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# Theoretical Investigation of the Stability, Electronic and Magnetic Properties of Thiolated Single-Wall Carbon Nanotubes

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**ABSTRACT:** The addition of SH and OH groups to single-wall carbon nanotubes (SWCNTs) was investigated employing first principles calculations. In the case of the semiconducting (10, 0) SWCNT the SWCNT-SH binding energy is weak, 2–4 kcal/mol. However, for the metallic (5, 5) SWCNT it is larger, 7–9 kcal/mol. Thus metallic SWCNTs seem to be more reactive to SH than the semiconducting ones. Indeed, the (6, 6) SWCNT is more reactive to SH than the (10, 0) SWCNT, by 2–3 kcal/mol, something that can be explained only considering the electronic structure of the tube, because the (6, 6) has a larger diameter. The binding energies are larger for the addition of the OH group, 25 and 30 kcal/mol for the (10, 0) and (5, 5) SWCNTs, respectively. When a single OH or SH group is attached to the metallic SWCNTs, we observe important changes in the DOS at the Fermi level. However, when multiple SH groups are attached, the changes in the electronic and magnetic properties depend on the position of the SH groups. The small binding energy found for the SH addition indicates that the successful functionalization of SWCNTs with SH, SCH<sub>3</sub>, and S(CH<sub>2</sub>)<sub>n</sub>SH groups is mostly due to the presence of defects created after acid treatment and to a minor extent by the metallic tubes present in the samples. Perfect semiconducting SWCNTs showed very low reactivity against the SH group. © 2008 Wiley Periodicals, Inc. *Int J Quantum Chem* 109: 772–781, 2009

**Key words:** carbon nanotubes; Siesta program; nanotechnology; covalent functionalization of carbon nanotubes, computational nanotechnology

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## Introduction

One of the easiest ways to functionalize single-wall carbon nanotubes (SWCNTs) is with hydroxyl groups [1, 2]. Indeed, in 2002, Pan et al. [1] reported the successful synthesis of hydroxylated SWCNTs by a mechanochemical reaction. They mixed 10 mg of SWCNTs and 200 mg of KOH in a milling ball for 10 h, to obtain a reaction mixture that after dissolution and centrifugation gave a black solid soluble in water, the hydroxylated SWCNTs. The multiple hydroxyl groups present in the SWCNTs are responsible for the enhanced solubility in water, about 3 mg/L. According to the X-ray photoelectron spectroscopy (XPS) results there is one OH group present per 10 carbon atoms. Another interesting property of the hydroxylated SWCNTs is that they readily self-assemble into aligned arrays through strong surface hydrogen bond interactions.

Sulfur has several properties in common with oxygen because both belong to the same group of the periodic table. However, the functionalization of SWCNTs with sulfur-containing groups has presented some problems. In most cases the researchers confirmed that some kind of sulfur functionality is bonded to the SWCNTs or multi-wall carbon nanotubes (MWCNTs), although they were not able to identify their characteristics [3–7]. Among the first successful functionalization of nanotubes with sulfur-containing groups, we can cite the work of Liu et al. [3] published in 2000. Employing a wet chemical approach they were able to organize SWCNT on gold surfaces. To achieve this goal, the SWCNTs were first chemically cut into short pipes and thioderivatized at the open ends. The ordered assembly of SWCNTs was made by their spontaneous chemical adsorption onto gold, via the Au-S affinity. In 2002, Konya et al. [4] employed a ball mill and  $\text{SH}_2$  and  $\text{CH}_3\text{SH}$  gases to introduce the thiol and  $\text{SCH}_3$  groups, respectively, onto the MWCNTs walls. XPS spectra showed one component at 163.6 ( $\pm 0.2$ ) eV, indicative of the presence of thiols. In addition to this, Konya et al. [4] observed the samples with infrared spectroscopy; they confirmed the presence of the  $-\text{SH}$  and the  $-\text{SCH}_3$  groups in the MWCNTs treated with  $\text{SH}_2$  and  $\text{CH}_3\text{SH}$ , respectively. The efficiency of the process strongly depends on the ball mill, because the cleavage of the CC bond takes place in the presence of  $\text{SH}_2$  or  $\text{CH}_3\text{SH}$ , and thus new

bonds between these reactants and the broken CC bonds are formed. Two years later, Plank et al. [5] employed a different method to thiolate SWCNTs. They exposed a mixture of elemental sulfur and SWCNTs to argon/hydrogen gaseous plasma. Raman spectroscopy indicated that the SWCNTs structure was preserved after the treatment. The method had the advantage that excess of oxygen is not present. The thiolated SWCNTs were found to self-assemble onto gold electrodes. Unfortunately, Plank et al. [5] were not able to identify the form in which sulfur was present. Thiolation of the sidewalls of carbon nanotubes has also been achieved by Curran et al. [6, 7]. To perform the functionalization, they used acid treated MWCNTs and  $\text{P}_4\text{S}_{10}$  in refluxing toluene. Employing electron energy loss spectroscopy they have determined that the amount of sulfur bonded to the SWCNTs was 0.6%, in terms of the atomic content of the samples. They proposed that the OH and COOH groups present after the acid treatment were converted into thiol ( $-\text{SH}$ ), thioester ( $-\text{CSOR}$ ), and dithiocarboxylic ester ( $-\text{CSSR}$ ) groups. Finally, in 2007, Nakamura et al. [8] attached sulfur-containing groups to the sidewalls of the SWCNT employing a method that involved the photolysis of cyclic disulfides. The diameter of the SWCNTs employed was between 0.9 and 1.2 nm. The cyclic disulfide opens and one end is attached to the tube while the other sulfur atom forms the thiol group. Subsequent attachment of gold on the surface of the SWCNTs was possible through the thiolalkylthiol linkage.

