

# Original Article



## Amino acids interacting with defected carbon nanotubes: ab initio calculations

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### Abstract

The adsorption of a number of amino acids on a defected single-walled carbon nanotube (SWCNT) is investigated by using the density-functional theory (DFT) calculations. The adsorption energies and equilibrium distances are calculated for various configurations such as amino acid attaching to defect sites heptagon, pentagon and hexagon in defective tube and also for several molecular orientations with respect to the nanotube surface. The results showed that amino acids prefer to be physisorbed on the outer surface of the defected nanotube with different interaction strength following the hierarchy histidine > glycine > phenylalanine > cysteine. Comparing these findings with those obtained for perfect SWCNTs reveals that the adsorption energy of the amino acids increase for adsorption onto defected CNTs. The adsorption nature has also been evaluated by means of electronics structures analysis within the Mulliken population and DOS spectra for the interacting entities.

**Keywords:** Amino acids; SWCNTs; Defects; Adsorption; Density functional theory

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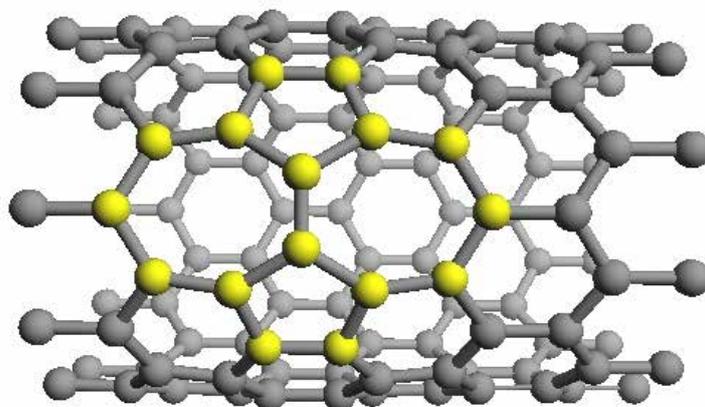
## INTRODUCTION

Since the discovery of carbon nanotubes (CNTs), critical investigation is ongoing in the effort to understand the tremendous potential applications of such nanostructures in diverse areas including flat panel displays, microelectronic devices, chemical and electro-mechanical sensors and fuel cells (Anantram et al. 2006). An exceptional line of research on CNTs focuses on the fusion of CNTs with a multitude of biological substances such as proteins, to form composite materials that benefit the electrical and mechanical properties of CNTs (Lin et al. 2004). Additionally, there is great potential for developing immobilization of biological substances, sensors and drug delivery through the functionalization of single-wall nanotube (SWNT) functionalization with biological molecules (Zhao et al. 2006; Star et al. 2003; Gao et al. 2004). It was shown recently that the hybridization between corresponding strands of DNA could be detected on the surface of a CNT (Star et al. 2006; Jeng et al. 2006) and thus could be applied to utilize CNTs for the precise detection of specific genes (Hwang et al. 2006). The roles of particular amino acids in direct protein interaction with nanotubes is suggested by the direct peptide bindings on CNTs (Wang et al. 2003; Trzaskowski et al. 2006), although it is recognized that we still require better grasp of the interfaces of these systems. A fundamental theoretical and systematic understanding on bridging carbon nanotubes with biological substances should be crucial in designing life sciences-related tools that employ these nanomaterials, whether it is for drug delivery

or for any other envisioned application. As a result, considering particular forms of samples and analyzing the adsorption properties may uncover the appropriate tube parameters like defects for optimizing the adsorption capability in nanotubes.

A couple of theoretical works based on simulation studies were released on the amino acid adsorption in SWCNTs. Roman et al. (2006) applied density functional theory (DFT) method to research the adsorption of amino acids on a very small-diameter ( $\sim 4 \text{ \AA}$ ) CNT. Furthermore, they restricted their calculations to the adsorption of amino acids on the exterior surface of the flawless nanotubes. We recently explored the interaction of amino acids with a perfect (10, 0) semiconducting CNT (Ganji, 2009).

