Hydrogen Adsorption and Associated Electronic and Magnetic Properties of Rh-Decorated (8,0) Carbon Nanotubes Using Density Functional Theory

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ABSTRACT: A systematic spin-polarized density functional theory (DFT) study of hydrogen interaction with pristine and Rh-decorated zigzag (8,0) single-walled carbon nanotubes (SWCNTs) was performed. The most stable decoration site for Rh atoms as well as atomic and molecular hydrogen adsorption inside and outside the SWCNT was studied. Hydrogen adsorption energy in Rh-decorated SWCNTs was improved compared to that of pristine nanotubes. In addition, Rh-decorated SWCNT systems present a magnetic moment. Density of states and work function (WF) were computed to study the bonding evolution and electronic structure. When hydrogen is considered on Rh-SWCNT and pristine SWCNT, the WF increased while band gap decreased compared to that of pristine SWCNT.

1. INTRODUCTION

Nowadays, carbon nanotubes (CNTs) are widely seen as a material with extensive potential for applications based on their electronic structure and one-dimensional geometry. Their application areas include single-electron transistors, nanostructure diodes, hydrogen storage, gas sensors, and cold emitters.1−2 Hydrogen-based energy sources are one of the promising solutions to environmental pollution because this approach could provide a bridge between fossil fuels and renewable energy. However, one of the major drawbacks is finding new materials capable of storing hydrogen at high per mass quantities at a low cost.3 There are several materials available for hydrogen storage,4 such as hydrides or carbon nanostructured materials.5−10 These materials must exhibit favorable thermodynamic properties, and they must have sufficiently fast kinetics of hydrogen charging and discharging.11 Although single-walled carbon nanotubes (SWCNTs) have many potential advantages for hydrogen adsorption over currently available adsorbents,12 they do not adsorb considerable amounts of hydrogen at normal conditions.13 The interaction between H or H2 and SWCNTs is of the van der Waals type.14,15 Nevertheless, hydrogen storage properties of SWCNT can be modified by addition of transition metals (TM) or alkali metals or by creating defects.16,17

Recently, the scientific community has also studied CNTs18 because of their great potential for use in spintronics devices.19,20 Zhao et al.21 have found that SiC nanotubes decorated by different atoms (H, Li, B, N, and F) can induce spontaneous magnetization.

The SWCNT (8,0) has been studied extensively and presents interesting physical and chemical properties.15,16,22 In addition, the adsorption of H atoms, H2, and/or TM atoms (particularly TMs with unfilled d orbitals) on SWCNTs can create an active site and induce magnetism in the CNT, making the impurity−SWCNT a potential system for both hydrogen storage and spintronics applications.16,23

Suarez-Martinez et al.24 studied the interface between Rh and CNT, suggesting that Rh is a good candidate for CNT contacts. DFT modeling of hydrogen adsorption on SWCNT-supported Rh is still an open question. Rh adsorption on (6, 6) SWCNTs was investigated by DFT,25 and the authors conclude from partial density of states (PDOS) and band structure calculations that magnetism of Rh adsorbed outside of SWCNTs is higher than that inside. Yang et al.26 studied the rolling effects of the (n, n) SWCNT with different curvatures on Rh adsorption behaviors. To the best of our knowledge, although there are some theoretical studies on Rh/SWCNT or Rh/graphene and H2 on pristine SWCNT, there is not a combined study of H and H2 on Rh-decorated SWCNT. Also, the published research is mainly related to hydrogen storage and some electronic properties relevant for spintronics are not addressed.

The paper is organized as follows: In section 2 we describe the computational method and model used for our calculations.

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The results and discussion are in section 3, which contains two subsections. The adsorption geometry of Rh, H, and H₂ on SWCNTs are discussed in section 3.1. Section 3.2 contains results of electronic and magnetics properties and the effects of H and H₂ on Rh/SWCNT(8,0). In section 4, results are summarized.

