Labeling the defects of carbon nanotubes with thiol groups

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Abstract Herein, we investigate the reactivity of perfect and defective single-wall carbon nanotubes (SWCNTs) with the SH group using first principle periodic calculations. The presence of Stone–Wales (SW) defect sites significantly increases the reactivity of SWCNTs against the thiol group. The most reactive site for the addition of the SH radical is the single vacancy defect; the sulfur atom reconstructs the SWCNT framework and the hydrogen atom becomes attached to a carbon atom. The cluster model calculations performed for perfect SWCNTs confirmed a very low reactivity with the thiol group, even for the small diameter and metallic SWCNTs. The reaction between the perfect SWCNT and SH results thermodynamically unfavorable. The different reactivities observed for perfect and defective SWCNTs suggest that the SH group can be employed to perform a chemical labeling of the defect sites present in carbon nanotubes. The SH radical group is quite unique because, even though it has an unpaired electron, it does not react with sp^2 carbon frameworks, unless they have defects or curvature similar to C60. The results are discussed in terms of the recent experimental investigations about thiolated SWCNTs. We were able to explain the Transmission Electron Microscopy images of thiolated nanotubes and the lack of reactivity at the tips. Finally, we discuss a possible route to synthesize sulfur-doped SWCNTs using thiol groups and their electronic properties.

Introduction

The discovery of SWCNTs by Ijima [1] has elicited tremendous attention from all areas of science due to their unique properties. However, there are significant problems that render the massive use of carbon nanotubes quite difficult. The major drawback is that the properties of the tubes are not similar. For example, some tubes present metallic character whereas others are semiconductors, depending on the chiral index [2]. In addition to this, the use of carbon nanotubes in devices is complicated by the presence of defects [3] and contaminants such as amorphous carbon, catalyst nanoparticles, etc. [4]. Most of these defects are created during the harsh purification treatments [4]. The presence of defects can be quantified employing Raman spectroscopy. The ratio between the intensities of the D and G bands is widely used to determine the disorder present in SWCNT [5]. In a recent study, Li et al. [6] showed that the defects of the SWCNTs can be labeled employing TiO_2 nanoparticles, they were chemically adsorbed at SWCNT defect sites via an ester-type linkage between the carboxylic acid groups and the surface of the nanoparticles. Wang et al. [7] were able to deposit metal oxides only at the defect sites of graphene, but not on a perfect sp^2 sheet. The chemical labeling of the defect sites permits direct determination of their density, distribution, and location. In addition to this, the groups attached to the defect sites open new possibilities for the selective attachment of chemical groups at vacancy defect sites. Therefore, to perform a chemical labeling it is necessary to find groups which are unreactive against perfect tubes, but

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react with defect sites like the vacancies and Stone–Wales defect sites, which are among the most frequently observed defects. In a recent study [8], we showed that perfect SWCNTs have a very low reactivity with the SH group. In effect, the (10,0) tube is almost unreactive against thiolation (binding energy, E_{bind}C–SH = 0.10 eV), whereas metallic tubes like the (5,5) one are slightly more reactive (E_{bind}C–SH = 0.34 eV).

In this study, we continue our investigations about the reactivity of SWCNTs with sulfur-containing groups [8–11] focusing our attention in the reaction between the SH group and defective SWCNTs. The results obtained showed that the defect sites can be chemically labeled employing SH radicals and also we suggest a possible route to synthesize sulfur-doped SWCNTs. The inclusion of sulfur functionalities in nanostructures is very important because they are one of the keys to the formation of self-assembled nanostructures [11–13], to the stabilization of biological molecules onto SWCNTs [14] and to connect carbon nanotubes functionalized with thiocarboxylic and dithiocarboxylic esters.

