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Dioxygen Adsorption and Dissociation on Nitrogen Doped Carbon Nanotubes from First Principles Simulation

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1. Introduction

The electronic and materials properties of carbon nanotubes (CNTs), like those of recent discovered graphene and earlier found fullerenes, attracted lots of research interests due to their appealing applications in the field of molecular electronics or for the refinement of materials, such as antistatic paints and shieldings, sensor, and catalytic functionality in fuel cells, etc. Like its two/three dimensional siblings graphene and graphite, CNTs consist $sp^2$ hybridized carbon atoms and are either semiconducting or metallic depending on their helicity. CNTs can be considered in structure as rolling up a single sheet of graphene into a cylinder. Polymer electrolyte membrane fuel cells (PEMFCs) are the best candidates for automobile propulsion owing to their zero emissions, low temperature, and high efficiency. Precious platinum (Pt) catalyst is a key ingredient in fuel cells, which produce electricity and water as the only byproduct from hydrogen fuel. However, platinum is rare and expensive. Reducing the amount of Pt loading by identifying new catalysts is one of the major targets in the current research for the large-scale commercialization of fuel cells. Specifically, developing alternative catalysts to substitute platinum for the oxygen reduction reaction (ORR) in the fuel cell cathodes is essential because the slow kinetics of this reaction causes significant efficiency losses in the fuel cells. Recent intensive research efforts in reducing or replacing Pt-based electrode in fuel cells have led to the development of new ORR electrocatalysts, including carbon nanotube–supported metal particles.³,⁴ In 2006, Ozkan and coworkers reported that nitrogen-containing nanostructured carbons and nanotubes have promising catalytic activity towards ORR.⁵,⁶ In a 2008 report, Yang et al. at Argonne National Laboratory showed that the vertically-aligned CNT arrays, which are functionalized through nitrogen and iron doping by a chemical vapor deposition (CVD) process, can be electrocatalytically active toward ORR.⁷ The functionalized CNTs show promise properties as an alternative non-Pt electrocatalyst with a unique nano-architecture and advantageous material properties for the cathode of PEMFC. They further identified FeN4 sites, which are incorporated into the graphene layers of aligned carbon nanotubes, being electrocatalytic active towards ORR, by their X-ray absorption spectroscopy and other characterization techniques.
In a 2009 publication in *Science*, Gong *et al.*\(^8\) reported that vertically aligned nitrogen-containing carbon nanotubes (VA-NCNTs) can act as a metal-free electrode with a much better electrocatalytic activity, long-term operation stability, and tolerance to crossover effect than platinum for oxygen reduction in alkaline fuel cells. They excluded the effect of metal contaminants and concluded that purely nitrogen doped CNT (metal free) as the active site for ORR. They also performed hybrid density functional theory (DFT) calculations for the hydrogen edge-saturated (5, 5) CNT, in which a nitrogen atom doped in the middle of the nanotube. Based on their experimental and DFT simulation results, they put forward an O\(_2\) reduction mechanism as a four-electron pathway for the ORR on VA-NCNTs with a superb performance. Hu *et al.*\(^9\) studied the triplet O\(_2\) adsorption and activation on the side wall of defect free NCNTs using the DFT based B3LYP method with different NCNT size. From application point of view, however, the defect and edge effects may play an important role in the real reaction environment.

To further understand the properties of nitrogen doped carbon nanotubes as a metal-free electrocatalytic electrode for dioxygen reduction, Yang *et al.*\(^10\) performed first principles DFT calculations for the nitrogen doped (10, 0) CNTs. The stable structure of nitrogen doped CNTs and the properties of the N-doped CNTs for the dioxygen adsorption and reduction were studied. The results show that the nitrogen doping on the open-edges of carbon nanotubes is the most stable structure, that is consistent with the previous experimental results of Ozkan *et al.*\(^4, 5\). To study the dioxygen dissociation, the minimum energy path searching based nudged elastic band (NEB)\(^11\) method was used to calculate the dioxygen dissociation energy barrier. In the following section of this review paper, the detailed method is described. Section 3 presents the optimized open end CNT (10, 0) and one nitrogen edge-doped CNT(10, 0) structures. Section 4 gives the results of dioxygen adsorption. In section 5, recent advance in dioxygen dissociation study is introduced. A brief conclusion is provided in Section 6.

