Carbon nanotubes interacting with vitamins: First principles calculations

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ABSTRACT

Electronic and structural properties of carbon nanotubes interacting with vitamins C and B3 radicals are analyzed through the density functional theory. The radical adsorptions result in modifications on the structural and electronic properties of the original carbon nanotubes. The strong adsorptions resulting from the combination of the carbon nanotubes with ascorbic acid and nicotinamide allow the manipulation of the resulting systems in a stable way. These results are extremely relevant in order to identify the potential applications of functionalized carbon nanotubes as drug delivery systems or molecule sensors.

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1. Introduction

Due to their prominent features, carbon nanotubes (CNs) have aroused huge curiosity on the scientific community. There is a great attention on how to combine these materials with substances of therapeutic purpose, being possible to connect biological molecules, such as drugs, on their shells [1].

CN associated with pharmaceutical compounds can develop promising systems for drugs dissemination. In this context, this work studies possible routes of vitamins C (ascorbic acid, labeled VTC) and B3 (nicotinamide, labeled VTB) molecules adsorption on the semiconductor (8,0) and on the metallic (5,5) CN surfaces. Both vitamins present certain instability that can be controlled by the association with other chemical species as CNs, which are highly stable molecules. The vitamins are soluble in water molecules and part of many other chemical complexes, and they are necessary for the appropriate working of the organism, beyond additional biochemical, therapeutically and cosmetic functions [2–6].

2. Methodology

The *ab initio* calculations of the ascorbic acid and nicotinamide molecules adsorbed on the single-walled carbon nanotubes (SWCNTs) are studied based on the density functional theory (DFT) [7,8], using the SIESTA code [9]. More details about the computational procedures are described in Ref. [1]. Vitamin B3 can occur in the nicotinic acid or nicotinamide forms, however this work includes only the CN interacting with nicotinamide molecules.

The binding energies (E_b) are calculated using the basis set superposition error (BSSE) [10]. This correction is done through the counterpoise method using "ghost" atoms, as the following equation:

$$E_b = -[E_T(SWCNT + X) - E_T(SWCNT + X_{ghost}) - E_T(SWCNT_{ghost} + X)], \quad (1)$$

where X = VTC- or VTB-radical and $E_T(SWCNT+X)$ is the total energy of the SWCNT interacting with the radical. The "ghost" SWCNT/X corresponds to additional basis wave functions centered at the position of the SWCNT/X, but without any atomic potential.

3. Results and discussion

The equilibrium geometries for the pristine (5,5) CN, isolated ascorbic acid and nicotinamide molecules are shown in Figs. 1(a), (b) and (c), respectively.

For the adsorption of the VTC molecule, one hydrogen atom was removed from one hydroxyl group, and then the resultant oxygen atom approached the CN surface, corresponding to the configuration labeled as VTC+(5,5)-radical-1H (Fig. 1 (d)) or VTC+(8,0)-radical-1H. For the nicotinamide molecule (VTB), one hydrogen atom was removed from the amine group with the nitrogen atom moving towards the CN, labeled as VTB+(5,5)-radicals-1H (Fig. 1(e)) or VTB+(8,0)-radicals.

In Table 1, the closest distances between CN and VTC- and VTB-radicals are listed. The VTC-radical-1H and VTB-radical-1H arrangements present the closest distances with (5,5) CN as 1.44 and 1.47 Å, respectively.

Covalent bonds between the CN and the radical are formed in the studied configurations. For the VTC+(5,5)[(8,0)]-radical-1H and VTB+(5,5)[(8,0)]-radical-1H configurations the resulting

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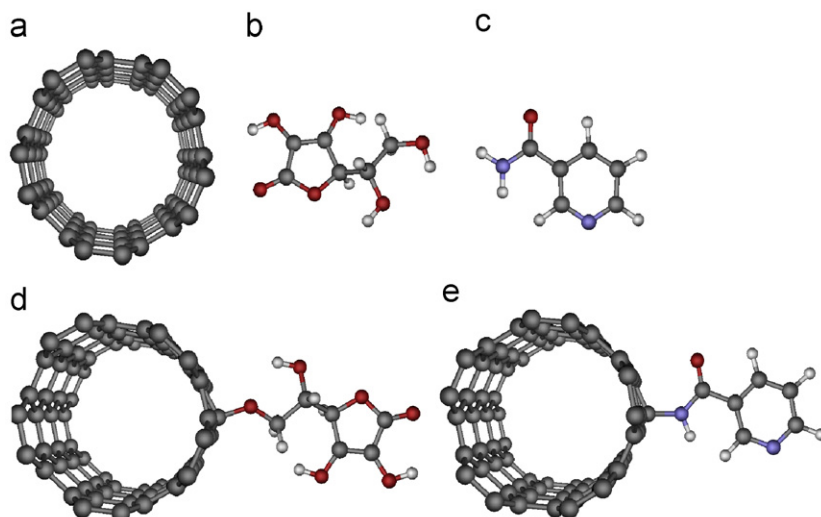
Fig. 1. Relaxed atomic structures for (a) (5,5) CN, (b) ascorbic acid and (c) nicotinamide molecules. In (d) VTC+(5,5)-radical-1H and (e) VTB+(5,5) -radical-1H.