Methods

The methodology applied herein is the same as the one we applied to successfully study sulfur-doped graphene [11], thiolated [10] and hydrogenated [15] graphene, magnetic graphite [16], thioepoxidated [9] and thiolated [8] SWCNTs, hydrogenated DWCNTs [17], and the adsorption of CH_4 on SWCNTs [18]. Briefly, we performed Density Functional (DFT) calculations employing the PBE functional [19], as implemented in SIESTA [20, 21], which carries out SCF calculations using numerical basis sets. For the latter, we have selected the double-zeta basis set with polarization functions and fixed the orbital confining cutoff to 0.01 Ry. The split norm used was 0.15. The DFT implementation in SIESTA can be prone to significant basis set superposition error (BSSE), even with relatively low degree of radial confinement [10]. To avoid this problem, we used the counterpoise correction suggested by Boys and Bernardi [22]. In all cases, we used relaxed structures to estimate the BSSE corrected binding energies and we took monomer deformation energies into account. The interaction between ionic cores and valence electrons was described by the Troullier–Martins norm conserving pseudopotentials [23]. We have checked the convergence of the Mesh cutoff; using a value of 200 Ry we obtained converged binding energies (within 0.02 eV). It is important to note that in our previous studies [8–11, 15–18] we performed methodology calibration against mesh cutoff and orbital confining cutoff values. By doing so, we were able to reproduce the results obtained without the use of

pseudopotentials. Cells were sampled employing a Monkhorst–Packard k-point sampling scheme of $1 \times 1 \times 75$ k points for geometry optimizations and $1 \times 1 \times 300$ k points to calculate the electronic properties. Geometry optimizations were pursued using the conjugate gradient algorithm until all residual forces were smaller than 0.01 eV/Å.

We performed periodic calculations for two models of defective SWCNTs. The defects considered were the single vacancy and the Stone–Wales (SW) [24]. In the case of the single vacancy, we employed 4 unit cells of a (5,5) SWCNT. The total number of atoms in the unit cell was 79. For the SW defect, we used 3 unit cells of a (10,0) SWCNT which amounts to 120 atoms. The lattice parameter along the c direction was fixed to 9.954 and 12.78 Å for the defective (5,5) and (10,0) SWCNTs, respectively. In both the cases the a and b directions were fixed to 20 Å, large enough to prevent lateral interaction between adjacent cells. It is important to note that the use of these cell parameters did not introduce significant stress. For the sake of completeness, for the tube with a single vacancy we optimized the lattice parameter in the c direction. The result was 9.933 Å, only 0.2% shorter than the value used by us. Thus, we can safely use the aforementioned lattice parameters. Finally, to confirm our previous results about the very low reactivity of perfect SWCNTs against the SH group we conducted cluster model calculations. The methodology employed was B3LYP [25, 26] along with the 6-31G* basis set [27]. The model was constructed employed 3 unit cells of a (5,5) SWCNT terminated with H atoms ($C_{60}H_{20}$), similar to the one described by Galano [28] to study the reactions of SWCNTs with several radicals. The B3LYP calculations were carried out employing Gaussian 2003 [29]. In all cases, the structures were confirmed to be a minimum in the potential energy surface performing vibrational frequency analysis. Gibbs free energies were estimated at 298 K and 1 atm.

