First-principle Studies on the Doping Behavior of the Coal-based Carbon Nanotubes

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Abstract. This work presents the studies of structure and functional properties of coal-based carbon nanotubes (CNTs) affected by nitrogen and silicon doping. The (6, 6) tube doped by silicon and nitrogen atoms were investigated by using the first-principles self-consistent field crystal orbital method. The relative stabilities, electronic conducting properties and young's modulus of coal-based CNTs affected by silicon or nitrogen doping are explored and discussed. The results suggest that the defect formations of nitrogen and silicon doping are both energetically unfavorable, especially for silicon doping. The band structure calculations show that the tube with nitrogen doping exhibits metallic conducting state, whereas the Si-doped tube becomes a semiconductor. Young's modulus results indicate that nitrogen doping could enhance the mechanical properties of coal-base CNTs.

Keywords: Coal-Based Materials, Carbon Nanotubes, Electronic Conducting, Mechanical Property.

1. Introduction

Carbon Nanotube (CNT), one of the allotropes of Carbon with great importance, can be considered one-dimensional tubular materials composed of graphite pieces. It has arisen much of concern in the chemistry, physics, materials science and nanotechnology due to the semiconductor/metal and superconductor properties [1], high carrier mobility [2] and good mechanical property [3] in recent years. Also it is good candidate of the new generation of electronic triode with good prospects in nanoscale electronic devices.

At present, the CNTs have been prepared by using the coal as raw materials in the laboratory by several research groups [4-9]. Obvious this opens up a low-cost preparation of carbon nanotubes. The studies have pointed out that the unit of Cn (n = 1, 2) is the building blocks in preparation of CNTs with high purity graphite electrode by using the traditional arc discharge method. However, the polycyclic aromatic hydrocarbons Cn (n = 6 or higher) now have been identified directly as a fragment to build the carbon networks in the preparation of coal-based carbon nanotubes. Therefore preparation of CNTs from coal as raw materials has double advantages: high efficiency and low price [6-8].

It is should be pointed that silicon, nitrogen atoms in the inorganic/organic components of coal may be incorporated into CNTs structures in the process of preparation of coal-based CNTs. These impurities will affect the quality and function characteristics of the CNTs [5-8]. In addition, the nitrogen doping could also achieved by adding some compounds in preparation of CNTs [10]. For instance Campos et al. recently announced that silicon doped CNTs were synthesized by using chemical vapor deposition method [11].

However, there are still few studies available for coal-based CNTs. Especially, the effects of nitrogen and silicon doping on the structures and functional properties of coal-based CNTs do not well understand. On the other hand, the movement of electrons in the low dimension materials, such as CNTs, is confined to close the de Broglie wavelength, and thus the wave feather becomes the overwhelming. In order to study the behavior of the carrier appropriately and describe the novel properties correctly of these low dimensional materials, it is desired to use computational chemistry research based on quantum mechanics.

This paper presents our quantum chemistry studies of coal-based CNTs containing nitrogen and silicon doping atoms by using the self-consistent field crystal orbital (SCF-CO) method. The studies mainly discuss the effects of nitrogen and silicon doping on the structure, energy electronic and mechanical properties of coal-based CNTs.

2. Models and Computational Methods

This article selects typical (6, 6) armchair CNT as the mother structure. This tube has the diameter of about 8 A, and can be obtained in many experiments [12-13]. Firstly we produce the single cell of tube (6, 6), and then extend to the structure with five unite cells containing 120 carbon atoms, as shown in Fig. 1. The initial models of the coal-base tubes can be built by replacing a carbon atom by a nitrogen atom or silicon atoms. In the calculations, the CNTs are treated as the one-dimensional infinite nanowires, under the consideration of periodical boundary condition. The model of armchair CNTs with five unit cells of armchair has the lengths about 12 Å. This distance means the interaction between two adjacent nitrogen or silicon doping defects in one-dimensional infinite model will be very small and this would not introduce much artificial error.

