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The Effect of Gas Adsorption on the Field Emission Mechanism of Carbon Nanotubes

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Abstract: We have investigated systematically the effects of various gas adsorbates (H_2, N_2, O_2, and H_2O) on the electronic structures and the field emission properties of open edges of single-walled carbon nanotubes by density functional calculations. All of the molecules, except N_2, dissociate and chemisorb on open nanotube edges with large adsorption energies. The Fermi levels are moved toward the valence (conduction) bands for O_2 (H_2, H_2O) adsorption induced by the Mulliken charge transfer on the tube edge. The Fermi level shift for N_2 adsorption is negligible. Adsorption of H_2O enhances the field emission current, whereas H_2 adsorption does not affect the field emission current much because of the absence of the density of states near the Fermi level. The correlation of the electronic structures and the field emission current is further discussed.

I. Introduction

Adsorption of gases on carbon nanotubes (CNTs) modifies their electronic structures in various ways. Changes in carrier (electron or hole) densities induced by the charge transfer between gas adsorbates and CNT lead to very sensitive molecular sensors.[1−3] It has been suggested that CNTs might become an effective hydrogen-storage material for fuel-cell electric vehicles, by utilizing the large adsorption capacity of CNTs.[4−6] Hydrogenation of the tube wall by atomic hydrogen transforms a metallic CNT to a semiconducting one.[6] A semiconducting nanotube can be converted into a metallic one by physisorption of oxygen gases on the tube wall.[1,7−9] Functionalization of the tube wall modifies more seriously the electronic properties of the CNT. The electric properties of the CNT can be made either metallic or semiconducting by fluorine decoration of the tube wall depending on the coverage and decoration type.[10]

The tube edge is another interesting site for adsorption. The tube edge is more viable to react with gas adsorbates than the tube wall, because it has either an open or a capped structure, and thus has dangling bonds or pentagonal defects. Oxidation reaction rates of tube caps are faster than those of a cylindrical tube wall.[11] The selective oxidative etching can purify raw CNT powders using the difference of etching rates between CNTs and other nanoparticles including fullerenes or amorphous carbons.[11,12] Chemically sensitive nanoprobes can be constructed by covalent modification of a tube edge. Tip-activated gas functionalization of CNTs provides nanotips for chemical force microscopy (CFM), which is applicable to chemically sensitive imaging of nanomaterials or biomolecules.[13]

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Field emission is defined as the emission of electrons from the surface into a vacuum under electric fields and is a phenomenon related to the end structures of molecules or clusters.[14] CNTs are promising materials for field emitters because of their unique structures and prominent stability[15] and, therefore, have been used as a tip material of the field emission display (FED) device.[16] Contrary to the case of conventional metal emitters, unusual field emission current saturations are observed under high electric fields.[17] This observation is attributed to gas adsorptions, although the field emission mechanism through gas adsorbates is not clearly elucidated. Understanding the field emission characteristics would be useful to the design of efficient field emitters, which can be applied to FED device, nanoscale lithography, electron microscopy, and microwave devices. Moreover, the activity of chemically functionalized CNTs could be estimated if the field emission mechanism is revealed in detail.

Adsorption of various gases on a tube edge leads to different field emission characteristics. Exposure to oxygen gas decreases the field emission current, increases the turn-on voltage, and further degrades the tip morphology, whereas exposure to water molecules increases the field emission current.[18,19] No appreciable change in the field emission current has been observed for H_2 and N_2 adsorptions.[18,19] Physisorption of H_2O or H_2 molecules on a capped CNT edge has been studied by theoretical models,[20] which explains that H_2O adsorption enhances field emission current because it lowers the ionization potential (IP) under electric fields. Another theoretical study shows that calculated field emission currents are increased when an O atom or O_2 molecules are adsorbed on a capped nanotube,[21] contrary to experimental observations.[18,19] Although both calculations assumed that the tip structure is a capped nanotube, it is more likely that the tip has an open edge. The closed tips of the as-grown CNT powder can be easily opened by an oxidative etching during the preparation process for field emitters.[11] In addition, the capped tubes also can be opened by the high-voltage annealing procedure in the experimental situation.[22] Under high electric fields, the local Joule heating can cause the degradation of CNT tips even for multiwalled CNTs.[23]

