Theoretical study of electronic properties of nitrogen doped carbon nanotubes

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Abstract. In this work, we have studied the effects of nitrogen (N) substitutional doping on the electronic properties of single wall carbon nanotube (SWCNT). The electronic density of states (eDOS) of these nanosystems has been calculated in the framework of tight-binding calculations method. The obtained results show that the semiconducting SWCNT could be a quasi-metallic one after N-substitution. We conclude that electronic properties of the N-doped nanotubes (SWCNNT) are sensitive not only to the concentration of nitrogen atoms but also to their distribution on the nanotube surface. Our main results are discussed in the light of the experimental data.

1. Introduction

The Ever since their discovery [1], carbon nanotubes (CNTs) have been proclaimed as the new wonder material of the future. Their extraordinary electronic and optical properties destine them to play an important role in nanoelectronics. Calculations show that the intrinsic electronic properties of SWCNTs can be either semiconducting or metallic, depending on their geometrical structures defined by the chirality and the radius of the tube [2]. The skill to generate defects or/and to introduce impurities into CNT could be the most promising way to change and modulate its electronic properties and thus have a significant bearing on a broad range of applications [3,4]. Recently, different works have been done addressing the changes of CNT properties induced by doping with hetero-atom.

Nitrogen substitution of carbon atoms in NTCs modified the electrical and structural properties of these nanomaterials [5, 19] [6–8]. Both experimental and theoretical studies stated that the hetero-atom doping has an important impact upon the electronic structure of the CNTs [9,10].

The properties of SWCNTs are very sensitive to the tube diameter and chirality, which are depending on the synthesis conditions. A modification of these properties by controllably placing hetero-atoms on the tube surface leads to huge technological applications, which justifies the number of experimental and theoretical investigations focused on this topic. In fact, the electronic properties of SWCNTs can be modified by manipulations the Fermi level, which can be done by chemical doping. It was found that the introduction of hetero-atoms such as boron or nitrogen into SWCNTs offers the possibility of tailoring their structural and electronic properties [11–17]. Recently, SWCNTs doped with nitrogen or boron have been synthesized by laser-ablation [18], arc-discharge [19] and substitution reaction methods [20]. The N doped carbon nanotubes are produced by in situ nitrogen...
substitution and are used, singularly or in multiples, in power transmission cables, in solar cells, in batteries and in composites [21–25] [26].

The electronic properties of individual nitrogen doped SWCNTs (SWCNNTs) have been calculated by density functional theory [27] and tight-binding approach [28]. In this paper, we study the electronic properties of SWCNNTs, by using a force constants model in which the interatomic force constants up to the fourth-nearest-neighbor interactions are fitted to experimental data, to explore the basic properties of nitrogen doping. For this purpose, we perform calculations of the density of states (DOS) and dispersion curves.

2. Models and method

Density functional theory (DFT) methods are the standard and the most used theoretical techniques for electronic structure calculations. The formalism of the DFT and its extension to the chemical reactivity indexes are subject of intensive research and many empirical concepts [29–36]. The method is chosen for a huge range of applications. Density-functional based tight-binding (DFTB) is an approximate method based on the density functional framework which does not require large amounts of empirical parameters. These parameters are obtained from DFT calculations of a few molecules per pair of atom typesTight-Binding (TB) and Force Constant models are semi-empirical methods that do not require a fully self-consistent process for the computation of electron and phonon dispersion curves, and thus are much faster compared to ab initio calculations. However, they require the prior knowledge of some given empirical parameters which are called onsite and hopping energies in electron study and force constant parameters in phonon study. These parameters are usually adjusted so that dispersion results from TB (or Force Constant) simulation fit well with that of ab initio calculation or experiments. Great successes were evidenced from many works using TB methods on many materials and devices, including carbon nanomaterials [37–42]. In this study our approach is based on TB methods correlated to ab initio calculations to describe the electronic properties of nitrogen doped SWCNT and the used TB parameters are $t_{CC} = 2.85$eV and $t_{CN} = 2.96$eV [43]. We focus on the electronic properties of different achiral nitrogen doped carbon nanotubes of different diameters. The variation of the band gap energy with the concentration of N atoms is investigated.

