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Effect of boron and nitrogen co-doping on CNT's electrical properties: Density functional theory

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ABSTRACT

In this work, we have theoretically studied the changes in electrical properties of three different geometrical structures of carbon nanotubes upon co-doping them with boron and nitrogen atoms. We applied different doping mechanisms to study band structure variations in the doped structures. Doping carbon nanotubes with different atoms will create new band levels in the band structure and as a consequence, a shift in the Fermi level occurs. Whereas, filling up the lowest conduction/ upper valence bands created an up/ downshift in the Fermi level. Moreover, dopants concentration and dopants position play a critical rule in defining the number of new band levels. These new band levels in the band gap region represented as new peaks appeared in the density of states. These new bands are solely attributed to co-doping carbon nanotubes with boron and nitrogen atoms.

1. Introduction

There are many sensing techniques used to detect toxic and harmful gases such as; electrochemical sensor [1], infrared sensor [1–5], ultrasound sensor [1] and semiconductor sensors [1,3–10]. Sensing devices based on semiconducting techniques are considered the most effective yet the lowest cost method. Nevertheless, the interactions of toxic gases require a low operating temperature [1,3,5,7,11–13]. However, the lifetime limitations in real sensors are the main obstacle as the metal nano-clusters suffer from thermal degradation [6].

Carbon nanotubes (CNT's) have a wide range of potential applications in the field of nano-sensors. The unusual properties of CNT's make them the best candidate as an active material for gas sensors [9,16,17]. Their electrical properties show electrical conductivity modification upon gas adsorption [9,14,15]. Unlike other gas sensors, CNT's gas sensor's mechanism can be recorded at room temperature [16,17]. However, pristine CNT's cannot detect gases without any surface modification [3,12]. Therefore, different strategies have been adopted to increase CNT's gas sensitivity, such as; acid treatment [1,18–21] or intentionally introducing impurities [4,6,8]. Introducing impurities (doping) is an effective method to tune the physical properties of CNT's based nanostructures [1,5–7,22]. Although dopant incorporation can be achieved during growth with no additional post-growth treatment steps [6]. Even though, it is a big challenge to tune the band gap and make it serve specific application through introducing impurities or creating defects in the nanotubes structure. For instance, it is not an easy task to control the dopants position in the nanotubes structure. Moreover, the natural choices for CNT's functionalization structures are nitrogen and boron [3–5,11,15,20,26]. In fact, it has been proven that both elements significantly tune the optical, electrochemical and electronic properties of CNT's. However, there have been no realistic studies of boron and nitrogen doped nanotubes at low gas concentrations [5,6]. In fact, it has been shown that CNT's doped with boron or nitrogen are sensitive to the presence of CO, H_2O, NH_3 and lately various organic solvents [1,6,16,21].

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Theoretically, it has been proven that graphene band gap can be tuned by controlling the dopants position and concentration [23].

In this work, we aim to present a modeling study of sensing properties of co-doped CNT's. We would like to study the effect of dopant's position on electrical properties of different types of CNT's. This will be achieved by studying the band structure variations upon co-doing the nanotubes.

2. Modeling and theoretical methods

In this work, we aim to study the effect of different doping schemes on electronic properties of single-walled carbon nanotubes (SWCNT's) upon boron and nitrogen co-doping. To perform this investigation, we carried out two main quantum-mechanical calculations. First, we performed geometry optimization calculations to obtain the most stable CNT structure (for both pristine and doped nanotubes). Then, we performed energy calculations to all geometry optimized structures in order to study the variations in the band structure and their corresponding density of states (DOS) of the nanotubes under study. All performed geometry optimization, and electronic energy calculations are based on density functional theory (DFT) code implemented in a DMOL3 code module in a commercial Materials Studio molecular modeling software packages (www.accelrys.com). The generalized gradient approximation (GGA) method with Perdew–Burke–Ernzerhof (PBE) parameterization was adopted to perform geometry optimization for the CNT's. Moreover, GGA functional with the PBE correlation gradient correction was also used to calculate the total energy along with electronic properties of the doped nanotubes. Self-consistent field tolerance was set to a medium tolerance of 10^{-5} a.u. In order to improve the calculation's quality, the energy convergence tolerance was set to $5 * 10^{-4}$ eV, while the maximum force convergence tolerance was set to 0.11 eV/Å with a maximum displacement “per iteration” of 0.005 Å. Besides, DFT Semi-core Pseudo potentials (DSPP) core treatment was used to optimize the computational time. The selection of semiconducting nanotubes and not metallic nanotubes was attributed to our interest in creating dangling bonds on the nanotubes. The Brillion-zone integration of the total energy was performed using 18 **k**-points for all nanotube unit cells from the Monkhorst–Pack grid. In order to choose an appropriate **k**-point mesh, we performed different geometry optimization calculations for the selected nanotubes and compared the energy changes for each sample. Furthermore, the unit cell dimensions were chosen to be large enough such that there will be no interactions between the simulated structure and its surrounding images in the performed periodic calculations. For all structures under study, the atomic coordinates were optimized to minimize the total energy in every structure and to ensure that the net force is zero on every atom in all studied structures.