In this report, we describe adsorption of various molecules on open tube edges and their effects on the field emission current from the result of density functional calculations. We find that molecules adsorb more strongly on CNT tips with an open edge than on those with a capped edge. We also find that H_2 adsorption does not affect the field emission current, although it also lowers the IP. We show that the available density of states near the Fermi level should be considered in addition to the IP to determine the change of field emission current correctly. The experimental results are well explained by the change in the Mulliken charges, ionization potentials, and densities of states.

II. Theoretical Approaches

We considered single-wall zigzag (10,0) and armchair (5,5) nanotubes with an open edge. The diameters of the nanotubes are 7.9 and 6.8 Å, respectively, and the average bond length is 1.42 Å. Eight and ten layers of carbon rings along the tube axis (z axis) are modeled, respectively,[24] where the bottom dangling bonds are saturated by hydrogen atoms to emulate the bulk properties. Thus, we have an open end for gas adsorption.

We used a self-consistent charge-density-functional-based tight-binding (SCC-DFTB) method[25] to determine the most stable geometries. Various adsorption sites of each molecule on both nanotubes are investigated by computationally less demanding tight-binding calculations.

Our total energy calculations and corresponding structure optimizations of the most stable geometries are based on the density functional formalism within the local density approximation (LDA) and the generalized gradient approximation (GGA), as implemented in DMol3 code.[26] The exchange-correlation energy in LDA is parametrized by Perdew and Wang's scheme,[27] and Becke's corrected exchange functional[28] is adopted in GGA. All-electron Kohn−Sham wave functions are expanded in a local atomic orbital basis set with each basis function defined numerically on an atomic-centered spherical-polar mesh. We used a double numeric polarized basis set, which is the most complete set available in DMol3 code. In this basis set, the 2s and 2p carbon orbitals are represented by two wave functions each, and 3d (2p) type wave functions on each carbon (hydrogen) atom are used to describe the polarization. No frozen core approximation is used throughout the calculations. For accurate binding energy calculations, GGA calculations are performed after geometrical optimization by the LDA. The forces on each atom to be converged during each relaxation are less than 10^{-3} au.

III. Results and Discussion

A. Adsorption Geometry. At first an adsorbate is placed far away from the tube edge and relaxed fully by the SCC-DFTB method. Once the most stable position is found, the geometry is further relaxed by the LDA to find a more accurate geometry. Figure 1 shows the most stable and fully relaxed geometries of various adsorbed molecules on a zigzag tube edge. H_2 molecules on a zigzag tube edge dissociate and chemisorb

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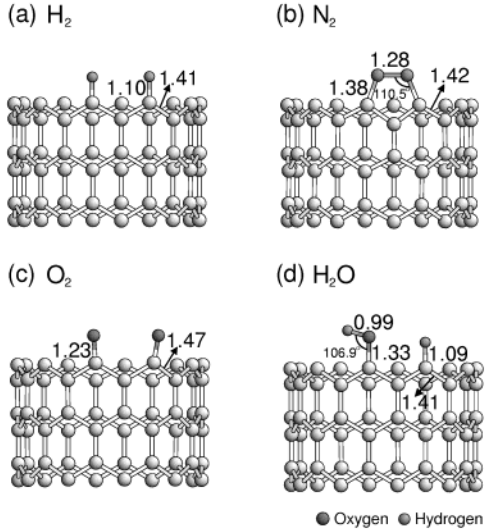

Figure 1. Optimized structures of various adsorbed molecules on the edge of the (10,0) nanotube by LDA: (a) H_2, (b) N_2, (c) O_2, and (d) H_2O adsorption. All bond lengths are in units of Å, and all bond angles are in units of degree.