### 2. Computational method

The first principles DFT calculations with the projector augmented wave (PAW) method\(^12, 13\) were performed. The relativistic effect was included in the calculations. The Vienna Ab-initio Simulation Package (VASP)\(^14, 15, 16, 17\) was used in the simulations. The exchange-correlation interaction potentials of the many electron system both in local density approximation (LDA) and in the generalized gradient approximation (GGA) with the same model and same parameters were employed. Two sets of data show that they give the consistent results in the stability studies of nitrogen doped (10, 0) CNTs. Thus for the O\(_2\) adsorption simulations, only the LDA results are presented. In these calculations, the 2s and 2p electrons of C, N, and O atoms were included in the valence states. The 1s electrons of the atoms are considered as the core states in a frozen core approximation. Short pieces of (10, 0) CNTs with 16 atomic rings (10 carbon atoms per ring) are included in the simulations. A total of up to 160 carbon atoms are included in the full self-consistent DFT calculations. The nitrogen substitutionally doped CNTs via replacing a carbon atom by a nitrogen atom were simulated. In all of the calculations, the plane wave energy cutoff is fixed at 500 eV. The self consistent energy converged to less than 0.001 meV. All of the atomic coordinates are fully relaxed in all of the DFT calculations and the residue forces are less than 0.05 eV/Å on all the atoms. The CNTs are set in a 17.0 Å × 17.0 Å × 24.9 Å super-cell with the vacuum space separations between CNTs on the sides and along the tube axis direction larger than 9 Å
the simulations, which is large enough to ignore the periodic boundary condition effect. We also performed some test computations and found that by changing the vacuum space separation from 9 Å to 20 Å, only a change of about 0.03 meV/atom in the calculated total energy and 0.0002 µB/atom in the calculated magnetic moment are observed. Since a relatively large super-cell is used, only the gamma point is enough in the k-space sampling. Both spin polarized and non-spin polarized DFT calculations are considered in the simulations. The transition state calculations for dioxygen dissociation adsorption were investigated by using the NEB method.  

3. Optimized carbon nanotube structures

The synthesized nitrogen-containing carbon nanotubes exhibit a bamboo-like structure. Distinctively, a great part of the bamboo-like nano-structures consists of open ends of relatively short CNTs. Individual short CNTs are weakly stacked one on top of the other to create a long nano-fiber. The observed bamboo-like structure along the nano-fiber length can be attributed to the integration of nitrogen into the graphitic structure, altering the nanotube surface from straight cylinder geometry. In order to simulate the open structure of the short carbon nanotubes, a short piece (10, 0) CNT with 16 atomic rings that have 10 carbon atoms per ring was used. There are a total of 160 carbon atoms in the short piece CNT that are included in the full self-consistent DFT calculations. The CNT has a diameter of 7.84 Å, through the center of the carbon atoms, and a total length of about 15.5 Å after the optimization of the structure. Different from the previous calculations, which utilized hydrogen atoms to artificially edge-saturate those CNTs to facilitate the convergence of the DFT computations, the open-edge of the short piece CNT was not saturated using hydrogen or other atoms. Wei et al. simulated the effects of nitrogen substitutional doping in Stone-Wales defects on the transport properties of single-walled nanotubes. They eliminated the open-edges of the short CNTs by matching to two pieces of perfect CNT unit cells. In this work, nitrogen-doped CNTs either at open-edge sites or in CNT walls was simulated. In addition, the open-edges of the short piece CNTs play an important role in the nitrogen doping, as demonstrated by the previous experimental work, as well as by the first-principles calculations as discussed later. In the first-principles self-consistent DFT calculations, all atomic positions are allowed to be fully relaxed. The calculated results show that the carbon atoms on the open-edge of the short CNT have a substantial relaxation, due to the existence of some dangling bonds of the carbon atoms at the open-edge sites. The calculated C-C bond length of the carbon atoms on the open-edge of the short CNT have a substantial relaxation, due to the existence of some dangling bonds of the carbon atoms at the open-edge sites. The calculated C-C bond length of the carbon atoms on the open-edge of the short CNT is 1.39 Å, which is shorter than the C-C bond length of 1.41 to 1.42 Å in the inner atomic rings of the short CNT. This reduction of the C-C bond length for the carbon atoms at the open-edge sites is mainly due to the absence of atoms on the empty side. The calculated bond length of the carbon atoms from the second to third atomic ring is 1.44 Å, which is slightly larger than those in the inner rings (such as those from the third to fourth atomic rings), away from the open-edge of the short CNT. The results indicate that the effect of the relaxation of the third atomic ring from the open-edge of the CNTs and other inner rings would be insignificant. The spin-polarized DFT calculations for the short piece CNT were also performed. It is interesting to see that the carbon atoms on the open-edge of the CNT possess a magnetic moment of about 0.59 µB/atom. Similar spin polarization effect was also shown on a recent study of Möbius graphene nanoribbons. Other carbon atoms away from the open-edge...
and in the inner wall of the CNT do not have a noticeable magnetic moment from our computational results. This property of the carbon atoms on the open-edge with a magnetic moment is attributed to the existence of some dangling bonds. In the next sub-sections, it is demonstrated that the absorption of other atoms to the open-edge of the CNT will reduce the magnetic moment of the carbon atoms, because the dangling bond is reduced.

