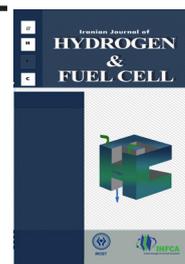


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## Study on the stability of Si, Ge, Fe and Co in the interior surface of a metallic carbon nanotube for hydrogen storage

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### Abstract

In this article, we have performed calculations for studying the stability of carbon group elements, such as Si and Ge, and also magnetic elements, like Fe and Co, via first principle investigations. We found that Si and Ge decoupled from the interior surface of carbon nanotubes, this fact was independent in curvature, radius, conductivity and number of atoms in the carbon nanotubes. But the magnetic elements bonded to the surface of the tube via the electronegativity factor. The binding energy calculated for Co was -3.82 eV which is more stable than that of Fe (-2.65 eV) due to a larger decrease in its magnetization. The magnetization of Fe and Co changed from  $4.00 \mu_B$  to  $3.40 \mu_B$  and  $3.00 \mu_B$  to  $1.75 \mu_B$ , respectively. Finally, we came to the conclusion that carbon group elements are favorable for hydrogen absorption inside the carbon nanotube, whereas magnetic elements are suitable for hydrogen adsorption on the nanotube surface.

## 1. Introduction

Since the discovery of single-walled carbon nanotubes (SWCNTs) by Sumio Iijima [1], they have come under intense attention. Carbon nanotubes have various applications due to their stable, electric, magnetic, thermal and optical properties [2]. One of the most important applications considered is

hydrogen storage [3]. Carbon nanotubes can accommodate hydrogen inside themselves [4] or adsorb it on their surfaces [5]. One of the most inevitable problems in carbon nanotube is having low storage efficiency due to their weak binding energy of carbon-hydrogen [6]. In order to improve the efficiency of the storage, carbon nanotubes are doped with different elements [7]. When a carbon nanotube

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is doped with metallic elements, two possible places for hydrogen adsorption are made. One is the metallic element and the other one is the surface of carbon nanotube. However, metallic elements transmit the electrons and increase the charge density of the surface leading to the enhancement of absorption. W. Liu et al. [8] showed that doping Li increased hydrogen uptake dramatically in single-walled carbon nanotubes.

Before hydrogen adsorption, the optimized position of the doped element has to be recognized. H.S. Philip Wong et al., and Lee, S. M. et al [9] mentioned that the maximum stable intercalation of hydrogen side of the nanotubes is predicted to about 14.3 weight percentage of hydrogen for hydrogen storage inside the carbon nanotube [9, 10]. Nanotubes generally expand in order to accommodate hydrogen. J. Davoodi et al. [11] performed calculations from the (4,4) to the (17,17) single-walled carbon nanotubes and observed that by increasing the SWCNTs radius the hydrogen storage inside the SWCNTs increases. Elements which are bound to the surface of carbon nanotubes and do not change their structural properties can be good candidate for hydrogen adsorption for hydrogen adsorption. Experimental circumstances showed that it is possible to synthesize Si, Fe and Co doped single walled carbon nanotubes [12,13]. In this article we used carbon group elements to study their interaction on the surface of carbon nanotube and also investigate the effect of doping Fe and Co on the electric and magnetic properties of the surface.

The aims of this article are:

- (i) Study the interaction of carbon group atoms Si and Ge and magnetic atoms Fe and Co on the interior surface of carbon nanotubes.
- (ii) Determine optimized geometry for these atoms in single walled carbon nanotubes in order to allow them to be applied favorably in hydrogen storage.

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## 2. Simulation Methods

We have used Siesta code [14], which carries out a fully self-consistent density functional calculation via solving the standard Kohn-Sham (KS) equations,