with a large adsorption energy[29] of −7.11 (−6.68) eV obtained by the LDA (GGA) calculations. The LDA result overestimates the adsorption energy as compared to the GGA result, as expected.[30] The relatively large adsorption energy mainly comes from the stabilization of an edge by recovering the zigzag edge energy of 6 eV.[31] On H_2 adsorption, the CNT recovers a complete sp^2 bonding character without appreciable changes of bond lengths and bond angles on the tube edge. Unlike H_2, which dissociates on adsorption, N_2 molecules do not dissociate when adsorbed, although the bond length is increased to 1.28 Å from the gas-phase bond length of 1.10 Å.[32] The C−N bond length of 1.38 Å is longer than the bond length of 1.17 Å of a CN molecule.[32] The adsorption energy of N_2 is −4.40 (−3.29) eV.

The adsorption of O_2 on a zigzag edge is an exothermic process[12] with an adsorption energy of −9.51 (−8.84) eV. The C−O bond length of 1.23 Å is longer than the gas-phase CO bond length of 1.13 Å.[32] Significant charge is transferred from the carbon atom to oxygen atoms, resulting in an increase of O−O distance. In this case, the C−C back-bond in the CNT is extended slightly to 1.47 Å, as shown in Figure 1c. The dissociative adsorption of the O_2 molecule is also observed on defective graphite surface.[33] A water molecule dissociates into a hydrogen atom and an OH group and then adsorbs on the edge. The large adsorption energy of −6.83 (−6.14) eV is attributed to the formation of a relatively strong C−OH bond and the removal of dangling bonds on the tube edge by the adsorption of a hydrogen atom. The adsorption energies are summarized in Table 1. We find that O_2 adsorption provides the largest adsorption energy because of the strong C−O bond, whereas N_2 provides the smallest adsorption energy because of

Table 1. Adsorption Energies from the LDA (GGA) Calculations[a]

LDA (GGA)	E_{ad}			
	H_2	N_2	O_2	H_2O
(10,0)	−7.11 (−6.68)	−4.40 (−3.29)	−9.51 (−8.84)	−6.83 (−6.14)
(5,5)-seat	−4.55 (−4.18)	−2.10 (−1.10)	−6.28 (−5.80)	−4.06 (−3.64)
(5,5)-top	−5.59 (−5.31)	0.24 (0.033)	−10.10 (−9.10)	−5.17 (−4.54)

[a] All adsorption energies are in units of eV.

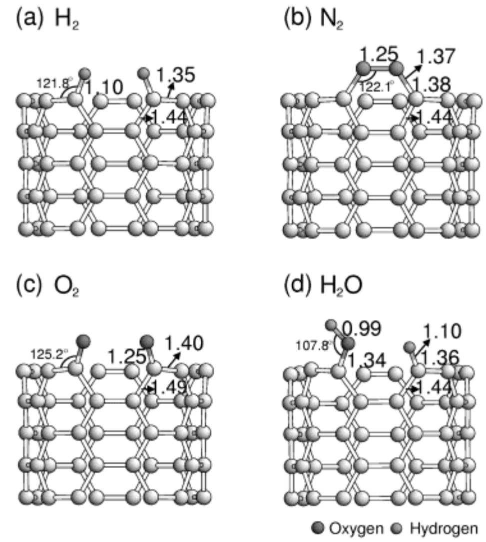

Figure 2. Optimized structures of various adsorbed molecules at the seat site of the (5,5) nanotube edge by LDA: (a) H_2, (b) N_2, (c) O_2, and (d) H_2O adsorption. All bond lengths are in units of Å, and all bond angles are in units of degree.

severe bond angle distortion (pentagon formation) and the relatively weak C−N bonds. We note that H_2, O_2, and H_2O, other than N_2, all lead to dissociative adsorptions on a zigzag tube edge. Such dissociative adsorptions of hydrogen,[34] oxygen,[35] and water[36] on the Si(001) surface were observed in experiments.