Fig. 1. (a) and (b) Side and top views of a N doped short CNT with N atom on the edge of the CNT; (c) and (d) Side and top views of a N doped short CNT with N atom in the middle side wall of the CNT; (e) and (f) Side and top views of a N doping in the side wall near a (5-7-7-5) Stone-Wales defect in the CNT; (g) and (h) Side and top views of a N doped CNT at the open-edge and a (5-7-7-5) Stone-Wales defect in the CNT wall. The blue ball stands for N atom; the grey balls represent C atoms. The supercell (17.0 Å × 17.0 Å × 24.9 Å) contains 159 carbon atoms and one N atom.

The nitrogen substitutionally doped carbon nanotubes, i.e., a nitrogen atom replacing a carbon atom in the short CNTs were then calculated. Four types of doping configurations were considered. They are, (i) a doping nitrogen atom substituting a carbon atom at the open-edge (Figure 1 (a) and (b)); (ii) a N atom substituting a C atom at the middle side wall (Figure 1(c) and (d)); (iii) a N atom doping at the middle side wall with a (5-7-7-5) Stone-Wales(SW) defect (Figure 1(e) and (f)); and (iv) a doping N atom at the open-edge with a (5-7-7-5) SW defect in the middle side wall of the short CNT (Figure 1(g) and (h)). We performed full self-consistent first-principles DFT calculations again. All atomic positions are fully relaxed. The calculated total energies of the four types of doping cases are -1534.58 eV, -1531.91 eV, -1530.17 eV, and -1532.54 eV, respectively. The first doping configuration (i.e., a nitrogen atom substituting a carbon atom at the open-edge of the short CNT) has the lowest total energy among the four cases and thus is the most stable configuration within the configurations studied. The total energy of a N atom substituting a C atom on the open-edge...
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The total energy of the N atom doped CNT at the middle side wall with a (5-7-7-5) Stone-Wales (SW) defect (case 3) is higher than that of case 2 by 1.74 eV and higher than that of case 1 by 4.41 eV. In the optimized structure of Case 3, the nitrogen atom in the side wall with the 5-7-7-5 SW defect is sitting between 5-5 and 7-7 defects, as shown in revised Fig. 1(e). Case 4, i.e., one N atom doped the CNT at the open-edge with a (5-7-7-5) SW defect in the middle side wall has a total energy higher than other three cases. The calculated results show that nitrogen atoms may prefer to stay at the open-edge sites of short CNTs. Both of the LDA and GGA calculations confirmed the same properties. This conclusion is consistent with the previous results of the first-principles DFT calculations of N-doped short carbon nanobells. It agrees with the previous experimental results of Ozkan et al.4,5 The above results are also consistent with the fact that at elevated temperature, the 5-7-7-5 SW defect in single wall CNTs is not stable and will eventually diffuse to the edges of CNTs and be healed by catalytic atoms, although it is possible that the 5-7-7-5 SW defect in single wall CNT could be meta-stable under weak stresses and in catalyst free syntheses environment.24 The finding is in contrast to the simulated results in a recent report for the hydrogen edge-saturated (5, 5) CNT, in which nitrogen atom is doped at the middle (5, 5) CNT sidewall.7 It should be noticed here that in the real multi-walled CNT application, the nitrogen side wall doped (5-7-7-5) SW defect may be relatively stable considering the existence of wall-defect and wall-wall interaction. To the best of our knowledge, no multi-walled CNT defect stability study report is found due to the relative large size and expensive computation cost. On the other end, the open edge may be considered as an enlarged defect thus at least partially showing the atom adsorption and catalytic property.