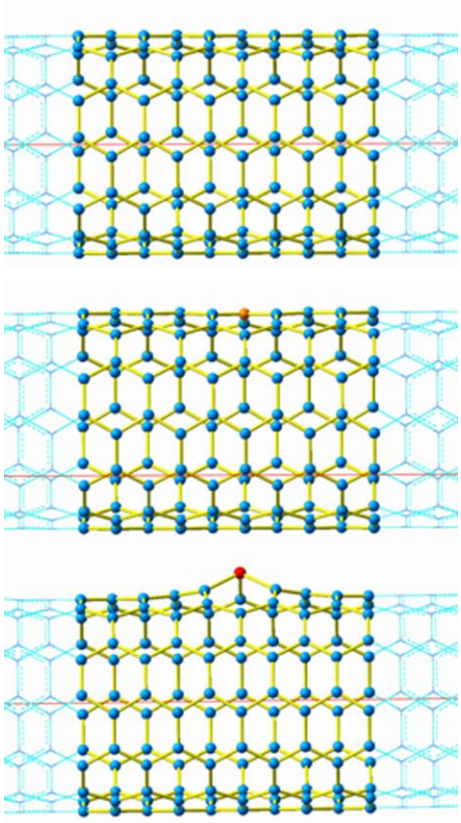

Fig. 1 The obtained (6, 6) tubes with geometrical optimization for the pure (top), N-doped (middle) and Si-doped (bottom) structures.

All the geometric structure optimization and the calculation of energy and electronic properties in this paper are performed based on density functional theory (DFT) combined with SCF-CO method. In the study, the hybrid functional method B3LYP at the 6-21G* theory level embedded in CRYSTAL09 package [14] are adopted to calculate the system of silicon, nitrogen doped CNTs. According to the previous calculations, the B3LYP method has been successfully applied to the theoretical studies on carbon-based materials obtained by doping the CNTs and fullerenes [15-17]. In the SCF-CO calculations, the default values of convergence criteria in CRYSTAL09 programs and 40 k-points sampling in the first Brillouin zone are used.

3. Results and Discussion

3.1. Energy and Relative Stability.

The computed total energies of the pure, N- and Si-doped tubes are listed in Table 1. To study the thermodynamic stability of the tube with doping defect, the defect formation energy (ΔE) of the doped tubes can be calculated by:

$$\Delta E = E_{\text{X-tube}} + E_{\text{C}} - E_{\text{CNT}} - E_{\text{X}} \quad (1)$$

Where $E_{\text{X-tube}}$ and E_{CNT} respectively are the energy of doped and pure CNTs, E_{C} and E_{X} are the ground energy of isolated carbon and doping atoms.

Table 1. Total energy (E_{total}), doping defect formation energy (ΔE), POAV and Young's modulus (Y) of the pure, N- and Si-doped (6, 6) tubes.

Tube	E_{total} (Hartree)	ΔE (eV)	POAV (°)	Y (GPa)	Y (eV/atom)
(6, 6)	-4567.9450769	/	5.0	1900	64.9
N-(6, 6)	-4584.5220155	4.571	5.4	2034	69.4
Si-(6, 6)	-4819.2384126	6.365	26.9	1871	64.5

As shown in Table 1, the defect formation energy of N- and Si-doped tubes are 4.571 and 6.365 eV, respectively. The positive values of indicate that the formations of the N- and Si-doping defect are both endoergic. Thus the formations of these two substitutional defects are energetically unfavorable from viewpoint of energy change in the reaction. Here ΔE of Si-doped defect gives 6.365 eV, and larger than 1.794 eV for N-doped tube. This fact means that the silicon doping is more difficult than nitrogen and it explains why the N-doping is more common than that of silicon [5-8].

In order to get more about the reason about the difference between the defect formation energies of N- and Si-doped tubes, we perform the Pi-Orbital Axis Vector, (POAV) analysis for the nitrogen, silicon and carbon atom in the pure and doped tubes. As shown in Table 1, the POAV angles are 5.4, 26.9 and 5.0 °for the nitrogen, silicon and carbon atom according to the POAV theory. It is observed that the silicon atom exhibits more obvious enhancement of POAV angle than that of Nitrogen. This can be ascribe to that the carbon atom is more close to that of Nitrogen, while obvious smaller than that of Silicon. Thus the structural deformation is more obvious for silicon doping than nitrogen doping. This is also confirmed by the geometrical structures shown in Fig. 1.