In the contemporary investigations, we have conducted geometric optimizations using the DFT method on the adsorption of amino acids Gly, His, Phe and Cys on the zig-zag (10, 0) SWCNT with structural imperfections. Comparison of the two sets of outcomes enables us to evaluate the impact that imperfections have on the interaction of amino acids with CNTs. To evaluate the role of structural defects on the amino acids adsorption, we have introduced defects like pentagon and heptagon in the hexagonal structure of the carbon nanotubes, as depicted in figure 1, and calculated the adsorption (binding) energies  $E_{ads}$  for different configurations with respect to these defect sites. The computational details for calculating the adsorption energies and the method of construction of amino acids/nanotubes complexes are given in detail in the next section.



**Figure 1. The optimized geometric structures of the defected (10, 0) single-walled CNT.**

## COMPUTATIONAL METHODS

We employed a supercell approach in all our calculations. The unit cell of a (10, 0) SWCNT consisting of a ring of 96 carbon atoms with a diameter of about 8 Å was repeated three times along the tube axis. In the direction perpendicular to the tube axis, a distance of at least 18 Å was kept between repeated units to avoid interactions between adjacent CNTs. We used a  $1 \times 1 \times 5$  Monkhorst–Pack grid for k-point sampling of the Brillouin zone.

The structural optimizations of carbon nanotubes and amino acids are carried out using the recently developed DFTB+ code (Aradi et al. 2007). The DFTB+ employs the density functional based tight binding (DFTB) method based on a second-order expansion of the Kohn-Sham total energy in density functional theory with respect to charge density fluctuations. The DFTB approach utilizes a tabulated set of integrals derived from ab initio DFT calculations (Seifert et al. 1996), leading to a substantial speed up of the method. Contrasting to the usual tight-binding method it is possible to produce parameterizations capable of accuracy close to local density approximation (LDA)/generalized gradient approximation (GGA) with minimal adjustable parameters and also transferable between different systems. Further details of the method have been fully reviewed for instance in references (Aradi et al. 2007; Seifert et al. 1996; Frauenheim et al. 2000; Frauenheim et al. 2002). In this study, the Slater-Koster type parameter set (Eltner et al. 1998) was applied. The dispersion corrects for the van der Waals interaction have also been considered via the Slater-Kirkwood type model (Eltner et al. 2001).

The total energy calculations for the interaction between CNTs and amino acids (binding energies) are carried out using the ab initio DFT code SIESTA (Ordejón et al. 1996; Soler et al. 2002). The GGA with the Perdew-Burke-Ernzerhof functional was adopted to treat electron exchange correlation (Perdew et al. 1996). The core electrons are represented by improved Troullier-Martins pseudopotentials, and a numerical atomic orbital basis with polarization is used for the valence electrons. All total energy calculations were done with a double- $\zeta$  plus polarization basis set. From the well known expression for calculating the molecular adsorption energies,  $E_{ads}$  are

obtained for various cases of our study.

