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STRUCTURAL, ENERGETIC AND ELECTRONIC CHARACTERIZATION OF THE CHIRAL CARBON-NITRIDE NANOTUBES

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The influence of possible defects of atoms due to deviations from the 1:1 stoichiometry of the chiral carbon-nitride nanotubes on structural, energetic and electronic properties has been considered in this paper. PM3 calculations demonstrate that small quantities of nitrogen (1%) incorporated into the carbon nanotube lead to thermodynamic instability. This doping of the carbon nitrogen nanotubes modifies significantly the bands in the vicinity of the Fermi level and these tubes can behave as semiconductors or insulators. Therefore, doping of tubes by nitrogen may lead to electronic properties that are more controlled by the chemistry (the amount of doping) than by a specific geometry of the tubes.

INTRODUCTION

Since their discovery,[1] carbon nanotubes and related materials have attracted much interest due to their many exceptional properties. Carbon nanotubes are promising systems for manufacturing of electronic devices, such as transistors, actuators and logic circuits.[2-7] The electronic properties of carbon nanotubes exhibit either semiconducting or metallic characteristics depending on their chiralities and diameters.[8,9] However, these geometric natures are very difficult to control experimentally, and this restrains the application of the carbon nanotubes.

Recently, nitrogen doping of carbon nanotubes has gained increasing attention[10, 11]. Up to date, only small quantities of nitrogen (<10%) have been incorporated experimentally into carbon nanotubes and filaments.[12-18]

This paper suggests exploration of theoretical models for examining the structural, energetic and electronic properties of some prototype (7, m) CN nanotubes with deviations from the 1:1 stoichiometry in order to use them to construct electronic nanodevices.

RESULTS AND DISCUSSION

Thermodynamic stability

The starting geometries of the basic (7, m)C nanotubes (see details in the Experimental Section) (m = 1, …6)[19] have been virtually doped with 0, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50 nitrogen atoms. After geometry optimisation we found that the carbon-nitrogen distances vary between 1.39 and 1.41Å, the C-N-C angles ranging from 117-120^0 and the N-C-N angles between 119 and 123^0. These values are in agreement with the experimental results.[20]

Fig. 1 giving the variation of the enthalpies of formation/atom of carbon and carbon nitrogen nanotubes, shows an almost linear dependence on the chiral vector, m and a thermodynamic stabilization with the increase of the diameter.

Fig. 2 shows the dependence of the enthalpies of formation (per atom) of the carbon nitrogen nanotubes with the nitrogen content (x). It comes out that the carbon nitride nanotubes are thermodynamically unstable with the increasing of x. This might explain the synthesis[21] of carbon-nitride nanotubes containing no more than 13%N.

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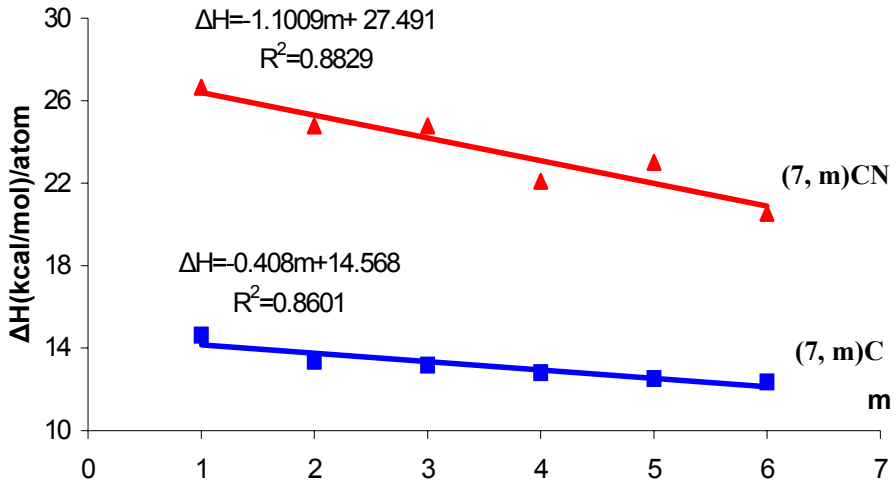

Fig. 1 – Enthalpies of formation (per atom) of the (7, m)CN tubes as a function of the chiral parameter (m).