to calculate the electronic and magnetic properties, charge density, and binding energy of doped elements on the interior surface of the (6,6) carbon nanotube with a diameter of 8.14 Å. In the calculation a double zeta basis set with polarization function has been selected [15]. The standard norm conserving Troullier-Martins pseudopotentials have been utilized [16]. The exchange-correlation energy functional of Perdew-Zunger [17] in the local density approximation (LDA) has been used. Energy cut-off was obtained at 120 Ry. The Brillouin zone has been sampled using  $1 \times 1 \times 8$  Monkhorst-Pack k-point grids [18]. All the coordinates of the atoms were relaxed until the Hellman-Feynman forces were less than 0.05 eV/Å for the entire geometry optimization. We chose the lateral separation between the centers of the tubes 16 Å to use as periodic-boundary conditions in order to insure that they did not react with each other. In all calculations, we defined the binding energy of the doped atom by having  $E_b = E_{\text{CNT+d}} - E_{\text{CNTs}} - E_d$ , where  $E_{\text{CNT+d}}$  is the total energy of carbon nanotubes with the accompanying doped atom,  $E_{\text{CNTs}}$  is the energy of pure carbon nanotubes, and  $E_d$  is the self-energy of the doped atom which should be subtracted from  $E_{\text{CNT+d}}$  [19].

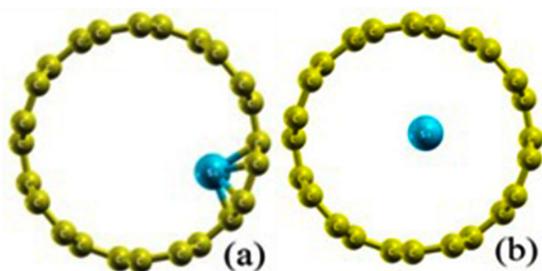
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## 3. Results and discussion

R. J. Baierle et al. [20] showed that when a Si atom was substituted for one carbon in CNTs the electronic properties of the carbon nanotubes changed. The local density of the states depicted that Si doped carbon nanotubes have more active surface than their pristine ones. Yuan et al. [21] demonstrated that silicon substituted armchair single-walled carbon nanotubes with different diameters have less binding energy than their pure structure, so this case is not suitable for hydrogen adsorption, because the binding energy of the structure should not be lowered. Therefore, the substitute Si carbon nanotubes are not appropriate for this study.

Jung Hyun Cho et al. [22] showed that the hydrogen storage capacity of 10 wt% Si-doped single walled

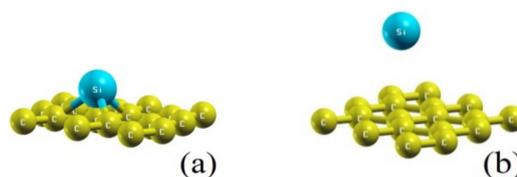
carbon nanotubes could reach a maximum of 2.5 wt%, almost twice the storage capacity of pure single walled carbon nanotubes, but this amount is distant from Department of Energy (DOE) volumetric capacities which is 5.5 wt% [9]. In this work we have investigated the behavior of a Si atom in the interior of a metallic (6,6) carbon nanotube with 24 C atoms in the unit cell. The C-C distances in the (6,6) are about 1.42 Å. Figure 1 demonstrates the initial placement of the Si atom in the interior surface of the (6,6) where the distance between Si and carbon atoms are approximately 1.86, 1.96, 1.90 and 1.76 Å. As seen in Figure 1(b), the Si atom decoupled from the interior of the surface of the (6,6) nanotube and was approximately relaxed in the center of the tube. This fact is similar to Timerkaera et al.'s work in [23]. They performed calculations for a helium atom inside a (13,0) carbon nanotube and found the most preferred position for the Helium atom is near the center of the tube.



**Fig 1. Position of Si atom inside the metallic carbon nanotube on the interior surface (a) before relaxation and (b) after relaxation.**

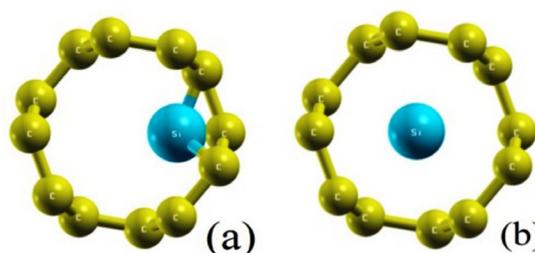
The binding energy of Si was calculated at + 3.48 eV which indicates that the Si atom has not maintained its initial place on the surface of the tube. The diameter of the tube increased to 0.2 Å, which is not considerable, and the bond length of C-C underwent no dramatic displacement. We studied several parameters to find out the decoupling behavior of the Si atom from the interior surface of carbon nanotube. We carried out the calculation for a graphene sheet whose unit cell has been tripled, shown in Figure 2, to consider the effect of curvature of the tubes.