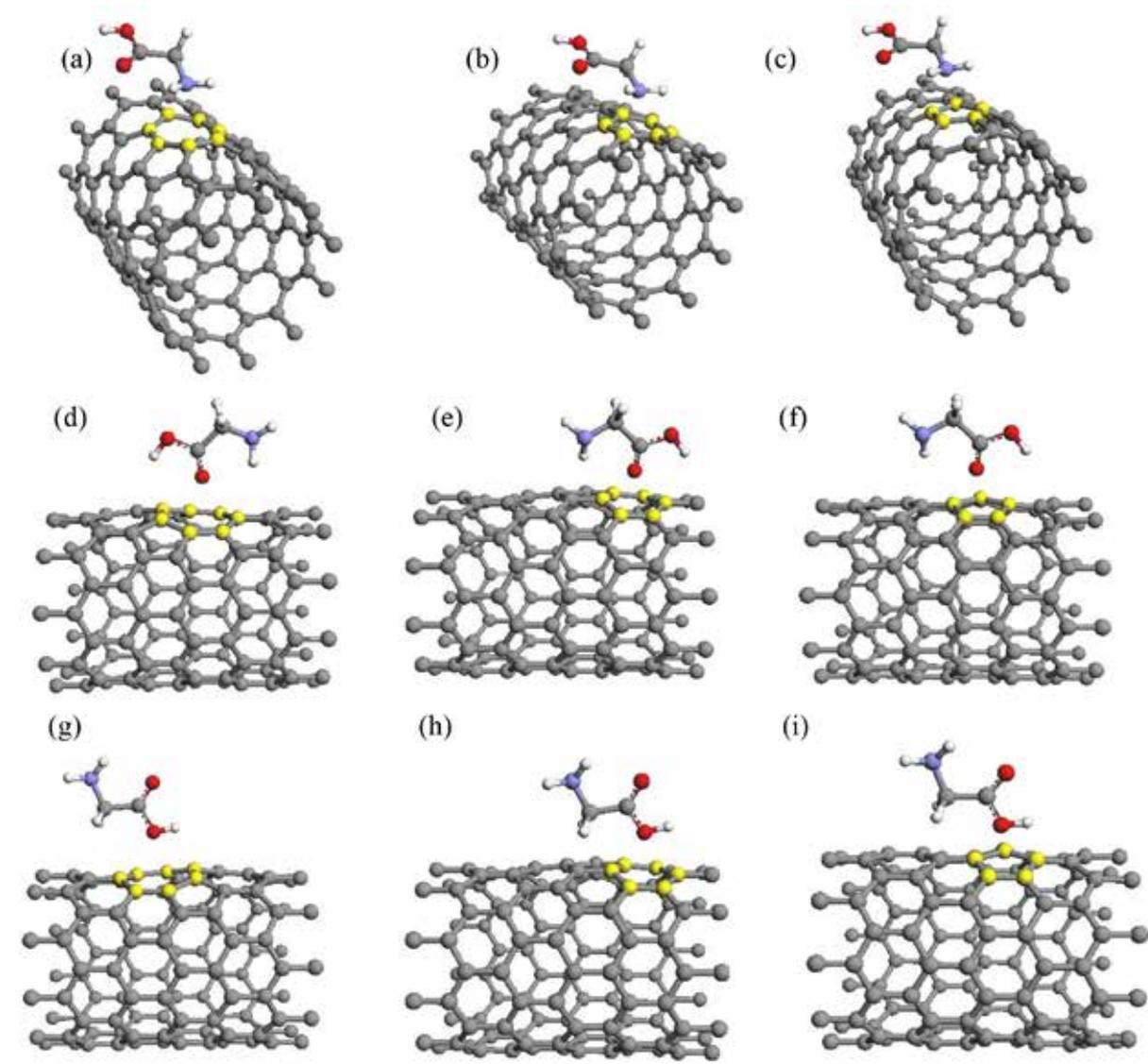
$$E_{ads} = E_{CNT-AA} - E_{CNT} - E_{AA}$$

where  $E_{CNT-AA}$  is the total energy of the CNT with an adsorbed amino acid molecule,  $E_{CNT}$  is the pure CNT and  $E_{AA}$  is the total energy of the isolated amino acid molecule. Our considered models for Gly involve the molecule in its non-ionic forms and the fragment that would form part of the polypeptide backbone ( $NH_2CHCOOH$ ) for His, Phe, and Cys have been replaced by terminating hydrogens. As the twenty most ordinary amino acids mainly differ through their corresponding side-chains, we focus on those sections only, somewhat due to decreasing the computational cost of the calculations (Roman et al. 2006). It should be noted that, the His is demonstrated by an imidazole ring with an attached methyl group, the sulfur-containing Cys with a methanethiol molecule, and Phe with toluene.

## RESULTS AND DISCUSSION

The introduced structural defects such as pentagon and heptagon may play a significant role in the electrochemical properties such as adsorption on the nanotubes. Several research works have studied the adsorption of various molecular systems on defected nanotubes. To evaluate the influence of structural defects on the amino acid adsorption in CNTs, two heptagons and two pentagons are inserted in the hexagonal structure of considered tube in this work.

