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## Atomistic Oxidation Mechanism of a Carbon Nanotube in Nitric Acid

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Motivated by recent experiments, we investigate how  $\text{NO}_3$ -SWNT interactions become energetically favorable with varying oxidation state of a single-walled carbon nanotube (SWNT) using first-principles calculations. Chemisorption becomes less endothermic with respect to physisorption when the SWNT oxidation state is elevated. Importantly, the dissociative incorporation of an oxygen atom into the SWNT sidewall becomes highly favorable when the SWNT oxidation state is elevated from electron density depletion in the vicinity, as caused experimentally using electrochemical potential. The elevation of the SWNT oxidation state through accumulating local charge transfer from the surrounding molecules does not have the same effect. Our investigation reveals the crucial effects of the SWNT oxidation state in understanding the molecule-SWNT interaction.

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A grand challenge for nanotechnology is to control fabrication with atomic precision, in order to construct novel materials with outstanding properties or functions. Reactions with isolated, single-walled carbon nanotubes (SWNTs) provide a promising case for directly connecting the experimental techniques for controlling single molecule chemistry to modern theoretical modeling. Recent experiments have revealed that the electrical conductance  $G$  of a SWNT is a very sensitive and effective transducer of individual chemical events on the SWNT sidewall [1–3]. This transduction allows experiments to construct devices with single bond modifications, an ideal situation for comparison to atomistic modeling.

Experimentally, oxidation and reduction reactions have been electrochemically promoted between electrolytes and electrically connected SWNTs. At an electrolyte-dependent threshold,  $G$  exhibits stochastic, discrete steps that are interpreted as single site reactions occurring on the SWNT sidewall. Discrete conductance steps provide a promising method of building and controlling with molecular precision, but the experimental data also indicate a great deal of temporal variability. The timing and magnitude of the jumps in  $G$  are found to vary, and some of the jumps are chemically irreversible [2]. Several distinct chemical mechanisms are believed to be responsible for all of the observed phenomena, and a clear model connecting different interactions with the observed effects remains to be understood. To date, most of the theoretical work in this area has explored the effects of SWNTs with different constructions [4,5]; very little work has considered the competitive conditions that might lead to bistability or irreversibility of the chemical functionalization itself, effects that are important variables in these experiments.

Here, we use first-principles calculations to investigate the fundamental molecular interactions in a representative

$\text{NO}_3$ -SWNT system. Our results show that the SWNT oxidation state has profound effects on the most stable chemical states and arrangements of the system. Furthermore, the energetic trends of the various chemical states depicted in Fig. 1 are consistent with what has been suggested from the experimental observations. These results substantiate the idea that control of the oxidation state can effectively direct molecular functionalization of a SWNT sidewall.

The electronic and structural properties of the systems considered in this work were obtained using density functional theory (DFT) calculations [6], employing a non-empirical gradient corrected exchange-correlation functional [7]. Ultrasoft pseudopotentials [8] are used to describe the valence-core interactions, and the wave functions and charge densities are expanded in plane waves with kinetic energy up to 25 and 160 Ryd, respectively. Spin-unrestricted calculations were performed with 3

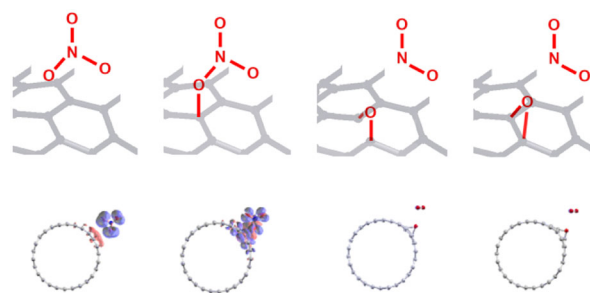


FIG. 1 (color online). Four chemical states investigated here include, from left to right, physisorbed, chemisorbed, ether-, and epoxide-incorporating configurations. Charge transfer between the molecule and SWNT is shown for the physisorbed and chemisorbed states. Blue isosurface indicates the accumulation of electronic charge while red isosurface indicates the depletion upon interaction.

