

## Systematic study of adsorption of single atoms on a carbon nanotube

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We studied the adsorption of single atoms on a semiconducting and metallic single-wall carbon nanotube from first principles for a large number of foreign atoms. The stable adsorption sites, binding energy, and the resulting electronic properties are analyzed. The character of the bonding and associated physical properties exhibit dramatic variations depending on the type of the adsorbed atom. While the atoms of good conducting metals, such as Cu and Au, form very weak bonding, atoms such as Ti, Sc, Nb, and Ta are adsorbed with relatively high binding energy. Most of the adsorbed transition-metal atoms excluding Ni, Pd, and Pt have a magnetic ground state with a significant magnetic moment. Our results suggest that carbon nanotubes can be functionalized in different ways by their coverage with different atoms, showing interesting applications such as one-dimensional nanomagnets or nanoconductors and conducting connects, etc.

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Single-wall carbon nanotubes (SWNT's) can serve as templates to produce reproducible, very thin metallic wires with controllable sizes.<sup>1</sup> These metallic nanowires can be used as conducting connects and hence are important in nanodevices based on molecular electronics. Recently, Zhang *et al.*<sup>2</sup> have shown that a continuous Ti coating of varying thickness and a quasicontinuous coating of Ni and Pd can be obtained by using electron-beam evaporation techniques. Metal atoms such as Au, Al, Fe, Pb were able to form only isolated discrete particles or clusters instead of a continuous coating of SWNT's. Low-resistance contacts to metallic and semiconducting SWNT's were achieved by Ti and Ni ohmic contacts.<sup>3</sup> Most recently, *ab initio* density-functional calculations<sup>4</sup> have indicated that stable rings and tubes of Al atoms can form around a semiconducting SWNT. It is argued that either persistent currents through these conducting nanorings, or conversely very high magnetic fields can be induced at their center.<sup>4</sup> It is expected that novel molecular nanomagnets and electromagnetic devices can be generated from these metallic nanostructures formed by adatom adsorption on SWNT's. As an example, one can contemplate to generate a nanodevice by the modulating adsorption of adatoms on a bare (8,0) SWNT, which is a semiconductor<sup>5</sup> with an energy gap of  $\sim 0.64$  eV. This band gap can increase to 2 eV by the adsorption of a hydrogen atom.<sup>6</sup> Then, a quantum well (or dot) can form between two barriers at the hydrogen covered sections of the (8,0) tube. This structure is connected to the metallic reservoirs through metal coated ends of SWNT's. This way a resonant tunneling device with metal reservoirs and connects at both ends can be fabricated on a single SWNT.

Clearly, the study of adsorption of atoms on nanotube surfaces is essential to achieve low-resistance ohmic contacts to nanotubes, to produce nanowires with controllable size, and to fabricate functional nanodevices. In particular, it is important to know the following: (i) How can the situation, where some metal atoms form strong bonding while others are only weakly bound, be explained? (ii) What is the geometry and character of the bonding between single atoms and SWNT's? (iii) How are the physical properties of SWNT's

influenced by the adsorption of a metal atom? (iv) Can certain adatoms, such as Ni, Fe, and Co, have triplet ground state to yield net spin? Our study covering several atoms revealed that some metal atoms can make bonds with SWNT's even stronger than Ti and most of the transition-metal atoms, including Cu and Au, adsorbed on SWNT's have magnetic ground state. We believe that the results of this work are important for further studies related to the functionalization and coating of carbon nanotubes.

