

# Ab initio calculations of dimensional and adsorbate effects on the workfunction of single-walled carbon nanotube

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## Abstract

The workfunctions of single-walled carbon nanotubes (SWNTs) with various geometries and adsorbates have been calculated by the ab initio plane-wave, pseudopotential method. The infinitely-long, capped, open-ended, and close-ended nanotubes show the workfunctions of 4.73, 4.8, 4.43 and 3.75 eV, respectively, and these results exhibit a good agreement with experiments. The effects of participation of foreign adsorbates on the nanotube surface both physically and chemically on the variations of workfunctions have also been studied. In the physisorption process, the electrostatic interaction between adsorbates and nanotubes leads to surface charge redistribution and to workfunction variations. In the chemisorption process, various values in workfunction can be understood in terms of the surface dipole of the terminated bond.

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## 1. Introduction

Carbon nanotubes have attracted considerable attention due to their unique geometry and prominent electronic properties which demonstrate potential applications in field emission displays [1] and other vacuum microelectronic devices [2]. Their high aspect ratio leads to a large electric field enhancement and a low emission threshold voltage. The other important factor which governs the field emission behavior is the workfunction of the emitter. Field emission from carbon nanotubes has been described by the Fowler–Nordheim tunneling theory [3], suggesting that emission act as a traditional tunneling process through high-aspect ratio carbon nanomaterials, with a workfunction similar to that of graphite. However, a more complicated emission mechanism is required to account for the observed changes in the slope of current–voltage characteristics. It is believed that adsorbates on the surface may be responsible for this behavior. For example, H<sub>2</sub> molecules do not affect the emission behavior noticeably but water vapor, however, is found to significantly enhance the

emission current. Although the workfunction of a filed emitter can be derived directly from the current–voltage characteristics, the uncertainty of local geometry of nanotubes leads to the unreliability of obtaining workfunction directly from the Fowler–Nordheim model. Several groups have attempted to estimate the workfunctions of single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs) by more sophisticated experiments and the values of workfunctions obtained vary from 3.7 to 5.6 eV [4,5]. In this paper, we have sought to apply the most sophisticated, ab initio, plane-wave, density functional theory (DFT) program to investigate the variations of workfunctions of SWNTs with different geometries and adsorbates.

## 2. Geometry

In our calculations, four types of cylindrical carbon cages are chosen to represent different geometrical structures of arm-chair (5,5) carbon nanotubes, which are (a) infinitely-long, (b) capped, (c) open-ended and (d) close-ended (H-terminated), respectively, as seen in Fig. 1. For the type (a) model, a supercell consists of 60 carbon atoms is constructed to model an infinitely-long carbon nanotube. A capped carbon nanotube is

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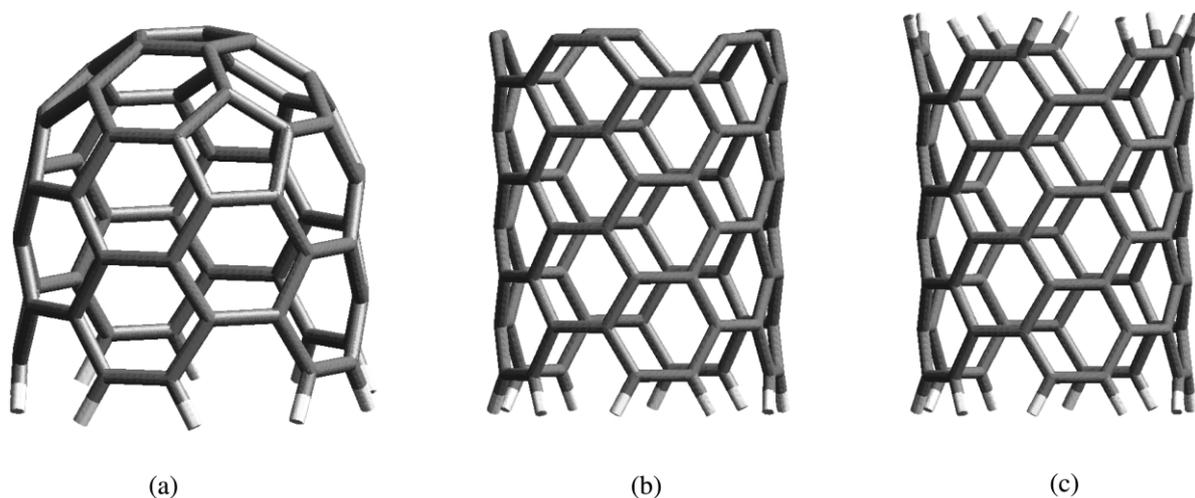


