

Adsorption of Gold Atoms on Carbon Nanotubes

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ABSTRACT

We investigate, using *ab initio* Density Functional Theory total energy calculations, the interaction of Au atoms with a (6,6) carbon nanotube. We found out that isolated Au atoms are weakly bound to nanotubes, and contrary to Al, Ti and Fe, the most stable site is on top of carbon atoms. The Au-tube binding energy for this site is between -0.3 eV and -0.7 eV, depending on the approximation used for the exchange-correlation functional. The Au atoms will diffuse very quickly through the C-C bonds, with a barrier along this pathway of ≈ 0.04 eV. When two Au atoms meet, a strong Au-Au bond is formed, with the resulting dimer being less bound to the nanotube when compared to isolated Au atoms. All these results are similar to what is found for the Al-nanotube interaction. This supports the picture that discrete metallic clusters will be formed on nanotubes when the interaction between them and the metal atom is weak. However, an analysis of Fe adsorption shows that further studies are still needed.

Keywords: Carbon nanotubes. Gold. Metals. Adsorption.

1 INTRODUCTION

Since the discovery of Multi-Walled (MWNT) [1] and Single-Walled Carbon nanotubes (SWNT) [2,3], a great deal of basic and applied research has been performed on these systems. In part this activity is motivated by the belief that carbon nanotubes will play a prominent role in the world of nanomaterials and nanotechnology. In particular, SWCNT present interesting electric transport properties, being either semiconductors or metals, depending on their diameter and chirality [4].

Recently, it has been shown [5,6] that upon adsorption of different molecules the properties of SWNT can be significantly altered, which may lead to interesting applications as sensors. Besides the adsorption of molecules, studies have also been performed where different metals are deposited on both SWNT [7-9] and MWNT [10]. One of the main goals was to study the possibility of using carbon nanotubes as templates to form metallic nanowires. However, the possibility of depositing transition metal atoms on nanotubes in order to functionalize them as catalysts has been recently demonstrated [11].

The studies of metal deposition have shown that the atoms can be located either outside [7,8] or inside [9,10] the

nanotubes. When located outside, it was found out that not all of the metals form continuous structures on the nanotube surface [7,8]. For example, Ti forms a continuous coating whereas Au, Al and Fe form discrete particles along the nanotube. It is believed that the weak interaction of these latter metal atoms with the nanotubes is responsible for such behavior [7,8]. In particular, Peng and Cho [12] have recently studied theoretically the interaction of both Ti and Al atoms with semiconducting (8,0) SWNT. They found out that both atoms prefer to adsorb over the center of a hexagon ring, however, whereas the binding energy for the Ti-SWNT is of the order of 2.3 eV, it is approximately 1.3 eV for Al-SWNT. Moreover, the diffusion barrier for Al diffusion was found to be only ≈ 0.05 eV, whereas it was found to be ≈ 0.4 eV for Ti. These results support the picture discussed above that the different coating behavior is related to the different Metal-SWNT binding energies.

Motivated by these experimental as well as theoretical studies, we have decided to perform systematic *ab initio* calculations to investigate the interaction of Au atoms and SWNT.

2 COMPUTATIONAL METHODS

In order to investigate the structural and electronic properties of Au atoms interacting with SWCNT we use first-principles total energy Density Functional Theory (DFT) [13] calculations, using numerical orbitals as basis sets. We have used the SIESTA code [14], which performs fully self-consistent calculations solving the Kohn-Sham (KS) equations. The KS orbitals are expanded using linear combinations of strictly localized atomic orbitals, as proposed by Sankey and Niklewski [15]. The extension of the orbitals is characterized by the confining energy shift (E_S) [14]. In all calculations we have used a split-valence double-zeta basis set with polarization functions [14]. For the exchange and correlation term, we have used either the Local Density Approximation (LDA) [13] or a Generalized Gradient Approximation (GGA) [16]. The ions-valence electrons attraction is described via the standard norm conserving Troullier-Martins pseudopotential [17]. A cutoff of 250 Ry for the grid integration was utilized to represent the charge density [14]. We have used 10 k-points for the Brillouin zone integration along the tube axis. Structural optimizations were performed using the conjugated gradient algorithm until the residual forces on every atom were smaller than 0.025 eV/Å.

For the calculations we use a metallic armchair (6,6) SWNT. In the supercell approximation with periodic-

boundary conditions we have 72 C atoms, corresponding to three primitive cells of the (6,6) nanotube, and one or two Au atoms. The lateral separation between tube centers is large enough to prevent any tube-tube interaction.