The inclusion of sulfur functionalities is very important. For example, it is one of the keys to the formation of self assembled nanostructures [9]. Employing the strong affinity between gold and sulfur it has been possible to build self-assembled monolayers of thiolated molecules over gold surfaces [9–11]. In biological applications, several groups have been able to functionalize gold nanoparticles with sulfur-containing groups. This process inhibited their aggregation into larger nanoparticles and allowed the tuning of several properties of the nanoparticles [12]. In a recent work [13], employing first principle calculations, we have showed that the thioepoxidation of small diameter (0.7–1.1 nm) SWCNTs is possible from a thermodynamic stand point. Thus, we consider that a theoretical characterization of one of the simplest sulfur-containing groups, such as the thiol, is necessary to continue our investigations about the interaction between sulfur and carbon nanotubes. We expect that this

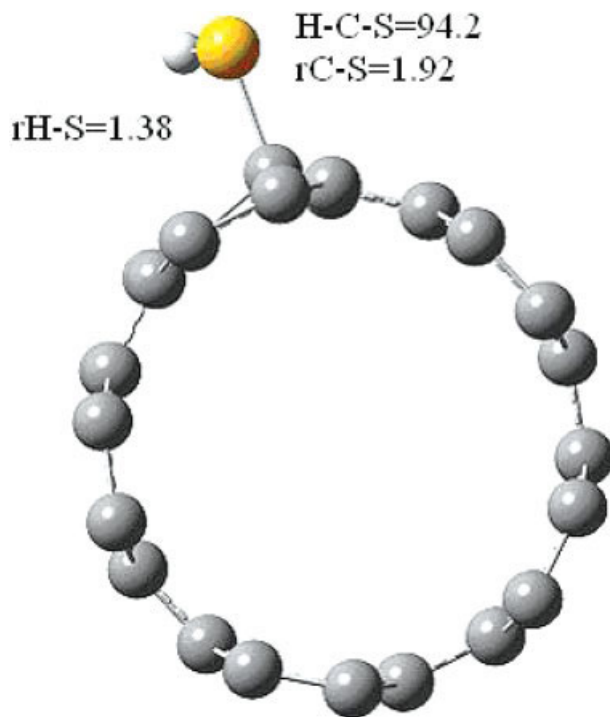
work can answer the following questions: how strong is the bond between the thiol group and the nanotube? Is the electronic structure of the nanotubes altered? And if it is, how? Can we expect some magnetic moment because of the attachment of the SH groups? Because the SH group has an unpaired electron, can we expect some differences in the reactivities of metallic and semiconducting SWCNTs? To answer these questions, we have performed density functional calculations with periodic boundary conditions (PBCs) for the armchair (5, 5) and (6, 6) SWCNTs and the zig-zag (9, 0) and (10, 0) SWCNTs. This work may help to understand the experiments performed to thiolate nanotubes and to guide the synthesis of stronger gold-nanoparticle-SWCNTs [14] hybrids, gold-nanoparticle-BNNTs [15] hybrids, and self-assembled nanostructures.

## Methods and Calibration

### METHODOLOGY

The methodology selected by us is the same as that we have calibrated to investigate the thioepoxidation of SWCNTs [13]. We have performed density functional calculations employing PBCs. The generalized gradient approximation (GGA) [16] (Perdew–Burke–Erzernhof (PBE) parameterization), was selected as implemented in the Siesta Program [17, 18] which performs SCF calculations using numerical basis sets. We have selected the double zeta basis set plus polarization functions (DZP). The GGA implementation in Siesta makes the results prone to big basis set superposition error (BSSE), and so we used the counterpoise correction suggested by Boys and Bernardi in 1970 [19]. In all cases, we used relaxed structures to estimate the BSSE corrected binding energies and we took into account monomer deformation energies. The interaction between ionic cores and valence electrons was described by the Troullier–Martins norm conserving pseudopotentials [20]. A cutoff of 200 Ry for the grid integration was selected to represent the charge density.