Fig. 1. Structural models of (a) capped, (b) open-ended, and (c) close-ended carbon nanotubes.

represented by a three-layer (30 atoms) stem where one mouth is capped by a half of a  $C_{60}$  molecule and the dangling bonds at the other end are saturated by hydrogen atoms to avoid the boundary effects, giving a final structure consisting of 70 atoms. The open-ended (5,5) nanotube consisting of 80 carbon atoms is constructed where one mouth is open with unsaturated carbon atoms and the other is H-terminated. The close-ended carbon nanotube is modeled by a similar orientation as the previous open-ended nanotube but with both ends terminated by hydrogen atoms. All these structures are constructed within a tetragonal supercell with a lattice constant  $30 \text{ \AA}$  along the  $z$ -axis to represent the vacuum slab and the separation of  $12 \text{ \AA}$  along the  $x$ - and  $y$ -axes to avoid the interaction between two adjacent nanotubes. These structures are then fully optimized until the force on each atom during relaxation is less than  $0.005 \text{ eV/\AA}$ . The equilibrium C–C bond length of the infinitely-long carbon nanotube is approximately  $1.43 \text{ \AA}$ . The optimized geometry of a capped (5,5) nanotube exhibits that the top atoms at the pentagon have an average bond length of  $1.44 \text{ \AA}$ . For the open-ended carbon nanotube structure, the carbon atoms at the mouth are found to move closer with a C–C separation of approximately  $1.23 \text{ \AA}$ . The close-ended nanotube structure shows an average C–C bond length of  $1.37 \text{ \AA}$  and an average C–H bond length of  $1.08 \text{ \AA}$  at both ends. To study the influence of different adsorbates on the workfunctions of carbon nanotubes, a systematic study of interaction between various adsorbates and the capped nanotube surface is carried out. Both physisorption and chemisorption on the carbon nanotube surface are taken into account. In the physisorption process, the adsorbate molecules,  $H_2O$  and  $H_2$  are initially located at a distance of  $1.5 \text{ \AA}$  above the nanotube tip and reach to a distance  $\sim 3 \text{ \AA}$  above the nanotube tip after relaxation. This

weak interaction primarily results from the electrostatic force in nature between molecules and nanotubes. To mimic the chemisorption on the nanotube surface, the top surface of the nanotube is terminated with H, O and OH atoms, respectively. The structural changes of carbon atoms terminated with these adsorbate atoms now become significant in accompany with bond formations and breakings.

### 3. Theoretical approach and computational details

The calculations are performed using the CASTEP code [6,7], which is a plane-wave, pseudopotential program based on density functional theory (DFT). Generalized gradient approximation (GGA) [8] is used with the exchange-correlation potential by Wang and Perdew (PW91) [9,10]. The ion–electron interaction is modeled by the non-local real space [11], ultrasoft pseudopotential [12]. A plane-wave basis with a cut-off energy of  $340 \text{ eV}$  and  $\Gamma$  point approximation are used for our calculations. The workfunction  $\Phi$  of a metal surface is defined as the energy needed to take an electron from the Fermi level  $\mu$  to the vacuum level, by  $\Phi = \varphi - \mu$  where  $\varphi$  is the electrostatic potential caused by a surface dipole resulting from the spilling-out of electron density at the metal surface [13,14]. Different from the solids, the surface of one SWNT is modeled by its wall and tip due to its unique geometrical characteristics. The electronic structure of a SWNT surface is then represented by that of its tip and wall. Therefore, the difference in potential energy of one electron between the highest occupied molecular orbital (HOMO) and the vacuum level is defined as the corresponding ‘localized workfunction’ which is different from the conventional definition of workfunction. The vacuum level in our calculations is defined as the

