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Structural and electronic properties of zigzag carbon nanotubes filled with small fullerenes

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Abstract

In this work we investigated the encapsulation of C_{20} and C_{30} fullerenes into semiconducting carbon nanotubes to study the possibility of bandgap engineering in such systems. Classical molecular dynamics simulations coupled to tight-binding calculations were used to determine the conformational and electronic properties of carbon nanotubes with an increasing fullerene concentration. We have observed that C_{20} fullerenes behave similarly to a ntype dopant while C_{30} can provide p-type doping in some cases. The combined incorporation of both types of fullerenes (hybrid encapsulation) into the same nanotube leads to a behaviour similar to that found in electronic pn-junctions. These aspects can be exploited in the design of nanoelectronic devices using semiconducting carbon nanotubes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discovery of fullerenes [1] and carbon nanotubes [2, 3] opened a new and enormous field in theoretical and experimental research. The development and improvement of the manipulation and fabrication methods of these structures, especially single-walled carbon nanotubes (SWNTs), have allowed a large number of technological applications. Hence, there is a growing need for a detailed understanding of the experimental results, as well as the exploration of promising properties due to the remarkable electronic and/or mechanical characteristics of these systems.

Depending on their structure, SWNTs are either metallic or semiconducting, a feature that has been intensively investigated and exploited in prototype devices. Armchair (n, n) SWNTs are metallic, while zigzag (n, 0) SWNTs, when n is not a multiple of 3, are semiconducting.

However, for zigzag tubes with large diameters, i.e., for large values of *n*, metallic behaviour is again observed [4].

An increasing interest is being devoted to the tuning of the electronic and mechanical properties through the process of incorporation of organic and inorganic compounds into SWNTs. The encapsulation of C₆₀ into SWNTs, generically called peapods [5], opened a wide research field in chemistry and physics, involving, for instance, molecular phase formation confined by the packing effect [6-8], and the transformation of peapods into double-walled carbon nanotubes [9, 10]. The encapsulation of C_{60} within SWNTs can not only affect the electronic structure, but it also alters the vibrational modes associated with the expansion and contraction of the tubes [11]. Okada et al [12], using density functional theory within the local density approximation, have obtained that the (10, 10) peapod presents a metallic behaviour, and it shows significant change of the electronic distribution either on the tube or over the C₆₀ chain. Esfarjani et al [13] have proposed that using donor atoms (potassium) on one side and acceptors (iodine) on the other, semiconducting (10, 0) SWNTs can work as nanodiodes, showing a nonlinear rectifying effect. Lee *et al* [14] have also shown that metallofullerenes can be used as bandgap modulators in semiconducting SWNTs. They also suggested that, with the insertion of different types of metallofullerenes, complex bandgap engineering could be possible. First-principles calculations have shown that the encapsulation of electrophilic (nucleophilic) organic molecules inside semiconducting SWNTs leads to a controllable p-type (n-type) doping [15].

While the encapsulation of C_{60} in small-diameter (<6.4 Å [12]) SWNTs occurs as an endothermic process, other smaller fullerenes, such as C_{20} and C_{30} , could potentially provide exothermic encapsulation and thus be more suitable candidates to modify the properties of semiconducting SWNTs through a peapod configuration. In recent years the interest in fullerenes smaller than C_{60} has considerably increased after the chemical synthesis of the cage C_{20} [16] and studies of the amazing thermodynamical stability of the fullerenes C_i (i = 30-82) [17, 18]. Using molecular dynamics simulations, Du *et al* [19] have studied the deposition of C_{20} fullerenes on a diamond surface used to produce diamond-like carbon films [20]. Recently, Zhou *et al* [21] have theoretically investigated three-dimensional configurations of encapsulated C_{20} and C_{28} in SWNTs. They have obtained similar configurations to the ones predicted for C_{60} encapsulation [6–8].

The diameter-selective encapsulation and the related energetics of C_{60} are relatively well known, and have been studied in several works [22–24]. Okada *et al* [23], for instance, found that the electronic properties of peapods could be modified simply by changing the available space between fullerenes and the nanotube. On the other hand, little is known about the physics of small fullerenes inserted into carbon nanotubes and the effect of the tube's diameter on the electronic structure of the resulting peapod. In this work we focus our interest especially on the feasibility of bandgap engineering in small-diameter zigzag semiconducting SWNTs through the encapsulation of small fullerenes.