Results and discussion

Thiolation of Stone–Wales defective SWCNTs

In our previous study about thiolated perfect SWCNTs [8], we showed that the (5,5) tube was more reactive against the thiol group than the (10,0) one. Since two-thirds of the as-produced tubes are semiconductors and also due to the lower reactivity of the (10,0) tube, we introduced the SW defect in a semiconducting tube. Two configurations are possible for this defect, depending on the orientation of CC bond rotated. We have chosen an orientation parallel to the tube axis because the defect produced is more stable than the one obtained by the rotation of a CC bond diagonal to
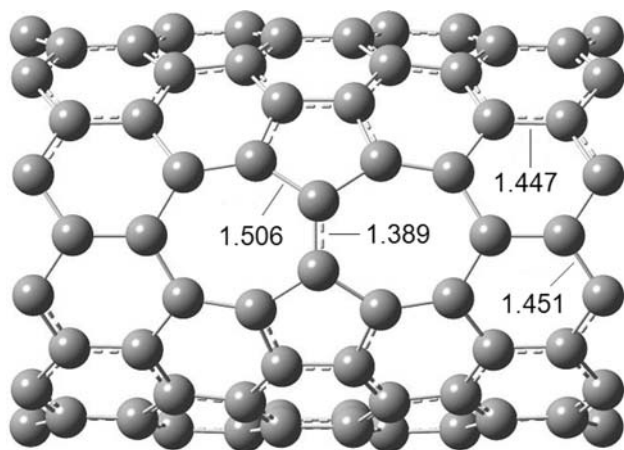
Fig. 1 Optimized unit cell obtained for the Stone–Wales defective (10,0) SWCNT (120 atoms). Only half section of the tube is showed for clarity (distances in Å)

Fig. 2 Optimized unit cell determined for the Stone–Wales defective (10,0) SWCNT functionalized with a SH group at the CC bond which connects both pentagons (distances in Å, angles in °)

the tube axis [30]. The optimized structure of the SW-defective (10,0) SWCNTs is presented in Fig. 1. The CC bond distance which connects both pentagons is 1.389 Å. This value is 0.019 Å longer than the one reported by Zurek et al. [30] for a (10,0) SWCNT, employing the PBE functional and plane waves. The energetic cost to create the 5/7/7/5 defect is 2.54 eV. This value is smaller than the one computed in [30] namely, 3.43 eV. We attribute these differences to the fact that Zurek et al. [30] employed 2 units cells of a (10,0) SWCNT and we used 3. Indeed, when they expanded the unit cell of the (9,0) SWCNT from two to three, the energy necessary to create such a defect was reduced by 0.39 eV.

In general, we would expect that the SW defect increases the reactivity of the SWCNTs because the CC bond which connects both pentagons has an increased electron density, as evidenced by a short CC bond length. In effect, it is 0.04 Å shorter than the CC bond length parallel to axis of the perfect (10,0) tube. However, it is important to note that Lu et al. [31] showed that for the addition of an oxygen atom to a (5,5) SWCNT this statement does not hold. The perfect tube is more reactive than the one containing a SW defect. In the case of the thiol group we have found that the SW defect significantly increases the reactivity. At the PBE level, the BSSE corrected C–SH binding energy is 0.98 eV. This value is significantly larger than the one reported by us for the perfect (10,0) tube: 0.1 eV [8] and also nearly twice the one computed by us for a SW-defective graphene sheet: 0.46 eV [10], showing a marked decrease of reactivity when the tube radius is increased. It is worth noticing that we expect a further increase of the C–SH binding energy if the SH radicals are paired on the same CC bond. Indeed, for a perfect (5,5) SWCNT, we observed that the C–SH binding energy per SH group changed from 0.34 to 0.50 eV
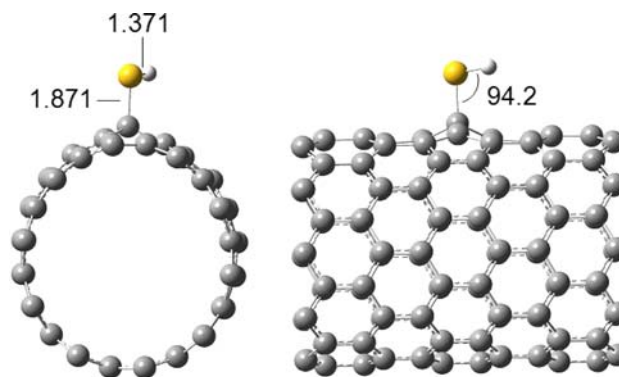
if two SH groups were attached to a CC bond perpendicular to the tube axis. Finally, the structure of the thiolated SW-defective (10,0) SWCNT is presented in Fig. 2. Its structure does not suffer important changes after the thiolation. The major modification is the lifting of the carbon bounded to the SH group. The C–S distance is 1.871 Å, typical for a weak C–S single bond. The band structures of the SW-defective (10,0) tube is presented in Fig. 3. The band gap of the unfunctionalized tube is 0.46 eV, just 0.16 eV smaller than the one computed for a perfect (10,0) SWCNT. Thus, the presence of a SW defect does not introduce significant changes in the electronic structure of the (10,0) tube. However, thiolation at the SW site induces a semiconductor-to-metal transition; although, it is worth noticing that this thiolated tube is not a good metal as evidenced by the band structure presented in Fig. 3.