The binding geometry and binding energy, and resulting electronic structure of 23 different atoms (Na, Al, Cu, Au, Ni, Fe, Ti, W, Nb, Mo, Pd, Pb, C, Si, Cr, Co, Sc, V, Zn, Ag, Pt, Ta, and Mn) adsorbed on a (8,0) zigzag SWNT and four different atoms (Au, Mn, Mo, Ti) adsorbed on a (6,6) armchair SWNT have been calculated by using the pseudopotential plane wave method<sup>7</sup> within the generalized gradient approximation.<sup>8</sup> Spin-unpolarized and spin-polarized (relaxed) calculations have been carried out for single-atom bare SWNT's and single-atom adsorbed SWNT's in a periodically repeating tetragonal supercell with lattice constants  $a_{sc} = b_{sc} \sim 15$  Å and  $c_{sc}$ . To minimize the adsorbate-adsorbate interaction, the lattice constant along the axis of the tube,  $c_{sc}$ , is taken to be twice the one-dimensional (1D) lattice parameter of the bare tube, i.e.,  $c_{sc} = 2c$ . Ultrasoft pseudopotentials<sup>9</sup> and plane waves up to an energy cutoff of 300 eV are used. The Brillouin zone of the supercell is sampled by (1,1,11)  $\mathbf{k}$  points within the Monkhorst-Pack special  $\mathbf{k}$ -point scheme.<sup>10</sup> For the adsorption of individual atoms we considered four possible sites (i.e.,  $H$  site above the hexagon,  $Z$  and  $A$  sites above the zigzag and axial C-C bonds, and  $T$  site above the carbon atom) as described in Fig. 1.

The binding sites are determined by optimizing all atomic positions (adsorbate atom and 64 carbon atoms of SWNT's), as well as  $c$  using the conjugate gradient (CG) method. Binding energies are obtained from the expression

$$E_b = E_T[\text{SWNT}] + E_T[A] - E_T[A + \text{SWNT}] \quad (1)$$

in terms of the total energies of the fully optimized bare nanotube ( $E_T[\text{SWNT}]$ ), free atom  $A$  ( $E_T[A]$ ), and the atom

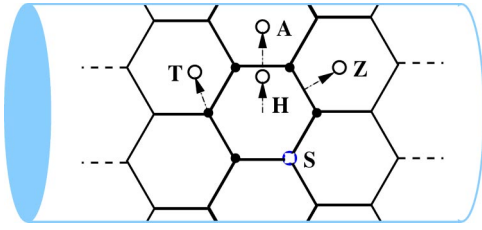


FIG. 1. A schematic description of different binding sites of individual atoms adsorbed on a zigzag (8,0) tube. Black and filled circles denote carbon and adatoms, respectively. *H*, hollow; *A*, axial; *Z*, zigzag; *T*, top; *S*, substitution sites.

*A* adsorbed on a SWNT ( $E_T[A+SWNT]$ ). The binding energies  $E_b$  are obtained from the lowest ground-state total energies (either magnetic or nonmagnetic) of both  $E_T[A+SWNT]$  and  $E_T[A]$ ; a bare nanotube has a nonmagnetic ground state with zero net spin.  $E_b > 0$  corresponds to a CG optimized stable structure and indicates the bonding (a local or global minimum on the Born-Oppenheimer surface). In Tables I and II, we present our results. We note that only the short-range (chemical) interactions are included in  $E_b$ . The

TABLE I. Calculated binding energies ( $E_b^{sp}$  spin polarized and  $E_b^{su}$  spin unpolarized) of individual atoms adsorbed on the (8,0) SWNT, the most favorable binding site, the average carbon-adatom bond distance ( $\bar{d}_{C-A}$ ), and the net magnetic moment ( $\mu$ ) of the adatom+SWNT system. Results for hydrogen and oxygen atoms are taken from Refs. 6 and 11.

Atom	Site	$\bar{d}_{C-A}$ (Å)	$E_b^{sp}$ (eV)	$E_b^{su}$ (eV)	$\mu$ ( $\mu_B$ )
Na	<i>H</i>	2.3		1.3	
Sc	<i>H</i>	2.2	1.9	2.1	0.64
Ti	<i>H</i>	2.2	2.2	2.9	2.21
V	<i>H</i>	2.2	1.4	3.2	3.67
Cr	<i>H</i>	2.3	0.4	3.66	5.17
Mn	<i>H</i>	2.4	0.4	3.4	5.49
Fe	<i>H</i>	2.3	0.8	3.1	2.27
Co	<i>H</i>	2.0	1.7	2.8	1.05
Ni	<i>A</i>	1.9	1.7	2.4	0.04
Cu	<i>A</i>	2.1	0.7	0.8	0.53
Zn	<i>H</i>	3.7	0.04	0.05	0
Nb	<i>H</i>	2.2	1.8	3.9	2.86
Mo	<i>H</i>	2.2	0.4	4.6	4
Pd	<i>A</i>	2.1	1.7	1.7	0
Ag	<i>A</i>	2.5	0.2	0.3	0.6
Ta	<i>H</i>	2.2	2.4	2.9	3.01
W	<i>H-A</i>	2.1	0.9	3.4	2.01
Pt	<i>A</i>	2.1	2.4	2.7	0
Au	<i>A-T</i>	2.2	0.5	0.6	1.02
Al	<i>H</i>	2.3		1.6	
C	<i>Z</i>	1.5		4.2	
Si	<i>H</i>	2.1		2.5	
Pb	<i>H</i>	2.6	0.8	1.3	0
H	<i>T</i>	1.1		2.5	
O	<i>Z</i>	1.5		5.1	