Molecules can adsorb at the seat and the top sites on an armchair edge, as shown in Figures 2 and 3. The adsorption energies of an armchair edge are smaller than that of a zigzag tube edge (see Table 1). This is expected, because the energy of an armchair edge is more stable by 0.79 eV per edge atom than that of a zigzag edge.[31] Adsorption at the top sites is shown in Figure 3. The H_2 molecule dissociates again and adsorbs at the top sites, as shown in Figure 3a. In this case, the H−H distance is farther than that in the seat site of an armchair edge (see Figure 2a), reducing the H−H repulsion. Only one C−C back-bond in CNT remains double-bonded. This results in a larger adsorption energy. N_2 adsorption at the top site forms a rectangular ring (see Figure 3b), and its strain makes the structure unstable with a positive adsorption energy. The geometry shown in Figure 3c is the lowest energy configuration among those discussed here including the adsorption structure on a zigzag edge, although two precursor states exist to reach this geometry.[12] Adsorption of H_2O at a top site is similar to that at a seat site with the OH group rotated by an H−H repulsion, as shown in Figure 3d.

(29) For an example, we define the adsorption energy (E_{ad}) of H_2 molecules as $E_{ad}(H_2) = E_{tot}(H_2 + CNT) - E_{tot}(H_2) - E_{tot}(CNT)$, where E_{tot} is the total energy of a given system.
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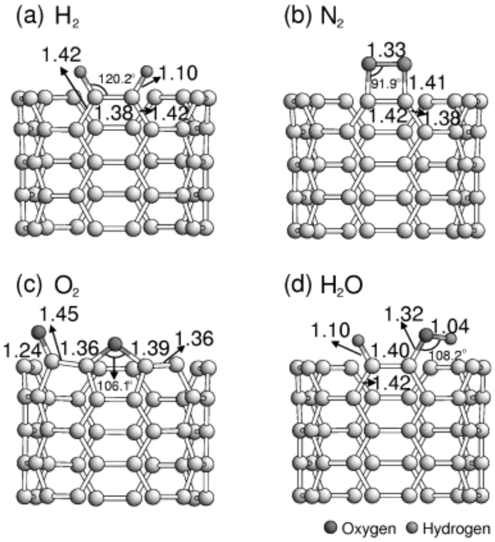

Figure 3. Optimized structures of various adsorbed molecules at the top site of the (5,5) nanotube edge by LDA: (a) H_2, (b) N_2, (c) O_2, and (d) H_2O adsorption. All bond lengths are in units of Å, and all bond angles are in units of degree.