As seen in Figure 2 (b), the Si atom decouples from the surface of the graphene again. It can also be seen



**Fig 2. Position of Si atom on the surface of graphene sheet (a) before relaxation and (b) after relaxation.**

that this behavior is independent to the curvature of the surface and takes place in a smooth surface. The surface and C-C bond length in graphene remained unchanged. The binding energy was calculated to be + 4.67 eV which is less than that of the (6,6) tube. We repeated the calculation for a (3,3) tube with 12 C atoms in its unit cell and a diameter of the 2.03 Å as depicted in the Figure 3. We tried to confine the diameter for the Si atom to adsorb it in the interior of the surface.



**Fig 3. Position of Si atom inside the (3,3) carbon nanotube on the interior surface (a) before relaxation and (b) after relaxation.**

As observed in Figure 3 (b), the Si atom again decouples from the interior surface after the process of relaxation which shows the number of carbon atoms and diameter of the tube is ineffective. The binding energy was calculated to be +2.67 eV which is less stable than the graphene sheet due to increased confinement of the Si atom by tightening the diameter of the tube. This indicates that the Si atom in the nanotubes is more stable than the graphene sheet.

We performed the calculation for a semiconductor carbon nanotube (10,0) obtaining 40 C atoms in its unit cell with diameter of 7.14 Å to study the interaction of a Si atom with the surface of the (10,0) tube, and to

ascertain if there was any difference with the metallic nanotube. Figure 4 (a) illustrates the initial position of the Si atom on the interior wall of the (10,0) tube before relaxation. As seen in Figure 4 (b), the Si atom decouples from the surface as in the previous cases, but the diameter of the semiconductor carbon nanotube increased to 0.5 Å which was more than the metallic nanotube.

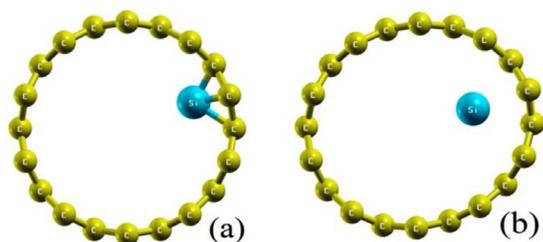


Fig 4. Position of Si atom inside the (10,0) carbon nanotube on the interior surface (a) before relaxation and (b) after relaxation.

Also, the Si atom prefers a region near the C atoms in comparison with the metallic nanotube, which indicates that the interaction of electrons in the outer electronic shell in Si with C atoms in the semiconductor carbon nanotube is stronger than the metallic nanotube. To scrutinize this behavior we studied and compared the magnetization of carbon nanotubes together. Calculations revealed that in both kinds of carbon nanotubes the initial spin polarization was zero as Si was placed on the surface (the electrons were in the antiparallel state). But when the Si atom was decoupled from the surface, its outer shell electrons were unbounded and achieved more freedom to produce magnetization. Figures 5 (a) and (b) are related to the metallic and semiconductor carbon nanotubes, respectively, and depict that desorption of the Si atom takes both types of carbon nanotubes into a magnetization state.

The spin polarization calculated for the (6,6) and (10,0) tubes were  $2.01 \mu_B$  and  $1.82 \mu_B$ , respectively. These amounts reveal that outer shell electrons in the Si atom react stronger with carbon atoms in the (10,0) than the (6,6) tube. So, the electrons come to antiparallel state more in the semiconductor tube. The

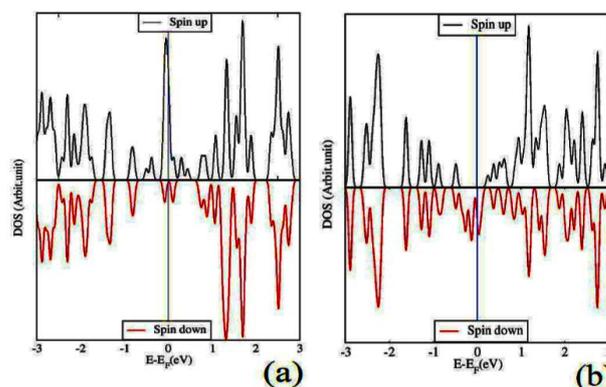
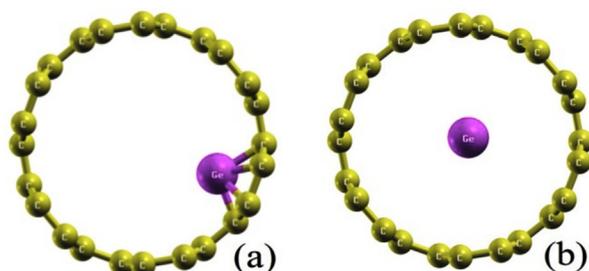


Fig 5. Spin up and down density of state (a) the (6,6), (b) the (10,0) carbon nanotube when Si atom decouples from the interior surface of them.