TABLE II. Same as Table I for the individual atoms adsorbed on the armchair (6,6) SWNT.

Atom	Site	$\bar{d}_{C-A}$ (Å)	$E_b^{sp}$ (eV)	$E_b^{su}$ (eV)	$\mu$ ( $\mu_B$ )
Ti	<i>H</i>	2.2	1.8	2.6	1.68
Mn	<i>H</i>	2.5	0.1	3.1	5.60
Mo	<i>H</i>	2.3	0.1	4.3	3.61
Au	<i>T</i>	2.3	0.3	0.4	0.79

long-range van der Waals interaction is expected to be much smaller than the calculated  $E_b$ .

The atoms which were observed to form continuous and quasicontinuous coating on the SWNT (Ti, Ni, and Pd) have relatively higher binding energies as compared to those atoms (Au, Fe, Pb) that form only discrete particles on the surface of the tube.<sup>1</sup> We also note that in forming a good coverage not only adatom-SWNT's interaction but also other factors, possibly adatom-adatom interaction, play a crucial role. Good conductors such as Au, Ag, and Cu have very weak binding. On the other hand, Na with 3s electron on the outer shell is bound with a significant binding energy ( $E_b = 1.3$  eV). The binding energy of Zn with the (4s)<sup>2</sup> outer shell is almost zero. While an individual Al atom is not bound to the graphite surface, its binding on the (8,0) SWNT is relatively strong. This can be explained by the curvature effect, since the binding was found to be even stronger at the high curvature site of SWNT's under uniaxial radial deformation.<sup>12</sup> In Tables I and II, most of the transition-metal atoms adsorbed on the (8,0) and (6,6) SWNT's have magnetic ground state, and hence they give rise to the net magnetic moment ranging from  $5.49\mu_B$  (for Mn) to zero magnetic moment (for Pd and Pt). While adsorbed Ni has a very low magnetic moment ( $0.04\mu_B$ ), the adsorbates such as Au, Ag, or Cu have magnetic moment in the range of  $0.4\mu_B$ – $0.6\mu_B$ . The magnetic ground states of SWNT due to the adsorbed transition-metal atoms can have important implications. For example, a SWNT decorated or coated with Fe may exhibit ferromagnetic properties and hence can be a potential candidate for nanomagnets. Such nanomagnets can serve as excellent probe tips in magnetic atomic force microscopy. SWNT's having conduction bands of one type of spin can be an interesting system for the emerging field of spintronics. The magnetization and hysteresis loops of iron nanoparticles partially encapsulated at the tips and inside of aligned carbon nanotubes have been demonstrated by recent experimental works.<sup>13</sup> The trends in Table I continue to exist in Table II for the transition-metal atom adsorbed on the metallic (6,6) SWNT. Here the binding energies  $E_b^{sp}$  and  $E_b^{su}$  and magnetic moments came out to be consistently lower than Table I, perhaps due to the curvature effect.<sup>12</sup> The transition-metal atoms with a few *d* electrons, such as Sc, Ti, Nb, and Ta, form strong bonds with a binding energy ranging from 2.4 eV to 1.8 eV, and hence can be suitable for the metal coating of SWNT's. These metals can also be used as a buffer layer to form uniform coating of good conductors such as Au, Ag, and Cu. Most of the adatoms we studied yield strongest binding at the *H* site. Ni, Pd, and Pt (column VIII elements) and Cu, Ag, and Au (column I-B elements)