2. COMPUTATIONAL METHOD AND MODEL

The DFT calculations were performed using the Vienna ab initio simulation package (VASP) code. This code uses a plane-wave basis set offering good access to the Hellmann–Feynman forces acting on all atoms in the supercell. Spin-polarized DFT with the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) and the projector-augmented wave (PAW) method were considered. The cutoff energy for the plane-wave basis was set to 700 eV.

A one-dimensional periodic boundary condition was applied along the tube axis. The supercell lattice constants a, b, and c were 20.00, 8.53, and 20.00 Å, respectively (Figure 1a).

Two unit cells of (8,0) SWCNT (64 carbon atoms) were used, and the distance from the carbon nanotube axis and its respective periodic image was 20 Å, ensuring no interaction between periodic images. The (8,0) SWCNT is a typical semiconductor CNT. We chose this particular chirality because it has physisorption properties. Fan et al. computed that (8,0) SWCNT has a significant curvature, which gives the SWCNT particular properties. These geometrical values are in good agreement with those previously reported in the literature.

In the Rh adsorption on SWCNT, the most stable site is placed between the hollow and the edge1 sites (Figure 2b). The Rh atom is located equidistant between two carbon atoms, being Rh–C distance of 2.09 Å. C–C bond lengths are elongated near the Rh adsorption site approximately 1% compared to the pristine SWCNT. It can be seen that Rhodium adsorption...
induces changes in the SWCNT diameter (Figure 2b). The diameter of Rh–SWCNT increases in the direction in which the Rh is adsorbed (from 6.37 to 6.43 Å), and a slight contraction in the perpendicular direction (from 6.37 to 6.32 Å) is noticed. The Rh adsorption energy is $-2.67$ eV (Table 1). These values are in good agreement with the literature.16 Regarding the possibility of Rh clustering, we performed some preliminary calculations because of the complexity of the problem. We studied the adsorption of small Rh clusters on pristine SWCNT ($8,0$). We found Rh$_2$ and Rh$_3$ to be unstable on pristine SWCNT ($8,0$). Suarez-Martinez et al. reported, by X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy in addition to DFT calculations, the formation of Rh clusters only at defects containing SWCNT ($8,0$).24 Shi and Sholl modeled the clustering of Rh$_n$ ($n = 1−5$) on alumina.59 They also found that the Rh$_2$ and Rh$_3$ are unstable or stable depending on the defects present on the surfaces.

With hydrogen atom adsorption on pristine outside SWCNT walls, significant geometric changes can be noticed. The most stable configuration for the H atom is located on top of a carbon atom at a C–H distance of 1.11 Å (Figure 3a,b) with adsorption energy of $-1.61$ eV; similar values were reported in the literature.17,40 It can be seen that hydrogen atom adsorption modifies C–C distances around 5% (Figure 3a). The SWCNT curvature increases from 6.37 to 6.72 Å in the H–C direction and it is contracted 1% in the H–C perpendicular direction (6.37 to 6.32 Å), as is shown in Figure 4a. For internal H atom adsorption, H is located in the center of the SWCNT

<table>
<thead>
<tr>
<th>system</th>
<th>$E_g$ (eV)</th>
<th>$\mu$ ($\mu_B$)</th>
<th>$\Delta VB$ (eV)</th>
<th>$\Delta CB$ (eV)</th>
<th>$WF$ (eV)</th>
<th>$E_{ads}$ (eV)</th>
</tr>
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<tr>
<td>pristine</td>
<td>0.58</td>
<td>0.0</td>
<td>0.01</td>
<td>0.57</td>
<td>4.39</td>
<td>$-$</td>
</tr>
<tr>
<td>Rh–SWCNT</td>
<td>0.46</td>
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<td>0.16</td>
<td>0.30</td>
<td>4.41</td>
<td>$-2.67$</td>
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<tr>
<td>H(I)/SWCNT</td>
<td>0.31</td>
<td>1.0</td>
<td>0.04</td>
<td>0.27</td>
<td>4.09</td>
<td>$-1.61$</td>
</tr>
<tr>
<td>H(II)/SWCNT</td>
<td>0.53</td>
<td>1.0</td>
<td>0.03</td>
<td>0.50</td>
<td>4.78</td>
<td>$-0.14$</td>
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<tr>
<td>H$_2$(I)/SWCNT</td>
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<td>0.01</td>
<td>0.57</td>
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<tr>
<td>H$_2$(II)/SWCNT</td>
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<td>0.0</td>
<td>0.06</td>
<td>0.51</td>
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<td>0.0</td>
<td>0.12</td>
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<tr>
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<td>0.03</td>
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<td>$-0.17$</td>
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<td>0.46</td>
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<td>0.17</td>
<td>0.29</td>
<td>4.42</td>
<td>$-0.30$</td>
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</table>