Thiolation of single vacancy defective SWCNTs

To construct a SWCNT with a single vacancy defect site we employed 4 unit cells of a (5,5) SWCNT. As explained by Ma et al. [32] there are two possibilities when a carbon atom is removed from the SWCNT framework. The vacancy can be reconstructed and thus a pentagon and a nine-membered ring are formed or it is possible to obtain a metastable state in which the pentagon is not reconstructed. In the case of a reconstructed vacancy there are two other possibilities, the CC bond formed to close the pentagon can be parallel or perpendicular to the tube axis. In this study, we studied the reactivity of the most stable one, which is the reconstructed vacancy with the pentagonal CC bond perpendicular to the tube axis [32]. The energy required to create this vacancy is 5.16 eV, just 0.44 eV lower than the value suggested by Ma et al. [32] employing plane waves, the PBE functional and 5–8 unit cells of a (5,5) SWCNT. In agreement with the results obtained by the latter authors [32] we find that the defective tube is metallic and has a
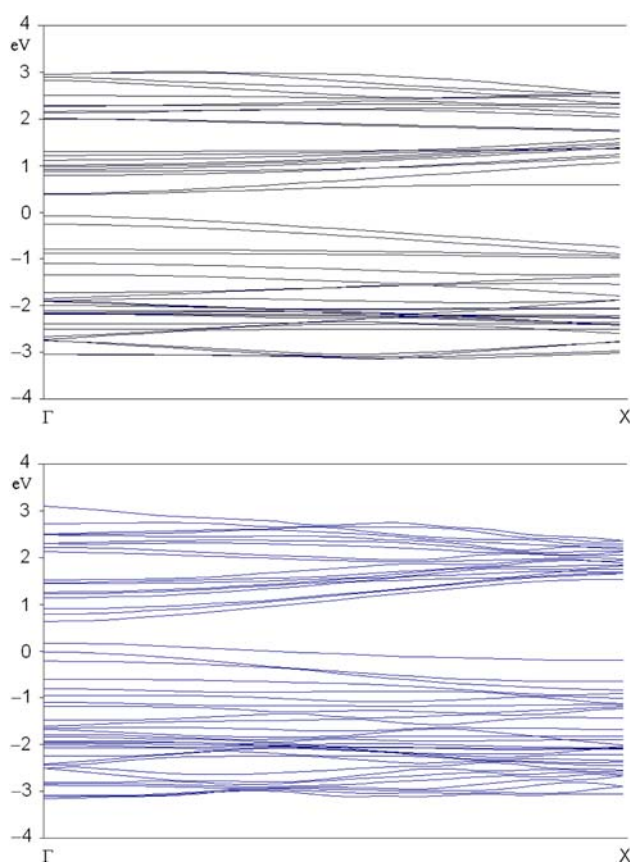
Fig. 3 Band structures determined for the (10,0) SWCNT containing a Stone–Wales defect (*top*) and the same tube functionalized with a SH group (*bottom*). For the thiolated tube we show only the spin-up bands, the spin-down are very similar

magnetic moment of 0.6 μ_B. This vacancy is extremely reactive and allows an easy attachment of a SH group, as shown in Fig. 4. The C–SH binding energy is quite large, 2.73 eV. However, this is not the most stable configuration. We have considered three other possibilities, namely

(a) the dissociative addition of the SH group, i.e., the H and S atom are separately attached to the vacancy,

(b) a structure in which the sulfur atom reconstructs the SWCNT framework and the H atom remains attached to sulfur,

(c) the sulfur atom reconstructs the SWCNT framework and the H atom is attached on a carbon atom that is bonded to sulfur.

