Molecular Modeling and Computer Simulation involving the Encapsulation of β-carot ene in Boron Nitride Nanotubes

Charles de A. O. Rocha, David L. Azevedo, Fábio F. Monteiro & Antonio L. de A. Fonseca

Introduction

The possibility of applying functionalized nanotubes with β-carotene in the form of nanocrystalline dyes in photovoltaic-type cells (DSSC) is the motivating element of this work. It is now known that the addition of nanocrystalline organic dyes possibly increases the efficiency of these electronic devices in converting solar energy into electrical energy. Vale, in due course, quotes the recent work of Grätzel at al [7, 8, 9] on this subject.

On the one instance, we have the β-carotene (BC), an orange pigment that has molecular formula C40H56. It is a natural dye that shows the photoluminescence phenomenon, a property proven by spectroscopy. On the other instance we pointed out the boron nitride nanotubes (BNNTs). These nanostructures have been theoreticallypredicted shortly after the discovery of carbon nanotubes (CNTs) by Rubio et al in 1994, and were experimentally manufacturedby Chopra et al, 1995[5]. All BNNTs are broadband semiconductors with gaps of approximately 5.5 ev[2, 3, 4]. Their high ionicity and high energy gap givetheirelectronic propertiesgreater uniformity and explain the use of thesematerials in the electronics field. In addition, BNNTs stand out for their chemical inertness and high thermal stability, potentially interesting properties for applications in thebiomedicine field and theengineering of biomaterials [3]. Unfortunately, it is noted that the applications of this and ofother boron nitride materials in biological domainsremain largely unexplored [6].

The objective of the present work is to investigate the encapsulation dynamics of BC molecule in single wallboron nitride nanotubes (SWBNNT) by means of computer simulations.Results produced by classical methods of molecular mechanics (MM) and Molecular Dynamics (MD) confirmed the encapsulation of said molecule in the two cases studied. In addition, density functional approximations associated with the Tight-Binding method to investigate possible changes in the electronic structure of the materials involved were carried out.

Thus, an interesting line of research is that which proposes the replacement of mesoporous titanium oxide by a sensitizer higher efficiency. Nanotubes functionalized with BC are potentially promising in this regard.

Methods

In this undertaking, we performed molecular dynamics computer simulations associated with the Universal Force Field (UFF) to investigate the possibility of encapsulation of BC molecule in a SWBNNT, within the conditions imposed. Classical results were combined with results based on Functional Tight-Binding Density (DFTB+)to investigate also changes resulting from this process.To perform these simulations, the Materials Studio was used, a Cerius computer simulation package as desktop.

The Molecular Mechanics (MM) is a classical and

simple method that uses newtonian mechanics equations to describe the potential energy surface (PES) and the physical properties of molecular systems through energy conformation calculation. In other words, with the application of MMyou want to get the optimized settings of the systems under study. The option of working with the so-called Universal Force Field (UFF) is conveniently categorical since the process one wishes to perform involves the interaction of an organic system with an inorganic system. The simulations describe the encapsulation of β-carotene into two specific nanotubes: a chiral SWBNNT (13,5) and an Armchair SWBNNT (9,9), with lengths and diameters compatible with conditions already described in the literature for CNTs.

The encapsulation process occurs with the application of molecular dynamics (MD). This is the method used to describe the time evolution of systems, through numerical integration of Newton's laws. The results obtained by these means provided information for their elastic energies calculations characterizing possible deformations besides allowing estimations on the spontaneity of the process.

Finally, one obtains quantum properties of systems through application of DFTB + module contained the Cerius package. The DFTB + uses the Tight-binding method (TB) associated with the Density Functional Theory (DFT) to gain accuracy and efficiency. The TB is in turn an approximation method suitable to the first neighboring situation. From this, analysis of energy and DOS of original systems andencapsulatedsystems allow us to make inferences about the gaps and other changes in the electronic structure of same.

Results and Discussion

In this study, we initiallytried to obtain the optimized and isolated structures of β-carotene molecule and the nanotubes (13, 5) and (9, 9). This optimization procedure involves the application of Force Field (UFF). Nanotubes were chosen with both open ends and lengths larger than the ones of the molecule so as to avoid edge effects. The BNNTs also have diameters compatible with the diameters of CNTs described in the experimental work of Yanagi et al. 1.

Once the structures in their most stable conformations were obtained, it urges to placeit in appropriate conditions for the initial development of the dynamics. Other procedures such as the choice of NVT ensebly and the randomness of the initial velocities seek to reproduce the experimental conditions in which the process usually occurs.