**Table 1.** Band Gap ($E_g$), Magnetic Moment ($\mu$), Distance between Fermi Level ($E_F$) and Valence and Conduction Band ($\Delta VB$ and $\Delta CB$), Work Function (WF), and Adsorption Energy ($E_{ads}$) for Rh-decorated SWCNT, H/SWCNT, H$_2$/SWCNT, H–Rh/SWCNT, and H$_2$–Rh/SWCNT

"(I): outside adsorption. (II): inside adsorption."
(Figure 3c,d). The SWCNT diameter is decreased from 6.37 to 6.32 Å, and H adsorption energy is 91% less than the outside adsorption (Table 1).

Regarding H₂ adsorption, it was found that the parallel adsorption is the most stable orientation. The H₂ molecule was externally adsorbed at the hollow site with a C–H distance of 2.89 Å and H₂ adsorption energy of −0.07 eV. These values are in good agreement with previous studies 38,40–44 (Figure 4a,b). This calculated adsorption energy value corresponding to a weak physisorption is due to the absence of a permanent dipole in both H₂ and SWCNT. 38 On the other hand, H₂ adsorption energy inside the SWCNT walls is more favorable compared to hydrogen adsorption energy outside SWCNT (−0.20 and −0.07 eV, respectively; Table 1). Moreover, it can be observed that H–H and C–C bond lengths as well as SWCNT diameter are negligibly changed after hydrogen adsorption. This occurs because the hydrogen molecule is not covalently bonded to SWCNT, see Figure 4c,d. While the adsorption energy of H₂ located inside SWCNT is energetically better than the adsorption energy of the H atom inside, the opposite occurs for H₂ adsorption outside SWCNT walls (Table 1).

The external hydrogen adsorption on Rh-decorated SWCNT elongate the C–Rh bond by around 3%, as we can see in Figure 5a,b. Regarding C–C bonds, no significant changes were found (Figure 5a,b). The SWCNT diameter lightly increases in the Rh–H direction (Figure 5b). For all H–Rh/SWCNT systems studied, hydrogen adsorption is more favorable compared to pristine SWCNT (Table 1). As a consequence of this, the Rh-decorated (8,0) SWCNT is a good candidate for hydrogen storage.

The Rh–H bond distance is 1.55 Å (Figure 5b). This value is in fairly good agreement with our calculations (Rh–H = 1.61 Å) and previous data reported on the literature. 45 In the case of internal H adsorption, the H atom is placed in a slightly eccentric position (Figure 5c,d). On the other hand, when H₂ is adsorbed outside Rh-SWCNT, the Rh–C distance is slightly decreased, while the H–H distance is the same as that in the H₂ gas phase (Figure 6c,d). Our results show that the H atom and H₂ molecule prefer to be adsorbed outside Rh-(8,0) SWCNT, as can be seen in Table 1. Moreover, all adsorption energy values obtained indicate that adsorption processes are exothermic.

3.2. Electronic and Magnetic Properties Analysis.
Density of states (DOS) curves are shown in Figures 7–11, and all computed physical properties are summarized in Table 1.
Figure 8. DOS curves for H adsorption on pristine (8,0) SWCNT: total (a) and PDOS (b) for H atom outside; total (c) and PDOS (d) for H atom inside.