These structures are presented in Fig. 4. The most stable one is (c) which is 1.53 eV more stable than the one with a SH group attached. Also, it is 0.72 and 2.49 eV more stable than configurations (a) and (b), respectively. These results differ from that obtained for thiolated graphene because the sheet favors the dissociative attachment of the SH group [10]. However, for a SWCNT, the reconstruction of framework by the incorporation of a sulfur atom is

preferred, this process being not observed for defective graphene. We attribute this difference to the fact that the energetic cost to create the sulfur substitutional defect for the tube is 1 eV lower than the one computed for graphene, due to the larger curvature of the SWCNT [11].

The present results suggest that the synthesis of sulfur-doped SWCNT may be possible using SH radicals. However, it is necessary to have pure carbon vacancies, something possible considering that, first Meyer et al. [33] observed the vacancy and SW defects with atomic resolution and second, Dato et al. [34] produced defective graphene sheets with no detectable oxygen or hydrogen. The synthesis of sulfur-doped SWCNT using SH radicals can occur via two paths:
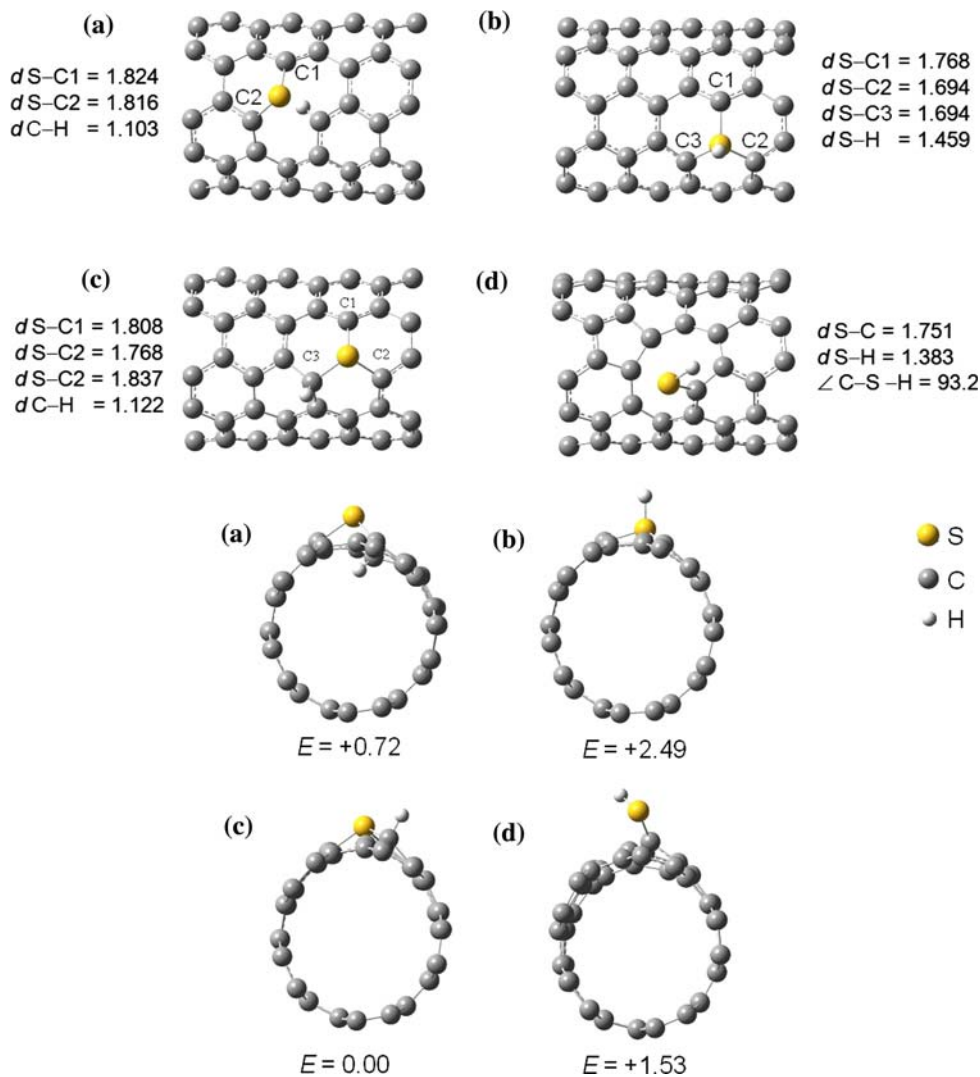
Path (1) first, a SH group becomes attached to the vacancy. Then, the sulfur atom reconstructs the framework of the tube maintaining the bonding with hydrogen. This process is not favorable because this structure is 0.96 eV less stable than the one with a SH group attached to be vacancy. However, since the H atom attached to sulfur is not an energetically favorable configuration (configuration b), it diffuses to the tube giving configuration (c), which is the most stable one, something very likely to occur considering that the S–H distance is very elongated, namely 1.459 Å. The diffusion of hydrogen is similar to the spillover of hydrogen observed for carbon surfaces decorated with metals [35]. Finally, by thermal annealing between 200 and 300 °C it is possible to remove the H atoms attached to the tube, as demonstrated by Nikitin et al. [36],