The stabilizing energy of the complexes SWBNNT + BC is obtained by comparing the energies of the complex before and after encapsulation. Stabilizing Energy Calculations confirmed the occurrence of encapsulation in its spontaneous form in both cases studied. Figure 1 and Figure 2 show, in sequence, the frames that highlight the encapsulation of BCat SWBNNT (13,5) and SWBNNT (9,9). Similarly, the elastic energy of the encapsulated BC was obtained by comparing the energy from the free molecule withthe one from theencapsulatedmolecule. Results from this energy values explain the emergence of geometric deformations of the molecule as a consequence of its weak interactions with the nanotubes walls.

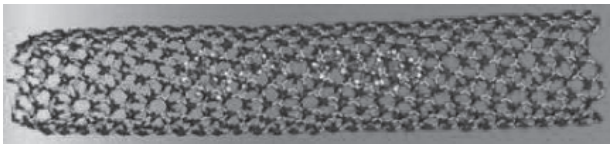

Figure 1.Frame in whichtheencapsulated BCinSWBNNT(13,5) is seen.

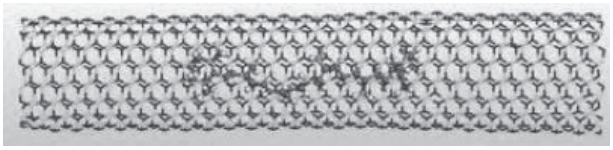

Figure 2. Framein whichtheencapsulated BCin SWBNNT (9, 9) is seen.

Data on energy and the DOS of encapsulated SWBNNT complex (13, 5) + BC and SWBNNT (9.9) + BC have also been generated by application of DFTB + method. Figure 3 and Figure 4 relate the normalized DOS per unit of states with the energy of the corresponding nanotube.

So we can compare the gaps of the nanotube with the gap of the encapsulated complex. Each figure highlights the region near the Fermi zone. The difference between the gap of the nanotube before and after encapsulation is indicative of the BC electronic coupling involved in both cases.

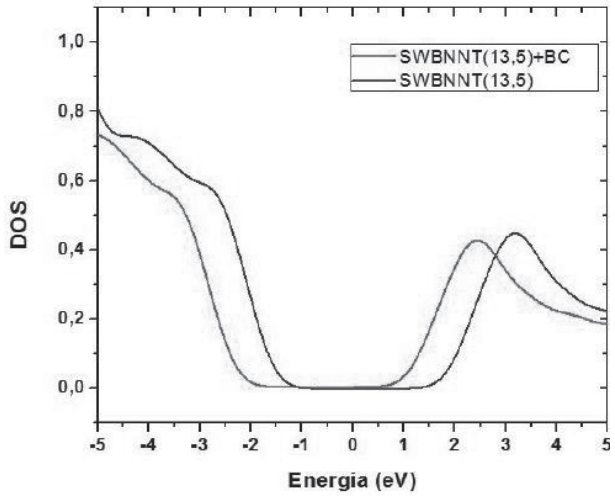

Figure 3.Curve depicting the DOS by unit of states as a function of the SWBNNT (13,5) energies. The blue line represents the pure nanotube and the red line represents the functionalized nanotube.

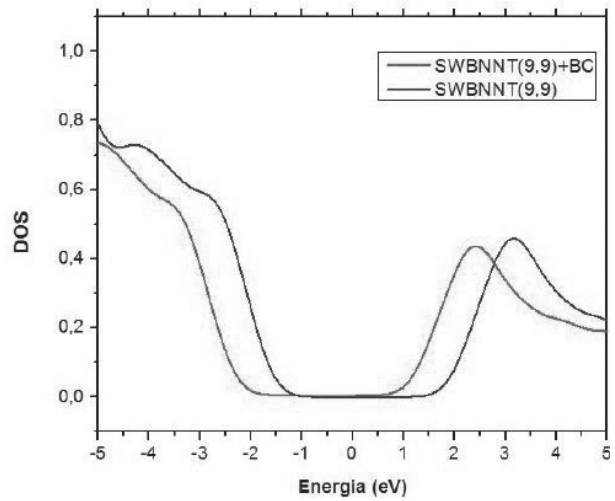

Figure 4. Curve depicting the DOS by unit of states as a function of the SWBNNT (9,9) energies. The blue line represents the pure nanotube and the red line represents the functionalized nanotube.

Conclusions

Our simulations showed that BC is encapsulated in SWBNNT nanotubes (13,5) and (9,9). Calculations relating to stabilization energies suggest that this process is spontaneous. Estimates of the elastic energy of BC point out deformations of the systems.

Analysis of the DOS of the investigated systems obtained by applying the DFTB + code, suggest the occurrence of electronic coupling due to the superposition of molecular orbitals.

Therefore,there have been changes in the electronic structure of the two nanotubes. Despite this evidence, the difference is remarkably small, so that both nanotubes keep their semiconductor properties.

Acknowledgments

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