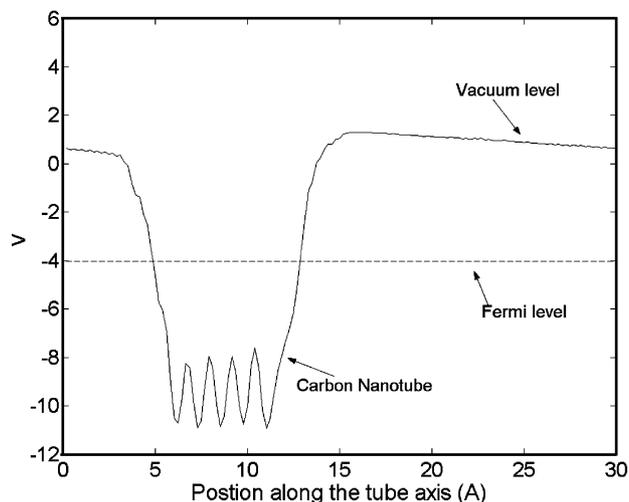


Fig. 2. Potential distribution along the carbon nanotube axis.

average value of potential energy distributions at the vacuum region during which the potential energy nearly comes to a constant value, as shown in Fig. 2.

#### 4. Results and discussion

The calculated workfunctions are summarized in Table 1. The infinitely-long and capped armchair nanotube are found to have a workfunction of 4.73 eV and 4.8 eV, respectively. These values show a good agreement with the recent experimental measurements of SWNTs bundles with a value of 4.8 eV by Suzuki et al. [4] using the ultraviolet photoemission spectroscopy. Although the (5,5) armchair nanotube is metallic, the

capped nanotube is found to be semiconducting with an energy gap of 1.6 eV between the HOMO and LUMO (lowest unoccupied molecular orbital), resulting from the half of a  $C_{60}$  molecule. The corresponding local charge densities of the HOMO and LUMO are found mostly localized at the side of the tip, not at the top of the hemisphere. The detailed electronic structure and localized states at carbon nanotube tips have been investigated by Carroll et al. [24]. The relaxed structure of the open-ended nanotube has a smaller diameter at its mouth with a shorter C–C bond length of 1.23 Å than 1.43 Å before relaxation. The formation of triple bonds at the tube mouth is also seen in the morphology of multiwalled carbon nanotubes [25]. The non-bonding valence electrons at the mouth of the open-ended nanotube give the states of higher occupied energy levels and this leads to a reduction of its workfunction with a value of 4.39 eV, lower in comparison with the previous molecular orbital calculation [15,16]. This implies that the open-ended nanotube will demonstrate better field emission properties with respect to the capped nanotube if a similar geometry enhancement factor is applied. The close-ended nanotube exhibits a further reduction in its workfunction with a value of 3.75 eV and the resulting lower workfunction can be attributed to the presence of a relatively small dipole on the C–H bond,  $C^{\delta-}-H^{\delta+}$  owing to the different electronegativity between C and H. The potential difference across the dipole lowers the distance between the Fermi energy and the vacuum level, leading to a reduction of workfunction. Similar phenomena are also seen in the H-terminated diamond surface, which leads to its negative electron affinities [17]. Our result is opposite to the previous report by

Table 1  
Workfunctions of carbon nanotubes with various geometries and adsorbates

Nanotube	Adsorbates	Workfunction (this work) (eV)	Workfunction (other groups) (eV)
Infinitely-long	None	4.73	4.68 <sup>a</sup>
Capped	None	4.8	5.08 <sup>b</sup>
Open-ended	None	4.39	4.86 <sup>c</sup>
Close-ended	10 H atoms (Termination)	3.75	5.44 <sup>c</sup>
	Physical adsorption		
Capped	1 water <sub>up</sub>	4.60	
Capped	1 water <sub>down</sub>	5.01	
Capped	1 H <sub>2</sub>	4.77	
	Chemical adsorption		
Capped	2 H atoms	3.95	
Capped	2 O atoms	5.22 <sup>d</sup>	
Capped	2 O atoms	4.79 <sup>e</sup>	
Capped	2 OH	4.9	

<sup>a</sup> Chen et al. [22].

<sup>b</sup> Ye et al. [23].

<sup>c</sup> Perdew et al. [8].

<sup>d</sup> Molecular adsorption.

<sup>e</sup> Atomic adsorption.

molecular orbital approximation, where the open-ended nanotube exhibits a lower workfunction than the close-ended one [15,16]. This may attribute to that the tight-binding (TB) calculations in [15,16] are unlike to get the correct workfunction because TB does not use real orbitals and therefore does not give dipoles properly.

