DENSITY FUNCTIONAL THEORETICAL STUDIES ON CARBON-BASED NANOTUBES MODIFIED WITH FUNCTIONAL MOLECULES

WANG YANJIN

DOCTOR OF PHILOSOPHY

CITY UNIVERSITY OF HONG KONG

MAY 2008

CITY UNIVERSITY OF HONG KONG
香港城市大學

Density Functional Theoretical Studies on Carbon-based Nanotubes Modified with Functional Molecules

功能分子修飾碳基納米管的密度泛函理論研究

Submitted to
Department of Physics and Materials Science
物理及材料科學系

in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
哲學博士學位

by

Wang Yanjin
王延金

May 2008
二零零八年五月

Abstract

Carbon nanotubes (CNTs), quasi-one-dimensional structures rolled from the two-dimensional hexagonal lattices of graphene sheets with the local bond arrangement conserved, provide opportunities for engineering novel physical properties suitable for ultimate device miniaturization. Recent interest in CNTs has focused on the various physical properties of nanotubes functionalized in different ways. The presence of weak interactions, e.g. van der Waals interaction and π-π stacking, is known to allow CNTs to aggregate into bundles and to make CNTs soluble in organic solvents. Modification of CNT surfaces with functional molecules is expected to give rise to novel materials with interesting properties and prospects for future nanodevice applications.

In the thesis, a conventional density-functional theoretical method and a self-consistent-charge density-functional tight-binding (SCC-DFTB) approach augmented by an empirical London dispersion correction (DFTB-D), were used to study the carbon based nanotubes modified with various functional molecules. Previous works have demonstrated that the DFTB-D method is an efficient way to deal with systems involving weak interactions.

In Chapter 3, noncovalent exo-modifications of CNTs with conjugated polymer were explored. Noncovalent surface modification is expected to open up the possibility of organizing CNTs into ordered networks without disrupting their electron conjugation characteristics. Our calculated results showed that the binding energies between poly phenylenethynylene (PPE) and (n, n) CNTs increase when the diameters increase for $n \leq 9$ and then decrease due to steric hindrance effect. It is evident that the combination is

made by π - π and van der Waals interactions with very small charge transfers involved. Significant blue shifts in the absorption and emission spectra of PPE upon interacting with the CNTs were revealed in the calculation, which are responsible to the optical quenching observed in experiment.

The mechanism of water transport through membrane channels has attracted great attention but still remains poorly understood because of the difficulty in separating generic causative features of transport from specific molecular and chemical details. Due to the similarities in the structures of the hydrophobic channels of transmembrane protein with CNTs, the simulated process of water transporting in CNTs is an excellent model for understanding water transport through membrane channels. In Chapter 4, the water chains encapsulated within CNTs were studied. The most interesting and important feature we observed is the diameter shrinking of CNTs when water chains are confined inside CNTs. The diameter shrinking of CNTs can be attributed to the van der Waals and H-π interaction between water chains and CNTs. Our calculated Raman spectra showed that the interactions between CNTs and water chains probably give rise to a kind of "mode hardening effect," consistent with the diameter shrinkage of CNTs when water chains are confined in CNTs. The calculated hydrogen bonding energy is 2.64 kcal/mol, suggesting the presence of weak hydrogen bonding when water is confined in the narrow tube.

Due to the high surface area to volume ratio, CNTs have been proposed to be a kind of possible hydrogen storage materials. In Chapter 5, we performed first-principles calculations based on DFT to study the electronic and atomic structures of fully hydrogenated CNTs which are relevant to hydrogen storage and device application. Our calculations showed that the exohydrogenated C atoms strongly stick out and the endhydrogenated C atoms moved strongly inwards, resulting in an inner endhydrogenated C cylinder and an outer exodhydrogenated C cylinder. The hydrogenation energy varies linearly with the inverse of the square of the tube diameter. The armchair structure has a larger binding energy than the zigzag structure, for a given diameter of fully hydrogenated CNTs (C_nH_n), suggesting that hydrogenation is more exothermic for the armchair nanotubes for a given tube radius. The band gap of CNTs is greatly increased by the hydrogenation of all carbon atoms of CNTs. The observed band gap opening via hydrogenation of nanotubes can be used in band gap engineering for device applications.