2. Methodology

We have considered three zigzag (n, 0) (n = 11, 13 and 17) SWNTs as the confining structures for the small fullerenes. Tubes made of 30 unit cells of the zigzag nanotubes were constructed corresponding approximately to 126 Å in the axial direction.

In order to envisage the possible realization of an SWNT-based pn-junction, i.e., a nanodiode, we have chosen to encapsulate fullerenes that might have complementary properties concerning their doping properties. Specifically, we need the highest occupied molecular orbital energy of one fullerene type to be close to the lowest unoccupied molecular orbital of the

other type. C_{20} and C_{30} fullerenes satisfy these conditions reasonably well, and they are thus good candidates (preferred to the pair C_{60} and C_{70} , which was also considered). Furthermore, due to their reduced size, these fullerenes can also be encapsulated into small-diameter SWNTs and therefore dope relatively wide bandgap structures.

The zigzag single-walled carbon nanotubes were initially optimized using the universal force field [25, 26], implemented on the Cerius2 package [27]. This force field includes van der Waals, bond stretch, bond angle bend, inversion, torsion and rotation terms, and it has been used with success in the study of dynamical properties of crystalline and complex carbon nanostructures [28]. In this work we have used the following Lennard-Jones 6–12 potential to describe the van der Waals interactions between carbon atoms, separated by a distance x,

$$E_{\rm vdW} = D\left[-2\left(\frac{x_0}{x}\right)^6 + \left(\frac{x_0}{x}\right)^{12}\right],\tag{1}$$

where *D* is equal to 0.105 kcal mol⁻¹ and x_0 is equal to 3.851 Å.

For each zigzag nanotube, 1–12 fullerenes C_i (i = 20 or 30) were inserted into the tubes. We label the first (second) group of structures $kC_{20}@(n, 0)$ ($kC_{30}@(n, 0)$) with n = 11, 13, or 17, and $1 \le k \le 12$. A third group was composed of SWNTs filled with 50% of C_{20} and 50% of C_{30} , and named $lC_{20} C_{30}@(n, 0)$ with n = 11, 13, or 17, with $1 \le l \le 4$ corresponding to the number of fullerenes of each type encapsulated into the nanotube. The total number of atoms for the different peapod configurations varied from 1300 up to 2100.

Classical molecular dynamics simulations were used to simulate the encapsulation of C_{20} and C_{30} molecules into SWNTs. Firstly, the fullerenes were placed at an edge of the nanotube. Secondly, a molecular dynamics simulation in the canonical ensemble at 300 K was run for 200–300 ps (time step = 1 fs) to encapsulate the fullerene. This procedure led to the structure $kC_i@(n, 0)$ (k = 1). The process was repeated until k = 12. The structure formed was then geometrically optimized to obtain the minimum energy of the system. These final geometrical optimizations were performed for two cases: one where the tubes are kept fixed (mimicking a multiwalled nanotube environment, where the tube deformation is small due to the confinement caused by the neighbouring tubes) and another where they are also relaxed (mimicking a real single-walled nanotube environment).

The geometries obtained from the molecular dynamics simulations were converted in supercells. The tubes in the supercells were placed 60 Å apart in the perpendicular direction from their periodic images of the neighbouring cells to avoid self-interaction. Using these supercells we have calculated the electronic band structure of $kC_i@(n, 0)$ and $lC_{20} C_{30}@(n, 0)$ using the tight-binding model of Porezag *et al* [29] implemented in the TROCADERO package [30]. This model employs a non-orthogonal s–p basis, in which the hopping matrix elements have been parameterized with density functional theory calculations using the same basis set, but disregarding three-centre contributions to the Hamiltonian. This method has been successfully applied to the prediction of allotropic forms of carbon [31], and it has proved to combine accuracy and reduced computational effort, especially for large systems. The use of the Γ -point for the Brillouin-zone sampling has been shown to be sufficient for the total-energy convergence for the structures considered here.

We have analysed the electronic structure of nanotubes containing C_{20} and C_{30} for two different configurations: firstly, the case of *pure* encapsulation, i.e., only one type of fullerene is inside the nanotube; secondly, the case of an ordered hybrid encapsulation (both types present, C_{20} at one side of the SWNT and C_{30} at the opposite side).

