

Functionalization of carbon nanotube by carboxyl group under radial deformation



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ABSTRACT

The dependence of the structural and the electronic properties of functionalized (5, 5) single-walled carbon nanotubes (SWNT) were investigated through *ab initio* density functional simulations when the carboxyl group is bonded on the flatter or curved regions. Radial deformations result in diameter decrease of up to 20 per cent of the original size, which was the limit reduction that maintains the SWNT functionalized structure. Changes on the electronic structure were observed due to the symmetry break of the SWNT caused by both the carboxyl group and the C–C bond distortions resulted by the radial deformation. It is observed that the functionalization process is specially favored by the sp^3 hybridization induced on the more curved region of the deformed SWNT.

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1. Introduction

Carbon nanotubes (CNT) represent one of the most attractive areas in nanoscience with potential for applications in new technologies. These nanostructures may exhibit metallic or semi-conducting behavior depending only on their chirality [1]. Single-walled carbon nanotubes (SWNT) are fundamental materials because they represent the basis of theoretical predictions and prior experimental observations [2–4].

Due to the high stability and chemical inertness of SWNT and their apolar character, the main barrier towards biologic applications is its insolubility in polar solvents such as water [5,6]. Thus, the functionalization of the SWNT is presented as an alternative to make them soluble in water, and the most common chemical group for this proposal is the –COOH radical [7], since it binds covalently to the carbon atom of the nanotube, making it easy to remove the –OH radical through a coupling agent [8]. Thus, a variety of potential applications has been suggested to apply the functionalized SWNT by the –COOH group in various areas [3].

At the same time, due to its tubular geometry, the CNT show high flexibility and high Young's modulus. Thus, many studies have been conducted in order to identify changes of structural, elastic and electronic properties of CNT under pressure [9,10]. Structural deformations can occur on CNT due to the growth, purification or devices production process. Therefore, the development of such

devices awakes, mainly, the need for understanding the electronic and structural properties of deformed SWNT [11,12].

Pressure or strain applications have been investigated in CNT using different approaches as radial deformations and uniaxial and torsional strain [13]. Axial strain studies show that the structural properties of CNT have a strong tendency to preserve its radius even under high tension and compression [10]. Already, in studies of radial deformation, the behavior of armchair nanotubes radially collapsed can be experimentally observed by scanning tunneling microscopy. These experiments show that changes in the electronic structure are directly related with the structural disturbances [14]. Similarly, theoretical studies show electronic transitions, as semiconductor–metal [15] and metal–semiconductor, for CNT radially deformed [16–18].

The functionalization associated with radial deformation of carbon nanotubes open new perspectives for the application of these nanomaterials. They are predicted for biological applications such as drug carrier [19] and in the theranostics diseases [20], once some cooperative deformations can occur due to the functional groups as seen by Nair et al. [21]. Additionally, they are also important systems in nanoelectronic devices as well as in nanomaterials subject to high pressures and high-impact. Being more specifically, the functionalized carbon nanotubes used in nanocomposites, have revealed to enhance their mechanical properties [22,23].

The main focus of this work is to evaluate the effect of the radial deformation on the functionalized SWNT with carboxyl group in comparison to the non deformed and pristine ones. From this point of view, as well as Veloso et al. [24], Saidi et al. [25], and Nair et al. [21] we have studied carbon nanotubes with no solvent

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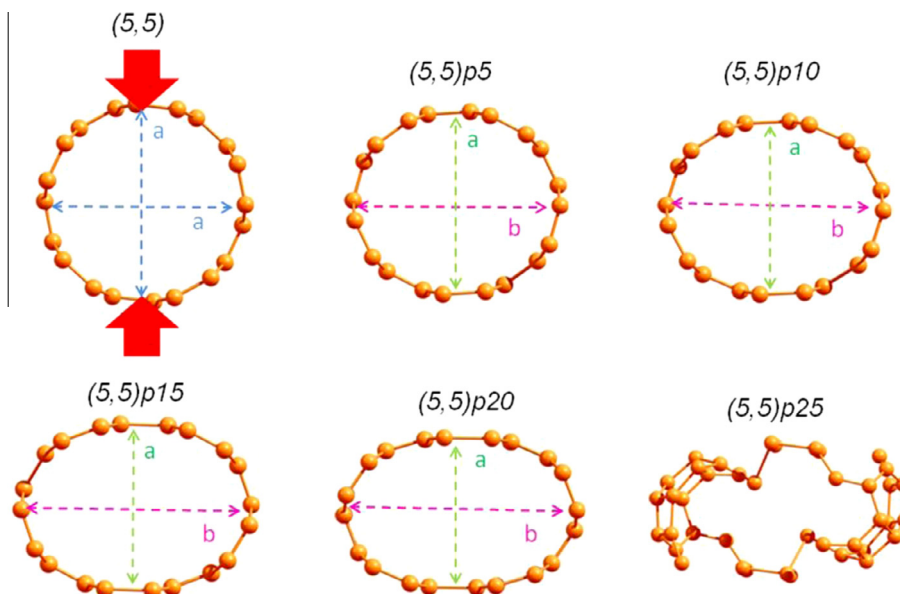