We first investigate the adsorption of glycine (Gly) amino acid on the outer surface of the defected (10, 0) SWCNT. The Gly molecule has three active sites, the amino nitrogen (N), the hydroxyl oxygen (OH) and the carbonyl oxygen (O) groups thus it is expected for Gly to interact with the CNTs via these active sites. In order to examine the adsorption of a Gly on the CNTs, nine possible configurations were selected for a molecule approaching the center of a heptagon/hexagon/pentagon of carbon atoms via its amino nitrogen (N), carbonyl oxygen (O) and hydroxyl oxygen (OH) active sites. The orientation schemes employed in modeling the Gly adsorption are shown in Fig. 2. The hollow site positions have similarly been adopted for the side chains of

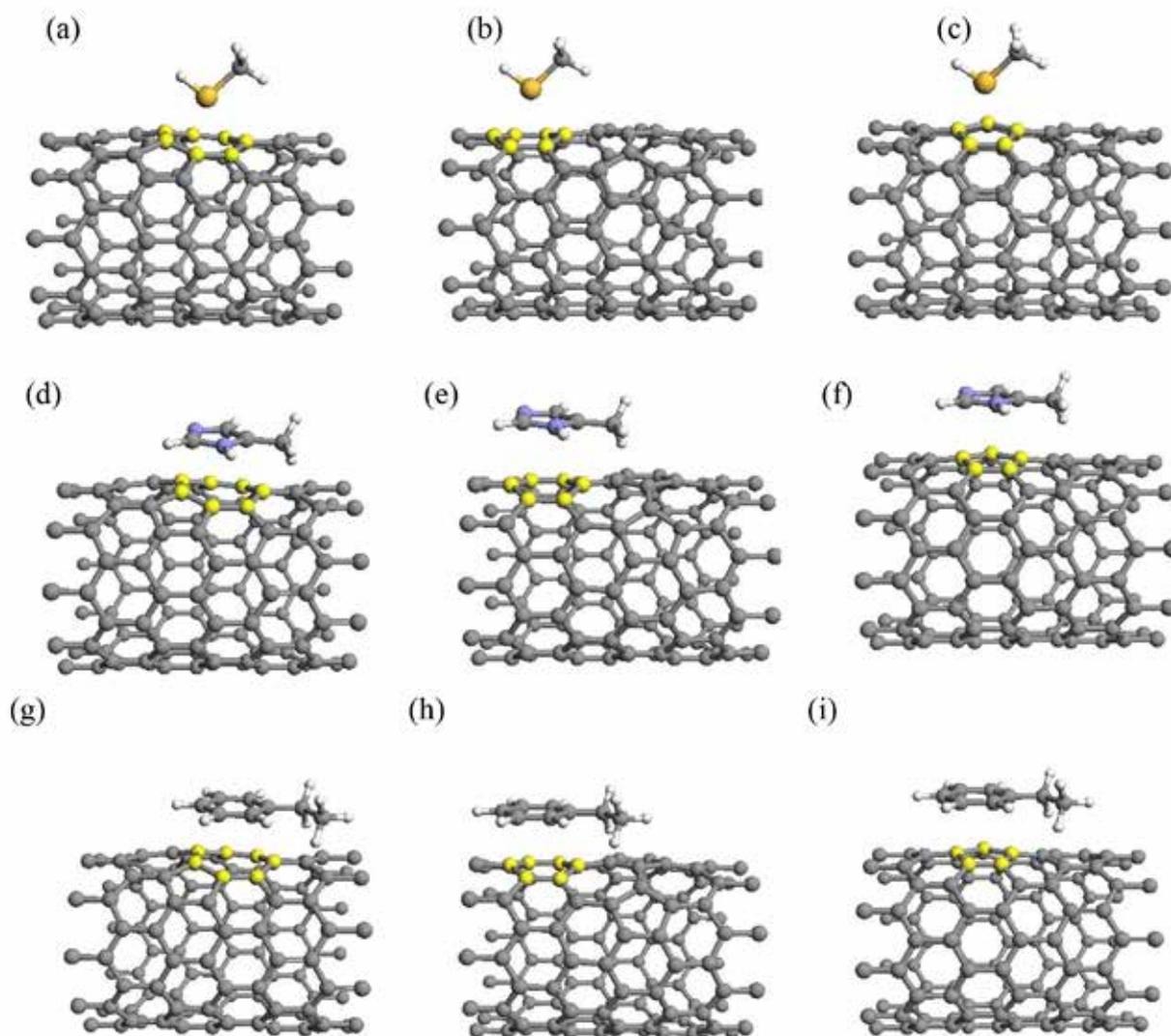


**Figure 2. Model for nine different adsorption states for a nonionic-glycine molecule on the defected sidewall of the (10, 0) CNT above a defect site heptagon substrate via (a) the amino nitrogen (N), (b) hydroxyl oxygen (OH) and (c) carbonyl oxygen (O) active sites. The similar adsorption states with respect to the hexagon and defect site pentagon rings represented in (d)-(i). Atom colors: grey—carbon, white—hydrogen, blue—nitrogen and red—oxygen.**

Cys, while the aromatic ring of Phe and His are AB stacked with respect to the substrate geometry (Fig. 3).

After full structural optimization of the considered systems, we find that His bound rather strongly to the pentagon/heptagon of carbon atoms of defected tube via its aromatics, while the binding for Cys with the CNT surface (pentagon ring) is the weakest. The binding energy for the energetically favorable

complex and the equilibrium distance between the closest atom of the His to the nanotube (C in CNT and H in His) are about  $-0.87$  eV ( $-20.06$  kcal/mol) and  $2.610$  Å, respectively (see Fig. 4(a)). The  $\pi$ - $\pi$  interactions between His and hexagonal ring of nanotube surface should promote adsorption of the molecule in introducing a stacking character to the amino acid-carbon substrate interaction, which is accompanied by charge transfers from the