The binding energy between a single Au atom adsorbed on site S of the SWNT is calculated as

$$E_B(S) = E[\text{SWNT}+\text{Au}(S)] - E(\text{SWNT}) - E(\text{Au}) \quad (1)$$

In the above equation, $E[\text{SWNT}+\text{Au}(S)]$ is the total energy for the fully relaxed system SWNT plus Au atom at site S, $E(\text{SWNT})$ is the total energy for the fully relaxed isolated SWNT, and $E(\text{Au})$ is the total energy for an isolated Au atom inside an identical supercell.

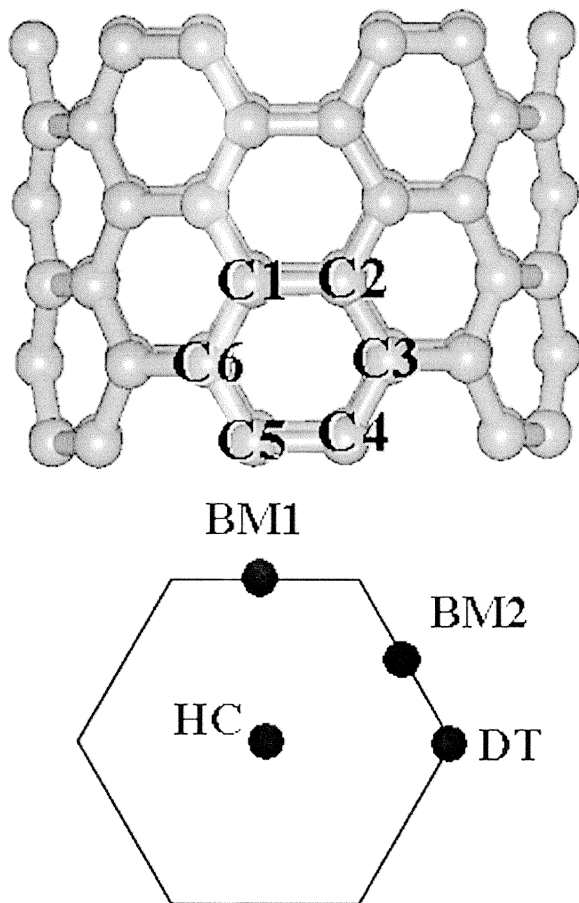


Figure 1: Upper panel shows a top view of the (6,6) SWNT, with the six C atoms in one of the hexagons marked from C1 to C6. The lower panel shows schematically one of these hexagons with labeled adsorption sites.

For a single Au atom interacting with the (6,6) nanotube, we have investigated four different adsorption sites, which are indicated in the lower panel of Figure 1: (1) The HC site has an Au atom adsorbed directly above the center of a hexagon. (2) The DT site has an Au atom adsorbed directly above a C atom. (3) The BM1 and BM2

sites are two non-equivalent sites where an Au atom is adsorbed directly above the middle of C-C bonds. All the results below are for energy shifts of $E_S=30$ meV for C and $E_S=1$ meV for Au atoms, which guarantees a convergence of approximately 0.01 eV for the binding energies.

3 RESULTS AND DISCUSSION

We present in Table 1 the results for the binding energies for an Au atom adsorbed at the DT and HC sites, for both LDA [13] and GGA [16] calculations. At both levels of calculation DT is the most stable site (see Figure 2). However, as is well known [18], the binding energy tends to be larger at the LDA level. Moreover, the differences between the LDA and GGA results are not the same for all sites. For example, for the DT site, the difference between the LDA and GGA binding energies is 0.42 eV, whereas the same difference is only 0.17 eV for the HC site. In both cases, however, the reduction in the binding energy from LDA to GGA is between 30-40 % of the LDA result (30 % for the HC site and 39 % for the DT site).

	Site	$E_B(S)$ (eV)	$d(\text{Au}-\text{C})$ (Å)
GGA	DT	-0.67	2.22
	HC	-0.40	3.56
LDA	DT	-1.09	2.12
	HC	-0.57	2.80

Table 1: Binding energies $E_B(S)$ for the HC and DT sites, as defined in Figure 1. Non-spin polarized calculations at both the GGA [16] and LDA [13] levels. $d(\text{Au}-\text{C})$ are the distances between the Au atoms and the nearest-neighbor carbon atoms.