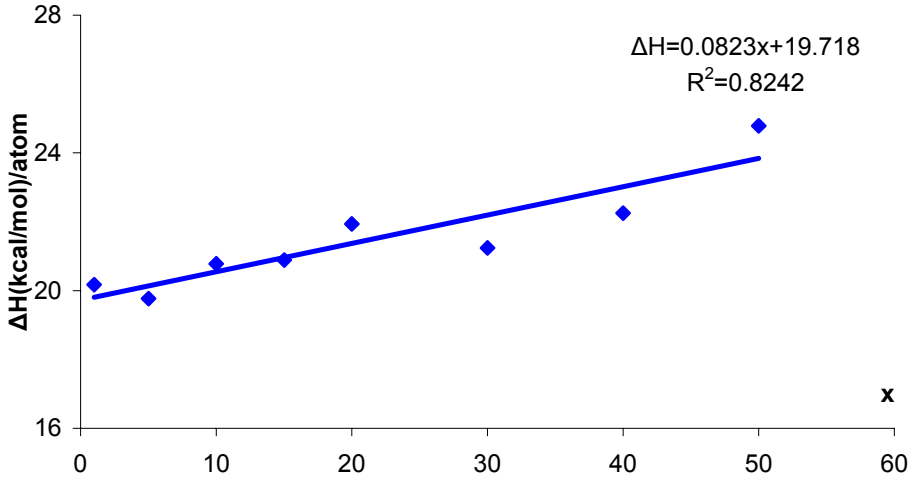

Fig. 2 – Enthalpies of formation (per atom) of the (7, 3)$C_{100-x}N_x$ tube as a function of nitrogen content (x).

Therefore, the synthesis of carbon nitride with high nitrogen content is difficult due to the greater thermodynamic stability of carbon and isolated nitrogen molecules.

Density of states

If one defines DOS(E)dE as the number of one-electron levels in the infinitesimal energy interval dE, then the total density of states is $DOS(E)=\Sigma_j\delta(E-e_j)$ (where δ is the Dirac function and e_j stands for the one electron energies). Partial Density of States (partial DOS or PDOS) reveals the specific contribution of an atomic orbital χ_μ to one-electron levels at certain energies.

The data obtained by us show that all (7, m) CN tubes can behave as semiconductors irrespective of their chirality, diameter or length of the tube. Fig. 3 shows an example of the DOS and PDOS plots for the (7,1) CN tubes. From these plots it is evident that the lowest bands (valence bands) are composed of N(2s) and C(2s) derived states and the conduction bands consist of N(2p) and C(2p) derived states.[22]

The incorporation of the defects brought by the deviations from the 1:1 stoichiometry modifies significantly the electronic properties. Interestingly, the chiral CN nanotubes can behave either as a semiconductor or as an insulator and only changing the composition controls their band gap, Fig. 4.

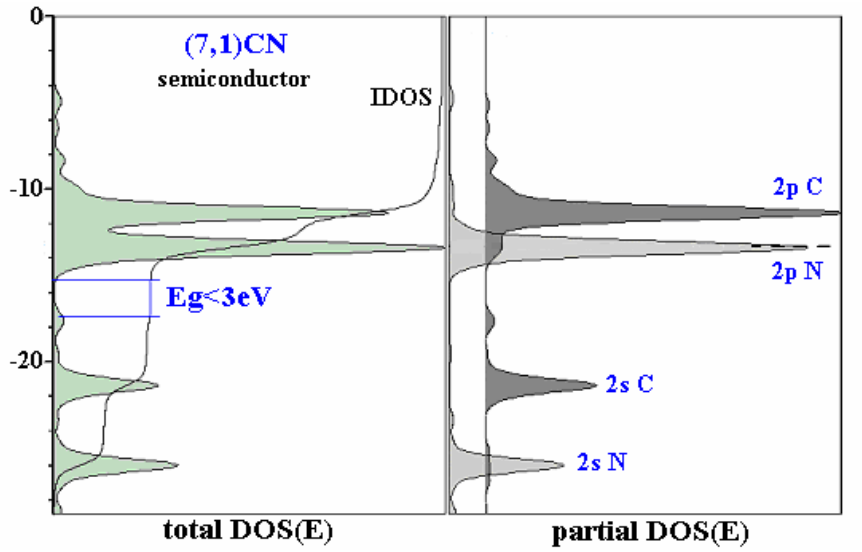

Fig. 3 – The total, partial *DOS* and *IDOS* diagrams for the (7, 1)CN nanotube.

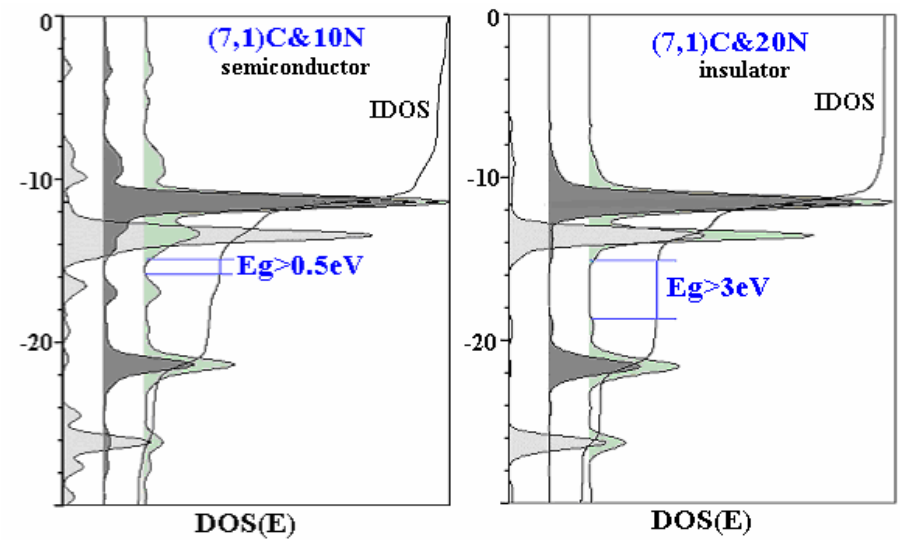

Fig. 4 – The partial, total *DOS* and *IDOS* diagrams for the (7, 1)C&xN tube where x =10, 20.