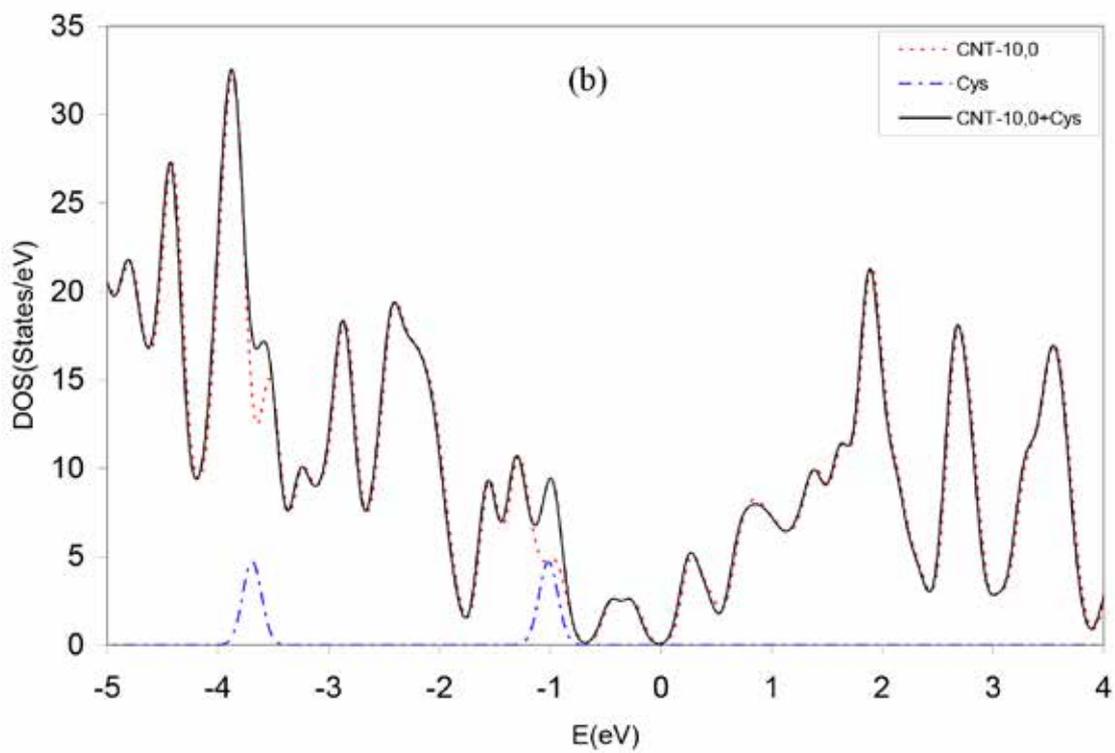
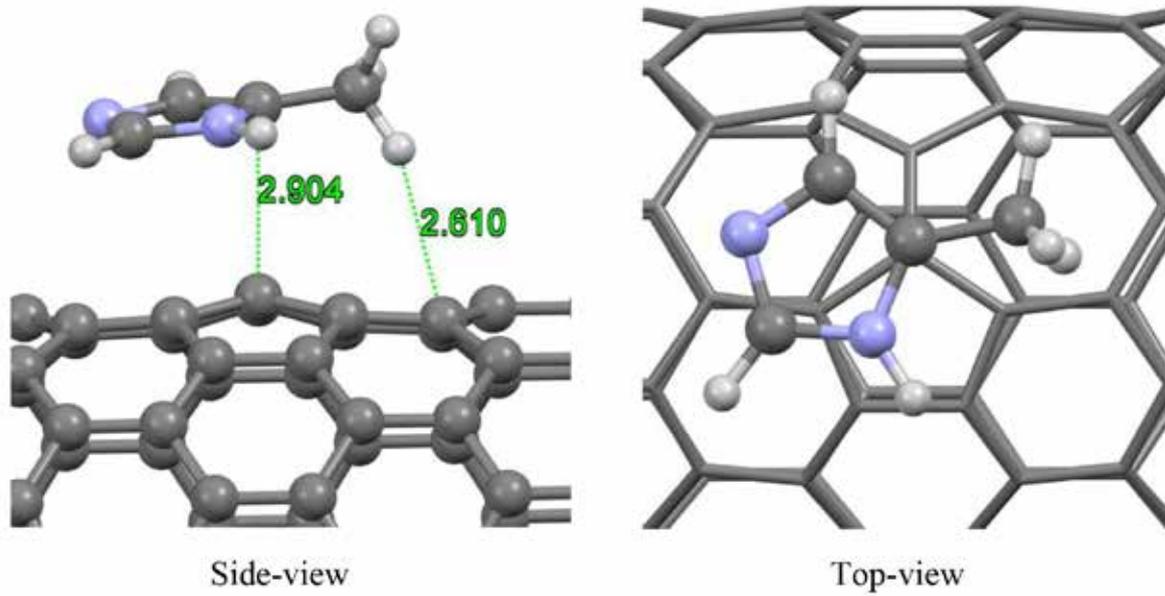
**Figure 3.** Model for three different adsorption states for a cysteine molecule on the defected (10, 0) CNT above a (a) heptagon (b) hexagon and (c) pentagon ring of the tube. The similar adsorption states for the phenylalanine and histidine amino acids with the imidazole ring oriented parallel to the substrate are represented in (d)–(i).