We have selected tubes that have similar diameter to the HiPco produced tubes ([21], i.e., 0.7–1.1 nm). For the zig-zag (9, 0) and (10, 0) SWCNTs, we have employed two unit cells, i.e., 72 and 80 atoms, respectively. In the case of the (5, 5) and (6, 6) SWCNTs, three unit cells were

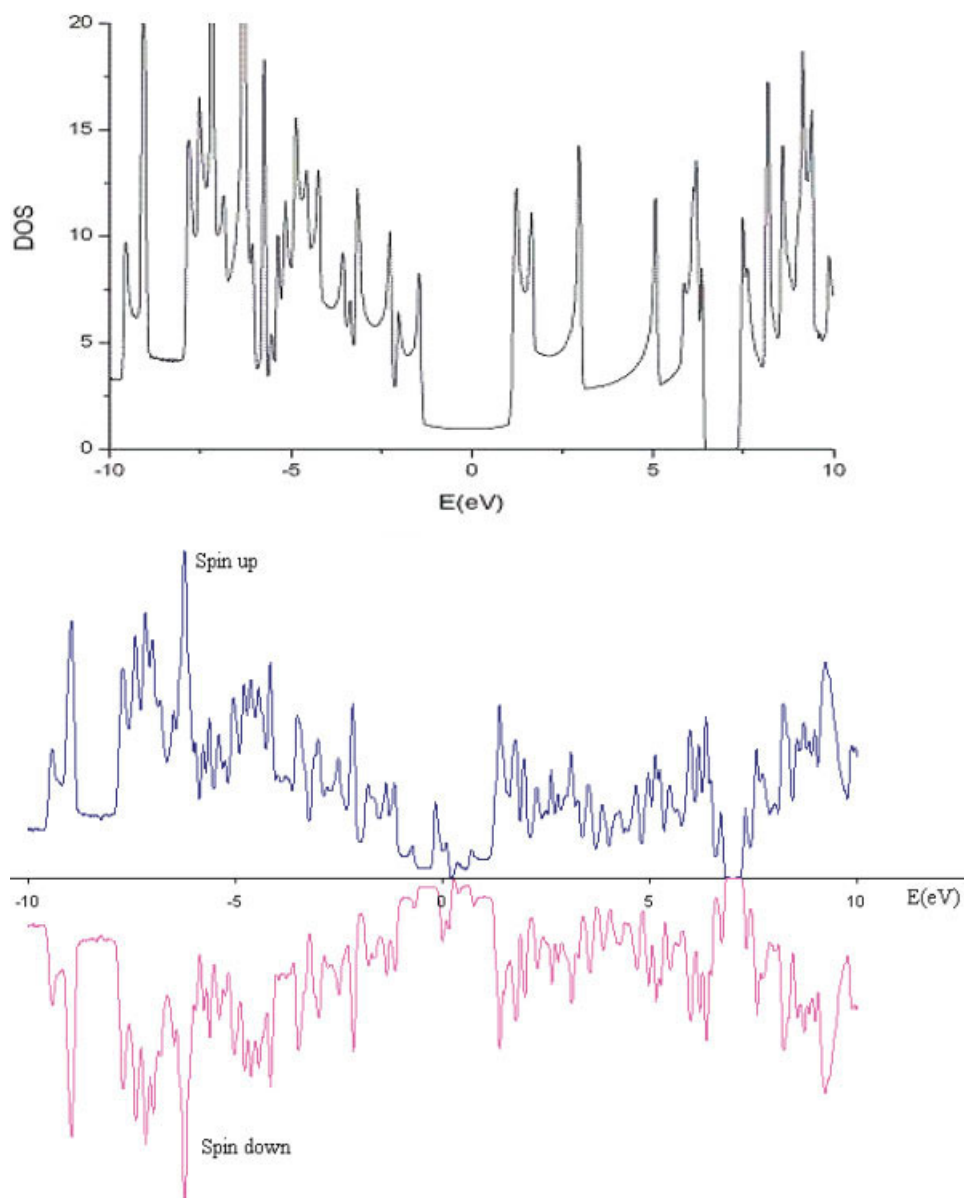


**FIGURE 1.** Optimized structure for the addition of the SH group to the (5, 5) SWCNT. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

employed, summing up a total of 60 and 72 atoms, respectively. The lattice parameter along the *z* direction was fixed to 7.38 and 8.52 Å for the armchair and zigzag SWCNTs, respectively, and 20 Å along the *x* and *y* directions; large enough to prevent lateral interaction between adjacent cells. To check the consistency of our values, we performed calculations for the (5, 5) SWCNT in which we doubled the size of the unit cell. The conclusions of the present work remained unchanged, thus two unit cell for the zigzag SWCNT and three for the armchair SWCNT is enough to study the thiolation of SWCNTs. Considering the symmetry of the SWCNT we used a Monkhorst-Pack sampling of  $1 \times 1 \times 75$ . The geometry optimizations were performed using the conjugate gradient algorithm until all residual forces were smaller than 0.01 eV/Å.

