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Physicochemical properties of armchair non-stoichiometric boron nitride nanotubes: A density functional theory analysis

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ABSTRACT

DFT–GGA calculations were carried out in order to analyze the structural and electronic properties of Boron Nitride nanotubes (BNNTs) for two cases: pristine and non-stoichiometric, this last rich in atoms of Nitrogen as Boron. After geometric optimization process, the doped BNNTs present an important reduction on values of HOMO-LUMO gap versus pristine case, as well as these systems have high polarity and low chemical reactivity. This effect in particular is enhanced for the nanotube with excess in Boron atoms moreover this indicates its potential application as drug delivery. An important structural feature was found for the above system due to they show very similar geometry with respect to B_{40} fullerene. The doped BNNTs possess low values of work function which fits to design devices for different applications.

1. Introduction

The nanostructures of Boron Nitride (BN) in particular those based on one dimension (1D); such as nanotubes have attracted the attention since past two decades of theoretical [1] and experimental [2] scientists. In these systems there is not dependency between their structure and properties, thereby specific studies should be made on zig-zag and armchair nanotubes according (n, 0) o (n,n) Hamada indexes [3], respectively. Furthermore a tendency has not been established yet, thus raises the needles to modify properties of interest by different process as functionalization or atomic defects on its surface; however some of these aspects have been considered and the creation of many devices was possible as glucose detection [4] and visible emission diodes [5]. The boron nitride nanotubes (BNNTs) which possess a similar morphology as carbon nanotubes, both with distinct properties; they appear to be potential candidates for biomedical applications due to their uniformity and stability under solution [6]. These are formed by a mesh of boron and nitrogen atoms showing a similar hexagonal structure as the carbon nanotube, where the atoms forming sp^2 hybridizations produce a semiconductor behavior (gap~5.5 eV) [7,8], besides they present high thermal stability, resistance to oxidation process and excellent mechanical properties. Despite of these great features, to modify their structure and properties to other kind of applications it is necessary a doping on the BNNTs. Thereby, recently Kim et al. [9], have addressed an interesting study on BNNTs rich in nitrogen and

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Bores atoms using quantum molecular simulation framework. In the model adopted after optimization process, the rich zone forms hexagons by 4B and 2N and they present B–B–B and N–B–N bonds and these last are good candidates to capture CO_2 in any geometry as zig-zag or (8.0) and (10.0) chirality. In general, the electronic and structural properties were obtained for non-stoichiometric BNNTs and the systems considered have the next chemical composition: $B_{55}N_{45}H_{20}$ (BNNT/Rich in Boron) and $B_{45}N_{55}H_{20}$ (BNNT/Rich in Nitrogen). Both with short length and open ends to facility its biologic application [10,11]. The chirality used was (5.5) due to high stability according its value of electronic gap [7]. Therefore, to modify this parameter is crucial to establish new applications, as well as improve its electrical conductivity by means atomic defects on their surfaces. This work is addressed in order to increase the physicochemical knowledge of these nanotubes.

2. Simulation models and methods

First-principles density-functional calculations were performed to study the armchair pristine and armchair non-stoichiometric boron nitride nanotubes (BNNTs). The geometry optimization process of the BN nanostructures was executed using the HSEh1PBE hybrid functional and the 6-31G(d) at the level of the general gradient approximation within the density functional theory [12] (DFT-GGA) implemented in the Gaussian 09 package [13]. The HSEh1PBE hybrid functional, actually derived from the Perdew-Burke-Ernzerhof exchange-correlation functional (PBE), was chosen to describe the non-covalent interaction reasonably. This functional includes 25% of the exact Hartree-Fock exchange energy [14]. This functional reproduced in a right way the HOMO-LUMO values for nanostructures based on BN [15–17]. Systems only with neutral charge were considered in this study. In order to ensure the lowest energy structures several multiplicities ($M = 2S_T + 1$; S_T = total spin) were considered, thus the differences energetic of $M = 1$ over $M = 3$ are $\Delta E = 5.85, 0.28, 3.81$ eV for the

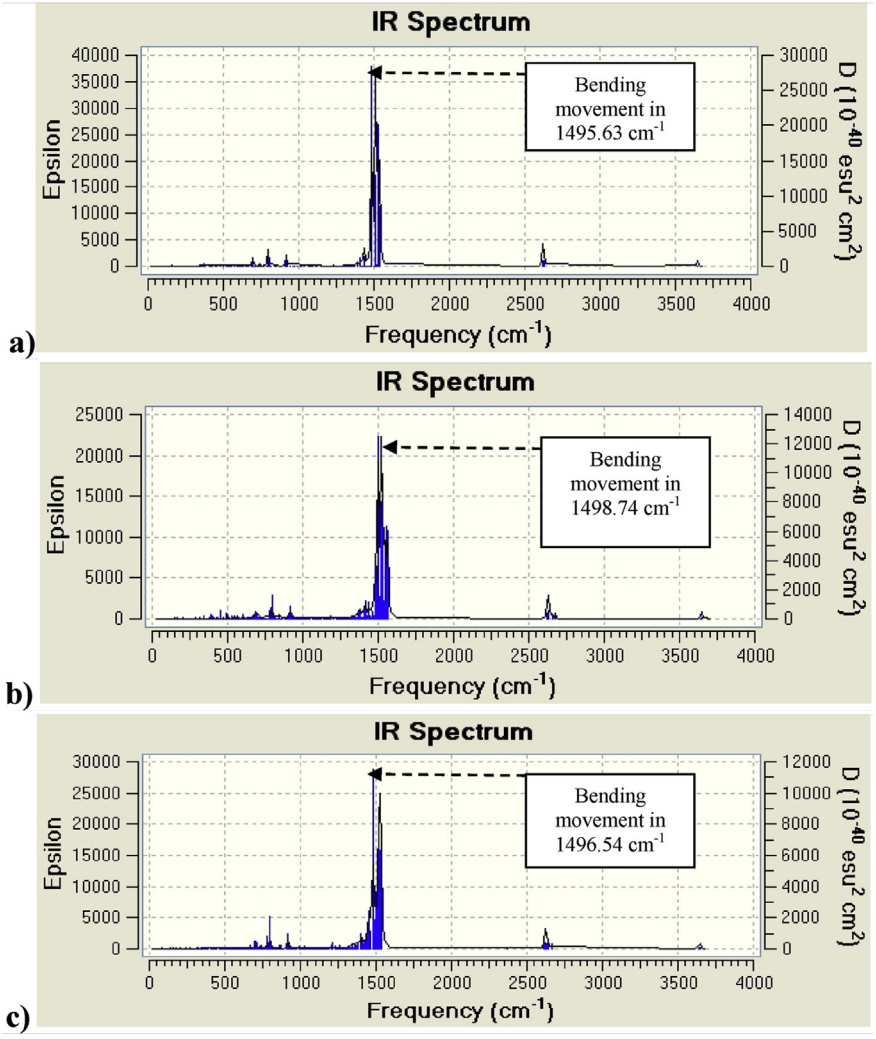

Fig. 1. IR Spectra for: **a**) pristine BNNT, **b**) BNNT/Rich in Nitrogen and **c**) BNNT/Rich in Boron.