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Modelling & Simulation Study of Interaction between Adsorbates with Carbon Nanotube for flat Display Applications

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Abstract: Nanomaterials have found potential application in many fields. In particular, Carbon Nanotubes (CNT's) have provided very promising application in the field of electronics. CNTs have very good electrical, optical, mechanical and vibrational Properties. Due to its high current density CNTs have applications in field emission for flat panel displays which can operate at low accelerating voltages. Using DMol[3] code, a first-principle density functional theory (DFT) calculation are carried out to analyze the effect of molecules interaction with carbon nanotube in the presence and absence of an electric field. In the absence of an, electric field the interaction between the polar molecules and nanotube is weak. In the presence of an externally applied electric field, the interaction between the polar molecules and nanotube is strong, and due to this there is an increase in the binding energy and a corresponding decrease in ionization potential (IP), at which electrons are easily extracted. The polar molecules and nanotube interactions increase the energy of the Highest Occupied Molecular Orbit (HOMO) in the nanotubes and in turn, this facilitates field emissions.

Keywords: Carbon nanotubes, field emission, first principles, DFT calculations, adsorption, HOMO (Higher Occupied Molecular Orbit).

1. Introduction

Carbon nanotubes are the allotropes of carbon with a cylindrical nanostructure. It has high aspect ratio of 132,000,000:1[1], which is significantly larger than any other material available today. These cylindrical carbon molecules have novel properties, making them potentially useful in many applications in nanotechnology, electronic, optics and other fields of material science. The chemical bonding of nanotubes is composed entirely of sp2 bonds, similar to those of graphite. These structures have fascinating properties [2] . They have metallic and semiconducting properties, depending on the tube geometry [3] . They show promising prospects for varied applications: mechanically they are extremely stiff

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and resistant to bending [4], and their suitability as a tip for scanning probe microscopy has also been demonstrated well [5]. Furthermore they have proven to be very good electron field emitters [6] - [10]. Field emission results from the tunneling of electrons from a metal tip into vacuum, under application of a strong electric field. CNTs can carry an astonishingly high current density, possibly as high as 10^{13} A/cm^2. Due to their small diameter and high aspect ratio, CNTs is very favorable for field emission. Even for moderate voltages, a strong electric field develops at the free end of supported CNTs because of their sharpness. These field emitters are superior to conventional electron sources and find their uses in many all kinds of applications, most importantly flat-panel display. Instead of a single electron gun, as in a traditional cathode ray tube display, CNT-based displays have separate electron guns for each individual pixel in the display. Their high current density, low turn-on and operating voltages, and steady, long-lived behavior make CNTs very attractive field emitters in this application [11, 13].

2. Computational Method

The interaction of the nanotube tip with Polar molecules were studied using the first-principles density functional theory (DFT) code DMol^3 [14] available from *Accelrys Inc*. In this code each electronic wave function is expanded in a localized atom-centered basis set with each basis function defined numerically on a dense radial grid [7, 8].

All-electron calculations were performed with a double numeric polarized basis set, the most complete set available in the code. Typical over binding associated with local density approximation was rectified through the use of the gradient-corrected PBE functional [15]. A finite basis-set cutoff of 4.0 Å was used to reduce computational time without any significant loss in accuracy [16].

A Metallic (5, 5) Armchair Carbon nanotube was chosen for our simulation. The tip consists of 30 carbon atoms which were crapped from the C60 Molecule resulting in the structure consisting of 60 carbon atoms.

A closed- cap structure was chosen because it is energetically favored with respect to an open tip even at large electric fields [12].

A uniform external field E_{FE}, directed toward the tube from the above was chosen to represent the electric field close to the tube tip under field emission conditions [9].

3. Result and Discussion

3.1. Zero Electric Field Calculation

In this section, the result of first principles density functional theory calculations for interaction between 1, 2, and 5 H_20, 1, 2 HCN, 1, 2 LiH, 1, 2 HCl molecules with nanotip in the absence of an electric field are presented and discussed.

Side views of 40 atom carbon nanotube whose structure is optimized and interacted with molecules was done and to improve the clarity, in most of the subsequence figures, the structure of the carbon nanotube are displayed using ball and stick representation as shown in fig. (1).

Table 1 lists the adsorption energy of an adsorbates with Nanotube in the absence of an electric field [E = 0]. Binding Energy is computed using following expression.

$$E_{binding[E=0]}=E_{nanotube[E=0]}+E_{adsorbate[E=0]}-E_{adsorbate+nanotube[E=0]}$$

Where use of different subscripts is self explanatory.