Monkhorst-Pack  $k$  points [9] along the tube's axial direction for Brillouin zone (BZ) integration of the simulation cell consisting 3 chiral turns (8.60 Å) with periodic boundary conditions. We used an orthorhombic simulation cell of dimensions 26.48/26.48/8.60 ( $x/y/z$ ) Å. A Fermi-Dirac distribution at 300 K was used for describing the electronic structure. Different chemical configurations were obtained by starting the system in different initial configurations before optimization.

In order to induce different SWNT oxidation states, an integer number of electrons ( $<1\%$  of total) were removed from the simulation cell with a uniform neutralizing background charge. This amounts to coarse graining the effects of positively charged  $H^+$  species that are explicitly present in the macroscopic experimental setup. An order of the error associated with this fictitious background charge on the reaction energetics was estimated to be no more than 0.02 eV [10].

Example experimental data for single site chemistry are shown in Fig. 2. Here, SWNT oxidation is promoted by applying a moderate electrochemical potential in concentrated  $HNO_3$ . In Fig. 2, the SWNT begins with a conductance of 2  $\mu S$ , limited primarily by contact resistances [11]. A first oxidation event at  $t = 0.9$  s reduces transmission along the SWNT sidewall by approximately 60%. The second event at  $t = 2.7$  s results in a bistable electronic state that ultimately settles at 1% of the initial transmission. Discrete steps in  $G$  suggest localized reaction events and their corresponding structural changes. However, after the accumulation of two or three such oxidation events, bistabilities are frequently noted. These dynamics are presumably due to competition between different oxidation routes or mechanisms.

At an atomistic level, two different mechanisms might contribute to the initiation of SWNT oxidation. The applied electrochemical potential depletes electron charge away from the SWNT into the bulk electrolyte. Simultaneously, individual  $NO_3$  molecules are attracted to the SWNT sidewall and oxidize it via accumulating local charge transfer (Fig. 1). Our calculations distinguish between these two oxidation mechanisms, using a semiconducting (13,0) SWNT representative of those used in the

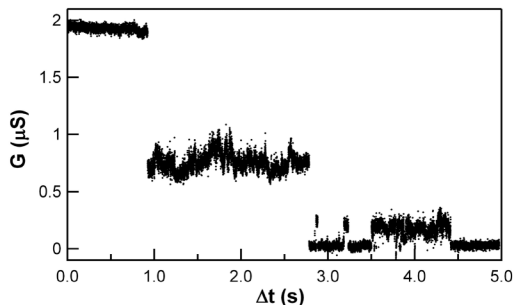


FIG. 2. Conductance during electrochemical oxidation of an isolated SWNT in concentrated  $HNO_3$ , showing multilevel fluctuations.

experiments. The relative importance of each mechanism is found to depend on both the number of  $NO_3$  molecules and the charging of the SWNT, although to varying extents.

First, consider the behavior of an electronically neutral system. In the simplest case of a single  $NO_3$  molecule approaching the SWNT sidewall, physisorption may occur. Lowdin charge analysis reveals that about  $0.4e^-$  transfers to the  $NO_3$  molecule from the SWNT. A density difference plot (Fig. 1) shows that this charge transfer is rather localized, and the distance from the sidewall to the closest  $NO_3$  oxygen atom is 3.10 Å. We do not observe a sizable deformation of the SWNT sidewall in this physisorbed state.