Path (2) the SH group is dissociatively attached to the vacancy to give configuration (a). Then the sulfur and the carbon atom which has the H atom attached form a covalent bond, giving configuration (c) which is the most stable one.

The sulfur-doped SWCNTs were discussed in our previous study [11] where we used 3.3% at. doping. In this study case we introduced 1 sulfur atom per 79 carbons, which corresponds to 1.3% at. The band structures of the pristine and the sulfur-doped (5,5) tubes are presented in Fig. 5. The doping with sulfur induces a metal-to-semiconductor transition; a band gap of 0.20 eV is opened. Thus, the sulfur doping is an attractive alternative to induce an inhibition the metallic character of SWCNTs.

Free energy changes

The free energy change under standard conditions is the thermodynamic magnitude which rules the spontaneity of a process. When periodic calculations are performed it is

Fig. 4 Optimized unit cells for the addition of a SH groups to (5,5) SWCNT containing a single vacancy defect site, *top* and *side* views. **a** Dissociative addition of SH, **b** the sulfur atom reconstructs the SWCNT framework and the H atoms remains attached to sulfur, **c** the sulfur atom reconstructs the SWCNT framework and the H atoms is attached on a carbon atom that is bonded to sulfur, **d** the SH group is attached to the vacancy defect site (distances (*d*) in Å, angles (∠) in ° and relative energies (*E*) in eV

