NUMERICAL CALCULATION OF OPTICAL PROPERTIES FOR CN_X AT LOW CONCENTRATION FOR DIFFERENT ZIGZAG CHIRALITIES.

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Abstract

We have performed a comparative numerical study of optical properties between three cases of zig - zag [(6, 0), (8, 0) and (9, 0)] single wall carbon nanotubes (SWNT´s) doped with small amounts of nitrogen. The optical description was obtained using the magnitude of the static dielectric constant through the use of *ab initio* in the relaxed C-C bond length, long-wavelength limit, calculation. The parameters of the optical properties were compared and discussed for each zig - zag SWNT´s between the nitrogen doped and not doped cases. According to our calculation, the main result is that the optical properties have a tendency to maintain a change as a function of chirality increment and/or decrement of nitrogen concentration.

Keyword: *ab initio, optical properties, carbon nanotubes*.

1. INTRODUCTION

Carbon nanotubes (CNTs) play an important role in different areas of nanotechnology due its particular structure and their semiconductor/conductor behavior that commonly depends on the (*n, m*) chirality index [1-2]. In this work, we present a comparative study trough *ab initio* calculations of SWNT with (6, 0), (8, 0) and (9, 0) chiralities using CASTEP software [3], in which we replace one carbon by a nitrogen atom, the later known for its similar structural properties of the replaced carbon. Some groups have focused on theoretical research using methods such as density functional theory (DFT) in order to investigate changes in CNTs structures and/or doping consequences [4-6]. For instance, Debnarayan Jana, et.al; developed a similar method to study the optical properties of SWNT alloyed with nitrogen only for the (8, 0) particular case.

Even though we know that during the experimental synthesis of CNTs is not easy to incorporate a foreign atom like nitrogen as a way of lowering the concentration trough doping, we are motivated by the importance that an acceptable knowledge behavior of the optical properties for this configuration is numerically possible and because recent advances in experimental synthesis have shown that nitrogen single atoms doping occurs in different bonding configurations such as graphitic and pyrrolic-like [7-9].

For the present numerical simulation, the imaginary part of the dielectric function was obtained from the change of the total energy for the CNTs hypothetical structure; consequently, all the optical quantities such as reflectivity and optical absorption were acquired from the calculated dielectric constant.

2. THE METHOD

The Kohn-Sham equation recreates the density of interacting particles without solving explicitly the Schrodinger equation. In this work CASTEP (Cambridge Sequential Total Energy Package) software was employed to

approximate pseudopotentials in the *ab initio* calculation of the total energy. From there, the electronic relaxation is calculated by minimizing the total energy. For our particular implementation, one super cell was designed for each nanotube with (6, 0), (8, 0) and (9, 0) chiralities and the geometric structure was built by replacing one of the C atoms in the hexagonal ring by one N atom.

The optical properties were calculated using the GGA –PBE functional, and cut-off energy of 700 eV was adopted for the grid integration with 24 K-point sampling for all the systems. Subsequently, we analyze the optical properties of the SWNT´s of the complex dielectric function defined by

$$\vec{D}(\omega) = \varepsilon(\omega)\vec{E}(\omega) = [\varepsilon_1(\omega) + i\varepsilon_2(\omega)]\overrightarrow{E}(\omega). \quad (1)$$

In fact, the study of optical properties is via the use imaginary part of the dielectric function since its relation to the joint density of states of the valence and conduction band [10-12].

3. RESULTS AND DISCUSSION

In Table 1, we show the obtained grid parameters of the typical 3D triclinic crystal structure of the CNTs for the three types of SWNT, where the systems of each structure represent a radius < 1 *nm* and the variation of distance parameters (*a,b*); in the case (8, 0) and (9 ,0) are equal; unlike to Debnarayan Jana, et., in which for the case (8, 0) the parameters of grid were a=18.80 Å; b=19.004 Å and c=4,219 Å. For the case of SWNTs doped with nitrogen, the percentage acquired for each structure were (6, 0; 4.16%), (7, 0 3.155%) and (9, 0; 2.77%).

