Study of Geometries and Electronic Properties of Pd and Pd-Ni alloy chains on Single-Walled Carbon Nanotubes

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Experiments showing the possibility of stable, suspended single atomic chains have been reported in the literature recently. Transmission electron microscopy studies reveal the quasi-continuous formation of Pd and Ni coatings on freely suspended carbon nanotubes. In this paper, we study the binding and geometries of isolated Pd and Pd-Ni atomic chains on two types of single-walled carbon nanotubes (SWNTs) theoretically. Pd and its alloys with Ni are commonly employed in hydrogen reactions and sensors. These calculations were performed using the pseudo-potential (PP) plane wave method within the density functional theory (DFT) and the generalized gradient approximation (GGA). Two configurations of straight and zigzag chains were studied. Cohesive energies calculations on free standing infinite Pd and Pd-Ni monatomic chains show stable formation of small angle zigzag chains, and a meta-stable formation of wide angle zigzag chains. Further studies of the electronic properties of Pd, Pd-Ni functionalized SWNTs and their possible contributions as novel sensing materials are underway.

I. Introduction

Recently, modifications of single walled carbon nanotubes (SWNTs) have attracted much interest because they allow control of the properties of bare tubes. A nanotube with adsorbed metals may significantly changes its physical properties, thereby providing a useful means for manipulating electronic transport for microelectronic devices. Our interest is in sensing materials. For example, a Pd nanoparticle modified SWNT based sensor was shown to exhibit high sensitivity and fast response to hydrogen at room temperature[1]. Pd loaded SWNTs also showed some advantages over conventional sensors for methane detection, while bare SWNTs showing no response to methane at all.[2] Thus, theoretical study of interactions of metal atoms SWNTs is important in understanding their potential applications in fabricating functional microelectronic gas sensor devices.

The contact of single metallic atoms with SWNTs has been systematically studied lately by DFT[3,4]. The influences of different single metallic atoms on the physical properties of SWNTs have been discussed. However, not much attention has been paid to the related properties of single atomic metal chains on SWNTs. No alloy chain formations on SWNTs have been explored. Earlier researches have shown the possibility of forming single atomic chains.[5-10] Experimentally, suspended stable gold monatomic chains were successfully fabricated between two gold electrodes, showing that a wire of at least four Au atoms can form linearly[6,7]. Theoretical calculations, on the other hand, demonstrate stable formation of infinitely long atomic chains with zigzag structures.[8,9] Molecular Dynamics (MD) simulations also show Au and Pt have the strongest tendency of forming chains than many other transition and noble metals.[10] Recently, both experimental[11] and theoretical[12] investigations have demonstrated well-defined bimetallic alloy chains, and their ability of stabilizing monatomic chains.

Pd materials are interesting due to their value in sensing hydrogen[13]. The solubility of hydrogen in palladium markedly exceeds that in the other elements in Group VIII over a very wide range of temperatures and pressures. Pd alloys, such as Pd/Ni and Pd/Pt, on the other hand, are important for hydrogen sensors to improve reliability and speed of the sensor response in detecting hydrogen[14,15] and other gases[16]. Applications of Pd decorated SWNTs as sensing materials[1-2,17] have recently provided new designs of high performance gas sensors, mainly because of the enhancement of adsorption of gases due to the large surface area of SWNTs, and dramatic electrical conductance changes due to the charge transfer mechanism.

In this paper, we present *ab initio* calculations on Pd and Pd/Ni atomic chain adsorbed SWNTs using density functional theory (DFT). Two types of SWNTs are used in this paper, semiconducting SWNT(10,0) and metallic SWNT(6,6), with similar diameters of 7.83Å and 8.14Å. First, geometries and stability of free standing infinite Pd and Pd/Ni monatomic chains are analyzed. Then, possible stable geometries of Pd and Pd/Ni chain are added on SWNTs to examine the formation of chains on tubes. Our primary goal is to reveal the character and geometries of the atomic Pd and its alloy chains on both semiconducting and metallic SWNTs, and understand their effect on the property changes of the tubes. We believe that the results will be important to both theoretical and experimental investigations of these materials in hydrogen and other gas sensor applications, by allowing the design and fabrications of novel microsensors.