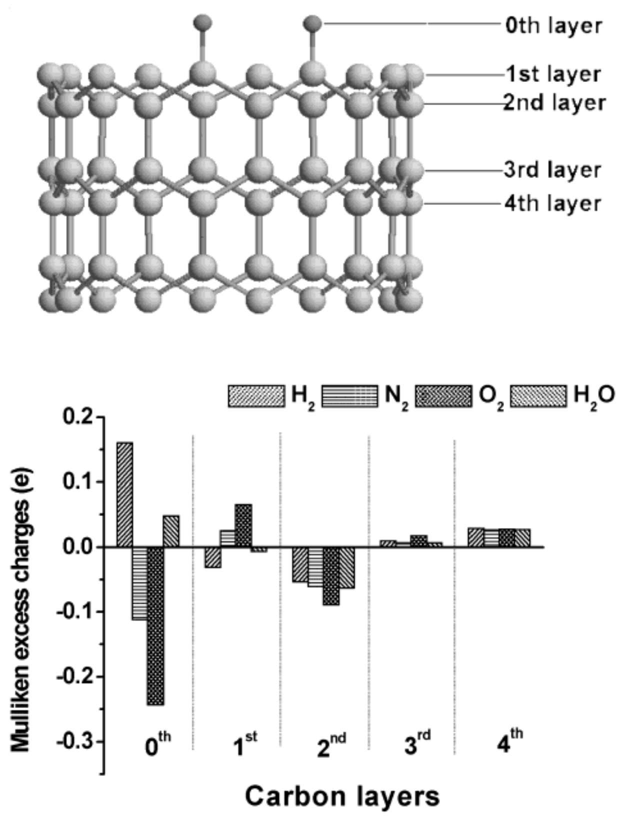

Figure 4. The Mulliken charge transfer for various adsorption geometries at the (10,0) nanotube edge. The charges are averaged for each layer indexed in the figure. The 0th layer indicates adsorbates, and the charges are also averaged for each atom. The Mulliken charges are in units of electron.

B. Field Emission Mechanism. The adsorption of these molecules on tube edges induces a charge transfer at the edge. Figure 4 shows the Mulliken charge transfer for various adsorption geometries at a zigzag edge. Charges are transferred from the adsorbates to the tube layers for H_2 and H_2O adsorptions,[37] whereas the opposite is the case for N_2 and O_2 adsorptions, following the trend of electronegativity of atoms. This phenomenon is very similar to that of graphite edge.[38] The excess charge is accumulated both in the first and in the second layer for the adsorption on a zigzag edge, whereas the excess charge is mostly accumulated in the first tube layer for the adsorption on an armchair edge. This may originate from the characteristics of a metallic armchair tube. However, the qualitative features of the charge transfer would be similar for different chiralities of CNTs, because the direction of the induced dipole moment is mostly determined by the electronegativities of individual adsorbates.

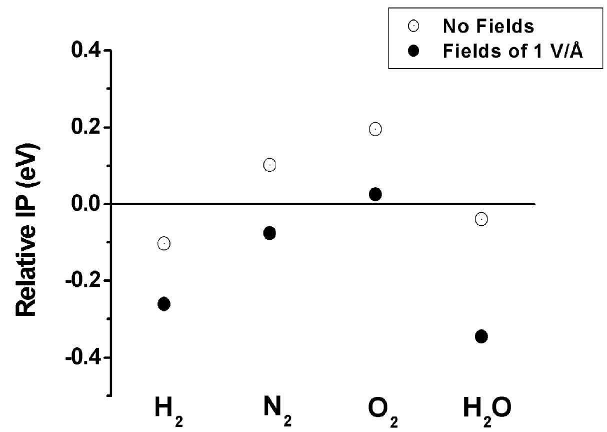

Figure 5. The relative ionization potential (IP) of the adsorbed (10,0) nanotube. The IP of the bare (10,0) nanotube is set to zero. The open circle (○) indicates the relative IP without electric field, and the filled circle (●) indicates the relative IP under the electric field of 1 V/Å.

Note that the charge transfer occurs from the zeroth layer to the rest of the tube atoms for H_2O adsorption, even in the presence of an O atom in the OH group. The excess charge transfer determines the direction of the dipole field at the edge and hence alters the magnitude of the ionization potential (IP) of a tube tip.

Figure 5 shows the IP of the adsorbed CNTs relative to a bare (without adsorbates) zigzag CNT.[39] The direction of the induced dipole field is upward (refer to the zeroth layer in Figure 4) for H_2 and H_2O adsorptions (reduce the thickness of the potential barrier when it is opposite to the direction of electric fields[40]). The IP of the CNT is thus lowered relative to a bare CNT; that is, it is easier to extract electrons from the system in these adsorption cases. The direction of the induced dipole field is reversed for N_2 and O_2 adsorptions. The IP decreases in all cases when the electric field is applied, as expected. Note that the adsorption of H_2 and H_2O lowers the IP significantly.