Figure 9. DOS curves for H₂ adsorption on pristine (8,0) SWCNT: total (a) and PDOS (b) for H₂ molecule outside; total (c) and PDOS (d) for H₂ molecule inside.
agreement with previous data.\textsuperscript{16,22} It has been shown that computing the band gap in several semiconductors and insulators, from Kohn–Sham formalism implemented in DFT, in general underestimates their band gaps.\textsuperscript{46} Nevertheless, the band gaps obtained in this work are in good agreement with other values reported in the literature. The spin up and spin down DOS contributions are symmetric, indicating that the SWCNT is antiferromagnetic with no magnetic moment. The Fermi level ($E_F$) is located at 0.01 eV of the valence band (VB) and 0.57 eV below the conduction band (CB). The small shift of $E_F$ is a common feature of DFT methods. Also, C s states contribute to the DOS curve below $-4$ eV with respect to the $E_F$. On the other hand, the C p states contribute in both VB and CB (Figure 7b).

When Rh is considered, significant changes in the electronic and magnetic properties of the SWCNT are found. The $E_F$ is shifted up to higher energy values, see Table 1. However, it still remains closer to the VB than the CB (0.16 and 0.30 eV, respectively). This relative shift in the $E_F$ could be important for nanotube-based transistors.\textsuperscript{7} In addition, Rh atom adsorption on (8,0) SWCNT induces novel states resulting in the band gap reduction. This reduction from 0.58 to 0.46 eV (Table 1) can be observed in Figure 7a,b. The VB and the CB do not start at the same energy values for the spin up and down DOS contributions. These facts are consistent with the computed magnetic moment ($\mu = 1.0 \mu_B$). Below the $E_F$, the most important contribution to the total DOS are the d states of the Rh atom and p states of the C atoms, and all states of the Rh and C atoms contribute to the CB. The intensities of the peaks near the $E_F$ of the total DOS curve increase because of the Rh d states, and they are more significant for the spin down contribution (Figure 7a,b).

For hydrogen atom adsorption, total DOS curve spin up and down contributions are not symmetric because of the hybridization among H s orbital and C p orbitals of SWCNT (Figure 8a). The net magnetic moment is 1.0 $\mu_B$ (Table 1). Similar results were reported by Ma et al.\textsuperscript{38} who found that H adsorption on SWCNT with vacancies presents an induced magnetic moment. It can be seen in the total DOS curves that the VB for spin up and spin down contributions have the same energy. However, contributions to CB have different energies when H is adsorbed outside CNT. In this case, the band gap for the spin up DOS contribution almost does not change while the spin down DOS contribution shows an important reduction of 46% in the band gap. Carbon atoms around adatom do not contribute significantly to the total DOS between $-3$ and 3 eV. Outside of this range, the C s state curve of spin up and spin down contributions have almost symmetrical. The C s electrons are not polarized when H is adsorbed. The C p states show changes due to the hybridization with H s states (Figure 8b). For H adsorption inside CNT, it can be noticed that an intense peak around $-1.5$ eV appears because of C p states. At the same time, we can see that the DOS curve is asymmetrical with a band gap similar to that of pristine CNT (0.53 eV) and a computed magnetic moment of 1.0 $\mu_B$ (Figure 8c,d).

DOS curves for H$_2$ adsorbed outside and inside (8,0) CNT are shown in Figure 9a–d. DOS curves for H$_2$–SWCNT are negligibly changed near the top of the VB and bottom of the CB with respect to DOS for pristine CNT. Moreover, the band

Figure 10. DOS curves for H adsorption on Rh-decorated SWCNT: total (a) and PDOS (b) for H atom outside; total (c) and PDOS (d) for H atom inside.
gap value does not change when H$_2$ is adsorbed on SWCNT, as can be seen in Table 1. In both cases, inside and outside adsorption, the charge transfer between (8,0) SWCNT and H$_2$ is negligible. This effect will be discussed in the next section. Regarding the magnetism, H$_2$ adsorption does not induce magnetism on pristine SWCNT (Table 1).