Table 1. Formation energy for the encapsulation of four fullerenes into the zigzag nanotubes considered in this work. Results from tight-binding calculations.

	$\Delta E \; (\text{kcal mol}^{-1})$	
SWNT	C ₂₀	C ₃₀
(11, 0)	476	1004
(13, 0)	-51	-30
(17, 0)	-71	-7

3. Results and discussions

The density of states (DOS) for the SWNTs without fullerenes shows an absence of states (gap) around the Fermi energy, indicating the semiconductor characteristic as expected. The bandgap, within the tight-binding method considered here, is about 0.8, 0.7 and 0.5 eV for (11, 0), (13, 0) and (17, 0) SWNTs, respectively. These values are in agreement with results from the theoretical prediction that the bandgap energy E_{gap} depends on the inverse of nanotube diameter d, i.e., $E_{gap} = 2\gamma_0 a_{C-C}/d$ [4] with the C–C tight-binding overlap energy $\gamma_0 = 2.7$ eV obtained from experimental data fitting [32], and the nearest-neighbour C–C distance $a_{C-C} = 0.142$ nm.

Depending on the relation between the nanotube and fullerene diameters (and assuming the absence of dynamical barriers) the encapsulation process (equation (2)) can be either endothermic ($\Delta E > 0$) or exothermic ($\Delta E < 0$):

$$kC_n + \text{SWNT}(n, 0) \to kC_n \otimes \text{SWNT}(n, 0) - \Delta E.$$
 (2)

In order to obtain information about the energetics of the encapsulation process of the structures investigated here, we estimated the required energy for the incorporation of C_{20} (C_{30}) molecules inside the (n, 0) SWNT for n = 11, 13 and 17, by calculating the total energy of the configurations represented in equation (2) and the formation energy (ΔE).

Table 1 shows the values of formation energy of the systems considered in this work for the resulting structures after full geometrical relaxation. The incorporation of C_{20} and C_{30} fullerenes into the SWNT (11, 0) turned out to be a highly endothermic process, but it is exothermic in the cases of SWNTs (13, 0) and (17, 0).

Previous theoretical studies using bond-order empirical potentials have demonstrated that the incorporation of C_{20} into (n, n) nanotubes occurs as an exothermic process when n > 8, forming a peapod configuration without tube deformation [21]. Our results confirm this tendency since the (13, 0) SWNT has approximately the (8, 8) SWNT diameter. This is an important point, as the exothermicity would greatly ease the encapsulation process.

In figure 1 we show the DOS of the endothermic system $C_{30}@(11, 0)$ in two complementary situations: single—where the tube is free to relax together with the encapsulated fullerenes—and multiwalled environments—in this case the tube is maintained fixed (see section 2). In both cases the fullerenes assume a linear configuration inside the tube. For the multiwalled environment the incorporation of C_{30} into the zigzag nanotubes leads to additional states in the DOS of the SWNT at the top of the valence band with no changes in the electronic structure of the tube. This is expected since the tube is not allowed to relax in this case. Furthermore, the position of the Fermi level is in the middle of the band generated by the C_{30} fullerenes. On the other hand, for the single-walled environment, smaller distortions of the C_{30} molecule occur together with tube deformations. This leads to changes in the electronic structure of the tube but still keeping the C_{30} states within the gap, similarly to the previous case. Thus, we can see that the common aspect in both cases is that the encapsulation of C_{30}

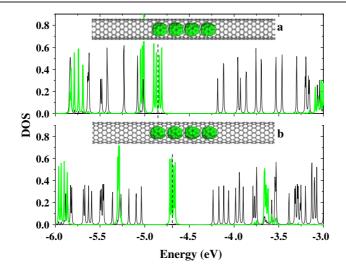


Figure 1. Partial density of states (DOS) of the carbon nanotube (black) and the C_{30} fullerenes (green/thicker) for the $4C_{30}@(11, 0)$ when the tube is (a) fixed and (b) relaxed. In all DOS graphs the dashed line indicates the value of the Fermi energy and the DOS units are in arbitrary units.