We now discuss the variations of workfunctions of nanotubes owing to the participation of foreign molecules during field emission behavior. Current recovery experiments [18–20] show that both physisorption and chemisorption are responsible for the observed current–voltage curve deviation from the typical Fowler–Nordheim tunneling model. For example, the emission current is found to be enhanced pronouncedly in the presence of water molecules, leading to a saturation of emission current. Such a current enhancement effect can be lowered after a higher temperature is applied, by removing the water adsorbates. The emission current can be then recovered after introducing water adsorbates again. Some adsorbates, like O<sub>2</sub>, on the contrary produce a substantial current degradation, resulting from chemisorption such as the formation of C–O dipoles. In our study, both physisorption and chemisorption on the nanotube surface are taken into account.

Firstly, in the calculation of physisorption, water and H<sub>2</sub> molecules are chosen to study their influence on the workfunction variations, respectively. According to our calculations, the polar water molecules above the capped nanotube have two stable structures in zero electric field, referred to water<sub>up</sub> and water<sub>down</sub>, respectively (water<sub>up</sub> represents the oxygen atom which is closer to the nanotube surface than hydrogen atoms; water<sub>down</sub> represents the hydrogen atoms which are closer to the nanotube surface than the oxygen atom). Both these structures are initially located at a distance of 1.5 Å above the cap and the fully relaxed models show that the water adsorbates migrate to a position of ~3 Å above the tube tip. The binding energy of an adsorbate is defined as

$$E_{\text{binding}}(\text{CNT} - \text{H}_2\text{O}) = E_{\text{total}}(\text{CNT} + \text{H}_2\text{O}) - E_{\text{total}}(\text{CNT}) - E_{\text{total}}(\text{H}_2\text{O})$$

where  $E_{\text{total}}(\text{CNT} + \text{H}_2\text{O})$  and  $E_{\text{total}}(\text{CNT})$  are the total energies of the carbon nanotube with and without a water adsorbate, respectively.  $E_{\text{total}}(\text{H}_2\text{O})$  is the total energy of an isolated water molecule. The binding energy of the water<sub>up</sub> and water<sub>down</sub> exhibit a similar value less than 0.2 eV, in agreement with the experimental observation that adsorption of water molecules on the CNT's surface is physisorption and can be easily removed under a higher temperature or electric field [18]. The calculated workfunction of the water<sub>up</sub>–nanotube model has a value of 4.60 eV, with a value of 0.20 eV lower than the clean nanotube. The workfunction of water<sub>down</sub>–nanotube system, however, shows a value 5.01 eV with a value of 0.21 eV higher than the

clean nanotube. Such a difference results from the charge redistribution on the nanotube surface caused by the participation of water adsorbates. In the water<sub>up</sub>–nanotube system, the H<sub>2</sub>O molecule consists of a negatively charged oxygen atom and two positively charged hydrogen atoms with a bond angle of 105°. The negatively charged oxygen atom will ‘push’ the spilling-out electron density into the nanotube surface, leading to a reduction of surface dipole and its corresponding workfunction. In the water<sub>down</sub>–nanotube system, however, the two positively charged hydrogen atoms ‘pull’ the electron density out of the nanotube surface into the vacuum, raising its surface potential and workfunction. The resulting charge redistribution on the nanotube surface by water adsorbates can be seen in Fig. 3. The charge density difference of water–nanotube is defined as

$$Q(\text{charge difference}) = Q(\text{CNT} + \text{water}) - Q(\text{CNT}) - Q(\text{water})$$

It is clearly shown that in the water<sub>up</sub>–nanotube system, the charge density above the tip surface decreases and the charge density below the tip surface increases, corresponding to a reduction of its surface dipole. This will lower its workfunction. On the contrary, in the water<sub>down</sub>–nanotube model, the charge density above the tip surface increases and the charge density below the tip surface decreases, corresponding to an enhancement of its surface dipole. This will raise its workfunction. Recent calculations [21,22] show that in the presence of electric field pointing from the tube tip to the tube stem, the water<sub>down</sub> molecule has a more stable configuration than the water<sub>up</sub> molecule due to the interaction of the adsorbate dipole with electric field. These water adsorbates produce tunneling states around the Fermi level under electric field. Charge transfer effects from nanotubes to water adsorbates become more significant through these states under electric field, which may account for the current enhancement effects in experiments. The non-polar H<sub>2</sub> molecule, located parallel to the top pentagon surface, is found to have less influence on the workfunction of the nanotube, giving a value of 4.77 eV similar to the clean nanotube of 4.8 eV. H<sub>2</sub> molecules are known to physisorb on the outer surfaces of carbon nanotubes [23] and are easily desorbed in a high field environment. This may explain the lack of influence of H<sub>2</sub> on the field emission characteristics of carbon nanotubes.