(a)
$d\,S–C1 = 1.824$
$d\,S–C2 = 1.816$
$d\,C–H\ \ = 1.103$

(b)
$d\,S–C1 = 1.768$
$d\,S–C2 = 1.694$
$d\,S–C3 = 1.694$
$d\,S–H = 1.459$

(c)
$d\,S–C1 = 1.808$
$d\,S–C2 = 1.768$
$d\,S–C2 = 1.837$
$d\,C–H\ \ = 1.122$

(d)
$d\,S–C = 1.751$
$d\,S–H = 1.383$
$∠\,C–S–H = 93.2$

(a) $E = +0.72$ (b) $E = +2.49$

(c) $E = 0.00$ (d) $E = +1.53$

S
C
H

often neglected because the evaluation of the zero-point energies and thermal corrections is a challenging task. A recent study by Galano [28] showed the importance of evaluating the free energy change when studying the addition of radicals to SWCNTs, due to the significant entropy loss of these reactions. In our previous studies about thiolated [10] and hydrogenated [15] graphene, and also during the investigation of the addition of azomethine ylides to C_{60}, SWCNTs and graphene [37] we have considered the free energy corrections and found that they are very important. They were evaluated employing cluster models. We concluded that the conversion from equilibrium energies to free energies is largely independent of the size of the carbon structure considered. In effect, when using the same functional group, they are nearly identical for ethene, pyrene, and a larger hydrocarbon model, $C_{48}H_{18}$. Thus, we used these corrections in conjunction with the reaction energies computed by employing periodic boundary conditions. In this case, the model employed is

composed by 3 unit cells of a (5,5) SWCNT terminated with H atoms. At the B3LPY/6-31G* level of theory, the equilibrium energy change for the addition of a SH group is 0 eV. This value confirms our previous finding [8] which suggested a very low reactivity of the perfect tube against the SH group. The small differences between the binding energy predicted by the periodic and cluster model calculations (0.3 eV) is due to the use of a finite model which cannot account for the metallic character of the (5,5) tube. The free energy change computed for our model at 298 K and 1 atm is 0.45 eV. Thus, we can estimate a correction of 0.45 eV to convert from total energies changes to free energies changes. Employing this value, we obtain a thermodynamically favorable addition of a SH radical to a SW-defective SWCNT with $-\Delta G° = 0.53$ eV. For a single vacancy defective SWCNT, a thermodynamically favorable addition of a SH radical is also observed with $-\Delta G° = 2.28$ eV. Therefore, the addition of thiol groups to Stone–Wales and vacancy defect sites is favorable from
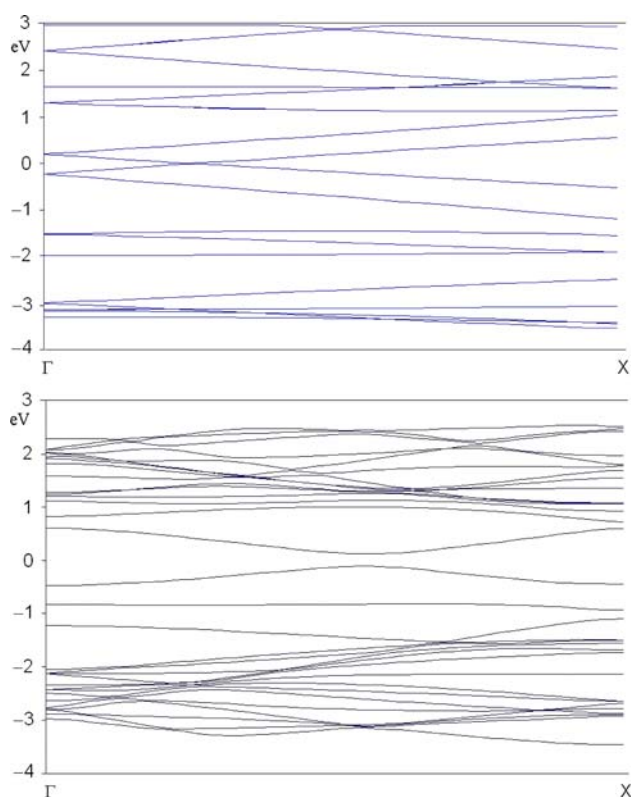
Fig. 5 Band structures determined for pristine (*top*) and sulfur-doped (*bottom*) (5,5) SWCNT. We introduced 1 sulfur atom per 4 unit cells

a thermodynamic stand point. However, the reaction with perfect tubes is not. These observations are in line with a successful chemical labeling of defects in SWCNT by employing SH radicals. If the diameter is increased, the results obtained for graphene suggests a reduction of the reactivity of the SW defect but not for the single vacancy. In effect, for the vacancy site the E_{bind}C–SH is nearly the same for a (5,5) tube and a graphene sheet [10]. However, for SW-defective graphene, E_{bind}C–SH = 0.46 eV, which is 0.52 eV smaller than the value obtained for the SW-defective (10,0) SWCNT. It is worth noticing that the SH group is a quite unique radical because, even though it has an unpaired electron, it does not react with the perfect sp^2 carbon framework of carbon nanotubes.