3. Results and discussion

In this section, we report calculation results obtained for the eDOS and dispersion curves of armchair and zigzag single walled carbon nitride nanotubes (SWCNNTs) with different diameters and for different nitrogen concentrations.

3.1 Band structure and eDOS of nitrogen doped carbon nanotubes

In Fig.1, we plot the dispersion curves (on the left) of undoped (17,0) SWCNT which is a typical semiconducting carbon nanotube. As shown, the Fermi level is centered at zero energy with a bandgap energy between conduction and valence bands close to $E_g = 0.6$eV These dispersion relations of a particular nanotube provide excellent information about the electronic properties of that nanotube, however, one may only require the eDOS which is deduced from the dispersion relations. Fig.1 (on the right) shows the electronic DOS of undoped (17,0) nanotube characterized by two separated large bands at low and at high energy.
When the concentration of nitrogen increases the profiles of the dispersion curves and eDOS are slightly affected, however one can see that the gap energy of the nanotube changes when C atoms are substituted by N ones on the surface of the tube. This behavior is well shown in Fig.2 where we plot the dispersion curves and eDOS calculated for doped SWCNNT at doping rate $\tau = 5\%$. At this concentration, the calculated bandgap energy is close to $E_g = 0.63\text{eV}$. To analyze effects of nitrogen concentration (the ratio between the numbers of N atoms and C ones) on the electronic structure of SWCNT, we display in Fig.3, the dependence of the bandgap with the doping rate $\tau$ (in %) for (10,10) N-doped carbon nanotube. We note that we have performed calculations on samples with low nitrogen density limit where N atoms are considered at impurity level. Our results are comparable with the results found in the following references [44,45].

As we can see from Fig.3, the electrical conduction behavior of the nanotube changes from a metal to semiconductor for doping rate $\tau$ ranging from 0% with a gap energy $E_g=0\text{meV}$ to 12% with $E_g=24.2\text{meV}$. In table 1, we give the calculated values of the bandgap for some doping rate and we state that for (10,10) SWCNNT this parameter increases linearly with rate doping.
| Rate doping(%) | Gap(meV) |
|---------------|----------|
| 0             | 0        |
| 2             | 6.8      |
| 4             | 10.7     |
| 6             | 13.4     |
| 8             | 18.2     |
| 10            | 22.5     |
| 12            | 24.2     |

**Table 1.** Gap energy variation with doping rate for (10,10) armchair SWCNNTs

![Graph showing band gap in function of rate doping for (10,10) armchair tube. The Fermi level is located at zero energy.](image)

**Fig. 3.** Band gap in function the rate doping for (10,10) armchair tube. The Fermi level is located at zero energy.

### 3.2 The gap variation with diameter of nitrogen doped carbon nanotube

In Fig. 4, we plot the calculated bandgap of SWCNNT versus diameter for (17,0) (panel a) and (10,10) (panel b) nanotubes with doping rates close to 8% and 5%, respectively. One can observe that for a given doping rate, the gap energy of armchair and zigzag SWCNNTs decreases when the diameter increases and can be represented by the relation: $E_g = A/D$ with $A$ depending on the doping rate, together with $A = 0.14eV.nm$ and $A = 7.47eV.nm$ for armchair tube (a) and zigzag tube (b) respectively. This behavior is analogous to the dependence of the RBM frequency with diameter stated for SWCNT whatever the chirality and the conductivity of the nanotube. These results state that metallic armchair nanotube becomes semiconductor under nitrogen doping.
4. Conclusion

In summary, we have performed band structure calculations on nitrogen doped carbon nanotubes within Tight-Binding approach. Due to nitrogen substitution doping effects, achiral nanotubes exhibit bandgap values linearly depending on the doping rate. The diameter effects study shows that the bandgaps of both zigzag and armchair tubes decrease when the diameter increases. We also note that armchair nanotubes have zero gap but when the doping rate increases these nanomaterials switch from metal to semiconductor. These results may provide guidance in practical engineering applications.

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