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First-principles study of the interactions of Ti and Zr with the tips of open-ended single-wall carbon nanotubes

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Abstract

Density functional theory is used to study the interactions of Ti and Zr with the tips of open-ended single-wall carbon nanotubes. It is found that Ti or Zr atoms can saturate the dangling bonds of a tip to make it closed. Zr displays much stronger interaction with the contacted carbon atom than Ti. The Fermi energies of the hybrid systems increase dramatically, and the peak values of the density of states near the Fermi levels increase significantly. The field emission properties are discussed qualitatively.

1. Introduction

Carbon nanotubes (CNT) have intrinsically suitable properties for field emitter use because of their unique electronic and atomic structures with high aspect ratio. They have been successfully applied in nanometre scale electron sources in field emission display (FED) devices [1] and in surface analysis instruments [2, 3]. The field emission properties of open-ended CNT have been widely studied in both experimental and theoretical aspects [4–7]. For open-ended CNT, the emission currents display low stability with strong fluctuations, and the emission tips are easily destroyed within the emission process. It is observed that when the tips are being heated in a high vacuum condition, the open-ended CNT are reclosed by forming some graphite cap-like structures on their ends [4, 5]. How to improve the field emission property and the structural stability of the open-ended CNT is an important question for their further application as electron sources. Previous experimental and theoretical studies show that the adsorption of water molecules on the tips can significantly enhance the field emission current [8, 9], which implies a new way to improve the field emission properties of CNT.

On the other hand, the interactions of CNT with different kinds of elements, especially metal elements, have attracted considerable attention [10–14]. It is interesting to note that Ti coated single-wall carbon nanotubes (SWCNT) have been obtained by using electron

beam evaporation techniques, which shows that Ti atoms have strong interactions with nanotubes [15, 16]. Theoretical simulations also support these experimental findings [17–19].

Tip functionalization of CNT is an attractive method for improving the properties of the ends of CNT probe tips. Carbon nanotubes terminated by hydrogen, oxygen, hydroxyl (OH) and other groups have been studied and it was found that tip functionalization can modify the electronic states and the chemical selectivity of CNT tips [20–22]. A recent experiment has obtained excellent field emission properties by depositing a thin film of Ti on the CNT emission tip [23], which indicates that Ti plays an important role in the field emission process. For CNT, it is not clear how Ti affects the stability of the emission tip and the field emission properties. With such questions, in this work, we investigate the interaction of Ti (Zr) with the tips of open-ended SWCNT by first-principles simulations. We consider Zr here because both Zr and Ti are IV_B elements. More importantly, both Ti and Zr can easily combine with C to produce stable TiC and ZrC solid. We will discuss the atomic structure, the binding property, the density of states (DOS) and the charge density of Ti (Zr)–SWCNT hybrid systems. The field emission properties are analysed qualitatively.

2. Method and computational details

We consider two typical SWCNT including armchair (5, 5) and zigzag (9, 0) forms, which have been widely used as model systems in many theoretical studies. The diameters are, respectively, 6.8 and 7.0 Å, and the average C–C bond length is 1.42 Å. The structural optimizations are performed by using smaller SWCNT models. Along the longitudinal direction, seven (70 atoms) and eight (72 atoms) layers of C rings are selected as the main body of SWCNT (5, 5) and SWCNT (9, 0), respectively. The dangling bonds of one open end are saturated by hydrogen atoms, and the other open end is taken as the emission tip. Considering the number of the C dangling bonds, we place a ring of 10 and a ring of 9 Ti (Zr) atoms on the top of the open-ended tips for SWCNT (5, 5) and SWCNT (9, 0), respectively. Since the dangling bonds are fully saturated, the hybrid systems can easily reach the stable state. We show the initial structures of the mouth of SWCNT (5, 5) with 10 Ti atoms ((5, 5) + 10Ti), SWCNT (9, 0) with 9 Ti atoms ((9, 0) + 9Ti), SWCNT (5, 5) with 10 Zr atoms ((5, 5) + 10Zr) and SWCNT (9, 0) with 9 Zr atoms ((9, 0) + 9Zr) in figure 1.

To make the whole simulation more realistic, we use larger SWCNT models to do total energy calculations. These models are constructed by appending the optimized pure SWCNT body to the optimized hybrid systems, about 24 Å in length (180–200 atoms).