Implications with experiment

In recent studies, Curran et al. [38] and Cech et al. [39] performed an experimental study of thiolated SWCNTs. They observed 0.6% of atomic content of sulfur. The bright-field TEM study followed by elemental maps of carbon and sulfur showed that: (a) the S atoms are located in specific zones forming lines or "sulfur islands" (b) the tips were not functionalized with sulfur-containing groups, unexpected result because the presence of pentagons suggests large curvature and thus larger reactivity. Since, the

nanotubes were exposed to harsh acid treatments, defects were created. Thus, the observation of sulfur islands is in line with the results obtained in this study. Only defective tubes react with the SH radical. This result in agreement with the recent study by Vasiliev and Curran [40] that showed the importance of surface defects when forming chemical bonds that connect nanotubes with each other. However, the lack of reactivity at the tips is more difficult to explain. For this reason, we evaluated the binding energy between the SH group and C60. At the PBE level using SIESTA the binding energy is 0.73 eV, but when the free energy correction is considered the $-\Delta G° = 0.28$ eV; the process is spontaneous. However, half of C60 is the cap of a small diameter SWCNT, like the (5,5) one. Thus, half-fullerenes larger than C60 will be necessary to close tubes with larger diameter, like the arc-produced ones, which were used in [36, 37]. Since, in general, fullerenes larger than C60 have lower curvature they are expected to be less reactive, explaining the lack of reactivity at the tips.

Conclusions

We have investigated the reactivity of perfect and defective SWCNTs against the SH group employing large unit cells and periodic DFT calculations. The presence of Stone–Wales defect sites significantly increases the reactivity of SWCNTs with the thiol group. Indeed, for a (10,0) SWCNT containing the SW defect the C–SH binding energy was determined to be 0.98 eV at the PBE level. In spite of having a significant entropy loss, the process is expected to be spontaneous with $-\Delta G° = 0.53$ eV. The single vacancy defect site is extremely reactive with the SH group, more than the Stone–Wales defect. In effect, the C–SH binding energy was 2.73 eV. However, the most stable configuration is not that with a SH group attached to the vacancy site. Instead, in the preferred configuration the sulfur atom reconstructs the SWCNT framework and the hydrogen atom is attached to a carbon atom that is bonded to sulfur. This result is different from the one reported for defective graphene. In this case, the SH group was disso-ciatively attached to the vacancy defect site, showing a reactivity similar to the one observed for a bare edge. We attribute this difference to the fact that the energetic cost to create the sulfur substitutional defect for the tube is 1 eV lower than the one computed for graphene, due to the larger curvature of the SWCNT [11]. The cluster model calculations indicate that even the small diameter and metallic SWCNTs like the (5,5) one have very low reac-tivity with the thiol group, and when free energy correc-tions are considered the process is not spontaneous. The different reactivities observed for perfect and defective SWCNT with SH, suggests a successfully chemical

labeling of the Stone–Wales and single vacancy defect sites present in carbon nanotubes. If the diameter is increased the results obtained for graphene suggests a reduction of the reactivity of the SW defect but not for the vacancy defect site. The SH group is a quite unique radical because, even though it has an unpaired electron it does not react with the perfect sp^2 carbon framework of carbon nanotubes. The experimental results which showed agglomeration of sulfur groups and lack of reactivity at the tips [38, 39], support the conclusions reached in this study: perfect carbon framework does not react with SH, unless they have defect sites or curvature larger than that of C60. Finally, we suggest a method to afford sulfur-doped SWCNTs by employing SH radicals.

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