### BENCHMARK

Prior to the investigation of the SWCNT-OH and SWCNT-SH hybrids, we performed a calibration of the methodology selected. For the later



**FIGURE 2.** Density of states determined for the pristine (5, 5) SWCNT (top) and (5, 5) tube + SH (bottom). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

purpose, we carried out comparative calculations for the addition of the XH groups  $X = (\text{O}, \text{S})$  to ethene. At the PBE/6-31G\* level [16, 22], with the aid of NWCHEM [23], we have determined that the energy change for the reaction  $\text{C}_2\text{H}_4 + \text{XH} \rightarrow \text{C}_2\text{H}_4\text{XH}$  is 36.2 kcal/mol for OH and 14.4 kcal/mol for SH. This result can be compared with the obtained employing the Siesta code and the parameters given in this section. If we take into account the BSSE corrections and the monomer deformation energies, we get that the energy

changes are 32.3 and 12.1 kcal/mol for OH and SH, respectively. These results are extremely close to the obtained at the PBE/6-31G\* level. Considering the differences observed between the results obtained with PBC and those calculated at the PBE/6-31G\* level, we expect that the SWCNT-XH binding energies are underestimated by 2–3 kcal/mol. Thus, we have corroborated that the methodology selected allow us to reproduce the results obtained without the use of pseudo-potentials and with more accurate basis sets.



## Results and Discussion

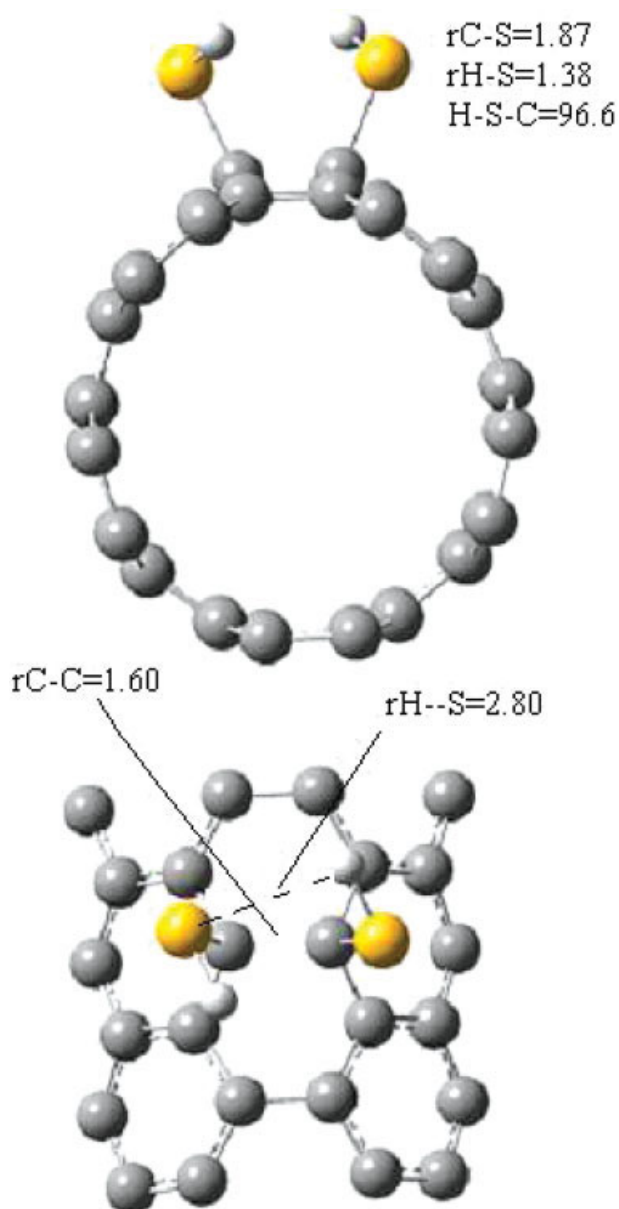
### HYDROXYLATION OF THE (5, 5) AND (10, 0) SWCNTs

The addition of a OH group to the (10, 0) SWCNT has been investigated previously by Pan et al. [2]. They have estimated that the SWCNT-OH binding energy is 18 kcal/mol at the PW91 level of theory. Our estimation is slightly larger, 24.9 kcal/mol, probably because we used the PBE density functional. It is important to remember that we underestimated the  $\text{C}_2\text{H}_4\text{—OH}$  binding energy (see the previous section) by 4 kcal/mol, and so we expect that the  $\text{C}_2\text{H}_4\text{—OH}$  binding energy is close to 30 kcal/mol. The addition of a OH group to the (10, 0) SWCNT induces a magnetic moment of 0.81 D, because one electron is taken from the  $\pi$  network of the SWCNT to create the new C—OH bond. Thus, a large magnetic moment may be expected from the nanotubes if multiple OH groups are attached. As observed by Pan et al. [2], the electronic structure of the (10, 0) SWCNT is modified by the inclusion of the OH groups. The pristine (10, 0) SWCNT has a band gap of 0.45 eV; in agreement with the results of reference [2] we observe a diminution of the band gap when the OH group is attached, 0.23 eV ( $\beta$  electrons,  $\alpha$  is 0.32 eV).

To investigate if there is some difference in the reactivity of metallic and semiconducting SWCNTs against OH, we studied the hydroxylation of the (5, 5) SWCNT. We have found that the binding energy is increased. At the PBE/DZP level it is 30.3 kcal/mol, 5.4 kcal/mol larger than that determined for the semiconducting (10, 0) SWCNT. The later fact is evidenced by a longer C—O bond distance in the hybrid formed by the (10, 0) SWCNT and OH. The C—O bond distances are 1.456 and 1.448 Å for the (10, 0) and (5, 5) SWCNTs, respectively. It is important to note that the lower reactivity observed for the (10, 0) SWCNT is also due to the fact that the semiconducting tube has larger diameter, 6.9 vs. 7.8 Å, (5, 5) and (10, 0) SWCNTs, respectively. The DOS of the (5, 5) SWCNT is modified at the Fermi level upon OH addition, but the tubes remains metallic. Perhaps multiple OH additions can transform the tube into semiconducting because of hole doping induced by the OH groups.