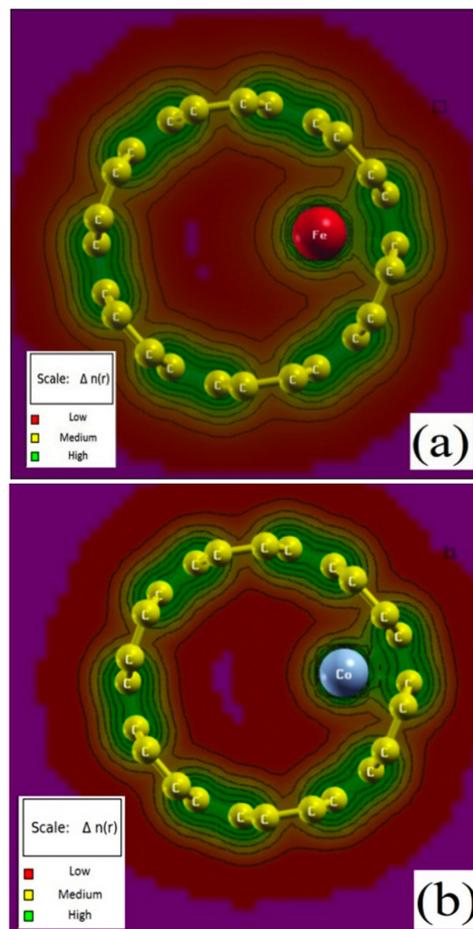
hybridization of s and p orbitals in the Si atom is a  $sp^3$  type [24] while the carbon nanotube is a  $sp^2$  [25]. The orbitals in a Si atom are bigger than carbon atoms spatially. The inhomogeneity and size of orbitals in the Si atom cause it to be desorbed from the surface. We recalculated the parameters for a Ge atom which is bigger than the Si atom in atomic mass and radius [26]. We came to the same results as the Si atom. Figure 6 shows the initial position of the Ge atom resembles the Si atom (a) before and (b) after relaxation. Decoupling the Ge atom indicates that carbon group elements have the same behavior, and the atomic mass and radius are ineffective to desorption. The diameter of the (6,6) tube increased to 0.25 Å while the C-C bond length showed no difference. The other reason for effective decoupling of Si and Ge on the interior surface of the carbon nanotube is that these atoms are metalloids, and there is a low electronegativity difference between metalloids and carbon atoms which prevents these atoms from reacting very well on the surface of the carbon. These elements can be a good candidate for hydrogen storage inside the carbon nanotubes because they can provide a circumstance to strongly bind four hydrogen atoms.



**Fig 6.** Position of Ge atom inside the metallic carbon nanotube on the interior surface (a) before relaxation and (b) after relaxation.

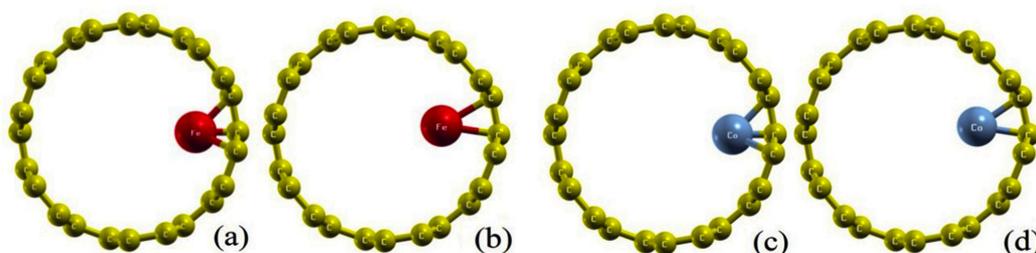
We performed calculations for magnetic elements Fe and Co and observed the different behaviors. Figures 7 (a) and (b) show the magnetic elements adsorbed on the surface of the carbon nanotube for Fe, and (c) and (d) for Co. Because the difference of the electronegativity between metals and carbon is rather good, their bindings are expected.