There exist all kinds of different length of the ultrasmall radius single-walled nanotubes grown from zeolite templates (e.g., AFI) by pyrolysis of tripropylamine (TPA) moleculs. In Chapter 6, we employed the density-functional tight-binding method to study the tube length effect on the structural, electronic, vibrational, and optical propterties of ultrasmall radius single-walled nanotubes.

The successful synthesis of BN nanotube has open up the possibility of the existence of tubular structures made of either noncarbon or partially carbon materials. For example, silicon carbide nanotubes (SiCNTs) have been produced via the reaction of Si with carbon nanotubes. SiCNTs are expected to have the advantages over CNTs because they may possess high reactivity of exterior surface facilitating sidewall decoration and stability at high-temperature. There are two possible structures for SiCNTs: one consists of alternating Si and C atoms and another one consists of pairs of C=C and Si=Si. In the thesis (Chapters 7 and 8), the two distinct types of SiCNT have been studied. Our results showed that the two distinct categories are close in energies, but show significant difference in electronic and transport properties. For the first type of structure (alternating Si and C atoms), both the cohesive and the strain energies vary inversely proportional to the square of the nanotube diameter, irrespective of the type (zigzag, armchair or chiral) of the SiCNTs. In contrast, the energy gap is very sensitive to both the diameter and the type of the nanotube. All three types of SiCNTs (zigzag, armchair and chiral) were found to be semiconductors with small band gaps (~1eV). However, the zigzag and chiral SiCNTs considered here show $n = 3k$ anomaly, with the band gaps of zigzag (n, 0) SiNTs being somewhat larger and approaching those of the armchair (n, n) SiCNT when $n = 3k$. For the second type of structure (pairs of C=C and Si=Si), the SiCNTs structures exhibit considerable distortions with one of the silicon atoms of the Si=Si bond being sp^3-like while the remaining silicon atom and the C=C bond being sp^2-like. As a result, the tube cross sections adopt interesting polygonal shapes. Both the cohesive and the strain energies vary inversely proportional to the square of the nanotube diameter. The armchair structure has larger strain energy than the zigzag structure, for a given diameter of SiCNTs. The calculated energy gap of SiCNTs decreases monotonically with increasing diameter and saturates at the calculated gap for graphitic sheet of SiC. The armchair structure has a larger energy gap than the zigzag structure, for a given diameter of SiCNTs.

Theoretical predictions played an important role in guiding experimental studies in the past and we expect that many findings reported in this thesis may have important implications in the nanodevice applications of these interesting systems.

Table of Contents

Abstract .... **i**
Acknowledgement .... **v**
Table of Contents.. **vi**
List of Figures .... **x**
List of Tables.. **xv**

Chapter 1. General Background and Introduction **1**
  1.1. General Background of Carbon Nanotubes **1**
  1.2. Physical Properties of Carbon Naotubes **2**
    1.2.1. Atomic and Electronic Structure **2**
    1.2.2. Geometric Structure and Energetics of Bare SWCNTs.. **5**
    1.2.3. Energy Band Structure **8**
  1.3 Chemical Properties of Carbon Naotubes.. **13**
    1.3.1. Aromaticity of SWCNTs and Clar Valence Bond (VB) Model Description... **13**
    1.3.2. Aromaticity and Chemical Reactivity: A Chemist's View.. **22**
  1.4 Our Approaches **23**
  1.5 References.. **26**
Chapter 2. Theories and Models.. **30**
  2.1 DFTB Method.. **30**
    2.1.1 Dispersion Energy Correction.. **36**
    2.1.2 Time-dependent DFTB (TD-DFTB).. **39**
  2.2 References.. **42**
Chapter 3. Noncovalent Modification of Carbon Nanotubes by Conjugated Polymer: A Theoretical Study.. **44**