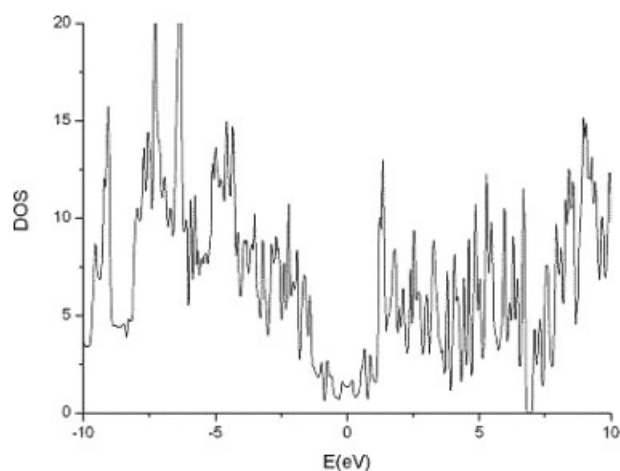
### THIOLATION OF THE (5, 5) SWCNT

The thiolation of the (5, 5) SWCNT is energetically favorable. The estimated exothermicity for the



**FIGURE 3.** Optimized structure for the addition of two SH groups to a bond perpendicular to the axis of the (5, 5) SWCNT, front (top) and top views (bottom). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

reaction  $\text{SWCNT} + \text{SH} \rightarrow \text{SWCNT-SH}$  is 7.8 kcal/mol, about 7 kcal/mol smaller than that observed for the addition of SH to ethene. The optimized structure is presented in Figure 1. The C—S bond length is 1.92 Å, reasonable considering the small binding energy between the SH group and the nanotube. The structure of the nanotube is changed



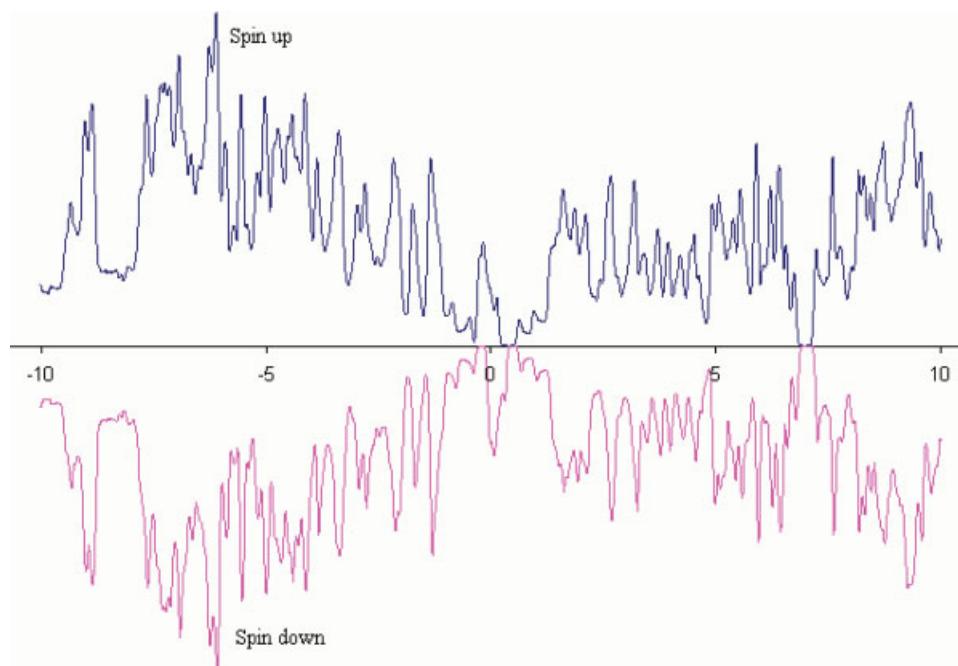
**FIGURE 4.** Density of states determined for the (5, 5) SWCNT functionalized with two SH groups (the SH are attached to a CC bond perpendicular to the tube axis).

upon addition of the SH group, the CC bond lengths between the carbon atom that bears the SH group and the neighboring carbons are close to 1.50 Å, about 0.07–0.08 Å longer than the observed in the pristine tube. The tube deformation energy is 17.9 kcal/mol. The DOS of the pristine and the thiolated (5, 5) SWCNT are presented in Figure 2. The electronic structure of the (5, 5) SWCNT is strongly modified upon addition of a SH group. The later fact was not expected considering the small SWCNT-SH binding energy and the results obtained for the hydroxylation of the (5, 5) SWCNT. However, it seems that the SH radical is in need for electrons and modifies the DOS at the Fermi level, about 0.3 eV above the Fermi level the DOS is nearly zero, in a very small interval. This result may indicate that we can expect the appearance of a band gap when more SH groups are attached to the SWCNTs. However, at least for certain configurations, this is not the case. We have considered the addition of two SH groups to two carbon atoms of the same CC bond. The optimized structure is presented in Figure 3. The structure of the tube is seriously modified. The CC bond is broken, the CC bond distance is 1.64 Å, and the SH groups adopt a configuration that allows some degree of hydrogen bonding. Indeed, the sulfur hydrogen distance is 2.8 Å, indicative of some kind of hydrogen bonding interaction. It is reasonable to expect a longer distance for the sulfur–hydrogen interaction because the hydrogen bonding properties of sulfur are not as good as those of oxygen. The carbon sulfur distances are shorter than that observed for the single