II. Method of Calculations

The Vienna *ab initio* simulation package (VASP)[18,19,20] was used to perform the periodic system calculations. The total energy and electronic structure calculations are carried out within the generalized gradient approximation (GGA) of PW91[21] using the pseudo-potential plane wave method. Both single atomic chains and SWNTs are considered as isolated and infinite in length, with lateral separation of more than 1 nm. The Brillouin zone of the supercell is sampled by 1×1×31 k-points within the Monkhorst-Pack special k-point scheme.[22] A large energy cutoff of 500 eV for the plane wave basis set is used for all large hexagonal supercells. Structural configuration of isolated SWNTs are fully relaxed to minimize their total energies by the conjugate gradient (CG) method. Same sized supercells are used next for adsorption, and all atomic positions of adsorbate and nanotubes are optimized until the remaining forces converge within 0.01 eV/Å.

The binding energy E_c for atomic chain structures can be calculated in terms of total energies of isolated atom and the chain formed by the same atoms, namely, the binding energies for Pd and Pd/Ni chains are calculated by the following equations respectively (the results are shown in two bonds):

$$E_b\left(\text{Pd chain}\right) = E_T\left(\text{Pd chain}\right) - 2E_T\left(\text{Pd}\right)$$

$$E_b\left(\text{Pd/Ni chain}\right) = E_T\left(\text{Pd/Ni chain}\right) - E_T\left(\text{Pd}\right) - E_T\left(\text{Ni}\right)$$

Similarly, the averaged adsorption energy E_{ad}, of each chain on SWNTs can be calculated by:

$$E_{ad}\left(\text{Pd chain}+\text{SWNT}\right)=E_T\left(\text{Pd chain}+\text{SWNT}\right)-E_T\left(\text{SWNT}\right)-E_T\left(\text{Pd chain}\right)$$

$$E_{ad}\left(\text{Pd/Ni chain}+\text{SWNT}\right)=E_T\left(\text{Pd/Ni chain}+\text{SWNT}\right)-E_T\left(\text{SWNT}\right)-E_T\left(\text{Pd/Ni chain}\right)$$

where E_T is the ground state total energy for different full-relaxed systems, N is the number of metal atoms in the system. Negative adsorption energies correspond to an energetically bound species.

Pd and Ni adsorbed SWNT systems have been reported having a zero or very small magnetic moment[3,23], and our calculations of a single Pd atoms also shows the nonmagnetic property. However in this paper, we still use fully spin-polarized DFT in our calculations to observe the possible change of magnetic moment in the interactions of Pd, and its vertical group elements Ni and Pt with SWNTs.

II. Atomic chain structures

Two configurations of chains were studied, namely, linear chain and zigzag chain. In the alloy chains, Pd and Ni atoms were located alternately. Results are shown in Fig.1, where the binding energy is plotted as a function of wire length. The binding energy curves show that Pd and Pd/Ni chains at local minima have larger binding energy than in their own bulk systems, which is -0.63eV/bond for Pd fcc bulk and -0.86eV/bond for Ni fcc bulk, indicating the many atom effect in the bulk.[24] The largest bonding energy of Pd linear chain is -1.21eV/bond, close to the -1.20eV/bond calculated by Bahn and Jacobsen.[23] The bonding energy of Pd/Ni linear chain at local minima is observed to be between that of the Pd and Ni linear chain and higher than pure Pd linear chain.

We observe that zigzag chains have much stronger binding than the corresponding linear chains, which indicates that a preferred geometry of single atomic chain is not linear. The highest binding energy of Pd zigzag chain can be found when Pd bonds form about 61.2° angle, a narrow angle, with d=2.5 Å. The other meta-stable state was found at d=4.0 Å, a wide angle, corresponding to a bond angle of 109.1°. As seen in Figure1, Pd/Ni zigzag chain also has overall lower binding energies than the pure Pd one, because of the stronger Ni-Ni bonding. Here, the differences between the binding energies are much smaller than for the linear chains. The first local minimum for Pd/Ni chain also appears at a bond length of 2.5 Å. The second local minimum turns up earlier than for the Pd chain, where the $d=3.7\text{Å}$ with a smaller bond angle of 98.1° than the wide angle for Pd due to the stronger interactions of Ni atoms.