3.1 Introduction **44**

3.2 Theoretical Methods and Models **47**

3.3 Results and Discussion **50**

3.3.1 Binding Energies **50**

3.3.2. Optical Spectroscopy **53**

3.4 Conclusions **59**

3.5 References **60**

Chapter 4. Signatures in Vibrational and Absorption Spectra of the Complex System of Water Chain Encapsulated in Carbon Nanotube Revealed by Density Functional Theory **63**

4.1 Introduction **63**

4.2 Computational Method **66**

4.3 Results and Discussion **68**

4.3.1 Geometrical Structures **68**

4.3.2 IR Spectra **72**

4.3.3 Raman Spectra **75**

4.3.4 Absorption Spectra **77**

4.4 Conclusions **79**

4.5 References **80**

Chapter 5. Full Hydrogenation of Carbon Nanotubes: Theoretical Studies **84**

5.1 Introduction **84**

5.2 Method of Calculations **86**

5.3 Results and Discussion **88**

5.3.1 Geometry 88
5.3.2. Hydrogenation Energy 93
5.3.3 Energy Gap 95
5.4 Conclusions 98
5.5 References 99
Chapter 6. Finite-length Single-walled 4 Å Carbon Nanotubes: A Theoretical Study **101**
6.1 Introduction 101
6.2 Computational Method 104
6.3 Results and Discussion 106
6.3.1 Geometry 106
6.3.2 Energy Gap 108
6.3.3 Radial Breathing Mode 111
6.4 Conclusions 116
6.5 References 117
Chapter 7. Silicon-Carbon Nanocomposites: A Theoretical Investigation **119**
7.1 Introduction 119
7.2 Computational Details 121
7.3 Results and Discussion 124
7.3.1 Geometry 124
7.3.2 Cohesive Energy 127
7.3.3. Strain Energy 129
7.3.4. Energy Gap 130
7.4 Conclusions 132

7.5 References **133**

Chapter 8. α Silicon in Silicon-Carbon Nanotubes: Theoretical Investigations .. **134**

8.1 Introduction **134**

8.2 Method of Calculations **136**

8.3 Results and Discussion **137**

8.3.1 Geometry **137**

8.3.2 Cohesive Energy **142**

8.3.3. Strain Energy **143**

8.3.4. Energy Gap **146**

8.4 Conclusions **147**

8.5 References **149**

Chapter 9. Summary **152**

Appendix. List of Publications **155**

List of figures

Figure 1-1. Inset: a schematic side view of a zigzag SWCNT, indicating two types of C–C bonds and C–C–C bond angles. These are labeled as d_1, d_2, θ_1 and θ_2. (a) Normalized bond length ($d_1/d_0$and d_2/d_0) versus the tube radius *R* (*d*0 = 1.41 Å). (b) The bond angles (θ_1 and θ_2) versus *R*. (c) The curvature energy, *E*cur per carbon atom with respect to graphene as a function of the tube radius. The solid curves are the fit to the data as *α/R*2.

Figure 1-2. A map of chiral vectors that determine the chirality of SWCNTs. Each vector is specified by the *(n,m)* indices. M, S and C denote metals, semiconductors and curvature induced of small gap semiconducting SWCNTs, respectively.

Figure 1-3. (a) Energies of the doubly degenerate π states (VB), the doubly degenerate π^* states (CB) and the singlet π^* state as a function of nanotube radius. Each data point corresponds to *n* ranging from 4 to 15 consecutively. (b) The calculated band gaps of [18] are shown by filled symbols. Solid (dashed) curves are the plots of equation (2) (equation (1)).

Figure 1-4. Clar VB representations of (a) pyrene ($C_{16}H_{10}$), (b) dibenzopyrene ($C_{24}H_{14}$), (c) triphenylene ($C_{18}H_{12}$) and (d) hexabenzocoronene ($C_{42}H_{18}$), where the aromatic sextets and the conventional two-electron *ð*-bonds are represented by circles and lines, respectively.

Figure 1-5. Clar VB representation of (12, 9), (12, 8), (12, 7), and (19, 0) SWCNTs.

