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Dependence of workfunction on the geometries of single-walled carbon nanotubes

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Abstract
The effective workfunctions of single-walled carbon nanotubes of armchair (5, 5) and zigzag (9, 0) with various geometries have been calculated by first-principles calculations. The results show that the capped and H-terminated zigzag (9, 0) carbon nanotubes exhibit a lower workfunction value than the armchair (5, 5) nanotubes with a similar diameter. The open-ended (without H termination) (5, 5) nanotube, on the other hand, shows a lower workfunction than the open-ended (9, 0) structure. The former exhibits a significant formation of triple bonds at its mouth part after relaxation, which reduces the surface dipole and lowers its workfunction, the latter exhibits a higher density of unsaturated dangling bonds, raising its surface dipole and giving a higher value of workfunction.

(Some figures in this article are in colour only in the electronic version)

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. Up to now, most field emission studies on carbon nanotubes have described the emission process by the Fowler–Nordheim tunnelling theory [3], suggesting that emission occurs by the quantum mechanical tunnelling of electrons through high-aspect ratio carbon nanomaterials, with a potential barrier similar to that of graphite. It is well known from experiments as well as band structure calculations that the electronic structure of the nanotube depends strongly on its geometrical parameters, like the diameter of the tube and its helicity [4]. Metallic and semiconducting tubes both exist. The tip of a carbon nanotube has different electronic properties from those encountered along the nanotube sidewall [5]. The workfunction is another critical quantity in understanding the field emission properties of carbon nanotubes. The workfunction Φ of a metal surface is usually defined as the energy needed to take an electron from the Fermi level μ to the vacuum level, by $\Phi = \varphi - \mu$, where φ is the electrostatic potential caused by a surface dipole resulting from the spilling-out of electron density at the metal surface [6, 7]. Experimental measurements on the workfunction of the single-walled nanotube bundles, determined by ultraviolet photoemission spectroscopy in a vacuum, exhibit the values ranging from 4.8 to 5.1 eV [8]. Recent first-principles calculations show that for the infinite long single-walled carbon nanotube, the workfunction of nanotube bundles exhibits a slightly higher value than individual tubes, and the value decreases dramatically upon metal intercalation [9]. It is believed that electrons are mainly emitting from the tip of a nanotube during the field emission process and therefore the electronic structure, as well as its workfunction at the tip, play a key role in determining its physical properties. The detailed electronic structure and the corresponding localized states at carbon nanotube tips have also been investigated in [10]. In this paper, we employ the first-principles calculations to study the variations of workfunctions of single-walled CNT tips with different geometries.

2. Theoretical approach and simulation models

The calculations are performed using the CASTEP code [11, 12], which is a plane-wave, pseudopotential program based on density functional theory (DFT). The generalized