The binding energy calculated for the Co atom was  $-3.82$  eV which is more stable than that of the Fe atom ( $-2.85$  eV). Figures 8 (a) and (b) show the electron charge density difference between the Fe and Co atoms with an isosurface value of  $0.08$  e/(a.u.), when the Fe and Co atoms have been attached on the surface of the carbon nanotube. Green and red colors indicate accumulation and depletion of electrons, respectively. Considering Figure 8, we see that a highly electronic charge density is observed around both of the magnetic elements. But the charge density around the Co atom (Figure 8 (b)) on the surface



**Fig 8.** The electron charge density difference between Fe and Co atom with the isosurface value of  $0.08$  e/(a.u.). Green and red colors are indicator of electron accumulation and depletion respectively.

is slightly higher than that of Fe (Figure 8 (a)) which explains why its binding energy is stronger. We also studied the partial density of state for Fe and Co doped carbon nanotubes in Figure 9 (a) and (b),



**Fig 7.** Position of magnetic atoms inside the (6, 6) carbon nanotube on the interior surface (a) before relaxation and (b) after relaxation for Fe atom, (c) before relaxation and (d) after relaxation for Co atom.

respectively.

By noticing Fe and Co doped carbon nanotube partial density, a highly considerable overlap between 3d Fe, Co and 2p carbon orbitals is observed, which is why

electrons are placed on the antiparallel spin binding two atoms to each other. The binding energy is increased due to this situation and vice versa. The greater reduction of magnetization in Co is

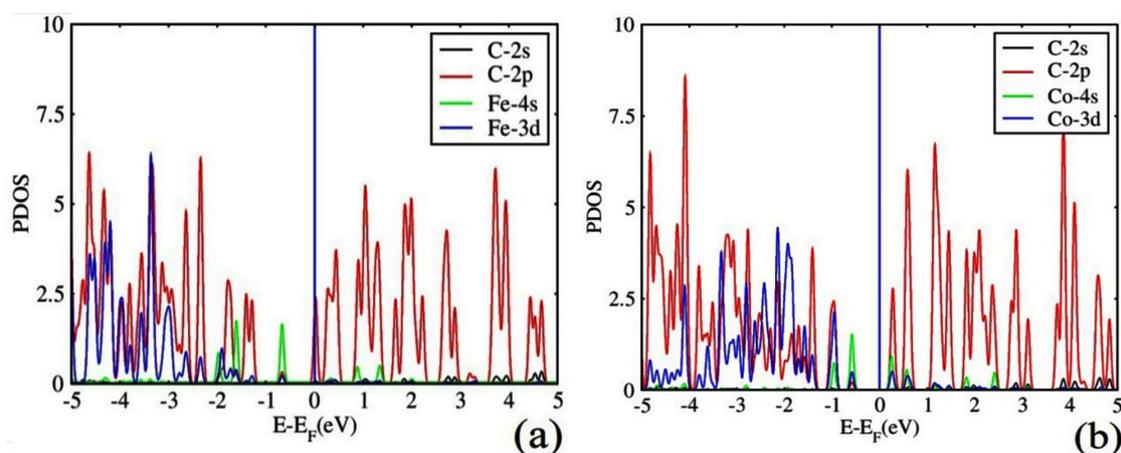


Fig 9. Partial density of state for (a) Fe and (b) Co doped carbon nanotube .

they bounded to the surface of the carbon nanotube. But as seen in the Figure 9 (a) which is related to the Fe doped carbon nanotube, a sharp peak is seen on the energy Fermi level concerning the 2p orbitals of carbon. It indicates that electrons in this level are willing to transfer to other states and are reluctant to be localized. When electrons are reluctant to be localized, the binding energy of the corresponding doped atom is less strong. To compare this state with Figure 9 (b), no seriously sharp peak is seen. This is another reason that binding energy in Co is stronger than the Fe atom on the surface.