Alternately, the  $NO_3$  may chemisorb to the SWNT sidewall. In the chemisorbed state, the distance between the SWNT and the binding  $NO_3$  oxygen atom is much shorter (1.60 Å), and the carbon atom binding to the  $NO_3$  protrudes outward by 0.43 Å. This strain causes the chemisorbed state to be energetically *less* stable than the physisorbed one by 0.64 eV. The energetic cost of covalently deforming the SWNT sidewall is therefore considerably larger than the energy gain from the bonding. Indeed, in a smaller (8,0) SWNT, the strain from curvature is much larger and the chemisorbed state is only 0.23 eV less stable than the physisorbed state according to our calculations. This difference can be explained in terms of the higher degree of  $sp^3$  character associated with the carbon atoms in the more strained graphene sheet of an (8,0) tube compared to that of a (13,0) tube.

The energetic difference between physisorbed and chemisorbed states decreases substantially when more  $NO_3$  molecules are added to the simulation cell. We consider two additional cases of 5 and 16  $NO_3$  molecules packed close to the SWNT sidewall, as shown in Fig. 3(a). The effect of each additional  $NO_3$  is to draw more charge from the SWNT surface, effectively increasing its average oxidation state. With only one  $NO_3$  molecule present, the calculation yields the SWNT oxidation state of  $+q/274$  C atoms, but this increases to  $+q/69$  C atoms and  $+q/38$  C atoms for 5 and 16 molecules, respectively. With 16  $NO_3$  surrounding, the SWNT surface area is fully packed, and placing an additional molecule at the SWNT surface merely displaces some other  $NO_3$ , resulting in no further accumulation of charge transfer. When multiple  $NO_3$  molecules are present, the increasing level of overall SWNT oxidation also reduces the energy difference between the chemisorbed and physisorbed states. The first column of Table I summarizes the relative energies of each chemisorbed state.

The trend and sign of these endothermic energies agrees with the experimental fact that graphitic carbons do not readily oxidize in  $HNO_3$  without the additional application of an electrochemical potential [12]. To simulate effects of the applied potential, up to six electrons were removed from each system to produce an elevated oxidation state of approximately  $+q/20$  C. Under these conditions, the en-

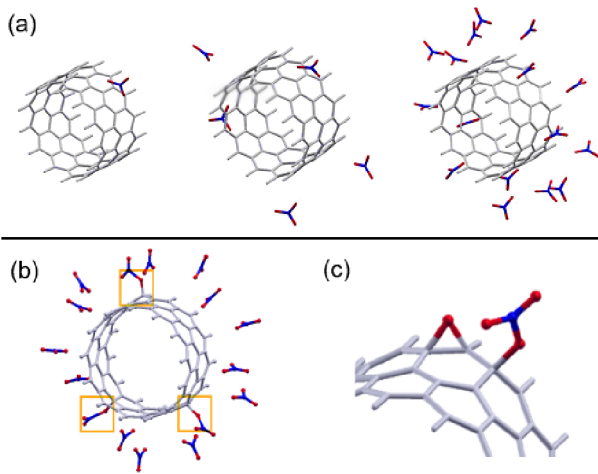


FIG. 3 (color online). (a) Atomistic configurations of three cases in which the number of reactant molecules was set to 1, 5, and 16  $\text{NO}_3$ . (b) 16  $\text{NO}_3$  configuration with 3  $\text{NO}_3$  chemisorbed. (c) Additional chemisorption after the oxygen incorporation.

ergetics of the aforementioned chemical states change considerably. The physisorbed state becomes rather unstable, with the  $\text{NO}_3$  molecule moving away slightly from the SWNT. The chemisorbed state becomes more energetically favorable, being only 0.41 eV higher in energy with respect to this weakly interacting physisorbed state while the difference was 0.64 eV without charging the SWNT as mentioned earlier. The combination of multiple  $\text{NO}_3$  molecules further reduces this energy as low as 0.04 eV (Table I). A graphical representation of the trends (Fig. 4) clearly depicts how the relative energy of the chemisorbed state depends on the SWNT's oxidation state.

By simulating conditions in the experimental situation, these calculations capture the onset of SWNT oxidation and clearly identify chemisorption as the primary reaction mechanism. Next, however, we consider further additional chemisorptions, and the nature of competing mechanisms that might drive bistable or metastable behaviors as observed in experiment (Fig. 1).