3.2. Energy Band structure.

The energy band structures based on the SCF-CO calculations under the formwork of DFT are shown in Fig. 2. As can be seen from the figure, the Fortier bands of pure (6, 6) tube touch each other, and they both cross with the Fermi energy level. This means that the partially filled energy band is present. Thus the pure (6, 6) tube shows metallic property. This fact agrees with the previous DFT calculations [1].

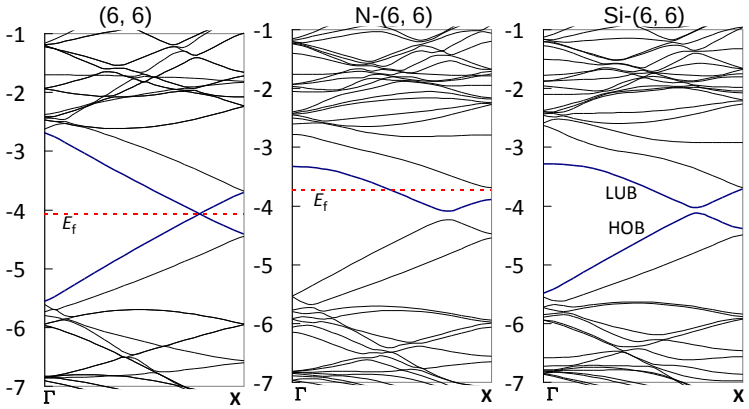

Fig. 2 Energy band structures of the pure, N- and Si-doped (6, 6) tubes

As for the N-doped tube, the Fortier bands cross with the Fermi energy level, and thus also exhibit conducting state. This indicates that the metallic property of the (6, 6) tube is not change upon the nitrogen doping. However, the situation is different for the Si-doped tube. As shown in the figure, the highest occupied band (HOB) and the lowest unoccupied band (LUB) do not touch each other, but open a energy gap with 0.108 eV. Thus the silicon doped (6, 6) tube exhibit semiconducting property with the direct gap of 0.108 eV. This is a very interesting result, which means that the silicon doping

could not only affect the geometrical structures, but also induce the metal/semiconductor transition for the armchair CNTs.

3.3. Mechanical Property.

The Young's modulus is one of the parameters with great important to study the mechanics of the materials. The calculation of Young's modulus here is based on the elastic stiffness of the 1D system using the second derivative of the strain energy of a unit cell with respect to the axial strain. The details for the calculations of Young's modulus can be seen previous studies [2]. As listed in Table 1, the calculated Young's modulus of CNT (6, 6) is 1.90 TPa, which agrees well with those obtained by the calculation and the experiment [2, 3]. The Young's modulus of the N-doped tube is 2.03 TPa with the same method. Thus the present of the nitrogen atoms in the CNTs could increase the stiffness of the tubes by about 7%. This means that the coal-based CNTs with nitrogen atom impurity exhibit better mechanical property. As for the Si-doped tube, the obtained Young's modulus is 1.87 TPa, and a bit smaller than that of pure one. Thus silicon doping would decrease the mechanical property along the axis of the tube.

4. Conclusion

The coal-based carbon nanotubes were studied by using the SCF-CO method based on the DFT calculations. The effects of nitrogen and silicon doping on the geometrical structures, energies, electronic properties and Young's modulus are investigated. The defect formation energy of silicon is larger than that of nitrogen because the silicon atom has a larger axial vector angle. According to the energy band structure, nitrogen doped tube still keep the original metallic conductivity while silicon doped tube becomes a semiconductor with energy gap 0.108 eV. The young's modulus results show that the young's modulus of silicon doped tubes slightly smaller than that of pure tube. However the nitrogen doping can enhance the mechanical properties of the coal-base CNTs.

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