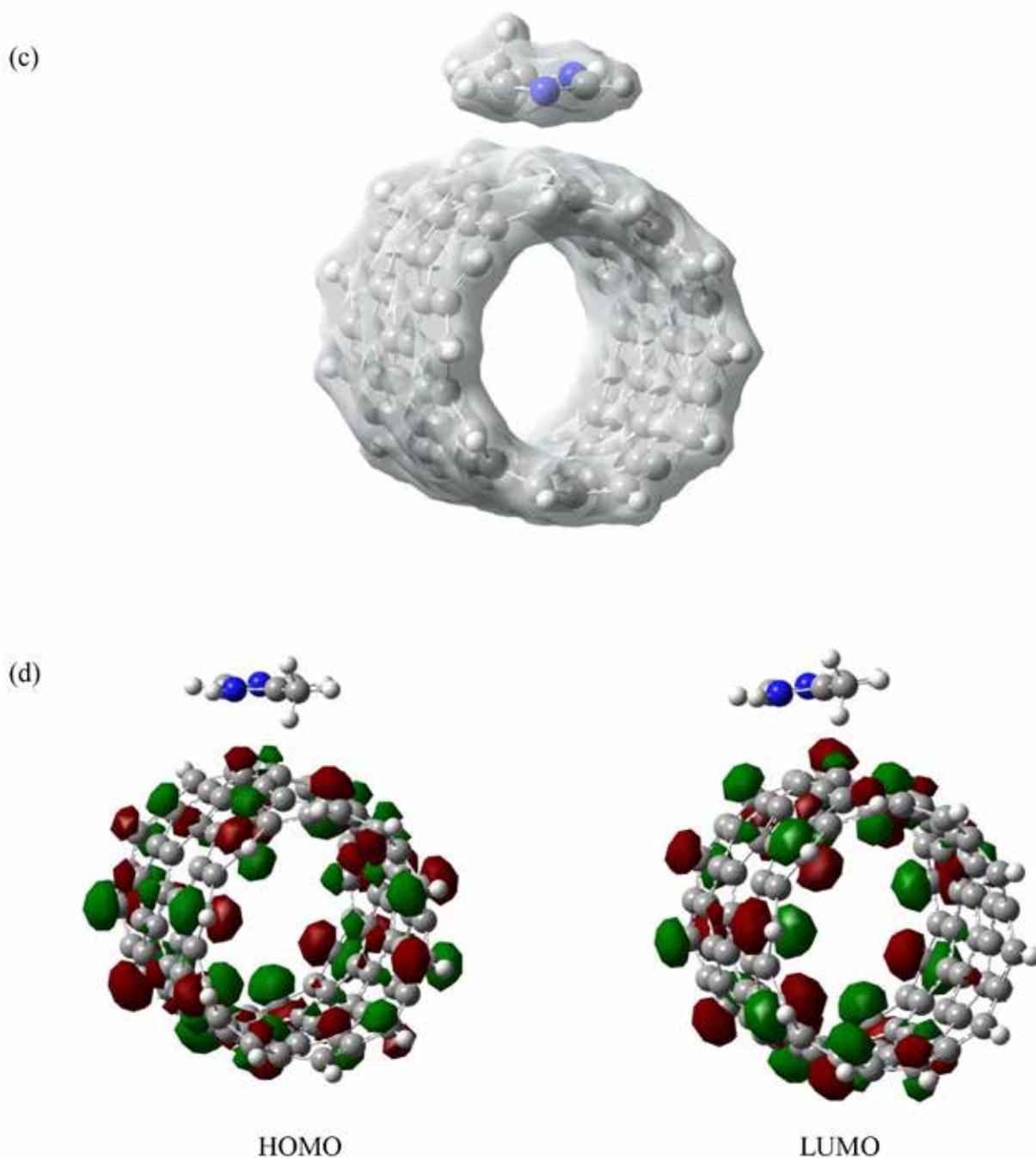
carbon substrate (Roman et al. 2006; Ganji, 2009).

The calculated binding energies  $E_b$  for all the considered systems are summarized in Table 1. It was found that adsorbed amino acids possess different interaction strength and calculated binding energies follow the hierarchy His > Phe > Gly > Cys. It can be understood from the comparison of the obtained binding energies with the previous study (Ganji MD, 2009), that except for the Gly amino acid the binding energy of all type of considered amino acids is increased ( $\sim 15\%$ ) for adsorption on the defected CNTs. The obtained results

reveal also that amino acids are physisorbed to the outer surface of the defected nanotubes, having adsorption energies comparable to the adsorbed nucleic acid bases and molecular gases on carbon based nanostructures (Ganji et al. 2010; Ganji et al. 2010; Ganji et al. 2013; Ganji et al. 2014; Ganji et al. 2015).