Table 1
Relevant interatomic distances and binding energies (E_b) for the VTC and VTB molecules, in different configurations, interacting with (8,0) and (5,5) CN.

Configuration	Bond	Distance (Å)	E_b (eV)
VTC-radical-1H-(8,0)SWCNT	C_{tube}–O	1.45	2.11
VTC-radical-1H-(5,5)SWCNT	C_{tube}–O	1.44	2.47
VTB-radical-1H-(8,0)SWCNT	C_{tube}–N	1.47	3.22
VTB-radical-1H-(5,5)SWCNT	C_{tube}–N	1.47	3.46
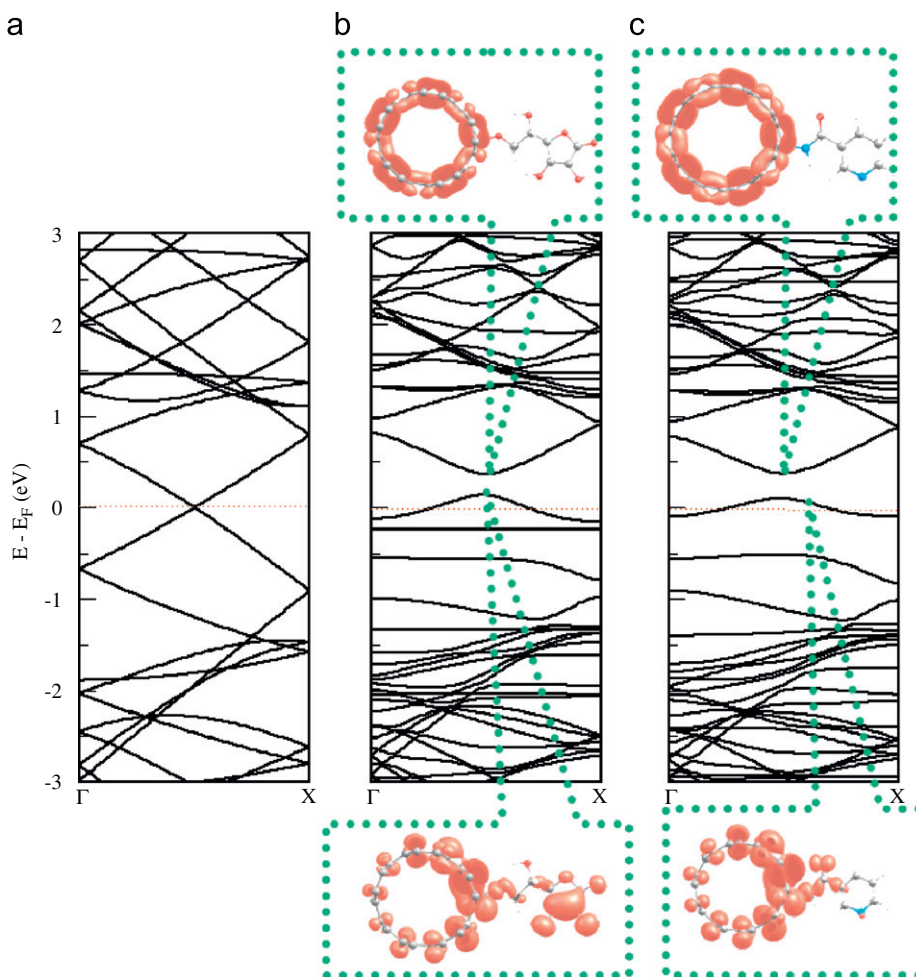
Fig. 2. Electronic band structures for the (a) (5,5) CN, (b) VTC+(5,5)-radical-1H and (c) VTB+(5,5)-radical-1H configurations.

binding energies are 2.47 [2.11] and 3.46 [3.22] eV, respectively. These values indicate that the VTC- and VTB-radicals form a strong chemical bond with the CN and that the systems could be manipulated in a rather stable way, similar to that previously observed with the functionalized CN with carboxyl, hydroxyl or amine groups [11–13].

The electronic band structures for the VTC- an VTB-radicals interacting with SWCNT (5,5) are presented in Fig. 2. The interaction lifts the degeneracy of the electronic bands close to the Fermi energy, breaking the CN mirror symmetry [13,14]. In both cases, there is one carbon atom of the CN that is sp^3-like hybridized due the interaction with the molecule radicals.

The isosurface plot for the valence and conduction electronic bands of the VTC+(5,5)-radical-1H and VTB+(5,5)-radical-1H are shown in the inset of Figs. 2(b) and (c), respectively. The valence states are localized on the CN and the vitamin radicals. However, for the conduction bands the electronic charge contribution are basically localized on the nanotube surface. These analyses also corroborate the strong interaction between the CN surface and the vitamin radicals.

4. Conclusions

In summary, the ascorbic acid and nicotinamide radicals interacting with the (5,5) and (8,0) CNs are reported using *ab initio* calculations. The results demonstrate that the strong interactions between VTC- or VTB-radicals and the CN lead to significant changes on the electronic properties. The resulting adsorption allows the manipulation of the systems in a stable way, resulting also in interesting possibilities for the drug carrier under appropriate circumstances. These observations are extremely relevant in order to identify the potential applications of CN as drug delivery or molecule sensors.

Acknowledgements

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