The structural optimization and the corresponding total energy calculation are performed by the DMol³ package [24–26], which is based on the density functional theory (DFT) [27, 28] with the generalized gradient approximation (GGA). The spin-unrestricted wavefunctions are expanded with a double numerical plus polarization (DNP) basis set [29], and the PBE exchange–correlation functional [30] is adopted for the GGA. The effects of core electrons are considered by the effective core potentials (ECP) [31, 32]. The energy gradient in the structural optimization is converged to be less than 8 meV Å^{−1}.

3. Results and discussion

We have tried different initial configurations and after structural relaxation it is found that the end of (9, 0) + 9Zr becomes closed, causing a Zr₉ cluster termination. For (5, 5) + 10Ti, (5, 5) + 10Zr and (9, 0) + 9Ti, each of them has two stable configurations. One is open ended and the other has a cluster termination. The latter is more stable. The total

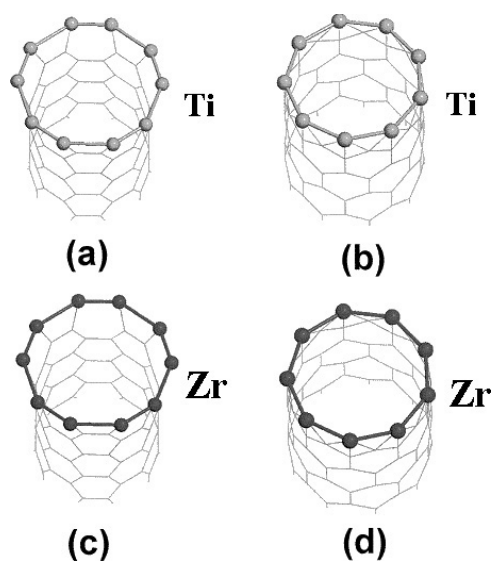


Figure 1. The initial structures of the mouth of (a) $(5, 5) + 10\text{Ti}$, (b) $(9, 0) + 9\text{Ti}$, (c) $(5, 5) + 10\text{Zr}$ and (d) $(9, 0) + 9\text{Zr}$ systems.

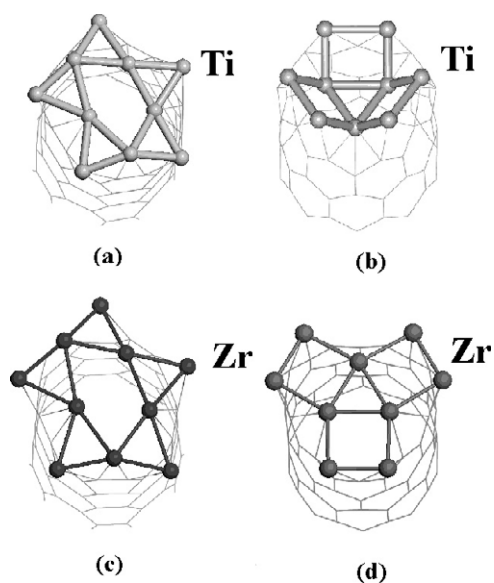


Figure 2. The optimized geometry for (a) $(5, 5) + 10\text{Ti}$, (b) $(9, 0) + 9\text{Ti}$, (c) $(5, 5) + 10\text{Zr}$ and (d) $(9, 0) + 9\text{Zr}$ systems.

energies of the closed-ended configurations are respectively 12.9, 13.7 and 5.1 eV lower than those of the open-ended configurations in these three cases, which can be attributed to the metal–metal bonding of the Ti (Zr) cluster. The open-ended configurations are considered to be metastable states.

The most stable optimized geometries of the hybrid systems are presented in figure 2. The reclosure of the open-ended SWCNT by doping with Ti (Zr) is really interesting. This

Table 1. The calculated average binding energy \bar{E}_b , Fermi energy E_f and effective work function Φ_{eff} for different systems.

	(5, 5) + 10Ti	(9, 0) + 9Ti	(5, 5) + 10Zr	(9, 0) + 9Zr	Pure (5, 5)	Pure (9, 0)
\bar{E}_b (eV)	2.78	3.10	2.92	3.56	—	—
E_f (eV)	-3.85	-3.97	-3.70	-3.77	-4.82	-4.90
Φ_{eff} (eV)	0.05	0.16	0.03	0.11	0.48	0.26

property may be used to encapsulate functional clusters in CNT to fabricate different kinds of hybrid nanostructures with tailored electronic structure and may have important applications in nanodevices.

