Effects of O₃ Adsorption on the Emission Properties of Single-Wall Carbon Nanotubes: A Density Functional Theory Study

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Abstract. In this study, we report density functional theory calculations to examine the effects of O₃ adsorption on the field emission properties of capped C(5,5) single-wall carbon nanotubes. Structural changes, adsorption energies, and the first ionization potential for possible adsorption sites are discussed, including an applied field in the calculations. The results suggest a suppression of the emission upon O₃ adsorption, explained by the charge transfer, while the favored adsorption for the etched structures rationalizes enhancement due to sharper tips upon opening of the carbon nanotube when ozonized, consistent with experimental observations.

1 Introduction

Applications of single-wall carbon nanotubes (SWCNTs) could be enhanced, or adversely affected, by surface adsorption, through non-covalent or covalent interactions (covalent surface chemistry was recently reviewed [1]). In this work we focus on the effects of surface adsorption on the field emission properties of carbon nanotubes, which attracted considerable attention for use in applications such as microwave amplifiers, X-ray sources, and flat panel displays, summarized [2], and improved upon [3]. It is notable, however, that despite significant technological developments, there are still unanswered questions, because the *I-V* characteristics often deviate from Fowler-Nordheim's relationship:

$$I = \alpha E_{\text{eff}}^2 \exp(-\beta / E_{\text{eff}}) \quad (1)$$

where α is a constant related to the geometry, E_{eff} is the effective field at the emitter tip, and β is proportional to the work function.

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Indeed, changes in the field emission of SWCNTs due to geometrical and local field effects were previously examined theoretically [4], while in our ongoing interest to enhance field emission characteristics of SWCNTs, we investigated the effects of Cs surface adsorption [5,6], which decreases the ionization potential (IP) of the SWCNT. Most recently, enhanced field emission was observed for HfC-coated carbon nanotubes, also attributed to the lower work function of HfC [7].

On the other hand, upon O₂ adsorption, a decrease in the output current was noted experimentally [8], consistent with our density functional theory (DFT) IP results [9], demonstrating a suppression of the field emission, particularly when including the effects of an electric field. At the same time, the effects of O₃ adsorption at a SWCNT tip have not yet been addressed theoretically, even though ozonized carbon nanotubes are often present in samples due to purification procedures [1]. The field emission characteristics upon ozonation were explored experimentally [10], suggesting that the observed enhancement with a longer time treatment by ozone of the sample, may be due to an opening of the carbon nanotube upon etching, resulting in sharper tips, thus leading to a higher emission current. In this study we carried out DFT calculations to study the effects of O₃ on the adsorption and field emission properties of SWCNTs.

2 Computational Details

2.1 Models

Calculations were performed by an all-electron linear combination of atomic orbitals DFT approach, applying DMOL3 [11], with the Perdew-Burke-Ernzerhof (PBE) [12] exchange-correlation functional within the generalized gradient approximation (GGA). A double numerical polarized basis set was used. The studied C(5,5) models are shown in Figure 1 (70 C; 10 H, saturating the SWCNT at one end), with the following adsorption sites: physisorption (config.-a); adsorption@h—h (config.-b); adsorption@h—p (config.-c); etched structure of adsorption@h—p (config.-d). An electric field was directed from above the tip to mimic the emission environment.

2.2 Computational Efficiency

DFT-based electronic structure calculations for molecular/periodic systems scale as ca. $O(N^3)$, where N is the number of basis functions (bf). We carried out timings for carbon nanotube model compounds, for one SCF iteration applying Gaussian03 [13] (defined as: molecular geometry; guess density matrix; evaluate integrals; solve KS equation) on a Compaq ES45, with up to 8100 bf. Calculations were carried out on 8 processors, and assuming linear scalability in this case, an $O(N^{3.45})$ scaling was noted. The serial efficiency of about 13% for an 180 atoms model (2700 bf's), when running on a 2GFlop processor, was consistent with NWChem results [14].

The bottlenecks in DFT include the electronic Coulomb problem, (x-c) quadrature, and the diagonalization of the Kohn-Sham (KS) matrix. Recent advances in achieving “linear scaling” in DFT consist, for example, of methods to tackle the Coulomb problem, based on the FMM, as reviewed [15], also by Beck [16], summarizing real-space techniques in DFT. An $O(N)$ real space technique has been applied by Bernholc's group [17].

3 Results and Discussion

3.1 Structural Parameters

Structural parameters of configurations (a)-(d) (Figure 1) are listed in Table 1. The increase in the C—C bond length at the adsorption site by 15% and 16%, for the h—h and h—p sites, respectively, demonstrated a weakening of the bonds upon O₃ adsorption, being similar to our results for sidewall ozonation [18], but larger than for O₂ [9], which is consistent with the well known reactivity of ozone [19]. In addition, a decrease of the bond angle in O₃ by 16% upon adsorption was notable. In the etched configuration, the dissociation of O₃ forms two adsorption sites (config.-d), an etched and an epoxide-type structure, for which an increase in the C—C bond distance of about 10% was noted. Small structural changes were shown upon physisorption, and the distance of O₃ to the SWCNTs was calculated to be ca. 3.2Å. These results are comparable to the results for the adsorption at the sidewall of a SWCNT [18].