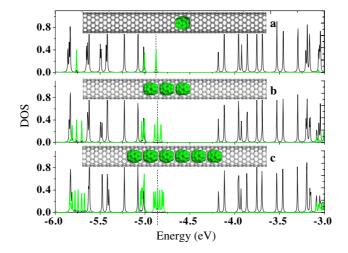


Figure 2. Partial density of states (DOS) of the carbon nanotube (black) and the C_{30} fullerenes (green/thicker) for the (a) $1C_{30}@(11, 0)$, (b) $3C_{30}@(11, 0)$, and (c) $6C_{30}@(11, 0)$ cases.

fullerenes in the SWNT (11, 0) alters the semiconductor characteristics of the empty tube, through the new states that appear in the gap region. However, there is a qualitative difference between the two cases. While for the multiwalled nanotube (modelled with a *frozen* single-walled tube, as explained in section 2) the C_{30} states are shallow and their use as acceptor states could be envisaged, the states associated with the fullerenes in the single-walled nanotube are rather deep to serve as doping levels, and their use in this sense should be questioned.

The width of the additional states is proportional to the fullerene concentration, similarly to the case of doping in semiconductors through the incorporation of impurities [33]. This can be clearly seen in figure 2 for the DOS of the configurations $1C_{30}@(11, 0)$, $3C_{30}@(11, 0)$, and $6C_{30}@(11, 0)$ for the multiwalled environment.

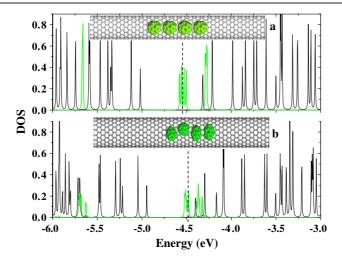


Figure 3. Partial density of states (DOS) of the carbon nanotube (black) and the C_{30} fullerenes (green/thicker) for the (a) $4C_{30}@(13, 0)$ and (b) $4C_{30}@(17, 0)$ cases.

When the tube diameter is increased, the encapsulation of C_{30} becomes exothermic (see table 1). For these cases we have not observed significant differences between the two types of environment considered, and the encapsulation in single-walled and multiwalled nanotubes has similar features. Figure 3 shows the DOS and the fullerene configurations of the systems $4C_{30}@(13, 0)$ and $4C_{30}@(17, 0)$. In both cases we can see that the incorporation of the C_{30} fullerenes also alters the electronic structure of the SWNTs, by reducing their bandgap value. Similarly to the case of $C_{30}@(11, 0)$ in single-walled nanotubes discussed above, the state associated with the encapsulated molecules appears too deep to be thermally activated and these molecules will likely act as carrier traps, rather than dopants. This is a serious inconvenience that shows that, although C_{30} encapsulation exhibits some promising properties, it can be simultaneously problematic.

For the kC_{30} @(13, 0) peapods (figure 3(a)) the linear arrangement is still observed but with the fullerenes not so compressed by the tube as in the kC_{30} @(11, 0) case. Thus, the whole band associated with the C₃₀ fullerenes inside the bandgap region is shifted towards the conduction band, also changing the Fermi level position. This behaviour also occurs in the kC_{30} @(17, 0) case (figure 3(b)) where the C₃₀ associated band is even closer to the bottom of the conduction band. However, in this case the larger diameter of the nanotube allows more mobility to the fullerenes and some disorder appears in the resulting zigzag arrangement.

For the $kC_{20}@(n, 0)$ structures, the encapsulation patterns of C_{20} into the (11, 0) and (13, 0) SWNTs (figure 4(a)) follows a linear arrangement, while for the (17, 0) SWNT, the arrangement of the fullerene molecules presents zigzag features (figure 4(b)). These arrangements are similar to those observed for ordered phases of C_{60} and they are a consequence of the confinement caused by the carbon nanotube [4, 6–8, 24]. Our calculations suggest that this can be a general feature, also common to small fullerenes.