In the following discussions, the properties of the nitrogen doping on the open-edges of the short CNTs are introduced. The nitrogen atom on the open-edge of the CNT bonds to two carbon atoms of the second atomic ring. The two N-C bond lengths are 1.31 Å and 1.34 Å, respectively. Because we only included one nitrogen atom substituting one carbon atom on the open-edge, the short CNT in the simulation did not have a cylindrical symmetry. The cross-section of the CNT is distorted and formed to nearly triangular shape by the N doping that can be seen from Figure 1(b). The distortion of the CNT cross-section is also partly attributed to the formation of new C-C bond of about 1.49 to 1.55 Å on the open-edge of the CNT, reducing the dangling bonds of the carbon atoms on the open-edge and forming in more stable $sp^2$ hybridization. The effective charge (Bader charge) and the charge transfer of the N and C atoms in the doped CNT were also calculated. The nitrogen atom on the open-edge of the CNT obtained about 3.0 electrons from the nearest neighboring carbon atoms, i.e., turning to N$^{-3.0}$. The C atom with a N-C bond length of 1.31 Å loses about 1.6 electrons to N atom; and the C atom with a N-C bond length of 1.34 Å loses about 1.3 electrons to the N atom. The calculated effective charge may have a computational uncertainty within an estimated range of about 0.1 electrons. The remaining of the charge transfer of about 0.1 electrons to the N atom can be attributed to the second nearest neighboring C atoms or to the computational uncertainty.

The spin-polarized DFT calculation for the short piece CNT with a doping N atom on the open-edge was then calculated. The results show that the nitrogen atom did not have a noticeable magnetic moment. In addition, some of the carbon atoms around the distorted locations of the open-edge of the short CNT have a strong relaxation and lose their magnetic...
moments. Only the carbon atoms on the open-edges of CNTs, which still have a dangling bond, possess a magnetic moment from 0.1 to 0.5 $\mu_B$/atom, depending on their local environments.

4. Dioxygen adsorption on one nitrogen open edge doped CNT(10, 0)

The first-principles DFT calculations to study dioxygen $O_2$ adsorption and reduction on the nitrogen edge-doped carbon nanotubes were performed. The calculated results show that the $O_2$ can chemisorbed on a site close to the nitrogen-carbon complex with a tilted slant away from the nitrogen atom and more close to a carbon atom (Fig. 2a and b, Pauling adsorption model). The O-O bond length of the dioxygen on the end-on Pauling site increased to 1.33 Å, which is longer than the calculated bond-length of 1.22 Å in free gas $O_2$ molecule state, see Table 1. The O(1)-C and O(2)-N distances for the Pauling adsorption are 1.31 Å and 2.64 Å, respectively. The dioxygen absorbed on the Pauling site obtained partial electrons from carbon-nitrogen complex. The calculated effective charges of two oxygen are $O(1)$-0.99 and $O(2)$-0.24, respectively. The effective charge of the nitrogen atom becomes $N$-2.9 after the dioxygen adsorption, which is not much different from that before the dioxygen adsorption. The electrons obtained by the dioxygen are mainly transferred from the neighboring carbon atoms. The adsorption energy of the dioxygen on the Pauling site is about 1.53 eV/atom. The magnetic momentum of the dioxygen at the Pauling site is greatly reduced from the gas state magnetic momentum of 2 $\mu_B$ to 0.027 $\mu_B$. The carbon atom that bonded to O(1) loses its magnetic moment to nearly zero, from about 0.5 $\mu_B$ before the dioxygen adsorption. The nitrogen atom still has no noticeable magnetic moment.