Table 1. Structural parameters

	Field (eV/Å)	Pristine	config.-a	config.-b	config.-c	config.-d
O—O—O°	0.0		117	100	101	
	0.5			100	101	
	1.0			100	100	
O—O (Å)	0.0		1.30	1.46	1.47	
	0.5			1.47	1.48	
	1.0			1.46	1.50	
C—O (Å)	0.0		3.19	1.45	1.44	epoxide: 43 ketone: 1.22
	0.5			1.46	1.47	epoxide: 1.45 ketone: 1.23
	1.0			1.48	1.51	epoxide: 1.48 ketone: 1.25
C—C (Å)	0.0	1.45 (h—p) 1.40 (h—h)	1.45 (h—p) 1.40 (h—h)	1.62 (h—h)	1.66 (h—p)	epoxide: 1.60 ketone: 2.75
	0.5	1.46 (h—p) 1.41 (h—h)		1.62 (h—h)		epoxide: 1.57 ketone: 2.76
	1.0	1.46 (h—p) 1.41 (h—h)		1.62 (h—h)	1.66 (h—p)	epoxide: 1.55 ketone: 2.76

3.2 Adsorption Energies

Our results showed a strong chemisorption of O₃, with binding energies of -1.4 eV and -0.74 eV for the h—h and h—p adsorption sites, respectively (Table 2). Most notable is the stronger adsorption upon etching, namely for config.-d, characterized by a higher adsorption energy (E_{ad}= -2.77 eV), as compared to O₂ adsorption (E_{ad}= -1.17 eV) [9]. These results are consistent with the O₃ reactivity, and may explain the enhancement of field emission for the etched sharp tips of the ozone treated carbon

pristine SWCNT

config. a

config.-b

config.-c

config.-d

Fig. 1. C(5,5) SWCNT models

Table 2. Ionization potentials and adsorption energies (eV). The percentage values indicate the increase of the IPs in comparison to the value in a pristine SWCNT.

eV	Field (eV/Å)	Pristine SWCNT	config.-a	config.-b	2O ₃ @h-h config.-b'	config.-c	2O ₃ @h-p config.-c'	config.-d
IP	0.0	6.17	6.24	6.25 (1%)	6.34 (3%)	6.28 (1.6%)	6.35 (3%)	6.31
	0.5	6.17		6.21		6.32		6.55
	1.0	6.17		6.18		6.60		6.90
Ead	0.0		-0.17	-1.40	-1.36	-0.74	-0.63	-2.77
	0.5			-1.72		-1.50		-3.93
	1.0			-2.20		-2.83		-5.62

nanotubes, as observed experimentally [10]. Indeed, in the presence of the electric field, higher adsorption energies were obtained (Table 2), once again, consistent with the experimental trend [10].

3.3 Ionization Potentials

The IP results indicate a slight increase upon ozonation, of about 1—2%, comparable to our previous results for O₂ adsorption [8], as well as for –COOH modification [20]. We note that although only small changes were calculated in the IPs upon O₃ adsorption, a slightly larger effect could be expected with an increase in O₃ uptake. This was demonstrated by the IP results for 2O₃@h—p and 2O₃@h—h (Figure 2), showing an increase of about 3%. In the presence of an applied field, although the changes in the IPs for config.-c and config.-d were larger than for config.-b (Table 2), variations are small overall, and the emission enhancement is mostly due to the etching of the carbon nanotube tips [10]. The changes in the HOMO values (Table 3) are consistent with the trend obtained for IPs, while variations observed for the two different adsorption sites are being further examined [18].

Table 3. HOMO, LUMO energies as a function of field strength for configurations –b and –c

	E (eV/Å)	HOMO (eV)	LUMO (eV)	Band-Gap (eV)
O ₃ @h—h	0.0	-4.879	-4.484	0.40
	0.5	-4.835	-4.526	0.31
	1.0	-4.811	-4.695	0.12
O ₃ @h—p	0.0	-4.912	-4.737	0.16
	0.5	-4.944	-4.702	0.24
	1.0	-5.208	-4.802	0.41

Mulliken population analyses show charge transfer to the adsorbed O₃ moiety, explaining the increase of the IP, as compared to pristine SWCNTs (Figure 2). A larger charge transfer was obtained for two O₃ adducts [18].

Fig. 2. Mulliken partial atomic charges (e) for O₃ adsorption @h—h and h—p sites; 0 (1) eV/Å applied electric field (corresponding values are given in parentheses)

4 Conclusions

In this study, we report DFT calculations to examine the effects of O₃ adsorption on the field emission properties of capped C(5,5) single-wall carbon nanotubes. The first ionization potential results, including an applied field in the calculations, for possible adsorption sites, have shown a suppression of the emission upon O₃ adsorption, explained in terms of charge transfer, while the favored adsorption for the etched structures rationalizes the enhancement due to sharper tips upon opening of the carbon nanotube when treated with ozone for a long period of time, consistent with experimental observations.

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