However, it is clear that in the absence of an electric field, the binding energy is small and, at room temperature, none of the adsorbates would be stable, let alone at an experimental temperature of up to 900K at which adsorbates-induced field emission has been observed [15]. For a better understanding of adsorption of 1, 2, 5 molecules to the carbon nanotube, an orbital analysis was carried out in the present work. The resulting electron density isosurfaces associated with the highest occupied molecular orbital (HOMO) is shown in Fig. (2).

It is noted that the 5 water molecules is adsorbed more strongly to the nanotube tip than the 3 molecules which can be due to the fact that both the (5, 5) nanotube and the five molecule posses five -fold symmetries.

3.2.1-eV/Å Calculations

In this section, the result of first principles density functional theory calculations for interaction between 1, 2, and 5 H_20, HCN, LiH, HCl molecules with nanotip in the presence of an electric field are presented and discussed. As mentioned earlier, an E_{EF} = 1-ev/Å electric field is applied since this value is comparable with the magnitude of the electric field at which field emission in the Carbon nanotubes yields a required level of field emission current.

Side views of the optimized molecules structure of the "clean" nanotube and the same nanotube containing a single molecule adsorbates are very similar to their zero electric field counter parts as shown in Fig. (1). The electric field under normal opening conditions is highly localized to the nanotip, the adsorption energy under an applied electric field [$E=E_{FE}$] is:

$$E_{binding[E=EFE]}=E_{nanotube[E=EFE]}+E_{adsorbate[E=0]}-E_{adsorbate+nanotube[E=EFE]}$$

For E_{FE} = 1eV/Å the adsorption energy for the adsorbates are given in Table 1.

This value is comparable to the binding energy of a chemical bond suggesting that adsorption of molecules to the nanotube tip changes from physorption (at E = 0) to chemisorptions (E_{FE} = 1 eV/ Å electric field).

For the better understanding of the phenomena, an attempt was made to identify the most important contribute to the increased interaction energy between adsorbates and the nanotip in the presence of an electric field. The electric field is applied along the tube axis where the dipole movements are directed. For E_{FE}=1eV/Å, the adsorption energy for a single molecule is found to be 20 Kcal/mol. The total charge density isosurfaces for the nanotube containing a 1, 2, 5 molecules are shown in fig. (2).

Table 1
Binding Energy of Adsorbates to the Nanotube in the Absence and Presence of an Electric Field

Adsorbates	*E=0 (Ha)*	*E=E_{FE}(Ha)*
1W	36.1	36.77
2W	72.37	73.38
5W	182.24	182.94
1HCN	129.69	129.90
2HCN	259.06	259.26
1LiH	36.68	36.80
2LiH	3.37	3.17
1HCL	56.51	56.48
2HCL	113.18	113.131

4. Adsorbates Enhanced Field Emission

To explain the experimentally observed adsorbates-enhanced field emission in carbon nanotube, ionization potential were computed for the clean carbon nanotube and the same nanotube containing 1,2,5 water molecules and 1,2 HCl,1,2 LiH, 1,2 HCN molecules. The Ionization Potential is defined in a standard way, i.e., the energy difference between a system with a +1charge and original system with zero charge. The lower the IP, the easier it is to extract an electron, and the higher expected field emission current at a given operating voltage. Since the "hole" left by an electron emitted from the nanotube tip is almost instantaneously filled with an incoming electron from the nanotube stem side, field emission is assumed not to alter the Zero-charge optimized molecular structure. The

