygen were both investigated. Three chiralities of SWCNTs were considered for both pristine and Fe nanowire-filled cases: (5,0), (3,3), and (5,5). These chiralities were chosen in order to compare oxygen adsorption on different diameters as well as different electronic properties. Half of the cases are metallic while the other half are semiconducting. Initial magnetic moments used are 2.0 μ_B for the oxygen atom and 2.4 μ_B for each Fe atom. The structures were optimized and compared to previous studies (Kasai et al., 2008; Kisaku et al., 2005; David et al., 2006; David et al., 2008). Three adsorption sites were considered for the adsorption of oxygen: bridge (B) site, top (T) site, and at the center of the hexagonal plane or hollow (H) site (Figure 1).

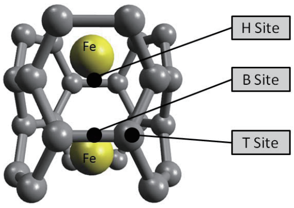

Figure 1
The Supercell for (3,3) **Fe-SWCNT**
C atoms in grey and Fe atoms in yellow; The adsorption sites are also indicated.

The adsorption of atomic oxygen was evaluated by placing an oxygen atom on the adsorption sites and the adsorption energies and optimized structures were obtained. On the other hand, the molecular adsorption of oxygen was investigated through single-point energy (SPE) calculations while the transition states and energy barriers associated with dissociation were obtained using the climbing nudged elastic band (cNEB) method. The triplet state of the oxygen molecule was used. Spin-polarized calculations based on density functional theory (DFT) (Hohenberg & Kohn, 1964; Kohn & Sham, 1965) using plane waves and pseudopotentials are performed using the Vienna *ab initio* Simulation (VASP) package (Kreese & Joubert, 1999). Generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional (Perdew, Burke, & Ernzerhof, 1996; Perdew, Burke, & Ernzerhof, 1997; Hammer, Hansen, & Norskov, 1999) was used for the exchange-correlation energy. The one-dimensional Brillouin zone was sampled using 35 Monkhorst-Pack k-points (Monkhorst & Pack, 1976) along the nanotube axis.

2. RESULTS AND DISCUSSION

The adsorption energies were obtained using the following equation,

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

where E_{sys} is the total energy of the system and E_{iso} is the sum of the energies of the isolated SWNT (pristine or Fe nanowire-filled) and oxygen (atomic or molecular). Optimized stable structures for atomic adsorption show that the oxygen atom prefers to be adsorbed on the bridge site in all the cases. The adsorption energies are about 1.0-1.2 eV weaker for the Fe nanowire-filled cases when compared with the pristine cases. Furthermore, the adsorption energies tend to decrease with increasing diameter, as observed for both the pristine and Fe nanowire-filled cases. The magnetic moments of the O and Fe atoms disappeared for the Fe nanowire-filled cases. The stable structures are shown in Figure 2.

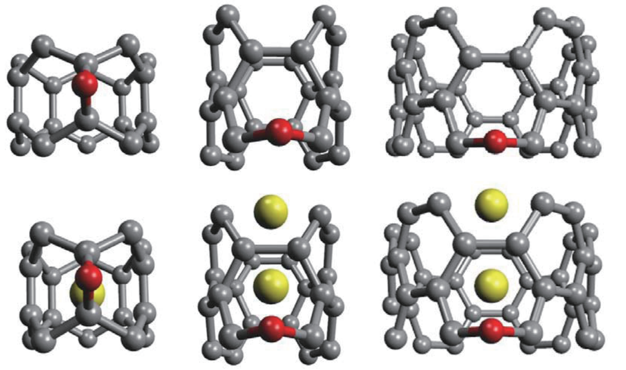

Figure 2
Stable Structures for Oxygen Atom Adsorption
Top row from left to right: (5,0) pristine SWCNT, (3,3) pristine SWCNT, and (5,5) pristine SWCNT. Bottom row from left to right: (5,0) Fe-SWCNT, (3,3) Fe-SWCNT, and (5,5) Fe-SWCNT.