Another important quantity to affect the field emission current is the density of states (DOS) localized at CNT tips and gas adsorbates. Figure 6 shows the density of states of the zigzag CNT adsorbed by various molecules. The open circle indicates the DOS localized at the adsorbates. The Fermi level shifts toward the conduction band for H_2 and H_2O adsorptions, whereas it shifts toward the valence band for N_2 and O_2 adsorptions. The directional changes of the Fermi levels agree

(37) The charge transfer in a zeroth layer is summed for the H atom and OH group for the H_2O adsorption case.
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(39) The ionization potential (IP) is defined as the total energy difference between the charged system with +1 charge and the neutral system with zero charge. We used the relative IP values to a bare CNT, because the absolute IP values depend on the number of carbon atoms in the model.
(40) The constant electric field is oppositely applied along the tube axis ($-z$ direction) to describe the experimental situation in the measurement of field emission current.

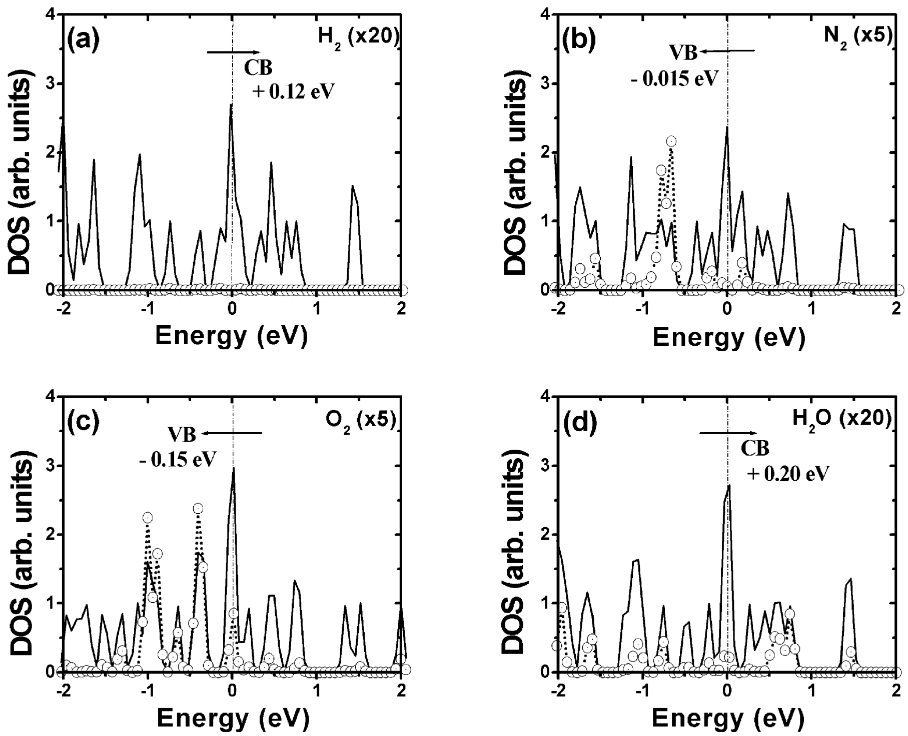

Figure 6. The electronic density of states (DOS) near the Fermi level for the adsorbed (10,0) nanotube: (a) H_2, (b) N_2, (c) O_2, and (d) H_2O adsorption. The solid line (−) indicates the total DOS of the CNT with an adsorption of each molecule, and the open circle (○) indicates the local DOS from the adsorbate only and is magnified by a factor given in each panel. The Fermi level is set to zero in all figures. The magnitude and direction of the relative shift from the Fermi level of the bare CNT are also marked in each panel. CB and VB are the acronyms for conduction band and valence band.

with those of the induced dipole fields at the edge. The amount of shift is negligible when N_2 is adsorbed. In the local DOS of adsorbates, no hydrogen state is available near the Fermi level, whereas the oxygen levels and OH levels coincide with the Fermi level.