![Fig. 2. (a) Side and (b) top views of the dioxygen $O_2$ adsorbed onto a nitrogen-carbon complex site of the short CNT (Pauling model). The red balls stand for oxygen atoms. (c) Side and (d) top views of the dioxygen $O_2$ adsorbed on the carbon-carbon long bridge sites away from the N-doping site of the short CNT.](www.intechopen.com)
effective charge of nitrogen did not change. The chemisorption energy of the dioxygen on this bridge site is 2.57 eV/atom. The results of the spin-polarized DFT calculations showed that the dioxygen loses its magnetic moment after the chemisorption on the long bridge site to nearly zero. The carbon atoms that adsorb the dioxygen also do not have noticeable magnetic moments, which are different from those of the carbon atoms on the open-edge of CNT with dangling bonds.

The second case of dioxygen adsorption in a short bridge-site on the open-edge of the CNT was also studied. In this case, near the dioxygen adsorption site, the open-edge of the CNT has a noticeable distortion that is attributed to the formation of new C-C bond. The dioxygen adsorption energy at this bridge site is about 0.015 eV/atom, which is much lower than that of the first case of the dioxygen adsorption discussed above. The calculated charges transfer to the two oxygen atom are O(1)-0.03 and O(2)-0.01, which is much smaller than that of the first case of the bridge-site adsorption discussed earlier. The O-O bond length is about 1.23 Å, which is nearly the same as that in the free O₂ molecule state. The O(1)-C(1) and O(2)-C(2) distances for this short bridge site adsorption are 3.65 Å and 3.76 Å, respectively. The dioxygen on this site maintained a magnetic moment of 2 µB, which is the same as that of the free gas state. All the data clearly show that the dioxygen adsorption on this short bridge-site is a physisorption, which is attributed to the loss of the dangling bonds of the carbon atoms on the open-edge of the CNT. To save space, this typical physisorption site graph is omitted here.

From Figure 2 (c) and the Bader charge analysis in Table I, it can be seen that the oxygen-carbon form a weak chemical bond (sp hybridization) at long bridge site, since the two carbon atoms at long bridge site would otherwise possess some dangling bonds, while there is strong C-C bond at the short bridge site on the open-edge of the short CNT, thus the interaction between O₂ and carbon atoms at short bridge site is weak physical adsorption.

<table>
<thead>
<tr>
<th>O₂ Site</th>
<th>O-C (Å)</th>
<th>O-O (Å)</th>
<th>MM(µB)</th>
<th>Bader charge change</th>
<th>E_{ad}(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pauling site (End-on C-N complex, Chemisorption)</td>
<td>1.31</td>
<td>1.33</td>
<td>0.027</td>
<td>O(1)\text{-0.09}, O(2)\text{-0.24}</td>
<td>1.53</td>
</tr>
<tr>
<td>Long Bridge site (Chemisorption)</td>
<td>1.34</td>
<td>1.57</td>
<td>0.001</td>
<td>O(1)\text{-0.91}, O(2)\text{-0.85}</td>
<td>2.57</td>
</tr>
<tr>
<td>Short Bridge site (Physisorption)</td>
<td>3.71</td>
<td>1.23</td>
<td>2.0</td>
<td>O(1)\text{-0.03}, O(2)\text{-0.01}</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 1. The calculated properties of dioxygen O₂ adsorption and reduction on the N-doped short CNTs. In the table, O-C is the shortest O-C distance; O-O is the O-O bond length, and MM is the dioxygen magnetic moment in µB. In the gas state, O₂ has a magnetic moment of 2µB and a bond length of 1.22 Å from our first-principles DFT calculation. E_{ad} is the low coverage adsorption energy (in eV) per atom.