To illustrate the stability and character of bonding of these three types of chain, we studied their electronic band structure, which is shown in Fig. 2. According to the band structure, all three chains are metallic. In the linear chain, the overlaps between the filled *d* states broaden the *d* bands slightly over the Fermi level. This overall band form of the band structure is maintained in the wide angle chain, except that the *d* bands are narrowed and less disturbed, which brings bands back below the Fermi level. However, the wide angle chain is more stable than the linear chain because of its relatively stronger electronic screening. The band structure of narrow angle chain shows some differences from the other two types of chain. In the narrow angle chain, the increased number of bands and band splitting in the narrow angle chain is due to the triangular geometry of the chain. In the PdNi chains, the s and d band decoupled. A band gap opens up at the boundary of the zone (kz=0.5) between valance s and underlying d band upon alloying. Zigzag PdNi chains have similar forms of band structure as Pd zigzag chains. In all cases, the lowering of density of states near Fermi level in the zigzag chain strengthens the binding than the straight chains. During the calculation, we did not observe obvious dimerization effect, such as Peierls distortion. The calculations were also repeated with full-potential linearized augmented plane wave (FLAPW) method,[25,26] and the same results of band structures were achieved.

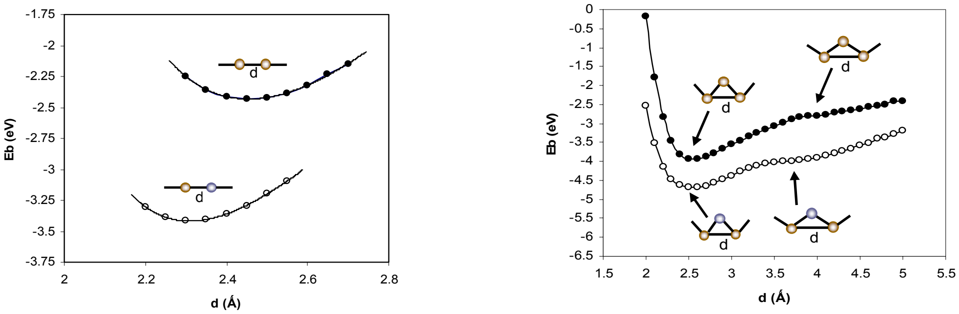


Fig.1 calculated cohesive energy of Pd atomic chain as a function of length of unit cell d. Two geometries: (left) straight, (right) zigzag chain with both narrow angle and wide angle, are shown at corresponding d values. The cohesive energy is calculated by total energy difference between isolated Pd atom and Pd monatomic chain.

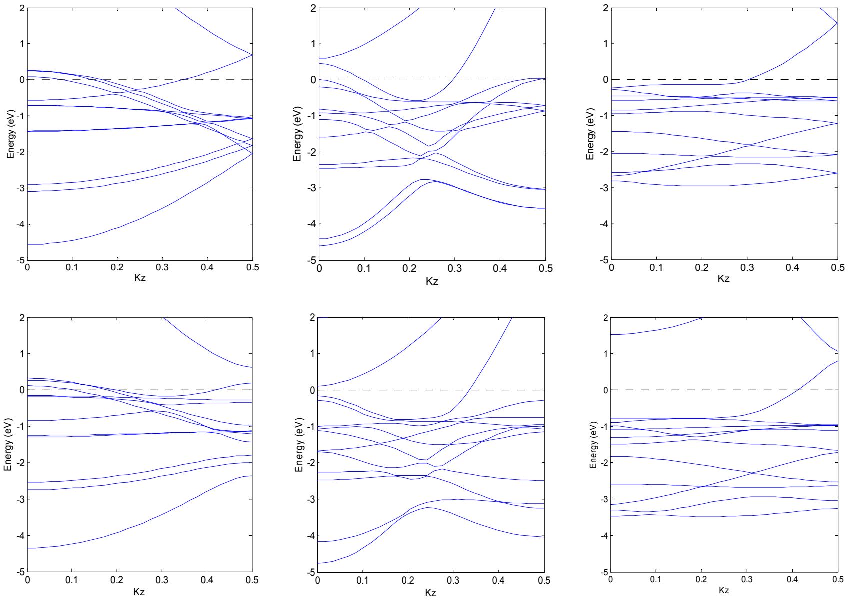


Fig. 2. Electronic band structure of the (upper panel) Pd chains and (lower panel) PdNi chains. From left to right: straight chains, narrow angle chains and wide angle chains shown in Fig. 1. Bands of linear chains are folded to compare with the zigzag structures. Fermi level is set at zero energy.