Both the Fermi level (or work function) shift and the available density of states near the Fermi level generally determine the field emission current. We expect that the field emission current would increase on H_2 and H_2O adsorptions because the Fermi level shifts toward the conduction band (decrease of the work function). H_2O adsorption would surely enhance the field emission current, because the density of states becomes available near the Fermi level on H_2O adsorption. No significant change in the emission current, however, will be observed on H_2 adsorption because of the absence of available states near the Fermi level. These results agree well with the experimental observations.[18,19] The emission current increase was also predicted even for the water molecules physisorbed on a capped tube edge.[20] The importance of the available charge density near the Fermi level is demonstrated in Figure 7 for a H_2O adsorption case. Although the highest occupied molecular orbital (HOMO) is not localized in the OH group, the field emission current emits through the available lowest unoccupied molecular orbital (LUMO) in the OH group, when the electric field is applied.[41]

No work function change is expected on N_2 adsorption because of a small Fermi level shift. Adsorption of O_2 induces large current degradation because of the large Fermi level shift toward the valence band (increase of the work function) and a large available density of states near the Fermi level. These expectations all agree well with experimental observations.[18,19]

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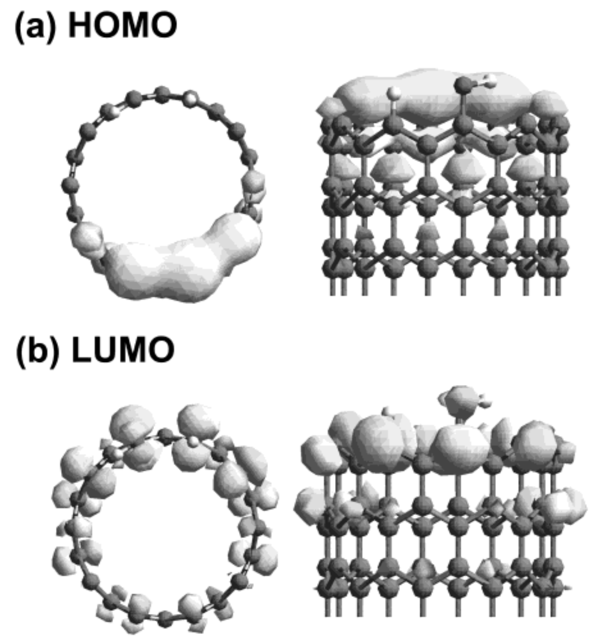

Figure 7. Top and side views of (a) HOMO and (b) LUMO: the (10,0) nanotube with an adsorption of H_2O molecule under the electric field of 1 V/Å.

IV. Conclusions

We investigated the adsorption of molecules (H_2, N_2, O_2, and H_2O) on CNT edges using density functional calculations. Possible field emission mechanisms of CNT through the gas adsorbate are suggested, and experimental results are well explained by these mechanisms.

(1) H_2O, H_2, and O_2 molecules dissociate and chemisorb on CNT edges with large adsorption energies, whereas N_2 does

not dissociate on adsorption. The adsorption energies depend on the structure and adsorption sites of the CNT edges and increase as follows: $N_2 < H_2O < H_2 < O_2$.

(2) Adsorption of these molecules induces a charge transfer and determines the direction of the dipole field at the CNT edges. Charges are transferred from the adsorbates to the CNT edges for H_2 and H_2O adsorptions, whereas the direction is reversed for N_2 and O_2 adsorptions.

(3) The relative ionization potentials reflect the trend of charge transfers. These values decrease under an electric field. We note that the ionization potential is significantly lowered by H_2 and H_2O adsorptions.

(4) According to the tendency of Fermi level (or work function) shift and the available density of states near the Fermi level, adsorption of H_2O enhances the field emission current, whereas adsorption of O_2 decreases the emission current from CNT tips. Adsorption of H_2 and N_2 does not affect significantly the field emission current. These results agree well with the experimental observations[18,19] and would help design efficient field emitters of molecular electronic devices.

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