For the exothermic cases, our tight-binding study reveals the presence of additional states (associated with the C_{20} fullerene) close to the bottom of the conduction band. The states associated with the $k C_{20}@(13, 0)$ and $kC_{20}@(17, 0)$ peapods (figure 4) turned out to be located well inside the conduction band, so they are depleted and their electrons fall to the bottom of the conduction band. Hence, the Fermi level is no longer pinned by the fullerene states and the peapod is metallic. Therefore, the effect of the C_{20} encapsulation can be seen as like an n-type

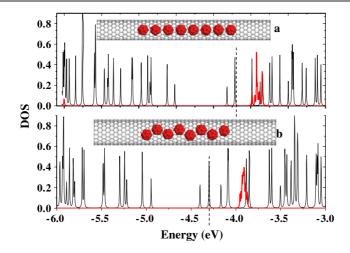


Figure 4. Partial density of states (DOS) of the carbon nanotube (black) and the C_{20} fullerenes (red/thicker) for the (a) $8C_{20}@(13, 0)$ and (b) $8C_{20}@(17, 0)$ cases.

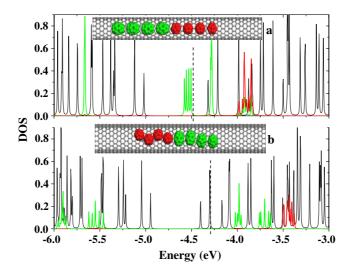


Figure 5. Partial density of states (DOS) of the carbon nanotube (black/thinner), C_{20} (red/thicker), and the C_{30} fullerenes (green) for the (a) $4C_{20} C_{30} @$ (13, 0) and (b) $4C_{20} C_{30} @$ (17, 0) cases.

doping process. The change of the molecular phase of C_{20} (linear to zigzag), possible in these larger SWNTs, does not significantly affect the characteristics of DOS distributions.

We have also considered the case where both fullerene types (C_{20} and C_{30}) are incorporated into the same nanotube, in order to investigate the possibility of these arrangements working as a pn-junction, envisaging an SWNT-based nanodiode. Figure 5 shows the results for the (13, 0) and (17, 0) SWNTs. For $4C_{20} C_{30} @(13, 0)$ we can see that the resulting density of states is the superposition of the cases of the pure encapsulation of C_{20} and C_{30} , with the C_{20} pushing the Fermi level towards the conduction band edge. Since this system exhibits a semiconductor aspect, it shows an example of a possibility of the construction of an SWNT-based nanodiode based on the encapsulation of both C_{20} and C_{30} fullerenes. For the encapsulation in larger tubes ($lC_{20} C_{30}@(17, 0)$) the disorder of the internal fullerenes is even higher, and it causes a larger spreading of the fullerene states over the energy region close to the Fermi level. In this case the influence of C_{20} fullerenes in the electronic structure is stronger, and the whole system presents a metallic behaviour.

4. Conclusions

We have investigated the electronic properties of zigzag carbon nanotubes filled with C_{20} and C_{30} fullerenes (peapods) by using force-field structural determinations and electronic structure calculations from a tight-binding approximation. The encapsulation of C_{20} and C_{30} fullerenes alters the electronic features of the peapod, which can behave as an n-type and p-type dopant, respectively. However, the latter case is especially critical, and we have shown that under certain circumstances the fullerene levels are too deep to be thermally activated and, instead of acceptors, they rather behave as traps. Comparatively, n-type doping is much more robust.

The presence of both fullerene types (C_{20} and C_{30}) into the (13, 0) (ordered hybrid encapsulation) yields to the superposition of the individual pure behaviours. In such cases, the donor state of the C_{20} pins the Fermi level close to the bottom of the conduction band, while the C_{30} provides new localized states close to the edge of the valence band, thus giving rise to an effective shrinking of the bandgap. In these systems, the peapod could work as a pn-junction, thus allowing the realization of an SWNT-based nanodiode.

In conclusion, the encapsulation of small fullerenes in small-diameter semiconducting (zigzag) single-walled carbon nanotubes can provide alternative ways for p- and n-doping, generating new possibilities for the bandgap tuning necessary in electronic devices using semiconducting carbon nanotubes. Under certain circumstances, the encapsulation might lead to deeper states that can potentially act as traps, decreasing the mobility of the device. Under this point of view, small fullerenes certainly offer some novel and promising properties—here reported for the first time—to dope carbon nanotubes, but also present the challenges typical of such a complex system. We hope that this work will stimulate experimental verification of these structures and further theoretical analysis, which are certainly needed.

Acknowledgments

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