Polarizability (α)

Polarizability measures the ability of an atom or molecule to deform the electric cloud in the presence of an electric field. Polarization means the separation of positive and negative charges in a system so that it results a net electric dipole moment per unit volume. Herein we use the mean polarizbilities $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ obtained with the Hyperchem package,[23] by applying a field strength of 0.0005 a.u.

The calculated data plotted in Fig. 5 demonstrate an almost liniar dependence of the polarizability values on the nitrogen content in the (7, 3) $C_{100-x}N_x$ tubes. So that polarizability decreases with the increasing of the nitrogen content.

In conclusion, the stability of the carbon nitride nanotubes decreases with the increase of the nitrogen content. The energy gap of the (7, 3) $C_{100-x}N_x$ tubes can be controlled only changing their compositions. Therefore, doping of tubes by nitrogen may lead to electronic properties that are more controlled by the chemistry (the amount of doping) than by a specific geometry of the tubes.

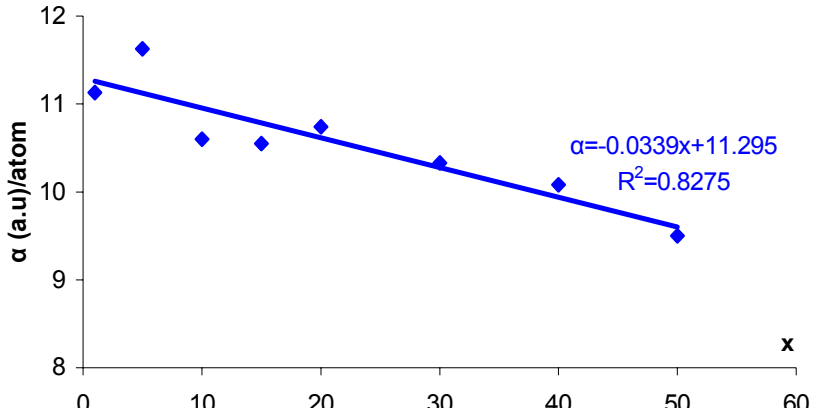

Fig. 5 – Polarizability (per atom) of the (7, 3)$C_{100-x}N_x$ tube as a function of nitrogen content (x).

EXPERIMENTAL

The significance of the (n, m) notation of the nanotubes is given in Fig. 6 and the geometries of the (7, m) C nanotubes have been generated by resorting to the software offered in ref.[19]. Then, 1 to 50 nitrogen atoms randomly replaced the carbon atoms and the new tubes were subjected to a preliminary optimization using the MMFF force field in Spartan'02.[24]

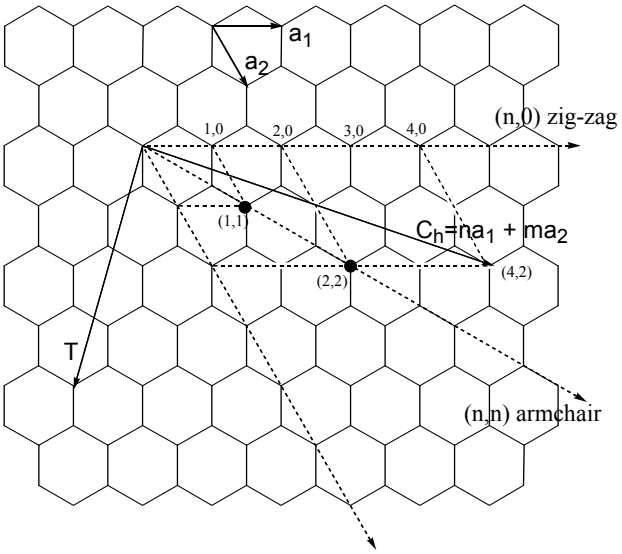

Fig. 6 – A graphene sheet showing the possible types of nanotubes in function of the chiral vector $\mathbf{C_h}(n, m)$ (perpendicular to the tube axis **T**). Tubes with n = m are called "armchair", those with m = 0 are called "zig-zag", otherwise they are called "chiral". $\mathbf{a_1}$, $\mathbf{a_2}$ are the unit vectors of graphene. In this particular case, $\mathbf{C_h}$ has n = 4, m = 2.

Further, the carbon-nitrogen nanotubes with chiral geometry were fully optimized by performing PM3-RHF[25] type semiempirical molecular orbital calculations using Spartan '02 package[24] followed by single point calculations within Hyperchem in order to determine the mean polarizabilities.

The densities of states (DOS) were calculated by the extended Hückel tight-binding method using BICON-CEDIT package.[26]

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