When an H atom is adsorbed externally on Rh-decorated SWCNT, the spin up and spin down DOS contributions are symmetrical (Figure 10a,b). The magnetic moment obtained is zero, indicating an antiferromagnetic behavior. This is in agreement with an electron spin resonance (ESR) investigation of changes in the electronic structure before and after purification of SWCN and exposure to hydrogen gas. The ESR signal in these nanotubes was due to paramagnetic impurities and diminished in intensity upon hydrogen adsorption.47 Wu and Hagelberg48 systematically explored by DFT the magnetic properties of axially confined, hydrogenated SWCNTs of the (n,0)-type with $n = 5$–24. They found for $n \geq 7$ antiferromagnetic (AFM) order is favored energetically over ferromagnetic (FM) order for all lengths investigated. Effect of doping of carbon nanotubes by magnetic transition-metal atoms has been considered by Esfarjani et al.49 In the case of semiconducting tubes, these authors found that the system has zero magnetization, whereas in metallic tubes the valence electrons of the tube screen the magnetization of the dopants; the coupling to the tube is usually antiferromagnetic (except for Cr). On the other hand, the first neighbors C atoms have a slight hybridization with Rh–H complex. While a stronger interaction is detected between the Rh and H atoms, the Fermi level is located closer to the VB than the CB (0.12 and 0.37 eV, respectively). Although the band gap of H–Rh/SWCNT is reduced by about 15% compared to pristine SWCNT, it increases compared to H-SWCNT and Rh-SWCNT systems (Table 1). For internal H atom adsorption on Rh-decorated (8,0) SWCNT, the net magnetic moment enhances from 1.0 $\mu_B$ (Rh-SWCNT) to 2.0 $\mu_B$ (H–Rh/SWCNT). Thus, the H–Rh/SWCNT system could have important applications in the spintronics area. The band gap of spin down contributions is smaller than the spin up contributions (Figure 10c,d).

Finally, hydrogen molecule adsorption on Rh-decorated SWCNT induces a magnetic moment. The net magnetic moment obtained is 1.0 $\mu_B$. Moreover, the band gap decreases by around 23% (Table 1). The $E_g$ shifts to higher values, but it remains closer to the VB (Table 1). It is important to notice that the spin down contribution has metallic behavior with zero band gap (Figure 11a–d).

Another important physical property to determine the electronic structure and the interaction at CNT/metal interface is the work function (WF).50 The WF is defined as the energetic distance between the vacuum level and the Fermi energy.22 The WF values for all studied systems are listed in Table 1. For pristine (8,0) SWCNT, the calculated WF is 4.39 eV. Similar values were reported by Horastani et al.,22 Su et al.,50 and Shiraishi et al.,2 who found a WF of about 4.34, 4.64, and 4.95 eV, respectively. Our results show that the WF is increased from 4.86 eV (H$_2$–SWCNT) to 4.39 eV (pristine CNT). When H$_2$ is adsorbed outside on Rh-decorated SWCNT, WF is increased by 13%.
Electronic properties such as band gap and work function are slightly affected by temperature and pressure. A recent study by Capaz et al. including the (8,0) CNT found a very small change in the band gap with pressure (between −0.17 and −0.08 meV/kbar), which is far from a useful pressure for hydrogen-based energy applications.\textsuperscript{51} The effect of temperature and pressure on the chemical potential of the gas phase, coverage, and adsorption energy will be addressed in a future investigation using Monte Carlo and molecular dynamics simulations.

The charge transfer was computed by Bader’s approximation for all studied systems.\textsuperscript{52} We can note that C atoms charge states are alternated, negative (0.03 e acquires) and positive (0.03 e loses), along the tube axis. This charge distribution is in agreement with the electrostatic potential curve behavior (Figure 12).