SH addition, 1.87 Å, and thus, the binding energy per SH group is larger, 11.6 kcal/mol. This fact is due to the attachment of both SH groups to the same CC bond. The tube deformation energy is 40 kcal/mol; it is important to remember that the tube deformation energy for the single SH addition to the (5, 5) SWCNT was 17.9 kcal/mol. Thus, for the double SH addition, the deformation is slightly larger, as expected because of the rupture of the CC bond length. In Figure 4, we present the DOS obtained for the dithiolated SWCNT. The DOS is different from that of the pristine (5, 5) SWCNT, although the tube remains metallic. Another difference with the single addition is that the dithiolated tube has no magnetic moment. This can be explained by the proximity of the carbon atoms that



**FIGURE 5.** Optimized structure for the addition of two SH groups in diametrically opposite sides of the (5, 5) SWCNT. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**FIGURE 6.** Density of states determined for the (5, 5) SWCNT functionalized with two SH groups (the SH are attached in diametrically opposite sides of the (5, 5) SWCNT). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

bears the SH groups: two  $\pi$  electrons are taken from the  $\pi$  network, without affecting the rest of the atoms. To confirm whether or not these results are true for other conformations, we have performed calculations for a dithiolated SWCNT with the SH groups added to carbon atoms that are in diametrically opposite sites of the SWCNT; the structure is presented in Figure 5. We can appreciate a strong deformation of the cross section of the SWCNT. The binding energy per SH group is 7.6 kcal/mol, 4 kcal/mol smaller than that observed for the previous dithiolation (that with two SH groups in the same CC bond), and similar to that determined for the single thiolation. The DOS determined for the tube dithiolated in opposite sides is presented in Figure 6; the tube is metallic but the DOS is zero 0.3 eV above the Fermi level, and the width of the interval is 0.20 eV. Therefore, the metallic properties are diminished when two SH groups are attached in diametrically opposite sites.

#### THIOLATION OF THE (10, 0) SWCNT

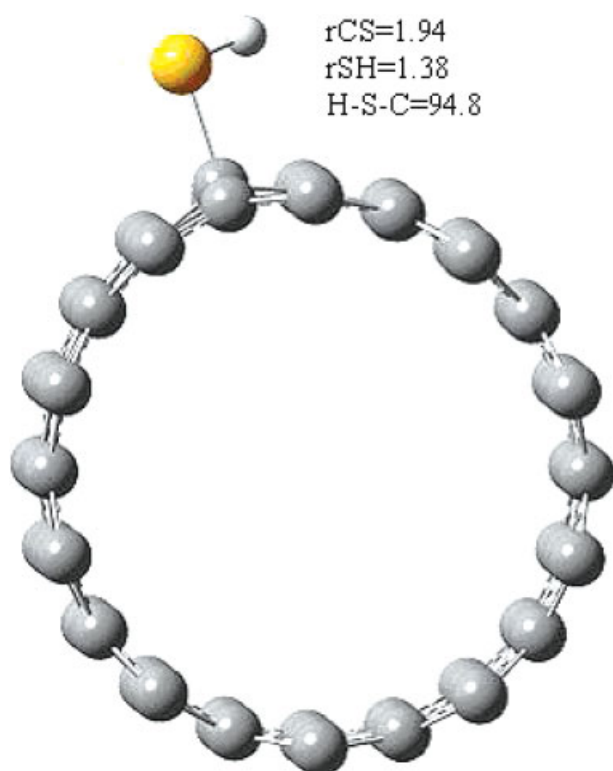
We have investigated the thiolation of the (10, 0) SWCNT; the optimized structure is presented in Figure 7 and the DOS in Figure 8. The C—S bond length is 1.94 Å, an indication of the weak interac-

tion between the nanotube and the SH group. Indeed, the SWCNT-SH binding energy is very small, 2.2 kcal/mol. This fact is very important because it shows that the metallic SWCNTs may have a stronger interaction with the SH group. The small binding energy can be explained by the semiconducting characteristics of the (10, 0) SWCNT and its smaller degree of curvature (the larger the diameter is, the smaller the reactivity is, because of the reduced  $sp^3$  characteristics). The deformation energy of the (10, 0) SWCNT upon addition SH is 21.0 kcal/mol per unit cell. In the case of the hydroxyl group, we have observed the same behavior. The binding energy determined for the semiconducting tube was 5 kcal/mol smaller, although the C—OH bond was stronger. As observed for the hydroxylated (10, 0) SWCNT, the SWCNT-SH hybrid has a magnetic moment of 1 D.