To further investigate the binding of amino acids to the outer surface of defected carbon nanotubes, the calculations of the Mulliken charge transfer between His and CNT and also Cys and CNT systems were also performed. Charge analysis shows 0.15 e charge transferred from the CNT to the adsorbed





**Figure 4.** (a) The optimized geometric structures of the His amino acid adsorbed on the hexagon of the defected nanotube. (b) Calculated density of states for an isolated cysteine molecule (Cys), an isolated defected CNT, and the combination of the two at equilibrium geometry (Cys–defected CNT). The calculated (c) total charge density and (d) orbital localized HOMO and LUMO of His/CNT system. (Red and green colors denote the negative and positive signs of the Wave function)

**Table 1. Adsorption energies Eads of adsorbed amino acids on the defected (10, 0) single-walled CNT.**

<b>(a) Pentagon defect</b>				
<b>Complex Acid/CNT</b>	<b>Cys</b>	<b>n-Gly (N/O/OH active site)</b>	<b>His</b>	<b>Phe</b>
Eb (eV)	-0.24	-0.65/-0.73/-0.48	-0.87	-0.77
<b>(b) Hexagon defect</b>				
<b>Complex Acid/CNT</b>	<b>Cys</b>	<b>n-Gly (N/O/OH active site)</b>	<b>His</b>	<b>Phe</b>
Eb(eV)	-0.28	-0.70/-0.85/-0.52	-0.82	-0.80
<b>(c) Heptagon defect</b>				
<b>Complex Acid/CNT</b>	<b>Cys</b>	<b>n-Gly (N/O/OH active site)</b>	<b>His</b>	<b>Phe</b>
Eb (eV)	-0.35	-0.75/-0.74/-0.52	-0.86	-0.78

z-Gly while for the Cys with CNT, 0.07 e were found to have been transferred from the CNT to the amino acid molecule. As a result, the relatively far equilibrium amino acids-carbon substrate separation, small adsorption energy, and absence of significant charge localization associated in strong chemical bonds all suggest the involvement of only non-covalent interactions in the adsorption.

To further understanding of the interaction between amino acids and defected CNTs, we also analyzed the density of state (DOS) for the combined system of amino acid/defected CNT and compared with the corresponding DOS for the individual parts, i.e., defected CNT and amino acid molecule separated. Figure 4 (b) shows the total electronic DOS for the Cys/CNT complex. It can be seen from the figures that the DOS of the combined system of Cys/CNT is almost exactly the superposition of the DOS of the individual parts. This finding highlights that the Cys and CNTs are interacting rather weakly, and that no significant hybridization between the respective orbitals of the two entities takes place, the unveiling the small interaction obtained quantitatively in terms of binding energies. Furthermore, the total charge density was calculated for the His molecule adsorbed on the defected CNT and depicted in Fig. 4(c). As it can be seen

from the charge density, the adsorbed His located far from the nanotube surface and the electronic charge distributions across the C atoms of CNT remain unaltered. This observation reveals that there is physical interaction between two interacting molecules. Finally, the isosurface plots of HOMO/LUMO on the His/CNT are calculated and shown in Fig 4(d). It can be found from the figure that densities of both the HOMO and LUMO states are located on the CNT. From the negligible overlapping of electron clouds between the His molecule and CNT one can conclude that there is no evidence of hybridization between the His amino acid and defected CNT and does not have significant influence on the electronic structure of the CNT in adsorption.

From the calculation results involving in this paper, one can predict that amino acids might readily form more stable bindings with the defected surface of carbon nanotubes in comparison to the perfect nanotubes. The present adsorption processes modeled here suggest that if for specific applications amino acids or even entire proteins are to be adsorbed on the defected nanotubes through the amino acids molecules discussed in this paper, then doing so through His and Phe amino acid may give the most favorable results.

## CONCLUSION

DFT based treatments have been performed on the interaction of amino acids with the defected (10, 0) SWCNT. The calculated results showed that the His molecule was adsorbed on the nanotube over the pentagon of carbon atoms can form most stable complex while the binding of cysteine to the hexagon of carbon atoms of the tube is the weakest. Comparing the present results with those obtained for ideal CNTs revealed that the binding energy of the amino acid molecules is increased for physisorption on defected CNTs. There is an increase in the adsorption binding energy of the order of 15% due to the presence of structural defects in CNTs, which will affect the amino acids adsorption in carbon nanotubes. Consequently, we could say that defects have an important contribution to the adsorption mechanism of SWCNTs.

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