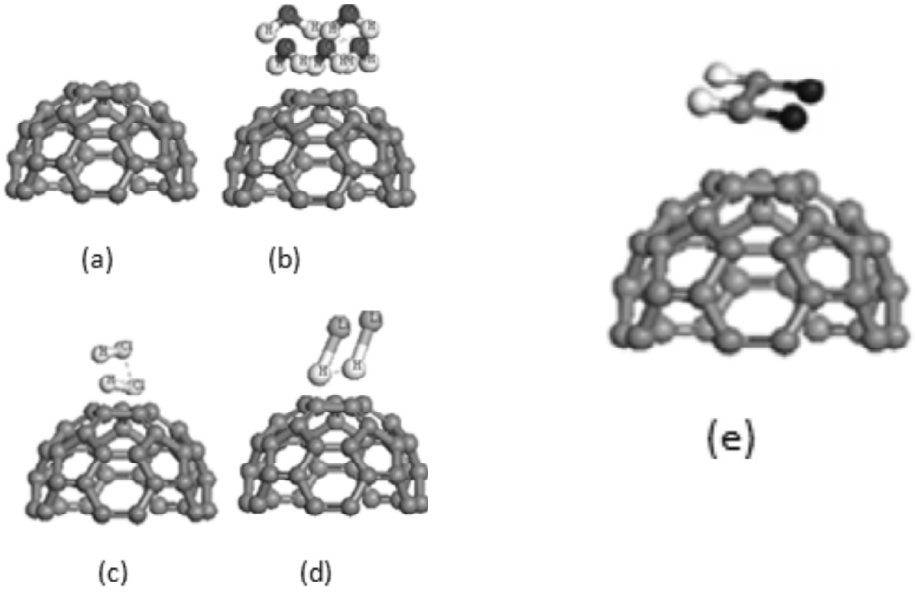

Figure 1: Optimized structures for different adsorbates on nanotip at E=0: (a) Carbon nanotube (b)five water molecule with nanotube (c)two HCl molecule with Nanotube (d) two LiH molecule with Nanotube (e) two HCN molecule with Nanotube

variation of the ionization potential with the corresponding HOMO energy in the clean nanotube and the same nanotube containing 1, 2, 5 Water molecule and 1, 2 HCl, 1,2 LiH, 1,2HCN molecules are shown in fig. (2). Table 2 displays the calculated IP for the systems.

Table 2
Ionization Potential and Position of HOMO for Nanotube and Nanotube with Adsorbates

System (at 1-eV/ Å)	*Ionization Potential (eV)*	*Position of HOMO*
Free Nanotube	6.4	-6.8
1W	6.15	-6.76
2W	6.09	-6.71
5W	5.9	-6.2
1HCN	12.02	-3.681
2HCN	11.9	-3.655
1LiH	12.023	-14.935
2LiH	9.67	-3.643
1HCl	5.45	-3.843
2HCl	4.716	-3.753

The presence of single adsorbates lowers the ionization potential by 0.1eV and multiple adsorbates lowers by 0.6 eV in the case of water molecule and 0.1 eV in other molecules. The lowering of the IP perfectly correlates with the lowering the stability of the HOMO level, as evident from the table 2.

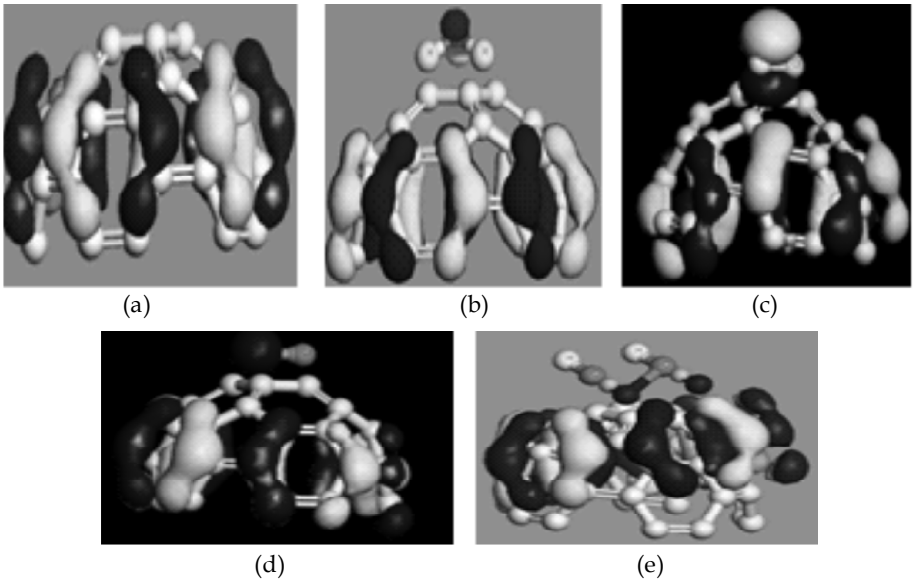

Figure 2: Highest Occupied Molecular orbital for the following : (a) Carbon nanotube (b)Two water molecule with nanotube (c) Two HCl molecule with nanotube (d) two LiH molecule with nanotube (e) two HCN molecule with nanotube

Conclusion

Based on the results obtained in the present work the following main conclusion can be drawn:

1. In the absence of an electric field the adsorbates are quite weakly adsorbed to the nanotube tip.
2. Under a 1eV/ Å uniform electric field directed along the nanotube axis, the molecules become chemisorbed to the nanotube tip and are likely to remain stable at the field emission temperature.
3. Electrostatic interaction between the adsorbates with the nanotube destabilizes the HOMO of the nanotubes which causes the lower ionization potential and promotes field emission.
4. The extent of reduction of the Ionization Potential results in the increase in field emission which in turns suggests that it can replace the electron gun in the flat panel displays can even operate at low accelerating voltages.

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