5. Dioxygen dissociation on one nitrogen open edge doped CNT(10, 0)

To study the dioxygen dissociation energy barrier, the NEB method was used to study the minimum energy path from the Pauling site to the dissociated N-O and C-O state. This
section will introduce the major results of the simulations and the detailed results will be organized and publish late. To save the computation time, only top ring atoms are relaxed since the bottom carbon atoms are relatively stable and the relaxation could be safely ignored. It should be mentioned that dioxygen dissociative adsorption minimum energy path from the NEB method is not necessary the only possible reaction path for the ORR or the most important step. However the relative energy barrier comparison can be used as a measure of reactivity.

The calculated initial Pauling site is shown in Figure 3 (a), the stable dissociated N-O(1) and C-O(2) state is shown in Figure 3 (c), while the transition state is shown in Figure 3 (b). The calculated minimum energy barrier is 0.55 eV which is reduced tremendously than the gas phase dissociation energy 5.1 eV. In the transition state (Figure 3(b)), the dioxygen bond length is elongated and the dangling O(1) is moved toward the nitrogen atom. The top carbon ring atoms have a slight re-adjustment to balance the residue forces. It should be emphasized here that in real PEMFC application, the Pauling site dioxygen may be dissociated through other channels even before it is dissociated into N-O(1) and C-O(2) considering the existence of the hydrogen atoms and OH. At the transition state, there is significant charge redistribution on nitrogen, O(1)-O(2), and bonded carbon atoms. It is the local electric field that weakens the O(1)-O(2) bond and dramatically decreases the transition barrier energy.

![Fig. 3. (a) Side view of the initial state of dioxygen O\textsubscript{2} adsorbed onto a nitrogen-carbon complex site of the short CNT (Pauling model, initial state). The red balls stand for oxygen atoms, green ball stands for N atom, while black be C atoms. (b) Side view of the transition state of dioxygen/NCNT complex. (c). Side view of the dissociated two O atom adsorption on the edge carbon and N atoms of the short CNT.](image)

6. Conclusions

In this review report, first principles spin polarized DFT simulations of nitrogen substitutionally doped (10, 0) carbon nanotube (CNT) for dioxygen adsorption and dissociation are performed. The calculated results show that nitrogen prefers to stay at the open-edge of the short CNTs. Two O\textsubscript{2} chemisorption sites are found, the carbon-nitrogen complex (Pauling site) and carbon-carbon long bridge (long bridge) sites. Dioxygen O\textsubscript{2} can be chemisorbed on and reduced on the carbon-nitrogen complex at the open-edge of the
CNТ and on the open carbon-carbon sites. The carbon atoms on the open-edge of the short CNТ can possess a magnetic moment of 0.59 μB/atom, which is due to the existence of the dangling bonds of these C atoms. The chemisorption of dioxygen O2 onto both Pauling site and long bridge sites at the open-edge of the short CNТs will reduce the magnetic moments of the carbon atoms to nearly zero. Further spin polarized NEB method minimum energy barrier simulations show that the Pauling site is the possible O2 dissociation site with a reaction barrier 0.55 eV. The unique open-edge structure and charge redistribution are crucial to the novel doped CNТ catalyst design.

7. Acknowledgements

The work is funded in part by the NSF-LASiGMA program (grant number #EPS-1003897), the NASA/LEQSF (2009-2012)-Phase3-03, the LaSPACE/NASA (grant number NNG05GH22H), DOE award No. DE-FE0004734 and DE-FE0003693, and the LONI institute. GLZ acknowledged the funding supports of the National Science Foundation (Award No CBET-0754821) and the Air Force Office of Scientific Research (Award No FA9550-09-1-0367).

8. References

Since their discovery in 1991, carbon nanotubes have been considered as one of the most promising materials for a wide range of applications, in virtue of their outstanding properties. During the last two decades, both single-walled and multi-walled CNTs probably represented the hottest research topic concerning materials science, equally from a fundamental and from an applicative point of view. There is a prevailing opinion among the research community that CNTs are now ready for application in everyday world. This book provides an (obviously not exhaustive) overview on some of the amazing possible applications of CNT-based materials in the near future.

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