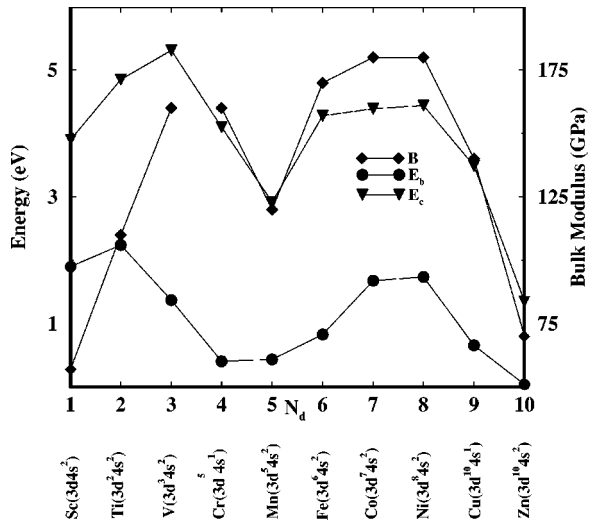


FIG. 2. Variation of the calculated binding energy  $E_b^{sp}$  (for spin polarized) of transition-metal atoms with respect to the number of  $d$  electrons  $N_d$ . The bulk cohesive energy  $E_c$  and the bulk modulus  $B$  from Ref. 16 are included for the comparison of the trend.

seem to prefer the  $A$  site. The average carbon-adatom distance  $\bar{d}_{C-A}$  ranges between 1.9 Å (minimum) and 3.7 Å (maximum); most of them occur at  $\sim 2.1$  Å.

In Fig. 2, we present the variation of the ground-state properties<sup>14</sup> (such as the cohesive energy  $E_c$  and bulk modulus  $B$ ) of the first row transition-metal elements with respect to the number of  $d$  electrons  $N_d$ .  $E_c(N_d)$  and  $B(N_d)$  curves show a minimum (at  $N_d=5$  for the  $3d^5 4s^2$  configuration of Mn atom) between two maxima of equal strength; the first maximum occurs at  $N_d=3$  or 4, the second one at  $N_d=7$ . This behavior of bulk properties was explained by the Friedel model.<sup>15</sup> Although the overall shape of the variation of the binding energies of first row transition-metal atoms with  $N_d$ ,  $E_b^{sp}(N_d)$  is reminiscent of the  $B(N_d)$  and  $E_c(N_d)$ , there are significant differences. The binding energy of Ti( $N_d=2$ ) is highest, and hence the first maximum is higher than the second one  $E_b^{sp}(N_d=7)$  and  $E_b^{sp}(N_d=8)$  corresponding to the binding energies of Co and Ni. While the binding energy of Sc( $N_d=1$ ) is close to that of Ti at the first maximum, the binding energy of Cu( $N_d=10$ ) is small, and it eventually decreases to almost zero for Zn, which has a filled valence shell (i.e.,  $3d^{10} 4s^2$ ). Interestingly, Cr and Mn atoms which have the same  $3d^5 4s^2$  configuration have similar binding energies forming the minimum between double maximum, but different  $E_c$  and  $E_b$ .

The parent atom C, and Si form rather strong bonds with the SWNT with  $E_b=4.2$  and 2.5 eV, respectively. These atoms can be used as spacers or bonders between individual SWNT's. In addition to the adsorption, the substitution of Si is of particular interest, because SiC is a stable crystal. The Si substitution is realized by replacing one of the carbon atoms of the (8,0) SWNT by Si, and subsequently by relaxing carbon atoms and Si until a practically zero force on all these atoms is achieved. To get an idea about the energetics of the Si substitution, we calculated the self-consistent total energies of two different systems. First is the total energy

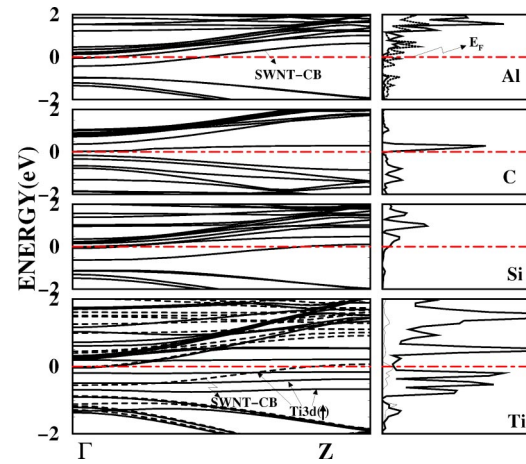


FIG. 3. Energy band structure and local density of states (LDOS) of Al, C, Si, and Ti adsorbed on a zigzag (8,0) tube. Continuous and dotted lines are LDOS's on the adsorbate (Al, C, Si) and on a hexagon of the SWNT at the close proximity of the adsorbate (Al), respectively. LDOS's of spin-up states of Ti and spin-down states on the hexagon of SWNT's are shown by continuous and dotted lines, respectively.