SWNT (Zig-Zag)	Angstrom diameter (Å)	Grid parameter
(6,0)	5.526	*a=b=18.6278 Å c=4.260Å α=β =90° γ=120°*
(8,0)	6.283	*a=b=20.1936 Å c=4.260Å α=β =90° γ=120°*
(9,0)	6.502	*a=b=20.9765 Å c=4.260Å α=β =90° γ=120°*

Table 1. Grid parameters from CASTEP (5.0)

3.1 Dielectric function

The graphs in figure 1 represent the resultant dielectric function for the three types of SWNT´s zig-zag (6, 0), (8, 0) and (9, 0) pure and doped (Fig. 1a, 1b, and 1c respectively). We can observe that the change in the optical properties depends on nitrogen concentration; for example in the pure case, the (6, 0) and (8, 0) behaves as a semiconductor and the (9, 0) as a conductor. In the nitrogen-doped case, the behavior for (6, 0) and (9, 0) are similar of a conductor and only in the case for (8, 0) the comportment does not change. The above observation indicates that a small percentage of nitrogen is enough to change the optical properties of SWNT´s, but equally important it is the type of chiralities since affects the number of atoms in the SWNT´s structure.

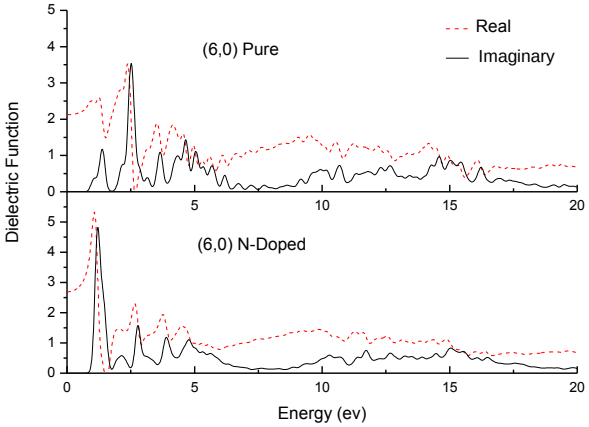

Fig. 1a. Dielectric constant of (6, 0) pure and doped.

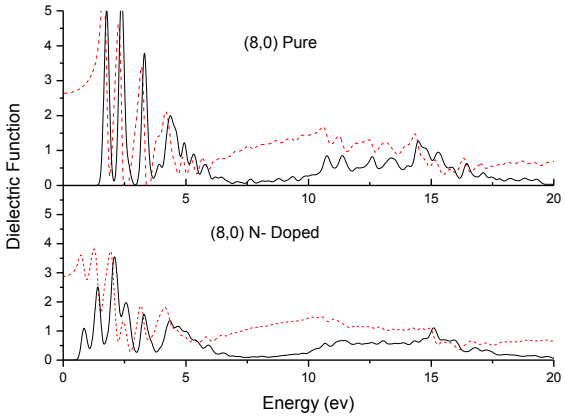

Fig. 1b. Dielectric constant of (8, 0) pure and doped.

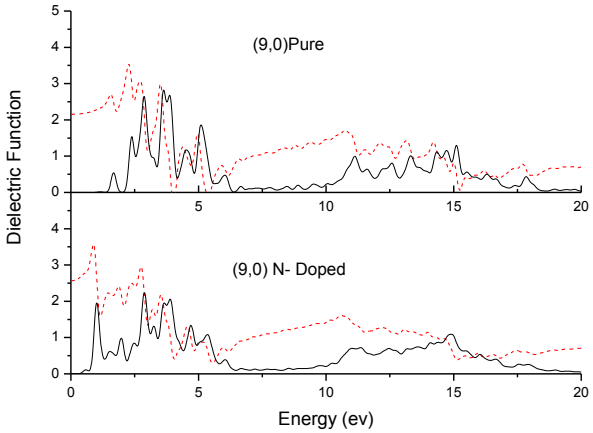

Fig. 1c. Dielectric constant of (9, 0) pure and doped with nitrogen.

3.2 Reflectivity

Figure (2) shows the typical reflectivity spectrum of the pure and doped SWNTs. Notice that the reflectivity has different behavior for the doped SWNTs. In all cases the spectra displays two peaks, however, the one in the region between 0-6 eV is more intense. In the case of (6, 0) doped, the overall peaks are around 1.13 eV when the SWNT is pure and 2.5 EV when is N-doped; for (8, 0) the overall peaks are around 2.5 eV when is pure and 2.7 eV doped, finally, in the case (9, 0) the peaks are 3.9 eV in pure and 3.8 eV in the N-doped; in addition, we detected that the reflectivity decreases its intensity when the number of atoms increases and lowers the amount of nitrogen concentration. It is also clear from the figure (Fig. 2), that the reflectivity behavior is present in the whole range of visible frequency.