We now consider the effect of chemisorption on the nanotube surface. The adsorbates under the high electric field during emission may result in several possible metastable forms, such as charged states or radicals. These metastable states may, furthermore, form chemical bonds with carbon atoms on the nanotube surface. The variations of workfunctions as a result of chemisorption between C atoms and different adsorbates are also shown

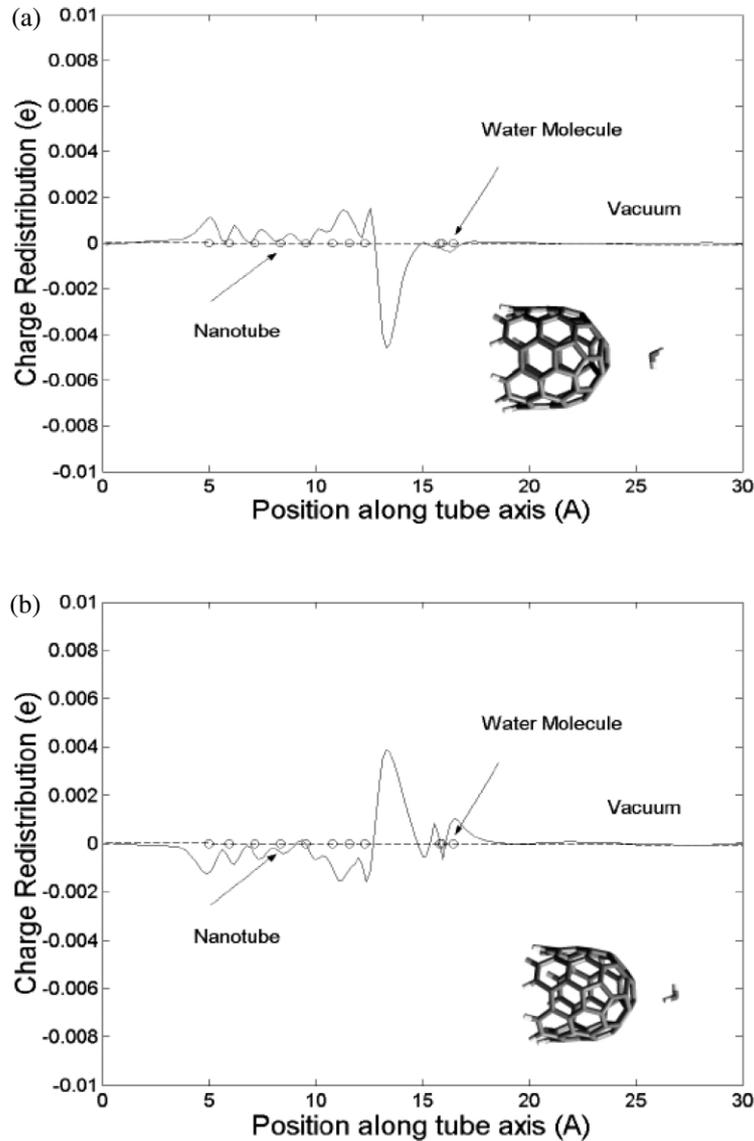


Fig. 3. Charge difference for water adsorbate and carbon nanotube surface (a)  $\text{water}_{\text{up}}$ -nanotube surface; (b)  $\text{water}_{\text{down}}$ -nanotube surface. (The circles indicate atomic positions.)

in Table 1. All these calculations are based on the structure of a capped nanotube with various adsorbates. The hydrogen-terminated capped structure has a C–H bond length of 1.11 Å and is found to have a lower workfunction of 3.95 eV than 4.8 eV for a clean capped nanotube. The C atoms vary from being a  $\text{sp}^2$ -like planar configuration before relaxation to being a  $\text{sp}^3$ -like tetrahedral configuration after relaxation. The reason for the reduction of workfunction for the H-terminated surface is mainly attributed to lowering surface potential similar to the discussions mentioned above. The models for the oxygen-terminated nanotube surfaces are shown in Fig. 4a,b, representing the molecular and atomic adsorption, respectively. For the molecular adsorption case, oxygen molecules are bonded with two carbon atoms on the tip to form a C–O–O–C four-membered