$E_T[\text{SWNT, Si}]$  of a (structure optimized) bare (8,0) SWNT and a single Si atom which was placed at the farthest point from the SWNT in the supercell. Second is the total energy  $E_T[\text{SWNT}(\text{Si}), \text{C}]$  of the structure optimized SWNT and a single C atom which was placed at the farthest point from the latter SWNT. The difference of energy  $\Delta E = E_T[\text{SWNT, Si}] - E_T[\text{SWNT}(\text{Si}), \text{C}]$  can give an idea about the energy involved in the Si substitution. We found that  $\Delta E$  is negative ( $\sim -6$  eV) and hence the substitution of Si is energetically unfavorable and corresponds to a local minimum in the Born-Oppenheimer surface. Following the definition by Baierle *et al.*,<sup>17</sup> i.e.,  $E_S = E_T[\text{SWNT}(\text{Si})] - E_T[\text{SWNT}] - (\mu_{\text{Si}} + \mu_{\text{C}})$ , we calculated the substitution energy of a single Si atom to be  $E_S = 2.75$  eV by using the bulk cohesive energies of Si and C for  $\mu_{\text{Si}}$  and  $\mu_{\text{C}}$ , respectively. This energy is comparable with the substitution energy of Si calculated for the (10,0) and (6,6) SWNT's.<sup>17</sup> If we use the adsorption energies of Si and C in Table I for  $\mu_{\text{Si}}$  and  $\mu_{\text{C}}$ , the formation energy is found to be 4.67 eV and hence becomes even more unfavorable.

An individual atom adsorbed on an (8,0) SWNT may give rise to resonance states in the valence and conduction bands, and also localized states in the band gap. However, owing to the supercell method used in this study, the energy states associated with an adatom form energy bands. Actually these bands correspond to a linear chain of adatoms with lattice constant  $c_{sc}$ . The dispersion or width of the bands is a measure of the adatom-adatom coupling. Moreover, the energy position of the bands indicates whether the associated localized state is a donor or an acceptor state. In Fig. 3, we present the band structures and the local density of states for Al, C, Si, and Ti. Upon Al adsorption, SWNT is metallized by the half-filled band derived from the conduction band of the bare SWNT. In the case of C, a small gap occurs between the bands derived from adsorbate states. Si yields an almost

doubly occupied band in the band gap, which may correspond to a doubly occupied donor state of the individual Si adsorbed on the (8,0) tube. The situation with the adsorbed Ti atom is complicated due to the magnetic ground state. Three bands formed from Ti  $3d(\uparrow)$  are fully occupied and accommodate three electrons of the adsorbed Ti atom. Other Ti  $3d(\uparrow)$  bands occur above  $E_F$ , but they overlap with the conduction band of SWNT. The dispersive and almost fully occupied spin-down band is formed from the states of carbon and hence derived from the conduction band of the bare SWNT. The SWNT is metallized upon the Ti adsorption, since this band crosses the Fermi level and also overlaps with the other conduction bands. The charge-density analysis performed by using difference charge densities and Mulliken scheme indicates that charge is generally transferred from the metal adsorbates to the SWNT.

In conclusion, our study shows that interesting physical

properties can be generated by the adsorption of a single atom on a SWNT. Higher coverage and decoration of adsorbed foreign atoms can produce nanostructures (such as nanomagnets, nanometer size magnetic domains, 1D conductors and thin metallic connects, and electronic devices) which may find interesting technological application, such as spintronics and high-density data storage, and interconnects between devices. The  $d$  orbitals of the transition-metal atoms are responsible for relatively higher binding energies, which display an interesting variation with the number of filled  $d$  states.

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