TABLE I. Relative potential energies (in eV) for chemisorbed, epoxide, and ether chemical states with respect to the physisorbed state, for the neutral and the charged case where the electron charge density was depleted to achieve an elevated CNT oxidation state of  $\sim +q/20$  C atoms.

Neutral			
	Chemisorbed	Epoxide	Ether
1 $\text{NO}_3$	0.64	0.87	0.83
5 $\text{NO}_3$	0.49	0.77	0.66
16 $\text{NO}_3$	0.28	0.54	0.56
Charged			
1 $\text{NO}_3$ ( $-5e^-$ )	0.41	-1.15	-1.13
5 $\text{NO}_3$ ( $-6e^-$ )	0.28	-1.51	-1.54
16 $\text{NO}_3$ ( $-6e^-$ )	0.04	...	-1.79

In the systems with multiple  $\text{NO}_3$  molecules present, it is straightforward to consider the case of additional chemisorptions after the first chemisorption event. Figure 3(b) shows a configuration with 16  $\text{NO}_3$  molecules around a SWNT, three of which are covalently bound. Compared to the initial endothermic chemisorption of 0.04 eV, the chemisorption of a second or third  $\text{NO}_3$  becomes increasingly more endothermic, with energies of 0.18 and 0.21 eV, respectively. This trend indicates that additional chemisorption of multiple molecules in a close vicinity becomes increasingly unfavorable, and may need to be ruled out as the most likely pathway to multiple oxidations.

A separate chemical pathway is for chemisorbed  $\text{NO}_3$  to dissociatively incorporate an oxygen atom in the SWNT sidewall, forming an epoxide with  $\text{NO}_2$  as a by-product. This configuration, and the very similar ether chemical state, are both depicted in Fig. 1. In each, the  $\text{NO}_2$  by-product is present as an electronically neutral nitrogen dioxide, having an O-N-O angle of  $\sim 132^\circ$ . The incorporation of the oxygen atom in an epoxide configuration stretches the C-C distance by 0.17 Å, with a C-O-C angle of  $67^\circ$ . In the case of the ether, the C-C distance opens up to 0.64 Å with a C-O-C angle of  $96^\circ$ . These results agree with previous calculations, which have studied these configurations in detail [13,14].

In our model, neither the ether nor the epoxide state is energetically favorable, regardless of the number of  $\text{NO}_3$  molecules in the simulation. Compared to the simple physisorbed states, these oxygen-incorporating states are 0.87 eV (epoxide) and 0.83 eV (ether) higher in energy, and approximately 0.2 eV less stable than the chemisorbed state.

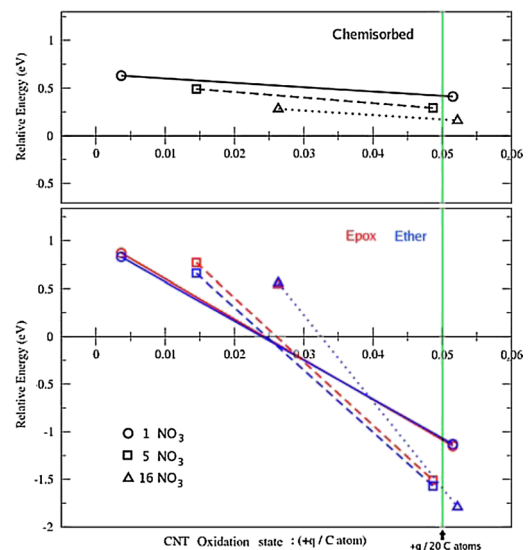


FIG. 4 (color online). Relative potential energy (eV) of the chemisorbed and epoxide or ether oxygen-incorporated states with respect to the physisorbed state. The effect of the CNT charging is represented by the lines connecting the neutral case (left end) and the charged case (to the oxidation state of  $\sim +q/20$  C atoms) (right end).