IV Chains on SWNTs

A Pure Pd chain on SWNTs

To form continuous chains on SWNTs, same sized supercells are chosen as the unit cell of SWNTs in tube directions. Previously, we have performed DFT calculations of a single Pd atom on the same tubes[27]. Four sites are considered for Pd adsorption, as shown in Fig. 2.

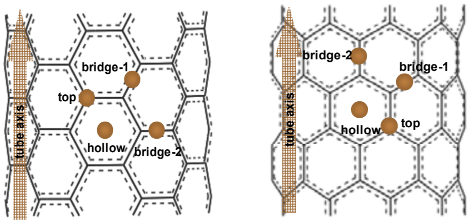
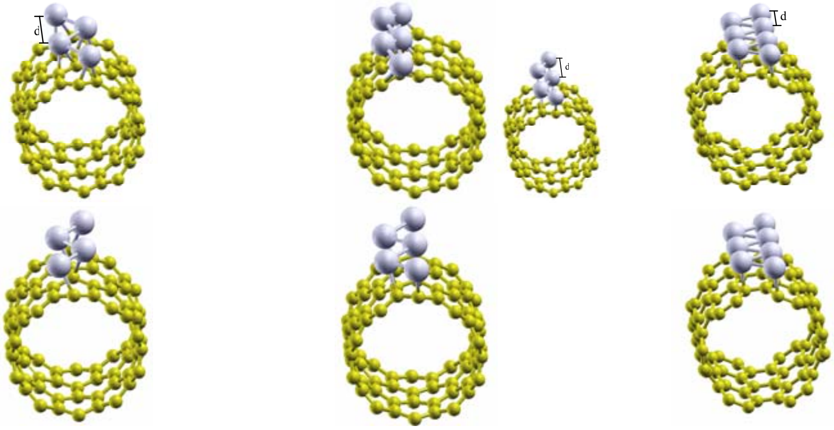


Fig. 3 Schematic drawing of top views of four possible sites for single Pd adsorption on the SWNT(6,6). Brown dots represent Pd atoms. Bridge-2 site is different from bridge-1 site because the former site located where the C-C bond is perpendicular to the tube axis. In the SWNT(10,0) case, bridge-2 site is located on a C-C bond parallel to the tube axis.

Calculations of adsorption energies have shown that for the (6,6) tube, the adsorption on bridge 1 site is the strongest, while for the (10,0) tube, the strongest adsorption site appear at bridge 2 site. However, due to different symmetries of (6,6) and (10,0) tubes, and required periodicity for DFT calculations, there are a few limited ways of putting chains on the SWNTs. As shown for the single chain calculations in Fig. 1, we decided to add Pd wide angle chains on (10,0) tube and narrow angle chains on (6,6) tube. The bond length or bond angle of the chains is slightly changed due to the curvature of the tubes. The initial geometry of Pd chains on carbon nanotubes is shown in Fig. 4. Single Ni atom was reported having larger adsorption energy than Pd atom on the (8,0) SWNT. The strongest adsorption sites are found as bridge 2 as well. Lately, continuous Ni nanowires have been coated on suspended SWNTs by electron-beam evaporation, indicating stronger interaction of Ni atoms with carbon nanotubes.[28] Both the theoretical and experimental work above shed light into the study of Pd/Ni alloy chain-tube interaction. In this paper, Pd/Ni alloy chains on carbon nanotubes have the same initial geometries, with one atom replaced by Ni.