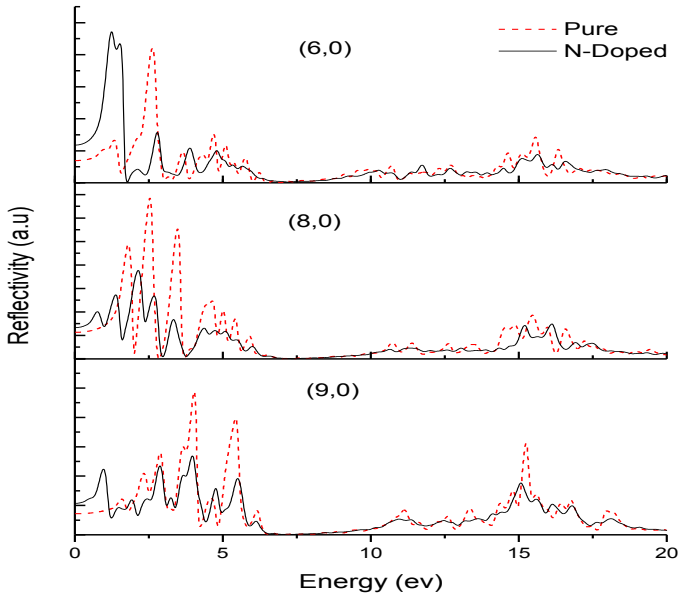

Fig. 2: Reflection spectra of (6, 0); (8, 0) and (9, 0) pure and doped SWNT

3.3 Absorption

In figure (3) we observe several peaks in the absorption spectra limited to the 10-20 eV range for all cases. The highest value of absorption coefficient occurs between 15-17 eV corresponding to the UV region. We can confirm that the maximum value of absorption increase with the number of atoms which reduces the percentage of nitrogen concentration in each type of chirality.

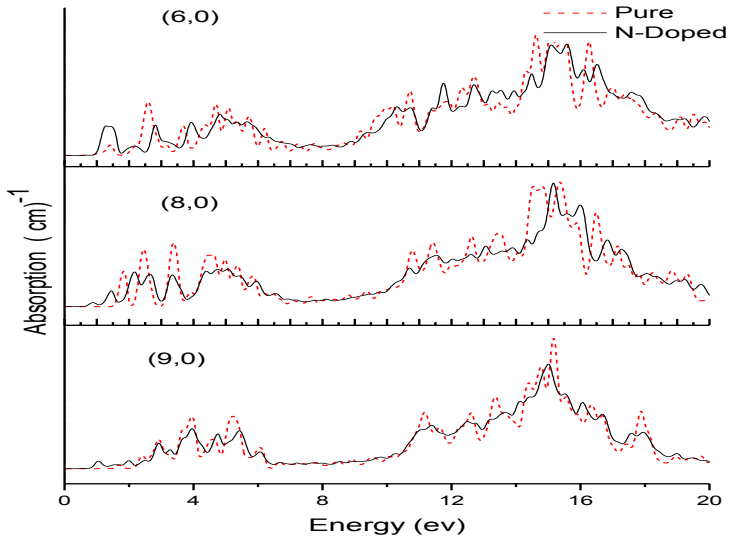

Fig. 3: Absorption spectra of (6,0) ; (8,0) and (9,0) pure and doped.

4. CONCLUSIONS

We determined that changes in the optical properties of SWNT's depend on the type of the chirality structures and the percentage of nitrogen concentration. Table 2 presents a behavior summary of the properties in relation to the system type.

SWNT	Reflectivity region		Percentage of intense peaks of reflectivity (%)		Absorption region	
	Pure	N-doped	Pure	N- doped	Pure	N- Doped
(6, 0)	Visible	Infrared	21	23	UV	UV
(8 ,0)	Visible	Visible	24	14	UV	UV
(9, 0)	Visible	Visible	34	24	UV	UV

Table 2: Summary of optical properties of systems.

Regarding the reflectivity parameter, we detected that only the structure (6, 0) doped with nitrogen has the maximum value in the infrared region when the concentration percentage is slightly larger than on the other structures. For the absorption case, the spectra do not show significant changes by any structures over the same region where as all systems had absorption activity in the UV region.

Furthermore; we know that the stability of the structure is associated with the total energy which is expressed in terms of the density of the DFT calculation in place of a wave function. Table 3 indicates the total energy of each system where we can perceive that the total energy becomes lower (more negative) when the structures are doped with nitrogen atoms indicating that the doped structures are more stable.

Total Energy (eV)		
SWNT	**Pure**	**N-doped**
(6,0)	-3737.65	-3854.65
(8,0)	-4690.24	-5105.63
(9,0)	-5615.55	-5703.89

Table 3: Summary of total energies by systems.

5. ACKNOWLEDGEMENTS

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6. LITERATURE

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