A most remarkable change occurs, however, when the SWNT oxidation state is further elevated to  $+q/20$  C by charging the SWNT. With additional charges on the SWNT, the reaction energetics change by approximately 2 eV from being endothermic to strongly exothermic. At  $+q/20$  C, the oxygen-incorporating epoxide and ether states become more stable than the physisorbed state by 1.15 and 1.13 eV, respectively. Furthermore, the effect is cooperatively enhanced by the presence of additional  $\text{NO}_3$  molecules, even at a constant oxidation state. As shown in Fig. 4 and Table I, the energy of the epoxide and ether states falls steeply as the number of  $\text{NO}_3$  molecules is increased from 1 to 16. Interestingly, in the full coverage limit of 16 molecules, only the ether defect is observed, not the epoxide one. Also, in this case the  $\text{NO}_2$  molecule exists as a nitronium ion with a linear symmetry and positive charge.

These findings are connected to another important experimental observation, that chemical defects appear to occur in very close proximity to one another [2]. In order to understand this local clustering phenomenon, we have investigated whether oxygen incorporation into the SWNT could facilitate chemisorption close to the defect site, as in Fig. 3(c). We found that with the epoxide present in an adjacent C-C bond, chemisorption is 0.18 eV more stable than physisorption in the charge depleted case, as opposed to being 0.41 eV more unstable without the nearby defect. This suggests that initial formation of the oxygen-incorporated defect induces further reactions locally on the SWNT.

Taken together, these results provide important insights into competing reaction mechanisms of SWNT oxidation. The chemisorbed state becomes more accessible when the SWNT oxidation state is elevated, though it always remains endothermic and does not allow for multiple spontaneous reactions. Spontaneous dissociation and oxygen incorporation is even more unfavorable. Following a chemisorption event, though, the elevated SWNT oxidation state causes the  $\text{NO}_3$  dissociation to become a highly exothermic process. The initial chemisorption event is probably a requisite intermediate in a two-step process of oxygen incorporation because of its role in sufficiently reducing the SWNT electron density at a site; logically, the dependence exists irrespective of how many  $\text{NO}_3$  molecules surround the SWNT. The resulting oxygen-incorporated epoxide or ether state is not only energetically very stable, it is likely to be structurally irreversible since the  $\text{NO}_2$  by-product is released and electrostatically repelled from the SWNT.

Oxidative metastabilities in the experimental data are much easier to interpret in light of this microscopic picture. Permanent, discrete drops in  $G$  are likely due to the rapid, two-step creation of a sidewall epoxide or ether. Bistable fluctuations, on the other hand, may indicate the fleeting instability of an endothermic  $\text{NO}_3$  chemisorbate. The observed interconversion between these two behaviors reflects the extreme sensitivity of  $\text{NO}_3$  dissociation to the

local oxidation state: a single elementary charge can change the dissociation probability by orders of magnitude and virtually halt the further accumulation of sidewall oxygens. Because the experimental SWNT is interacting with both a supporting substrate and the surrounding electrolyte, charge inhomogeneities are certain to exist.

Lastly, we comment on the effects of solvation on the reaction energetics discussed above. In this work, only the first layer of  $\text{NO}_3$  molecules surrounding the SWNT are included in the calculations for understanding how different chemical states become energetically more stable as a function of the SWNT oxidation. In experiments, hydronium ions are explicitly present, forming hydrogen bonds to this first layer of  $\text{NO}_3$ . While the most important effect of such solvating molecules is likely to be on the entropy rather than on the electronic properties of the interacting system, the solvating layer could indirectly perturb the stability of the physisorbed state, which is characterized by the charge transfer to the SWNT. The extent of charge transfer would certainly be modified by the solvating hydronium ions as a result of their hydrogen bonding to the  $\text{NO}_3$ , making the interaction to the SWNT weaker and the physisorbed state less stable. This would cause the relative stability of other chemical states to be shifted by a constant amount although the qualitative behavior described here would remain unchanged.

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