The SPE calculations for the oxygen molecule was performed by calculating the adsorption energies for different values of the oxygen molecule bond length, r and the distance of the oxygen molecule from the adsorption site, z. Since the bridge site was found to be the most stable site for atomic adsorption, the reaction path considered for molecular adsorption has the oxygen molecule approach the SWCNT in such a way where both oxygen atoms would adsorb on opposite bridge sites. The resulting potential energy surfaces (PES) were analyzed. Figure 3 shows the PES for the case of (3,3) Fe-SWCNT. The oxygen molecule approaches the SWCNT surface, it encounters an energy barrier of about 1.3 eV before it can dissociate. The minimum energy before the barrier, which we shall call the molecularly adsorbed state, was found to be -0.21 eV at a height of 2 Å from the SWCNT surface. After the barrier we have a second minimum energy at -1.35 eV and the oxygen atoms are 1.2 Å from the SWCNT surface and are separated by 2.48 Å. We shall call this the dissociated state. With the molecularly adsorbed and dissociated states from the PES calculations, we employ the cNEB method to obtain the transition state (TS) and corresponding energy barrier. The TS energy for the (3,3) Fe-SWCNT was 1.14 eV, corresponding to an energy barrier of 1.35 eV, which is comparable to the obtained value from the PES. The results of the other cases, summarized in Table 1, reveal a consistent trend—that the oxygen molecule is stable with low adsorption energy that is characteristic of molecular physisorption and that a significant energy barrier must be overcome for dissociation to occur.

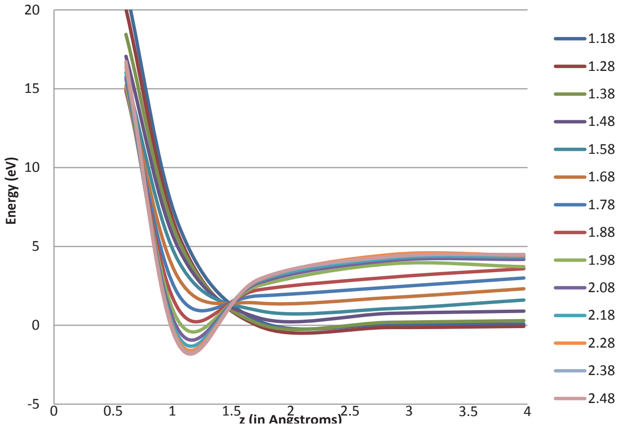

Figure 3
Potential Energy Surface (PES) **for Oxygen Molecule Adsorption on** (3,3) **Fe-SWCNT**

Table 1
PES Analysis and cNEB Data for Oxygen Molecule Adsorption

System	E_i (eV)	E_f (eV)	E_B (eV)	E_{TS} (eV)
(5,0) Pristine	-0.22	2.12	5.05	4.89
(5,0) Fe-SWCNT	-0.29	1.26	3.29	3.32
(3,3) Pristine	-0.17	-1.35	1.94	2.01
(3,3) Fe-SWCNT	-0.21	-0.53	1.30	1.35
(5,5) Pristine	-0.03	0.27	0.45	0.55
(5,5) Fe-SWCNT	-0.10	0.18	0.37	0.42

E_i and E_f are the adsorption energies of the initial and final states from the PES; E_B is the energy barrier also from the PES; and E_{TS} is the energy barrier of the transition state from the cNEB.

However, the energy of the dissociated state for the (5,0) and (5,5) cases are above the reference energy. Thus we conclude that dissociation is not favored for these cases. The obtained results are consistent with the experimental work by Barberio et al. (2009) on pristine SWCNTs as well as previous theoretical calculations on pristine SWCNTs (Giannozzi, Car, & Scoles, 2003; Dag, Gulseren, Yildirim, & Ciraci, 2003). Moreover, when comparing the reactivity of oxygen on Fe-SWCNT with the pristine cases, the general trend is that the molecular physisorption energies are stronger whereas the adsorption energy of the dissociated cases and its corresponding energy barriers are lower for Fe-SWCNT cases. This can be attributed to the modified electronic structure of the nanotube due to the effect of Fe. The surface carbon atoms in the vicinity of Fe have a depletion of occupied states near the Fermi level as compared to the surface C atoms of the pristine SWCNT (Kasai et al., 2008). This explains the weaker adsorption of dissociated states on Fe-SWCNT. However, there is a slight enhancement of the charge transfer from the surface carbons atoms of Fe-SWCNT to the molecularly adsorbed oxygen, thus explaining the stronger molecular physisorption. This combination makes Fe-SWCNTs better than pristine SWCNTs for oxygen reduction as it promotes stronger molecular adsorption, as well as easier desorption of the dissociated atoms.

SUMMARY

The atomic and molecular adsorption of oxygen on pristine and Fe-SWCNTs were investigated. The results for atomic adsorption showed that the oxygen atom adsorbs strongly on the bridge site in all the cases studied. The magnetic moments of O and Fe atoms disappear as O is adsorbed on the SWCNT surface. Also, the oxygen atom weakly adsorbs on the Fe-SWCNTs compared to the pristine cases. Similarly, the presence of Fe resulted in enhanced molecular adsorption as well as lower chemisorption energies and energy barriers for oxygen dissociation on SWCNTs. Thus the presence of Fe enhances the oxygen reduction capabilities of SWCNTs. This knowledge can be useful in designing better catalysts for oxygen reduction in various applications such as in the cathode of the PEMFC.

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