We also report in Table 1 the distances between the Au atoms and their nearest-neighbor C atoms, $d(\text{Au}-\text{C})$. For the DT site this corresponds to the Au-C3 bond distance (see Figure 1), and for the HC site there are six equivalent distances, from the Au atom to either one of the six labeled C atoms of Figure 1. The $d(\text{Au}-\text{C})$ result for the DT site has a quite similar value at both the LDA and GGA level. This result is not very different from what would be obtained from the sum of half the value of molecular Au-Au bond length and half the value of the C-C bond length in the nanotube (this sum gives approximately 2 Å). For the HC site, on the other hand, there is a large change in the $d(\text{Au}-\text{C})$ result when comparing the LDA and GGA calculations. Even though the binding energy does not show a drastic difference between the LDA and GGA calculations, the Au atom moves away from the C atoms by approximately 0.8 Å when changing from the LDA to GGA. In any case, however, the Au-C bond lengths are quite large (2.8 Å for the LDA calculations and 3.56 Å for the GGA calculation), indicating that the Au atom is weakly bound at the HC center. This should be contrasted to both Al and Ti atoms,

that prefer to adsorb at the HC site according to Peng and Cho [12]. We have also recently found, using a similar method as described here, that Fe atoms prefer to adsorb at the HC sites. Finally, by displacing the Au atom slightly away from the HC site, we observe that it is not a local minimum of the Au-SWNT adsorption potential energy surface, at both the LDA and GGA level of calculation.

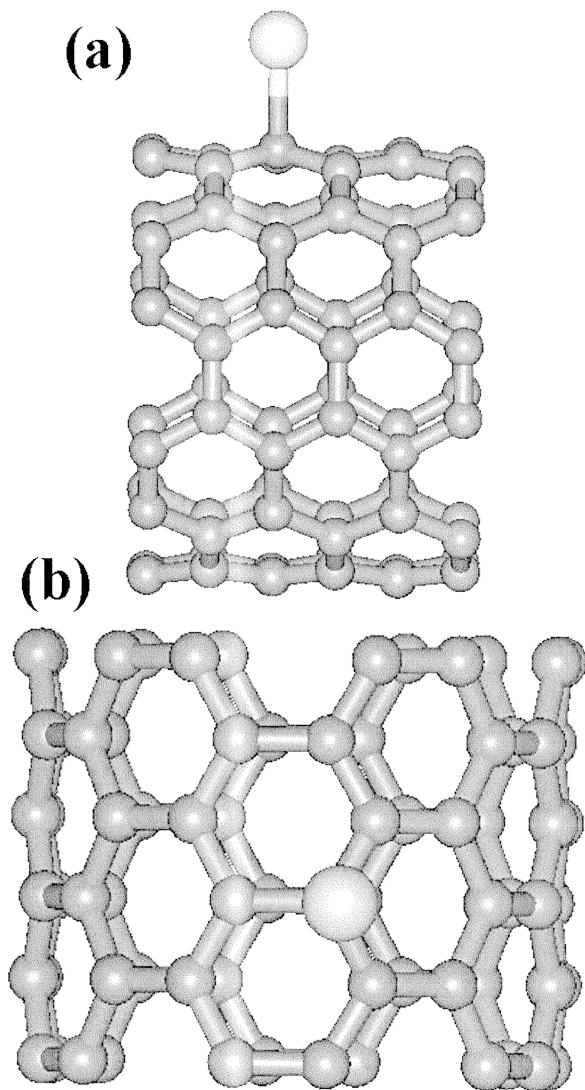


Figure 2: Configuration of lowest energy (DT site) for one Au atom adsorbed on a (6,6) nanotube. (a) Side view. (b) Top view.

In Table 2 we present the results for the binding energies for an Au atom adsorbed at the DT, HC, BM1 and BM2 sites (see Figure 1), for the GGA [16] calculations. As discussed before, the DT site (see Figure 2) is the most stable one. Differently from the results in Table 1, the binding energies shown in Table 2 are obtained from spin-polarized calculations, for both the isolated as well as the bound systems. As can be seen comparing the results of

Table 1 and Table 2, the spin-polarized calculations tend to reduce the binding energies by 0.3 to 0.4 eV. Most of this reduction comes from the lowering of the isolated Au atom total energy (the $E(\text{Au})$ in Equation (1)). The Au-C distances, on the other hand, are not altered in the spin-polarized calculations.

Site	$E_B(\text{S})$ (eV)	$d(\text{Au-C})$ (Å)
DT	-0.28	2.22
HC	-0.12	3.56
BM1	-0.18	2.52
BM2	-0.24	2.47

Table 2: Binding energies $E_B(\text{S})$ for the HC, DT, BM1 and BM2 sites of Figure 1. All results are obtained from spin-polarized, GGA [16] calculations. $d(\text{Au-C})$ are the distances between the Au atoms and the nearest-neighbor carbon atoms.

From the results of Table 2, we obtain that Au atoms will be very weakly bound to SWNT, and will have very small barriers for diffusion (of the order of 0.04 eV), similar to Al atoms [12] in SWNT.

Finally, we present in Figure 3 two possible configurations of Au dimers adsorbed on the (6,6) SWNT. In Fig. 3(a), the Au-Au bond is oriented along the nanotube axis, and each Au atom is approximately at a DT site. So we will call this configuration DT2_{\parallel} . The Au dimer configuration of Fig. 3(b) has the Au-Au bond oriented perpendicular to the nanotube axis, and the Au atoms are again approximately at DT sites. Therefore, we will label this configuration DT2_{\perp} .