The last parameter we inspected was to compare the value of magnetization in each atom. As seen in Figures 10 (a) and (b), both metallic elements created magnetization in the metallic carbon nanotube. By subtracting spin up electron density from spin down, the magnetization can be achieved. Spin density calculation showed that the initial magnetization for the Fe atom was  $4.00 \mu_B$  and decreased to  $3.40 \mu_B$ , while for the Co atom it was  $3.00 \mu_B$  which dropped to  $1.75 \mu_B$ . The difference between final and initial density reflexes is the binding energy. When magnetization decreased, it indicates that more

another justification of its stronger binding energy. This relaxed position on the surface of the metallic carbon nanotube explains that these elements can be potentially favorable for hydrogen adsorption in carbon nanotubes. Yosuke Yagi et al. [27] also studied the stability of Co on the surface of a (8,8) carbon nanotube. They concluded the most favorable position for Co was on the interior surface of the carbon nanotube which was stronger in comparison with its outer position on the surface.

#### 4. Conclusions

First principle calculations were performed to study the stability of Si, Ge, Fe and Co on the interior surface of a metallic (6, 6) carbon nanotube. Our results showed that Si desorbed from the surface and was relaxed in the center of the tube. This behavior is independent of the curvature, diameter, and numbers of carbon atoms and conductivity of the carbon nanotube. Desorption took place for the Ge atom obtaining larger atomic radius and mass than that of Si atom which indicates that mass and radius of carbon group elements are

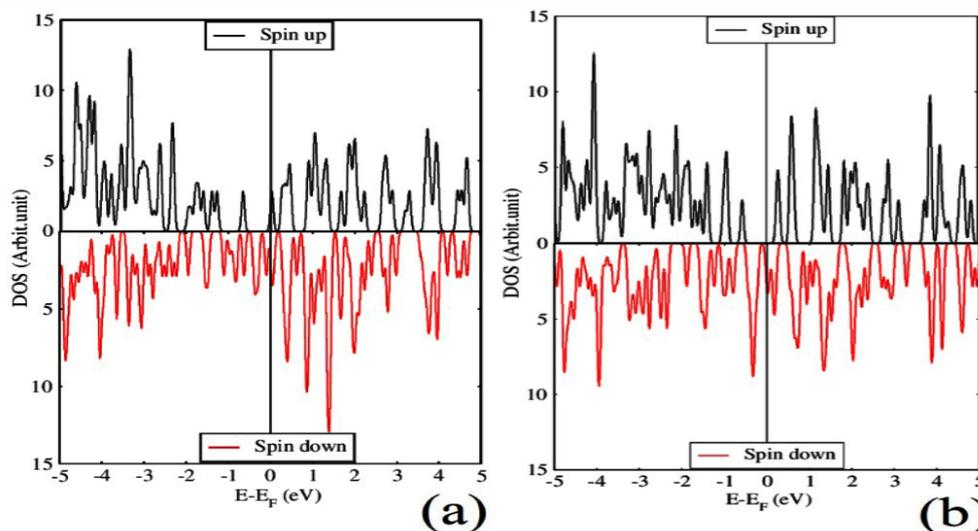


Fig 10. Spin up and down density of state (a) concerning Fe doped carbon nanotube and (b) Co doped carbon nanotube.

ineffective to adsorption. The greater interaction of the Si atom on the interior (10, 0) carbon nanotube caused a larger increase in diameter of the (10, 0) tube. Decoupling of the Si and Ge atom and being placed in the center of the carbon nanotube make them a good hydrogen absorbent inside the carbon nanotube.

Calculations for magnetic elements depicted that in spite of Si and Ge, they were bounded to their initial position. Binding energy calculated for Fe and Co was -2.85 and -3.82 eV, respectively. The Partial density of state showed that there is considerable favorably overlap between the 3d orbitals and carbon 2p orbitals of these elements. Also, the charge density for these elements showed that there is more electron accumulation around the Fe and Co atom. But for the Fe doped carbon nanotube there is a sharp peak in the Fermi energy level which is related to the 2p orbitals of carbon. The presented peak indicates that the electrons of the C atom are not localized and reluctant to be bounded. While in the Co doped carbon nanotube, no peaks were observed in the Fermi energy level. The binding energy was stronger in the Fe atom since its magnetization changed from  $4.00 \mu_B$  to  $3.40 \mu_B$  while the Co atom changed from  $3.00 \mu_B$  to  $1.75 \mu_B$ . The greater decrease in magnetization causes the

larger increase in binding energy. Bounding of these elements on the surface of a carbon nanotube makes them a valuable candidate for hydrogen adsorption.

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