(a) (b) (c)

Fig. 4 Considered geometries of the Pd chain-tube structure (upper) before and (down) after relaxations. (a) Pd wide angle chain on bridge 1 sites of (10,0) tube, (b) Pd wide angle chain on bridge 2 site of (10,0) tube, (c) Pd narrow angle chain on top site of (6,6) tube. From (a) to (c) respectively: d=4.268 Å, 4.268 Å, and 2.460, α=98.32°, 120.68°, 60.00°. Same initial geometries are used in the PdNi chains. (The geometry of Pd wide angle chain on bridge 2 site was initially suggested as the small picture shown beside (b). However the energy did not converge during relaxation. Therefore (b) is used for the initial geometry of wide angle chain on (10,0) tube.)

The Pd chains mostly maintain their overall initial geometries after relaxations. The angle between Pd atoms on (6,6) tube is 53.23°, with same d=2.460 Å. The curvature of the (6,6) tube and the stronger interactions of Pd-Pd atoms induces an unequal Pd-C distance of 2.241 Å and 2.280 Å between the Pd atoms and their nearest carbon atoms, which are also longer than the Pd-C distance formed by single Pd atom on top site of the (6,6) tube. The b1-site adsorbed Pd atoms form an angle of 107.21° with d=4.260 Å. This angle and distance d are close to what is obtained in the isolated wide angle chain, shown in Fig. 1. We also observed a significant change of the Pd arrangement on the tube during the relaxation: the Pd adatoms rise above the b1 site, and are disconnected from one of the Carbon atoms. The stronger Pd-Pd forces attract Pd atoms closer but the repulsive force and Pd-C interaction separate them again and finally shift Pd atoms to the bridge 1 site on the other side of the tube. The distances between the Pd atoms and nearest C atoms are 2.136 Å and 2.123 Å, which are smaller than the value of 2.170 Å obtained from single Pd adsorption on b1 site of a (10,0) tube. Pd chains on the b2-site also try to get close to their energy favorable geometry, where the angle between Pd atoms reduced from 120° to 99.51°, with a slightly smaller d=4.261 Å. Pd-C distances of 2.180 Å and 2.177 Å are also higher than 2.144 Å from the single atomic adsorption calculation. Unlike b1 absorption, Pd atoms keep the connection with four b2-site Carbon atoms all the time during the relaxation.

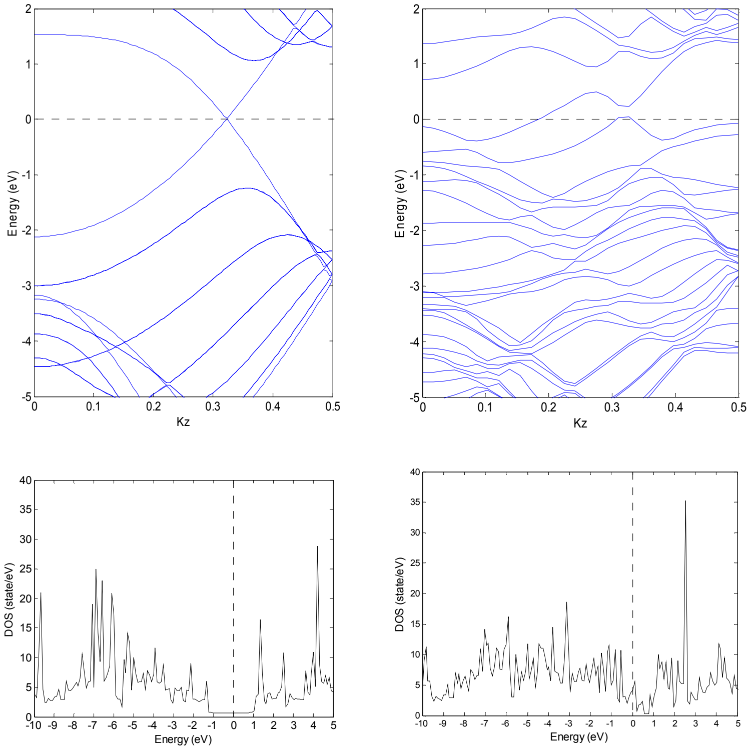
The calculated adsorption energy of a Pd atom adsorbed on SWNT(6,6) and SWNT(10,0) are listed in Table 1. As reported before, the adsorption energies of Pd atoms on four different sites range from ~-1 to ~-1.4eV. The average Pd-tube bond length occurs in the range of 2.0-2.1Å. In this case of Pd chain formation on carbon nanotube, the adsorption energy of each Pd atom is ~-0.45 to ~-0.62 eV, smaller than that of the single atomic adsorption. This is due to the strong Pd-Pd coupling in the chain, while Pd-SWNT bond is weakened. The Pd atoms have larger adsorption energy on the (10,0) tube than on the (6,6) tube because of the smaller curvature of the (6,6) tube. The higher adsorption energy from the b2 site than the b1 site is consistent with the single Pd atom adsorption results. However, the bond length between Pd and two neighbor C atoms is higher by ~0.05 Å on b2 sites. We attribute this to the initial geometry difference between the chains.