ring and the weaker  $\pi$  bonds between two carbon atoms are replaced by two stronger C–O  $\sigma$  bonds, exhibiting a four-fold configuration of carbon atoms. This model is found to have a workfunction 0.4 eV higher than the clean nanotube. Due to the larger electronegativity of O atoms, the C–O bond will produce a surface dipole,  $\text{C}^{\delta+}\text{--O}^{\delta-}$ , lowering the band energies inside the surface with respect to the fixed vacuum level. The magnitude of increase in workfunction will become more significant if more oxygen molecules adsorb on the nanotube surface. This may account for experimental results that  $\text{O}_2$  exposure increases the turn-on field of carbon nanotubes and lowers the emission current. Such current degradation results from the formation of C–O dipoles, not from permanent structural damage. For the atomic adsorption case, two oxygen atoms are initially located

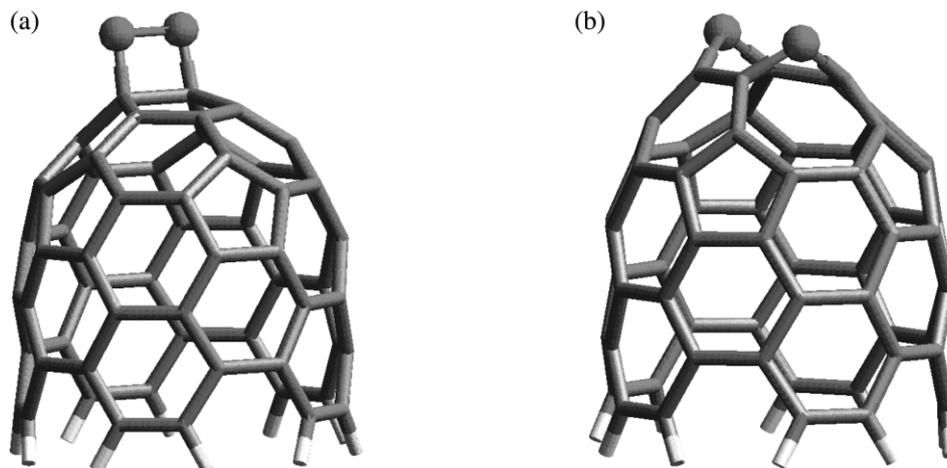


Fig. 4. Oxygen adsorption configurations: (a) molecular adsorption, (b) atomic adsorption.

over the pentagon–hexagon bonds on top surface and bonding rearrangements have been found after relaxation. The C–C bonds break and C–O bonds are formed as seen in Fig. 4b. Although oxygen might be expected to raise the workfunction, the carbon atoms, unlike in the molecular adsorption, still keep a three-fold configuration with non-bonding valence electrons which lower the workfunction. The calculated workfunction of this model therefore shows a similar value of 4.79 eV to the clean nanotube. The OH-terminated surface does not show an apparent change on the workfunction of carbon nanotube. The influence from oxygen and hydrogen atoms on the nanotube surface seems to cancel each other, giving a slightly higher workfunction of 4.9 eV. However, the situation will be more complicated due to the C–O–H bond angle.

## 5. Conclusion

In summary, we have performed the studies of workfunction variations of a series of carbon nanotubes with different geometries and adsorbates based on *ab initio*, plane-wave pseudopotential, density functional theory calculations. The capped nanotube shows a workfunction of 4.8 eV in a good agreement with experimental findings. The open-ended nanotube has a lower workfunction of 4.39 eV due to the non-bonding valence electrons at the mouth giving higher energy levels. The close-ended nanotube has, furthermore, a lower workfunction as a result of the presence of surface dipoles on the C–H bonds which lower the distance between the Fermi energy and the vacuum level. The effects of adsorbates on the workfunctions of nanotubes exhibit different behavior between physisorption and chemisorption. In the physisorption process, the electrostatic interaction between adsorbates and nanotubes results in surface charge redistribution leading to the variations of

workfunctions. In the chemisorption process, the formations of chemical bonds between adsorbates and nanotubes leads to the change of surface dipoles and to the variations of workfunctions. It is found that H-terminated surface will lower the workfunction and O-terminated surface will raise the workfunction, which may account for the observed substantial current degradation after oxygen exposure during field emission.

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