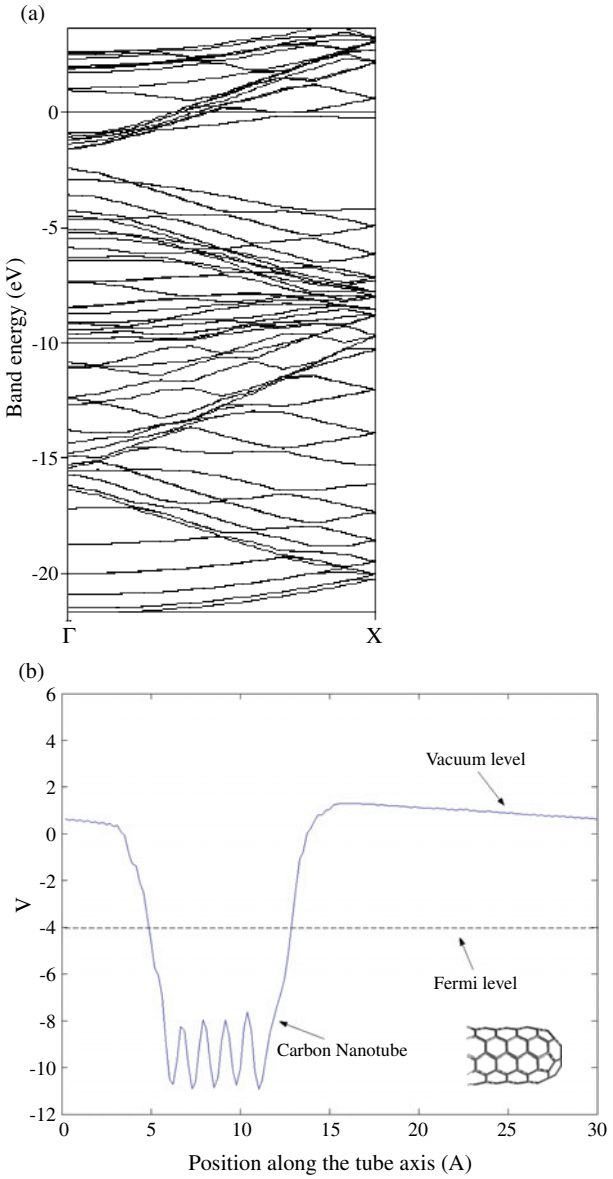

Figure 1. (a) Band structure of an infinitely-long (10, 0) carbon nanotube. It shows a good agreement with the previous *ab initio* calculation by [17]. (b) Typical potential distribution along the carbon nanotube axis.

gradient approximation (GGA) [13] is used with the exchange–correlation potential by Wang and Perdew (PW91) [14]. The ion–electron interaction is modelled by the non-local real space [15], ultrasoft pseudopotential [16]. A plane-wave basis with a cut-off energy of 340 eV and Γ point approximation are used for our calculations. For comparison, we have also calculated the band structure of an infinitely long (10.0) CNT, as shown in figure 1(a), and the result shows a good agreement with the previous first-principles calculations by [17]. In this study, we compare the electronic properties of six types of CNTs. They are the armchair (5, 5)/zigzag (9, 0) capped nanotubes, the (5, 5)/(9, 0) open-ended nanotubes and the (5, 5)/(9, 0) H-terminated nanotubes with hydrogen termination at their mouths as shown in table 1. These two types of carbon nanotube have a similar diameter. The model of an armchair (5, 5) capped single-walled carbon nanotube is represented by an eight-layer (80 atoms) stem with its mouth capped by half a C_{60} molecule. The eight-layer stem is chosen to ensure that its corresponding workfunction converges to a constant value. The dangling bonds at the other end are saturated by hydrogen atoms to avoid the boundary effect, giving a final structure consisting of total 120 atoms. The zigzag (9, 0) capped nanotube is similarly constructed with eight layers of carbon rings capped by half a C_{60}. In this study, the surface of one SWNT is modelled by its wall and tip due to its unique geometrical characteristics. The difference in potential energy of one electron between the highest occupied molecular orbital (HOMO) and the vacuum level is defined as the corresponding 'effective workfunction', which is different from the conventional definition of the workfunction of a solid. The vacuum level in our calculations is defined as the average value of potential energy distributions at the vacuum region during which the potential energy nearly approaches a constant value. The typical potential distribution along the tube axis is shown in figure 1(b).

These structures are then constructed within a tetragonal supercell with a lattice constant 30 Å along the z axis to represent the vacuum slab and the separation of 15 Å along the x and y axes to avoid interaction between two adjacent nanotubes. These atomic coordinates are fully optimized until the force on each atom during relaxation is less than 0.005 eV $Å^{-1}$. The optimized geometry of a capped (5, 5) nanotube shows that the atoms at the top pentagon have an average bond length of 1.44 Å compared to 1.42 Å at the side wall, whereas the average bond length at the top of a capped (9, 0) tube is about 1.43 Å. The relaxed structure of the open-ended (5, 5) nanotube as shown in figure 2(a) 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 [18]. The diameter of the relaxed open-ended (5, 5) structure slightly decreases. The relaxed structure for the open-ended (9, 0), on the other hand, does not show the significant bond formation of triple bonds as seen in the (5, 5) open-ended nanotube. The average bond length is about 1.39 Å, leaving dangling bonds at the tip. The diameter of the relaxed open-ended (9, 0) structure slightly increases. For the H-terminated (5, 5) and (9, 0) nanotubes, the dangling bond at the tip are saturated by hydrogen atoms and the relaxed structures show an average C–H bond length of 1.08 Å.