#### THIOLATION OF THE (9, 0) AND (6, 6) SWCNTs

We have performed two final tests to confirm that the metallic SWCNTs are more reactive against SH than the semiconducting ones. The first test was performed for the (9, 0) SWCNTs. Our calculations indicate that the tube is semimetallic and has a





**FIGURE 7.** Optimized structure for the addition of the thiol group to the (10, 0) SWCNT. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

pseudo gap of about 0.05 eV. This result is in good agreement with the results obtained by Ouyang et al. [24], who determined a band gap of 0.08 eV for the (9, 0) SWCNT. Therefore, as the (9, 0) SWCNT is semi-metallic (or narrow gap semiconductor as stated by Ouyang et al. [24]), and considering that its diameter is only 0.2 Å larger than that of the (5, 5), we can expect a reactivity just a bit lower than that observed for the (5, 5) SWCNT. Indeed, our DFT calculations predicted that the C—SH binding energy for the (9, 0) SWCNT is 5.6 kcal/mol, only 1.6 kcal/mol lower than that determined for the single thiolation of the (5, 5) SWCNT, and 3.4 kcal/mol larger than that determined for the (10, 0) SWCNT.

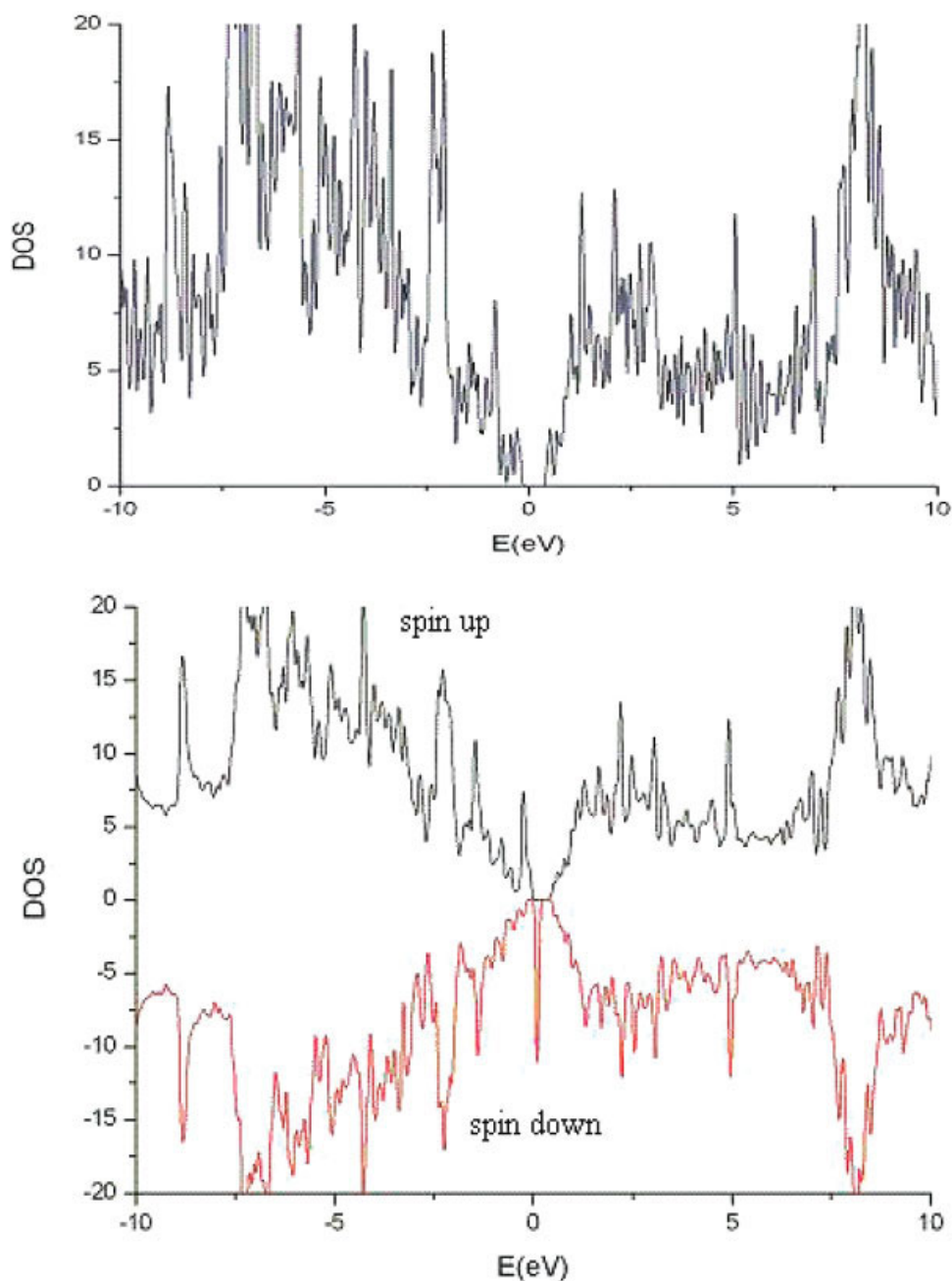
The final calculations were performed for metallic SWCNT that has a larger diameter than that of the (10, 0) tube. The tube selected was the (6, 6) one which has a diameter of 8.29 Å, 0.39 Å larger than the observed for the (10, 0) SWCNT. The binding energy determined for the SH group and the (6, 6) tube is 3.8 kcal/mol, 1.6 kcal/mol larger than that observed for the semiconducting (10, 0) SWCNT.