Fig. 1. Scheme adopted to evaluate the increasing radial deformation until 25% of reduction in the SWNT diameter. The a and b axis of each configuration is indicated.

Table 1
The C–C bond distances (d_{C-C}), θ_{CCC} angles, electronic 0 charge transfer (the + sign means that the charge is transferred from the SWNT to the carboxyl group), spin polarizations, binding energies (E_b) as well as the a/b axis ratio.

Configuration	d_{C-C} (Å)	θ_{CCC}	E_b (eV)	Charge transfer (e^-)	Spin Polarization (μB)	a/b
(5,5)-COOH	1.55	109.50	2.03	+0.15	–	1
(5,5)p5-curve	1.54	110.05	2.10	+0.15	–	0.88
(5,5)p10-curve	1.54	110.32	2.18	+0.15	–	0.80
(5,5)p15-curve	1.54	114.46	2.27	+0.14	–	0.73
(5,5)p20-curve	1.55	114.41	2.41	+0.15	–	0.66
(5,5)p5-flat	1.55	113.42	1.69	+0.14	–	0.88
(5,5)p10-flat	1.56	112.56	1.52	+0.13	–	0.80
(5,5)p15-flat	1.62	99.67	1.42	+0.11	0.80	0.73
(5,5)p20-flat	1.62	98.25	1.45	+0.11	0.84	0.66

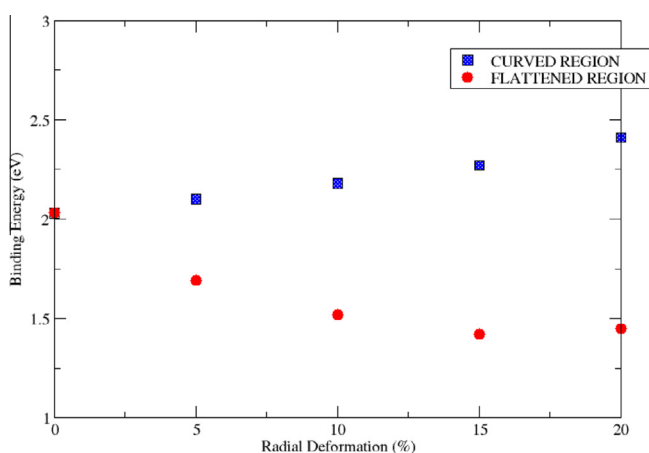


Fig. 2. Binding energy values versus the radial deformation for the carboxyl group attached to both the more curved and the flatter region.

interactions, vacancies or defects. This option is due to the fact that we are not interested exactly on the specific carboxyl group functionalization mechanism or process once this procedure is still not yet well established from the theoretical calculation standpoint. Although, it is identified that structural defects on the hexagonal

structure of the CNT are known to raise their reactivity [26]. Then, in this paper, the influence of the radial deformation of the (5, 5) SWNT functionalized by chemical groups, that can introduce sp^3 hybridization, is evaluated through an *ab initio* study.

2. Methodology

The structural and electronic behavior of the –COOH groups localized in different positions on radially deformed (5, 5) SWNT was studied by electronic structure calculation with the SIESTA program [27], which implements the density functional theory by solving the Kohn–Sham equations [28]. In all calculations we used the local density approximation (LDA) parameterized by Perdew and Zunger [29] to describe the exchange–correlation potential. The interactions between the core and the valence electrons were employed through Troullier–Martins pseudopotentials [30], whereas the molecular orbitals were made use of a localized double zeta plus polarization (DZP) basis set, through a limited energy shift of 0.03 eV. For the Brillouin zone integration along the tube axis it was used 16 Monkhorst–Pack k -points.

In order to characterize how these systems are interacting, the binding energy (E_b) between the carboxyl groups and the SWNT was analyzed through the following equation:

$$E_b = E_{total} - E_{SWNT} - E_{COOH}. \quad (1)$$

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