3. Result and discussion

The calculated workfunctions of nanotubes with different geometries are summarized in table 1. The capped armchair (5, 5) nanotube is found to have a workfunction 4.78 eV which shows a good agreement with the experimental measurements of single-walled carbon nanotube bundles with a value of 4.8 eV by Suzuki *et al* [8]. Although the (5, 5) armchair nanotube is metallic, the capped nanotube is found to be semiconducting with an energy gap of 1.4 eV between the HOMO and LUMO (lowest unoccupied molecular orbital), resulting from half of a C_{60} molecule. For the open-ended (5, 5) nanotube, as mentioned above, the formation of triple bonds at the tip leads to charge redistribution after structural

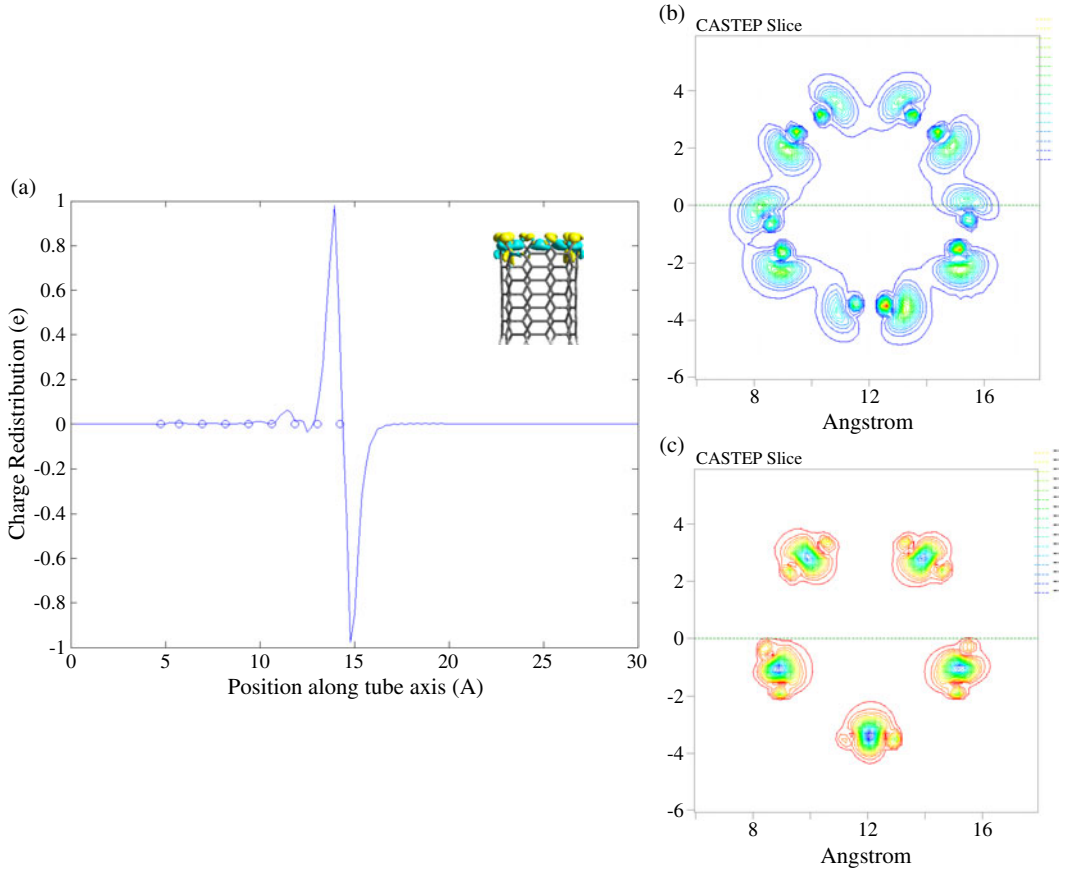

Figure 2. Charge redistribution of an open-ended carbon nanotube after structural relaxation. (a) The increase of charge densities between neighbouring C atoms indicates the formation of C≡C. (b) Shows the decrease of charge densities and (c) shows the increase of charge densities.

