Electronic and Structural Properties of Organic Molecules inside Carbon Nanotube

Rodion V. Belosludov, Hiroshi Mizuseki, T. Takenobu, Y. Iwasa and Yoshiyuki Kawazoe

Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan Phone:+81-22-215-2469 Fax:+81-22-215-2052 E-mail: rodion@imr.edu

1. Introduction

The outstanding discoveries of the fullerenes [1] and carbon nanotubes [2] have created a new field of research at the boundary of chemistry and condensed matter physics, and the properties of these carbon materials have been the subject of much attention from both experimental and theoretical viewpoints. Moreover, they have the potential to provide new classes of structural materials, sensors, electronic devices, gas storage materials and many other applications. They also can be used as framework in order to stabilize novel one-dimensional systems of different atoms or molecules [3, 4].

For molecular electronics applications carbon nanotubes are also very attractive materials because they have molecular-scale diameters. In the case nanoscale interconnections between electronic devices, it is important that the molecular wires should have metallic characteristics. Thus, carbon nanotubes (CNTs) are very attractive materials among the different candidates for molecular wires. Unfortunately, there are some limitations to using these materials. For instance, separation of metallic CNTs from semiconducting CNTs is still a significant challenge for experimentalists. This problem can be solved by doping both metallic and semiconducting CNTs in order to enhance the metallic features of the nanotubes. Recently, the possibility of CNT doping with different organic molecules has been reported experimentally [5], exemplifying importance of estimating the electronic and conductance properties of doped semiconductor CNTs.

Since the size of these molecular devices is a few nanometers, first-principles calculations have become important tools for predicting new electronic devices with the desired physical characteristics in parallel with the development of effective fabrication technologies. Despite the fact that the first-principles methods are either computationally expensive, they are important because can propose novel nanodevices as well as enrich experimental intuition.

Recently, using the first-principles calculations it was shown, that the semiconducting single-wall carbon nanotube (SWNT) can be doped by tuning the electron affinity or ionization potential of encapsulated organic or organometallic molecules [6] in agreement with the optical adsorption measurements on organic molecules doped SWNTs [5]. However, the selected intercalation density of organic molecules (molecule/ C_{128}) was smaller than experimentally estimated values (molecule/ C_{140}). This imposed a limitation on possible configuration of organic molecules inside CNTs because the diameter of selected (16,0) SWNT could be smaller than in experiment. Here, we try to overcome this limitation using the SWNTs with large diameter than one used previously [6].

2. Computational method and model

The firs-principles calculations were performed within density functional theory, using the pseudopotential method and a plane-wave basis set. Exchange correlation was included using the generalized gradient corrected functional. The energy cutoff was set to 350 eV and the convergence in energy and force were 10^{-4} eV and 3×10^{-3} eV/Å, respectively. The $(1 \times 1 \times 5)$ Monkhost-Pack point mesh were used. All calculations were performed using the Venna Ab Initio Simulation Package (VASP) [7]. In order to compare with experimental date, the intercalation density of organic molecules (molecule/ C_{140}) in the case of metallic (12,12), (10,10) and density (molecule/C₁₃₆) in the case of semiconducting (17,0) SWNTs have been selected. The calculated model includes two organic molecules in one supercell with total number of carbon nanotube atoms are 280 and 272, in the cases of metallic and semiconducting SWNTs, respectively.

The methods employed permit accurate intercalation energies to be calculated from the energy differences between the binding energy of the intercalation systems and those of empty SWNT and free molecules.

$$\Delta E = E_{SWNT/2MOL} - E_{SWNT} - 2E_{MOL}$$
(1)

where E_{SWNT} , E_{MOL} , and $E_{SWNT/MOL}$ represent the binding energies of the empty SWNTs, free organic molecules, and the intercalation systems, respectively. The negative value of ΔE means that the corresponding configuration of inserted molecules is thermodynamically favorable.

3. Results and Discussion

At the first step, we investigate the configuration of anthracene molecules inside metallic (12,12) SWNT. As mentioned before, the density of inserted molecules has been selected as in experiment [5] and the different possible configurations of anthracene dimer inside carbon nanotube have been chosen. Figure 1 shows the optimized structures of anthracene dimer inside (12,12) SWNT. It has been found that the most stable structure has face to-edge geometry (see Fig. 1d) as in free space [8]. In this case, the interaction energy between anthracene molecule and carbon nanotube is equal to -0.140 eV. The S-shape ("stacked") configurations have lower interaction energies that the most stable T-shape configuration and the energy values depend on the angle between molecular plane and tube axis. The interaction energies of anthracene with nanotube in co-planar configurations are equal -0.039eV, -0.045eV and -0.091eV, for parallel, rotated on 45 degree, and perpendicular structures, respectively. Thus, in the case of (12,12) SWNT, the carbon nanotube does not affect on configuration of organic molecules.



Fig. 1 Configuration of anthracene molecules inside (12,12) SWNT: (a) S-shape, parallel; (b) S-shape, rotated on 45 degree; (c) S-shape, perpendicular; and (d) T-shape structures.

However, in the case of (10,10) nanotube, the most stable configuration of anthracene dimer is changed and the planar geometry along tube axis has highest interaction energy (Fig. 2a). In this case, the value of intercalation energy is -0.145 eV which is the same as in the case of the most stable structure in (12,12) SWNT. The perpendicular S-shape (Fig. 2c) and T-shape (Fig. 2d) structures have positive value of ΔE (+0.271 eV and +0.142 eV, respectively).



Fig. 2 Configuration of anthracene molecules inside (10,10) SWNT: (a) S-shape, parallel; (b) S-shape, rotated on 34 degree; (c) S-shape, perpendicular; and (d) T-shape structures.

It is also found that the previous proposed configuration [6] (in the case of (16,0) SWNT) has lower intercalation energy (-0.138 eV) than the most stable one. In the case of anthracene doped SWNT, there is no charge transfer between inserted molecules and wall of nanotube (see Fig. 3a) and the interaction of anthracene molecule with SWNT is van der Waals one. This result is well correlated with experimental observation of optical adsorption measurements [5].

The situation is changed in the case of doping (10,10) SWNT by tetracyano-*p*-quinodimethane (TCNQ). In this case, the interaction between TCNQ and SWNT is much stronger than that in the anthracene/SWNT case. The value of intercalation energy of TCNQ is equal to -0.549 eV in the case of parallel S-shape configuration. The favorable intercalation is associated with the charge transfer ($\Delta q = 0.7$ e, see Fig. 3b) from SWNT to organic molecule followed by delocalization of a negative charge on the N atoms. Again

the structure, which is found to be stable in the case of (16,0) SWNT [6], has lower intercalation energy than one in the most stable case. It is also obtained that the TCNQ molecules in planar case can slide over each other which indicate that the configuration of TCNQ molecules is more likely random than the regular one-dimensional stacking.



Fig. 3 Charge density contours of (a) anthracene and (b) TCNQ in (10,10) SWNT.

4. Conclusions

The electronic and structural properties of different organic molecules inside SWNT have been investigated by firs-principles calculations. It has been found that the configurations of organic molecules are sensitive to changes in diameter of SWNT from 12.53Å (16,0) to 13.56Å (10,10). The sliding ability of the TCNQ inside (10,10) nanotube is in agreement with experimental XRD measurements which did not indicate any extra XRD peaks attributable to the regular one-dimensional configuration of organic molecules in SWNT [5].

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