Site	$E_{\text{Au-Au}}$ (eV)	$d(\text{Au-Au})$ (Å)	$d(\text{Au-C})$ (Å)
DT2_{\parallel}	-0.09	2.60	3.44 - 3.46
DT2_{\perp}	-0.08	2.63	2.48 - 2.52

Table 3: Binding energies $E_{\text{Au-Au}}$ for the adsorbed Au dimers (see Fig. 3) considering as reference an isolated Au-Au molecule. Our calculated equilibrium bond length for an isolated Au-Au molecule is 2.59 Å. All results are obtained from spin-polarized, GGA [16] calculations. $d(\text{Au-C})$ are the distances between the Au atoms and the nearest-neighbor carbon atoms, and $d(\text{Au-Au})$ is the Au-Au adsorbed dimer bond length.

As can be seen from the results of Table 2, we obtain that upon dimerization the Au atoms become much less bound to the nanotube. The isolated Au-Au binding energy, according to our calculations, is of the order of -2.0 eV. This implies that the Au atoms are much more strongly bound to each other than to the nanotube. Moreover, the Au-Au bond lengths for the adsorbed dimers are almost the same as the Au-Au molecular bond length. Finally, as can

be seen from Table 3, the Au-SWNT distance increases upon dimerization.

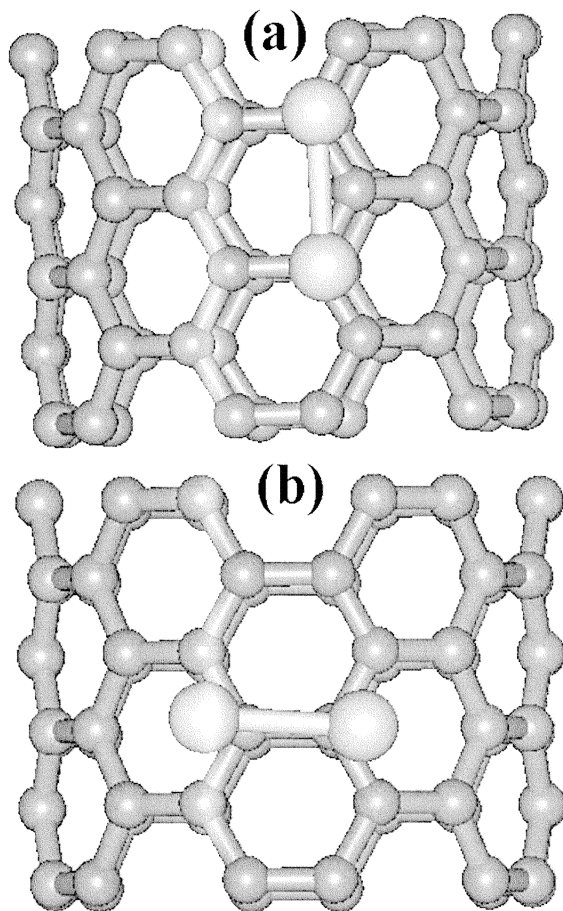


Figure 3: Two possible configurations for Au dimers adsorbed on the (6,6) SWNT. (a) The dimer is oriented with the Au-Au bond (a) along the tube axis ($DT2_{\parallel}$ configuration), and (b) perpendicular to the tube axis ($DT2_{\perp}$ configuration).

4 CONCLUSIONS

In conclusion, we have shown that isolated Au atoms are weakly bound to SWNT, the most stable site is on top of carbon atoms, and the Au(DT)-SWNT binding energy is somewhere between -0.3 eV (GGA) and -0.7 eV (spin polarized LDA calculation). Experimental estimates for the binding energy of Au on graphite give values of approximately -0.3 eV/atom [20] for large clusters and -0.8 eV for isolated atoms [21]. The Au adatoms will most likely diffuse very quickly, probably through the C-C bonds, since the barrier along this pathway is of the order of 0.04 eV. Upon encountering another Au atom, a strong Au-Au bond will be formed, and the resulting dimer will be less bound to the SWNT when compared to the isolated Au atom. All these results are similar to the Al-SWNT interaction [12], what would lend support to the picture that metallic clusters will be formed on SWNT when the

interaction between metal-nanotube has such properties. However, we have found [19] that the Fe-SWNT binding energy is of the order of -2.14 eV, with a diffusion barrier of approximately 0.4 eV [19]. These values are similar to what is found for the Ti-SWNT [12] interaction. Thus, as Ti forms a continuous coating whereas Fe forms discrete particles on SWNT, further studies are still needed to better understand the properties of the adsorption of metals on SWNT.

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