3. Results and discussion

In this work, chiral (10, 5), zigzag (10, 0) and armchair (10, 10) SWCNT's were studied. The diameters for (10, 5), (10, 0) and (10, 10) nanotubes are 10.36 Å, 7.83 Å and 13.56 Å, respectively. Depending on the dopant atoms position, four different major cases were considered, refer to Fig. 1. Where “CO-BN” code represents co-doping with boron and nitrogen dopants at the same time, and A, R, Θ, Z represents the doping criteria: axial, radial, angle and zig-zag direction respectively. D represents the distance between boron and nitrogen atoms in Angstrom unit length. Four different angles were used for all nanotubes under study with $\Theta_4 > \Theta_3 > \Theta_2 > \Theta_1$. The angles measured as following; we fixed boron atom position, and we modified the angle by manipulating the nitrogen atom position with respect to boron atom at a fixed distance. We studied the dopants position effect in the axial direction for both (10, 0) and (10, 10) nanotubes since (10, 5) nanotube has no atom on the axial direction.

3.1. (10, 5) nanotube

Starting with (10, 5) pristine CNT, we found that the band gap energy equal to 0.735 eV, as presented in Fig. 2(a), which consistent with previous investigations [24–26], whereas the red dashed line represents the Fermi level. In order to confirm the above result, we calculated the density of state (DOS) for (10, 5) pristine CNT, refer to (Fig. 2b). Upon doping (10, 5) CNT with only a boron atom, we found that there is a clear decrease in the band gap energy with respect to pristine (10, 5) CNT. Whereas, the band gap for boron doped (10, 5) CNT is equal to 0.653 eV, with almost 11% decrease, refer to Fig. 2(c) and Table 1. Furthermore, the valence band is up-shifted upon boron doping which consistent with what we mentioned before, see Fig. 2(c). In addition, upon doping (10, 5) CNT with a nitrogen atom, we noticed a downshift in the band gap to 0.650 eV with 14% decrease, refer to Fig. 2(d). We also noticed that doping (10, 5) CNT with nitrogen has almost the same effect as doping CNT with boron, see Table 1. However, unlike boron doping, the conduction band downshifted upon nitrogen doping with a significant decrease in the band gap, refer to Fig. 2(d). It is worth mentioning here that we co-doped all nanotubes with boron and nitrogen at the same time. We also controlled the positions of dopants in such a way we covered all possible positions that might occur in reality, refer to Fig. 1. First, we modified the angle between the two dopants and keep the distance between them nearly fixed. We noticed that changing the angle between the dopants has no effect on band gap energy; refer to Fig 3 and Table 1. We also found that changing the distance between boron and nitrogen atoms on the zigzag path practically has no effect in the band gap energy; refer to Figs. 4, and Table 1. However, because of the (10, 5) nanotube chirality, there is neither co-doping on the axial direction nor on the radial direction.

3.2. (10, 0) nanotube

We calculated the band gap energy for (10, 0) pristine CNT using the band structure generated by the DFT calculations. Upon doping (10, 0) CNT with boron atom, we noticed that there is a clear drop in the band gap energy compared to pristine (10, 0) CNT.