Rh acts as an electron donor, losing 0.9 e of its charge. In Figure 12 we can observe that a valley of 0.6 eV depth appears close to $z = 10.6 \text{ Å}$. Rh decoration provides adsorption active sites for new species. In Table 1, we can see that the work function in this system is increased by 0.5% compared to that of pristine CNT.

The H atom adsorbed on the outside of pristine SWCNT acts as an electron donor and loses 0.03 e. The C atom bonded to H atom also loses some charge (0.04 e). This leads to a redistribution of charge around the C–H pair. The charge is transferred from the C–H pair to their near neighbors (nn). Regarding the electrostatic potential curve in Figure 13, an increment of 0.5 eV around $z = 8.5 \text{ Å}$ is due to the H located nearby. Also, we can observe that H adsorption provides adsorption active sites. These results agree with those listed in the previous section. When H is located inside, SWCNT loses 0.02 e and its charge is transferred to the nn C atom (around 0.02 e). When H atom is adsorbed inside SWCNT, we can notice that the valley increases compared to H adsorbed outside SWCNT (Figure 13). When H\textsubscript{2} is considered, the charge transfer between the SWCNT and the H\textsubscript{2} is negligible. However, electrons tend to transfer from the SWCNT to H\textsubscript{2} and the H\textsubscript{2} adsorption results in a surface net charge transfer; this effect is reported by Horastani et al.\textsuperscript{22} Particularly, for H\textsubscript{2} outside adsorption on pristine SWCNT there is a reduction of electron concentration that gives rise to a slight electron depletion zone around 10.5 Å, as can be seen in Figure 13.

In the case of H atom adsorbed externally on Rh-decorated SWCNT, the Rh atom loses 0.5 e; its charge is transferred from Rh to its nn C atoms and H atom. When H atom is located inside Rh-SWCNT, the Rh and H atoms lose 0.4 e and 0.02 e, respectively. The charge is transferred from Rh and H to nn C atoms. In both adsorption cases, the electrostatic potentials

![Figure 12. Electrostatic potential in the normal direction of increase SWCNT (z) for the pristine and Rh-decorated SWCNT.](image)

![Figure 13. Electrostatic potential in the normal direction of increase (8,0) SWCNT (z direction) for hydrogen adsorption on the pristine and Rh-decorated SWCNT. (I) and (II) correspond to outside and inside adsorption on the nanotube, respectively.](image)
are similar to those obtained for Rh-decorated SWCNT (Figures 12 and 13). After H₂ adsorption on Rh-SWCNT, we can notice a behavior similar to that of H atom adsorption on Rh-SWCNT. Then Rh decoration improves the adsorption of new species.

The effect of other n- and p-type impurities and metal clustering at defective CNTs on the electronic and magnetic properties will be the subject of a forthcoming investigation.

4. CONCLUSIONS

Using periodic DFT calculations, it was found that the interaction between the SWCNT and non-nanotube components (atomic and molecular H and Rh atom) can further be used as an appealing route to modifying or producing specific (8,0) SWCNT properties in a controlled way.

The Rh-SWCNT, H−Rh−SWCNT and H₂−Rh-SWCNT systems have a magnetic moment of around 1.0 μB. Furthermore, a metallic behavior for spin down DOS contribution and semiconductor behavior for spin up DOS contribution were noticed. These asymmetries in the DOS curves at E₀ are useful in spin-injection device and a spin-polarized FET, among others.

On the other hand, it was seen that some electronic properties of SWCNT are sensitive when hydrogen is adsorbed on Rh-SWCNT. The WF is increased and E₀ is decreased compared to pristine SWCNT. In addition, the computed electrostatic potential shows that in the Rh-SWCNT, H−Rh−SWCNT, and H₂−Rh-SWCNT systems there is an active site for adsorption of new species. Then these systems could be appropriate candidates for use in sensing and measuring applications such as gas detection.

Finally, the hydrogen adsorption energy improves when the nanotube is Rh-decorated, i.e., from −0.07 eV (H₂−SWCNT) to −0.99 eV (H₂−Rh-SWCNT).

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Notes
The authors declare no competing financial interest.

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