Table 1. The effective workfunction of CNTs with different geometries. CAP-(5, 5) represents the capped CNT-(5, 5). Open-(5, 5) represents the open-ended CNT-(5, 5). Open+H-(5, 5) represents H-terminated CNT-(5, 5). CAP-(9, 0) represents the capped CNT-(9, 0). Open-(9, 0) represents the open-ended CNT-(9, 0). Open+H-(9, 0) represents the H-terminated CNT-(9, 0). The bond length of C≡C at the mouth of the open-ended CNT-(5, 5) is 1.23 Å.

	CAP-(5,5)	Open-(5,5)	Open+H-(5,5)	CAP-(9,0)	Open-(9,0)	Open+H-(9,0)
						
Φ (eV)	4.78	4.47	3.75	4.14	5.10	3.18

relaxation, leading to a substantial decrease of spilling-out of electron density at the nanotube tip after structural relaxation, as shown in figures 2(b) and (c), which reduces the surface dipole. The 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 lower value of 4.39 eV compared to the (5, 5) capped nanotube of 4.78 eV. The H-terminated (5, 5) CNT exhibits a further reduction in its workfunction with a value of 3.75 eV. 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 as shown in figure 3. The potential difference across the dipole lowers the distance between the Fermi energy and the vacuum level, leading to a further reduction of workfunction. Such enhanced field emission properties from CNTs by hydrogen termination have also been reported by the recent experiment carried out by Zhi *et al* [19] using hydrogen plasma treatment on CNTs. Similar phenomena are also seen in the H-terminated diamond surface, which leads to its negative electron affinities [20]. Our result is opposite to the previous report by molecular orbital approximation, where the open-ended nanotube exhibits a lower workfunction than the H-terminated one [21]. This may contribute to the fact that the tight-binding (TB) calculations in [21] are unlikely to get the correct workfunction because TB does not use real

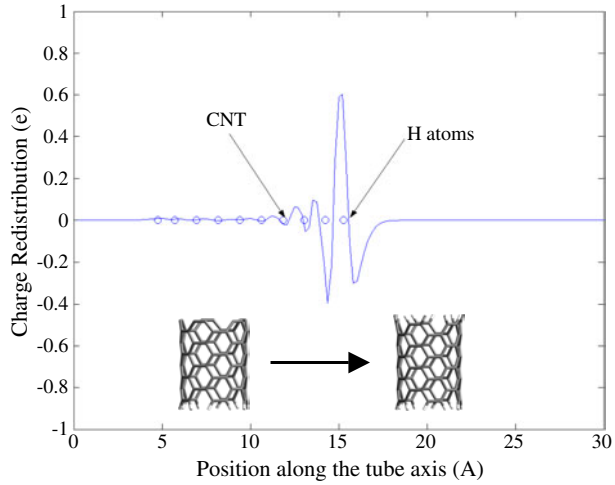

Figure 3. The charge redistribution of the carbon nanotube surface terminated by hydrogen and atoms indicating that charge transfers from H atoms to C atoms.

orbitals and so does not give dipoles properly. For the capped zigzag $(9, 0)$ nanotube, the workfunction shows a value of 4.14 eV, lower than the capped $(5, 5)$ nanotube, indicating that the capped $(9, 0)$ nanotube should demonstrate better field emission properties if the same geometry enhancement factor is applied. For the open-ended $(9, 0)$ nanotube, significant discrepancies are found compared to its open-ended $(5, 5)$ counterpart. Unlike in the open-ended $(5, 5)$ nanotube, where the unsaturated bonds are able to form triple bonds with a short bond length of 1.23 Å, the dangling bonds at the mouth of the open-ended zigzag model still prevail with an average C–C bond length of 1.39 Å. The unsaturated dangling bonds at its mouth give a substantial increase of spilling-out of electron density at the nanotube tip, which raises its surface dipole. The open-ended $(9, 0)$ nanotube therefore gives a higher workfunction value of 5.1 eV. The H-terminated $(9, 0)$ nanotube shows a lowest workfunction value of 3.18 eV among the six models we studied here. The reason for a significant reduction of workfunction after the introduction of H atoms at the unsaturated sites of $(9, 0)$ zigzag nanotube is similar to the above discussion for the H-terminated $(5, 5)$ nanotube case. Figures 4(a) and (b) show the density of states (DOS) of capped armchair $(5, 5)$ and zigzag $(9, 0)$ nanotubes respectively. For comparison, the intensities of DOS are then normalized by dividing the total number of atoms at the cap and sidewall parts respectively. As the states near the Fermi level are believed to be responsible for field emission, we compare the DOS of cap and sidewall parts from -5 eV below E_f to 5 eV above E_f. It is shown that the capped region has a slightly higher DOS than the body region of about 5% for the $(5, 5)$ armchair nanotube and 7% for the $(9, 0)$ zigzag nanotube. Recent x-ray absorption spectroscopy experiments indicate that the DOS near E_f increases with the curvature of the CNT graphite sheet [22], not only from defect and dangling states. From the above discussion, it is suggested that the capped and H-terminated zigzag $(9, 0)$ carbon nanotubes have better field emission properties than the capped and H-terminated armchair $(5, 5)$ nanotubes, respectively, if the same geometrical factor is applied. The open-ended zigzag $(9, 0)$ nanotube, on the other hand, shows a higher value of