Table 1. Adsorption energy of Pd atom on SWNTs.[a]

System	E_{ad} (eV)	$d_{Pd\text{-}C}$ ($Å$)	$d_{Pd\text{-}C}$ ($Å$)	ΔQ (e)
Pd chain + SWNT(6,6)	-0.90	2.241	2.280	+0.10
Pd chain + SWNT(10,0) on b1	-1.14	2.136	2.123	+0.20
Pd chain + SWNT(10,0) on b2	-1.24	2.180	2.177	+0.22

[a] $d_{Pd\text{-}C}$ is the distance between Pd and its nearest neighbor Carbon atom. ΔQ is the electron charge transfer from tube to adatoms, where positive means tube gains charge.

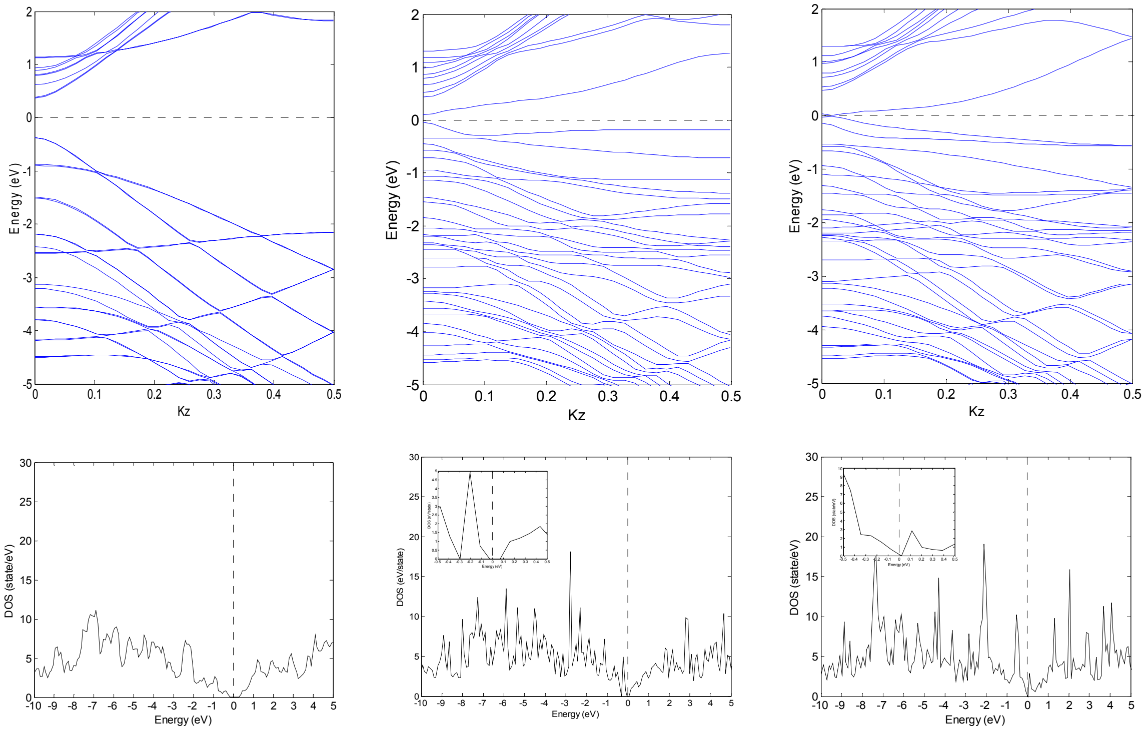
The electronic structures of the bare (6,6) and (10,0) tube affected by Pd atomic chains are shown in Fig. 5-6. To check the results of chain adsorption, we firstly investigate bare tubes. Figure 5(a) shows the band structure and DOS of a (6,6) tube. The π conduction band and π valence band cross at Fermi level at about kz=0.67 indicating that the tube is metallic. The separation between two van Hove singularities around Fermi level is 3.65 eV, which is in agreement with results of Reich *et al.*[29] Figure 6(a) shows the band structure and DOS of the semiconducting (10,0) tube. The band gap between the bottom of the conduction band and top of the valence band at kz=0 (Γ point) is about 0.75 eV, in agreement with previous results.[30]