For (5, 5) + 10Ti and (9, 0) + 9Ti, the Ti–C bond length alternates between 2.01 and 2.31 Å, compared with the bond length 2.16 Å of bulk TiC [33, 34]. The Ti–Ti bond length alternates between 2.28 and 2.85 Å, smaller than that of the bulk Ti (2.89 Å). For (5, 5) + 10Zr and (9, 0) + 9Zr, the Zr–C bond length alternates between 2.13 and 2.44 Å, compared with the bond length 2.35 Å of bulk ZrC [35, 36]. The Zr–Zr bond length alternates between 2.66 and 3.10 Å, which is smaller than that of bulk Zr (3.18 Å). These results indicate that there are both strong Ti–C (Zr–C) and Ti–Ti (Zr–Zr) bonds at the emission tips of SWCNT. Thus the emission properties of Ti (Zr) coated CNT are probably different from those of pure CNT.

To test the binding properties, we calculate the average binding energy \bar{E}_b of Ti (Zr), which is defined as

$$\bar{E}_b = [E_T(\text{SWCNT}) + E_T(\text{Ti}_N) - E_T(\text{SWCNT} + \text{Ti}_N)]/N, \quad (1)$$

where $E_T(\text{SWCNT})$, $E_T(\text{SWCNT} + N\text{Ti})$, and $E_T(\text{Ti}_N)$ are the total energies of the pure SWCNT, the hybrid system and the cluster of N Ti atoms separated from the hybrid system with unchanged geometry, respectively. The \bar{E}_b excludes the metal–metal interaction and can be used to measure the interaction between Ti (Zr) and SWCNT. From the results listed in table 1, we can see that the interaction of Zr atoms with open-ended SWCNT is much stronger than that of Ti. The chirality can also affect the interaction between SWCNT and Ti (Zr) atoms. The interaction of Ti (Zr) atoms with SWCNT (9, 0) is stronger than that of SWCNT (5, 5). The structure (9, 0) + 9Zr is the most stable one among all the cases.

Figure 3 displays the calculated DOS, including the total DOS of the pure SWCNT, the total DOS of the hybrid system and the Ti (Zr) d partial DOS. The DOS is aligned by the Fermi energy, which is generally defined in DMol as the energy of the highest occupied molecular orbital (HOMO) in the case of the HOMO being fully occupied by electrons. Compared with the pure SWCNT, the hybrid systems show great differences. The DOS in the energy range from -1 to 2 eV increases significantly. It should be noted that the DOS near the Fermi level has high values, which may result in a high tunnelling probability and could make the electrons easily emitted by an external electric field [7, 22, 37].

From figure 3 it is found that the increases of the DOS are mainly contributed by d orbitals of Ti (Zr) atoms, which have the feature of metal–metal bonding and hybridize evidently with p orbitals of C atoms. Compared with the total DOS of pure SWCNT, we can see that below -2 eV, the total DOS shifts obviously to the lower energy range. These results may be mainly attributed to the effects of metal–metal bonding of the Ti (Zr) cluster. The Ti (Zr) cluster formation is most likely the prime reason for these DOS changes. After doping with Ti (Zr), the average electrostatic potential at the tip seems to be more negative (see below, as shown in figure 6), resulting in a rigid shift of the eigenvalues.

Figure 4 presents the isosurfaces of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for different systems, which show very

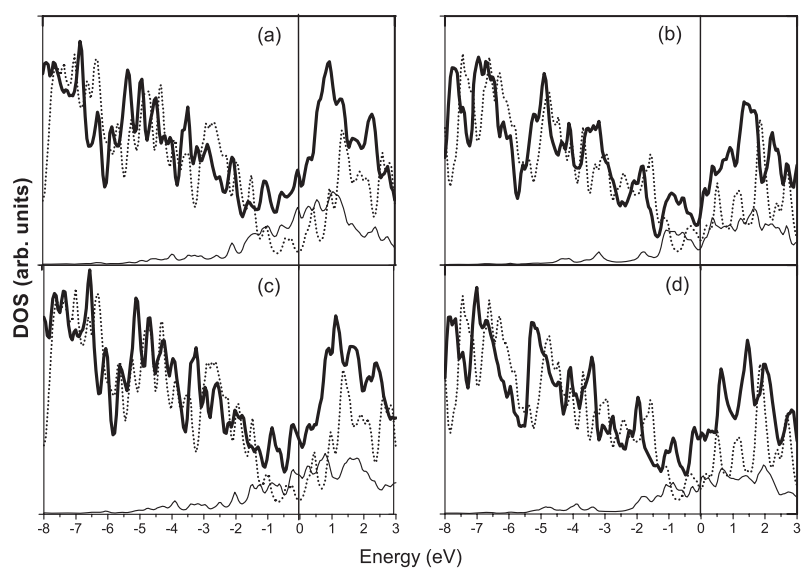


Figure 3. The calculated DOS in (a) (5, 5) + 10Ti, (b) (9, 0) + 9Ti, (c) (5, 5) + 10Zr and (d) (9, 0) + 9Zr systems. The dotted, bold solid and thin solid lines represent the total DOS of the pure SWCNT, the total DOS of the hybrid system and the Ti (Zr) d partial DOS, respectively. The Fermi level is set to be zero.