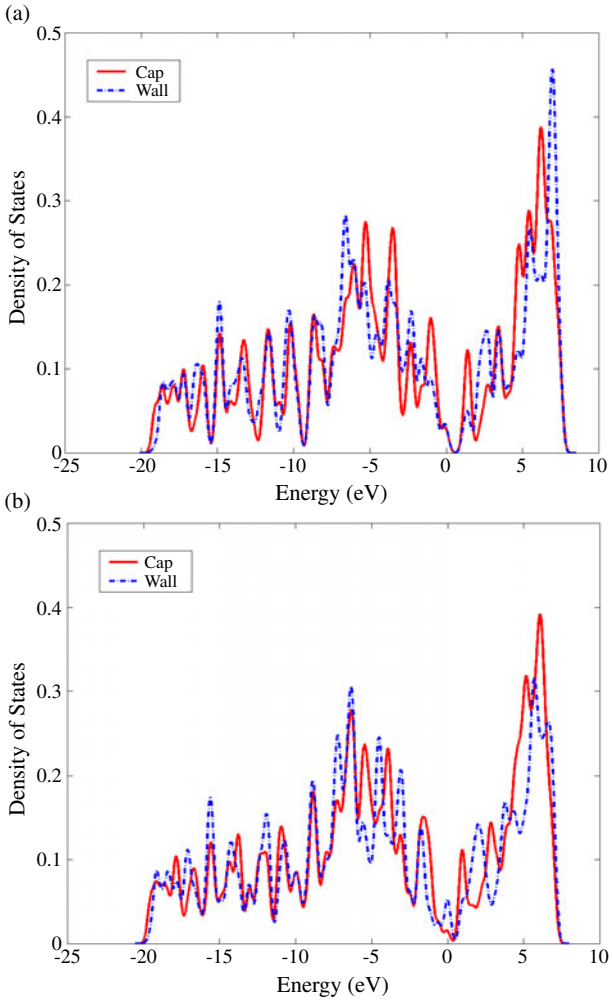

Figure 4. The DOS of capped carbon nanotubes at the cap and sidewall parts for (a) $(5, 5)$ and (b) $(9, 0)$ CNTs, respectively. The ratios between the DOS (cap) and DOS (sidewall) from -5 to 5 eV for $(5, 5)$ and (9.0) carbon nanotubes are 1.05:1 and 1.07:1 respectively. The Fermi energy is 0 eV.

workfunction than the open-ended armchair $(5, 5)$ nanotube due to the high dangling bond density at the tip end.

4. Conclusion

We have calculated the workfunction values of carbon nanotubes with different geometries by the first-principles calculation. The armchair $(5, 5)$ and zigzag $(9, 0)$ carbon nanotubes with capped, open-ended and H-terminated structures are studied. The results show that the capped and H-terminated zigzag $(9, 0)$ carbon nanotubes exhibit a lower workfunction value than the armchair $(5, 5)$ nanotubes with a similar diameter. The open-ended $(5, 5)$ nanotube, on the other hand, shows a lower workfunction than the open-ended $(9, 0)$ structure. The former exhibits a significant formation of triple bonds after relaxation, which reduces the surface dipole and lowers its workfunction, the latter having a higher density of unsaturated dangling bonds, giving a higher value of workfunction.

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