(a) (b)

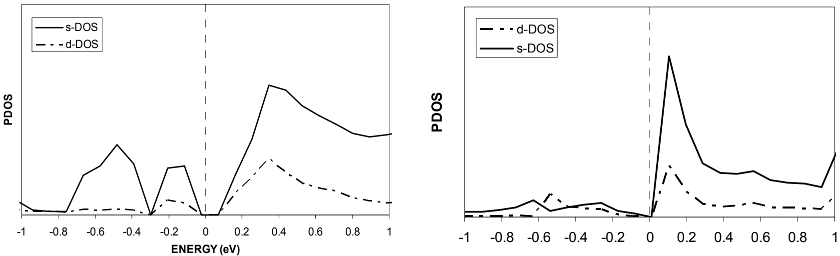
Fig.5 Band structure and DOS of (a) SWNT(6,6) ,and (b) Pd narrow angle chain adsorbed SWNT(6,6). Fermi level is set as zero.

Upon adsorption of Pd chains, the electronic properties of both SWNTs have many significant changes. As we can see from 5(c) and 6(b,c), new bands were created, and original bands from bare tubes were perturbed. The crossed or almost degenerated states are split in both valance and conduction bands due to the perturbation by the Pd chain, which reduces the symmetry of the wave function in the tube. As shown in 5(c), the metallic nature of the (6,6) tube is not affected. This is because even though π and π^* bands are lifted by the perturbation, the d bands of Pd chain are inserted around Fermi level, which makes the system stay metallic. The charge transfer study shows there is only 0.1eV electron transferred from Pd atoms to the tube. The band structure of (10,0) tube shows different electronic property change upon the adsorption of Pd chain on different sites. In the b1 site adsorption, band gap of the bare tube is significantly reduced due to the insertion of bands from Pd chain. PDOS shows the contribution of two new bands are from hybridized $\sigma-\pi$ and $\sigma^*-\pi^*$ bands. The Fermi level is about 0.5 eV above valence band and 1.0 eV below the conductance band. However, when Pd chain is added on the b2 sites, a metallic behavior is observed through the crossing of the two bands at the Fermi level. A perusal of the DOS in figure 6(c) reveals that the DOS in the neighborhood of E_f is equal to 0.17 state/eV. Approximately 0.2~0.22 electrons transferred from Pd to the (10,0) tube, with a slightly more transfer in the b2 adsorption case. The above suggests that carbon nanotube can be functionalized in different ways by their coverage with Pd chains at different sites. The semiconducting property of the tube may be either retained or changed based on the adsorption sites.



(a) (b) (c)

Fig.6 Band structure and DOS of (a) SWNT(10,0), (b) Pd wide angle chain adsorbed SWNT(10,0), and (c) Pd wide angle chain adsorbed SWNT(10,0). Fermi level is set as zero.



(a) (b)

Fig.7 Projected density of state (PDOS) of Pd atoms on (a) b1 site functionalized SWNT(10,0), and (b) b2 site functionalized SWNT(10,0)

B. PdNi alloy chains on SWNTS

We also studied the PdNi alloy chain functionalized on the same tubes by simply substitute one Pd atom with Ni atom, and then relaxing the systems. Ni and Pd are in the same vertical group in the periodic table, therefore they have the same outmost electronic structures. Ni atoms are reported to have a stronger binding with semiconducting tube (8,0)[3] , and Ni can also improve the reliability of Pd nanomaterials, especially in hydrogen sensing applications[31,32]. These studies are underway and results will be reported later.

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