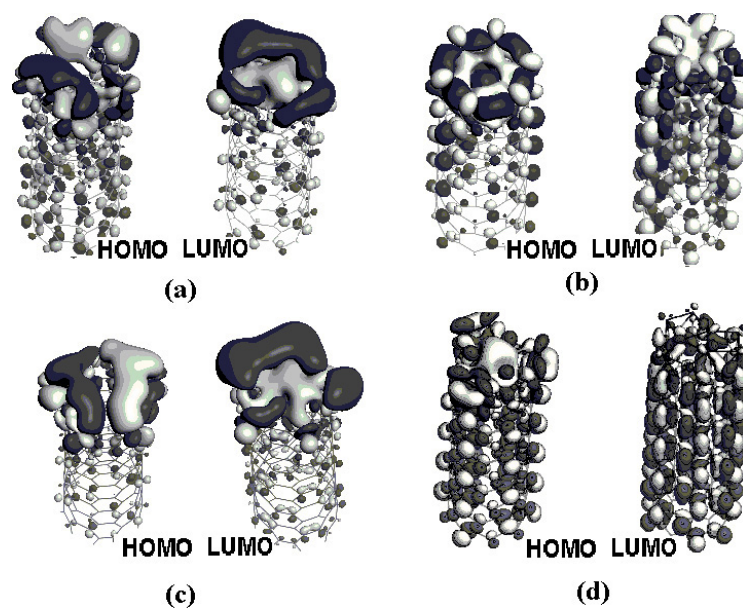


Figure 4. The isosurfaces of the HOMO and LUMO of (a) (5, 5) + 10Ti, (b) (9, 0) + 9Ti, (c) (5, 5) + 10Zr and (d) (9, 0) + 9Zr systems.

complicated characteristics. For (9, 0) + 9Ti and (9, 0) + 9Zr, the HOMO and LUMO diffuse to the whole tube body and the Ti (Zr) d and C p orbitals have comparable contributions. This is consistent with the result from the DOS analysis that the Ti (Zr) d and C p orbitals have evident

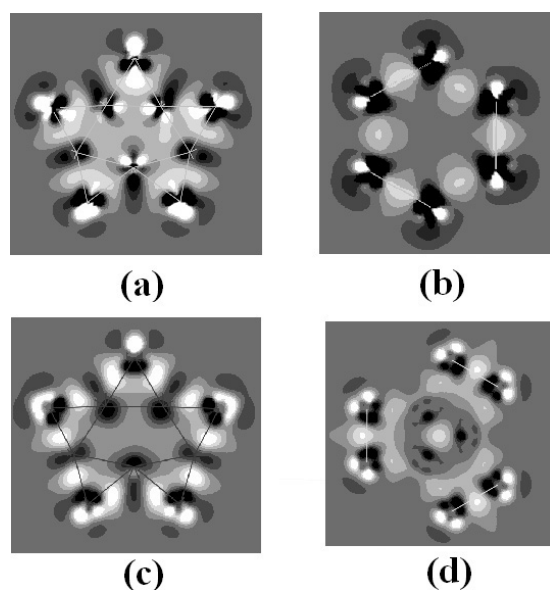


Figure 5. The charge density difference (in $0.1 e \text{ au}^{-3}$) of the top layer for (a) $(5, 5) + 10\text{Ti}$, (b) $(9, 0) + 9\text{Ti}$, (c) $(5, 5) + 10\text{Zr}$, (d) $(9, 0) + 9\text{Zr}$ systems. The black (white) denotes negative (positive) value.

hybridization. For $(5, 5) + 10\text{Ti}$ and $(5, 5) + 10\text{Zr}$, the contribution of the Ti (Zr) d orbitals accounts for a large proportion. The corresponding HOMO and LUMO are basically localized on the tip.