Thus, in spite of having a larger diameter, the (6, 6) SWCNT is more reactive than the (10, 0) one, confirming our hypothesis of the selective reactivity of the metallic SWCNTs.

The different reactivity observed for the small diameter metallic and semiconducting SWCNTs suggests that it may be possible to use the thiolation of the SWCNT to distinguish by their diameter or by its electronic properties. A procedure to can be designed to attach SH groups selectively to small diameter SWCNTs or metallic SWCNTs and then use the strong affinity between gold and sulfur to separate the metallic tubes. However, one issue may be problematic, i.e., the presence of defects. Our preliminary calculations indicate that vacancy defect sites and Stones–Wales defects are much more reactive against SH. Thus, to separate SWCNTs employing SH functionalization, the number of defects must be very small. Perhaps, annealing at high temperatures could reduce the number of defects, improving crystallinity as observed for DWCNTs by Jung et al. [25].

## Conclusions

The results obtained for small diameter SWCNTs indicated that the addition of XH groups ( $X = O, S$ ) to semiconducting and metallic SWCNTs presents a different behavior and it depends on the gap. The binding energy between the SH group and the semiconducting (10, 0) SWCNT is very weak, 2–4 kcal/mol; but for the metallic (5, 5) SWCNT the binding energy is larger, 7–9 kcal/mol. However, in both cases it is relatively small. The electronic structure of the SWCNT is strongly modified upon XH ( $X = O, H$ ) addition. For a single OH or SH addition to the metallic SWCNTs we have observed important changes in the DOS. However, when multiple SH groups are attached the electronic and magnetic properties depend on the position of the SH groups. If two SH groups are attached to the same CC bond, the tube remains metallic, the system has zero magnetic moment, and the binding energies per SH group are increased by 4 kcal/mol. This result is in good agreement with the bright field TEM images reported by Cech et al. [7]. Indeed, the elemental maps showed that the S atoms prefer to be added in specific zones forming lines or “sulfur islands.” If the SH groups are added in diametrically opposite sites the metallic characteristics of the (5, 5) SWCNT are diminished. Thus, it will be extremely difficult to control the metallic and magnetic properties of



**FIGURE 8.** Density of states determined for the pristine (10, 0) SWCNT (top) and (10, 0) SWCNT + SH (bottom). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

thiolated carbon nanotubes if it is not possible to control the position of the SH groups attached.

The present results are difficult to understand in terms of some of the experimental observations. First, we need to consider that for all the SWCNTs investigated in this work, binding energy between the SWCNT and SH is small, in particular for semiconducting SWCNTs. In addition to this, we can expect a

further diminution of the reactivity when the diameter of the SWCNTs is increased because of the reduced  $sp^3$  character of the C atoms. Therefore, most of the SWCNTs used in the experiments will not form a strong bond with the SH group. These results led us to conclude that the SH and  $SCH_3$  groups attached to the SWCNTs walls are due to the defects created by the aggressive ball milling and purification processes,

and, to a minor extent, due to the presence of metallic tubes. Indeed, most of the functionalized MWCNT are very short [3, 4], an indication of the severe conditions employed to achieve the functionalization (100 h in a ball mill [4]), and the extreme acid treatments used to purify the tubes [3–8]. Another point that warrants discussion is the issue of the cyclic disulfides attached to the SWCNT by Nakamura et al. [8]. The SH group is very similar to the SCH<sub>3</sub>, because the CH<sub>3</sub> can be considered to be electronically similar to the hydrogen. Thus, we can expect similar binding energies for both groups to the SWCNT. If we consider the simplest disulfide, SCH<sub>3</sub>SH, can we expect strong bond energy between this group and the SWCNTs? It is very difficult that the CH<sub>3</sub>SH group can induce strong bond energy between the nanotube and the SCH<sub>3</sub>SH group. Thus, as indicated earlier, the reactivity of the SWCNTs is due to the introduction of defects in the purification treatments—defect sites are in general more reactive [26–29], and, to a minor extent, due to the presence of metallic SWCNTs. Mawhinney et al. [26] found that after acidic oxidation (HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> method) 5% of the carbon atoms present in close ended SWCNT are located on defect sites [26]. As the nanotubes used by Nakamura et al. [8] were purified, we can expect the presence of defects and explain the observed reactivity. Further experimental and theoretical works are necessary to understand the functionalization of SWCNTs and MWCNTs with sulfur-containing groups. In particular, further calculations with larger diameter SWCNTs and defective SWCNTs are under progress in our laboratory. Our preliminary calculations suggests that graphene (4 × 4 × 1 supercell) does not react with the SH group. Thus we can expect that large diameter SWCNTs will not react with SH too.

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