The charge density difference of the tip is shown in figure 5, which is defined as the difference between the total charge density and the atomic ones. It can be seen clearly that Ti (Zr) atoms bond to each other at the mouth of the open-ended SWCNT. For SWCNT with different chirality, these bonds display different spatial orientation. The results indicate that Ti (Zr) atoms can be used to stabilize the open end of SWCNT by forming strong Ti–C (Zr–C) and Ti–Ti (Zr–Zr) bonds.

We now turn to the field emission properties. An important factor indicating the field emission capability is the field enhancement factor β ($\beta = E_{\text{loc}}/E_{\text{app}}$, where E_{loc} is the local electric field at which electron tunnelling occurs and E_{app} is the applied electric field [38]). The field enhancement factor relies on the geometry of field emitters [39]. For open-ended nanotubes, the β value near the open mouth is much higher than that near the capped mouth, which leads to a higher current density. This has been supported by many experiments [4, 5]. Our results shown in figure 2 suggest that coating the open-ended tip of SWCNT by the Ti (Zr) element may be used to modify the geometry of the field emitters and modulate the emission currents.

To discuss the field emission properties of the systems qualitatively, we define the effective work function (Φ_{eff}) as the energy difference between the Fermi level (E_f) and the LUMO [40]. Table 1 lists the calculated E_f and Φ_{eff} , from which we can find that doping Ti (Zr) at the open-ended tip will increase E_f and decrease Φ_{eff} efficiently, especially for the case of Zr. We also show the electrostatic potential at the tip before and after adding Ti (Zr) atoms to the open-ended tip in figure 6. We can see that distinct energy wells emerge around the metal atoms after doping with Ti (Zr). The energy wells at the tip become much deeper and wider than that of the pure carbon nanotube near the carbon atoms, especially for SWCNT $(5, 5)$. All these

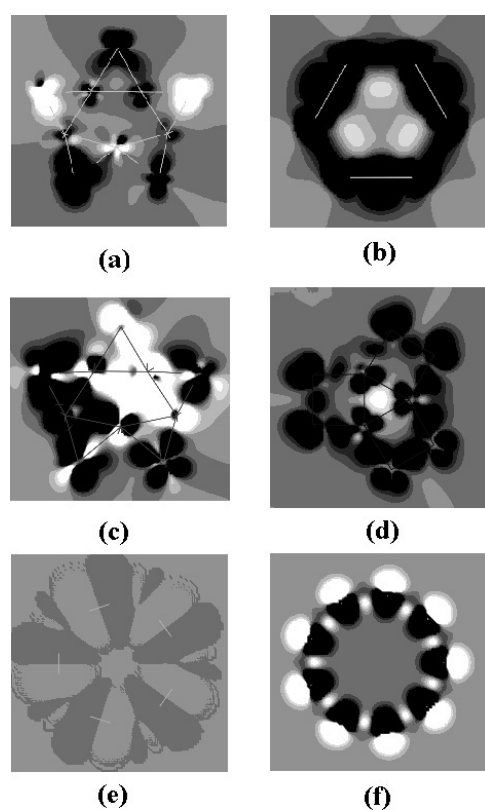


Figure 6. The electronic potential (from -0.01 to 0.01 au) of the top layer for (a) $(5, 5) + 10\text{Ti}$, (b) $(9, 0) + 9\text{Ti}$, (c) $(5, 5) + 10\text{Zr}$, (d) $(9, 0) + 9\text{Zr}$, (e) pure $(5, 5)$, (f) pure $(9, 0)$ systems. The black (white) denotes negative (positive) value.

results suggest that the electrons can be easily emitted from the Ti (Zr) atoms by means of an external electric field. This is consistent with the recent experiment [23], where a thin Ti film is deposited on the open-ended tip of CNT and the turn-on E field decreases dramatically.

4. Conclusions

In this work, we have studied Ti and Zr doped open-ended SWCNT and obtained stable hybrid structures at the open mouth by first-principles simulations. We find that the interaction of Zr with open-ended SWCNT is much stronger than that of Ti. The chirality of SWCNT also has an effective influence. Doping carbon nanotubes with Ti (Zr) atoms can increase the Fermi level of the system and decrease the work function. The density of states near the Fermi level also increases significantly. Ti (Zr) atoms can saturate the dangling carbon bonds and seem to have the function of stabilizing the open ends of carbon nanotubes. All of these results have demonstrated that doping open-ended carbon nanotubes with Ti or Zr atoms can improve the field emission properties and may have important applications in nanodevices.

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