Figure 1-6. Planar representations of short (12, 9), (12, 8), and (12, 7) CNTs shown with the Clar VB structures. Filled circles represent the magnitude of the average of the NICS values inside and outside the CNT, with the radius normalized to the largest value. Red is negative, and green is positive.

Figure 1-7. Schematic structures and color-coded NICS (ppm) maps of finite-length (*n*,*n*) SWCNTs (*n* = 5 and 6). Hydrogen atoms are omitted for clarity. Chemical bonds are schematically represented by using single-bond (solid single line; bond length > 1.43 Å), double-bond (solid double line; bond length < 1.38 Å), single-bond halfway to double bond (solid-dashed line; 1.43 Å > bond length > 1.38 Å), and Clar structures (i.e., fully benzenoid). NICS coding: red, aromatic < -4.5 ppm; blue, nonaromatic > -4.5 ppm.

Figure 1-8. HOMO/LUMO levels and band gap oscillation of the finite-length (5,5) CNTs ($C_{10j}H_{20}$). The values were determined by PM3 level calculations, and the trend parallels the one observed in the B3LYP/6-31G* calculations (for $C_{40}H_{20}$ until $C_{120}H_{20}$).

Figure 1-9. Reaction energies (in kcal mol-1) for the addition of fluorine atom to (5,5) SWCNT models $C_{30}+10nH_{20}$ (*n* = 0-18) as computed at the (U)B3LYP/6-31G* //(U)PBE/ 3-21G level of theory.

Figure 2-1. Comparison of CPU usage for different methods including the quantum chemical INDO/S approach as well as TDDFRT with different basis sets. Shown in the figure is the total CPU time in seconds for the complete set of organic molecules.

Figure 3-1. The optimized structures of (a) PPE, (b) (5, 5) CNT, and (c) CNT-PPE.

Figure 3-2. The dependence of "Binding energy" of PPE adsorbed on the exterior. surface of CNTs and the "Distance" between the CNT and PPE backbone on the diameters of the (n,n) CNTs.

Figure 3-3. Optical gaps of (n, n) CNTs (n=3-10) versus the radius of the tubes.

Figure 3-4. The emission and absorption spectra at UV-visible region of the armchair (5, 5) CNT, PPE and CNT-PPE complex.

Figure 3-5. The frontier orbital energy levels of the PPE, (5, 5) CNT and CNT-PPE respectively.

Figure 4-1. The optimized structures of (a) (6, 6) SWCNT, (b) Water Chains and (c) Water chains /CNT.

Figure4-2. The IR spectra of pentagona(a) (6, 6) SWCNT, (b) Water Chains and (c) Water chains /CNT for the absorption frequency between 0 and 4000 cm^{-1}.

Figure 4-3. The Raman spectra of (a) (6, 6) SWCNT, and (b) Water chains /CNT for the absorption frequency between 0 and 2000 cm^{-1}.

Figure 4-4. The absorption spectra of (a) (6, 6) SWCNT and (b) Water chains /CNT.

Figure 5-1. Ball-and-stick model of finite sections of fully hydrogenated single-walled carbon nanotubes (SWCNT): (a) armchair (5, 5), (b) zigzag (10, 0). The arrows in the figure indicate those kinds of bonds that are aligned "along" the tube axis, other bonds are considered as that aligned “around” the tub circumference.

Figure 5-2. Hydrogenation energy vs 10^3/diameter^2 for he fully hydrogenated CNTs.

Figure 5-3. Band gap vs 10^3/diameter^2 for the fully hydrogenated CNTs.

Figure 5-4. The model of metal-insulator heterojunctions.

Figure 6-1. Ball-and-stick model of finite sections of 4Å single-walled carbon nanotubes (SWCNT): (a) armchair (3,3) and (b) chiral (4,2). The arrows indicate those kinds of bonds that are aligned “along” the tube axis, other bonds are considered as that aligned “around” the tub circumference.

Figure 6-2. Schematic structures of finite-length (3, 3) CNTs: (a) Kekule network, (b) incomplete Clar network, and (c) Clar structures.

Figure 6-3. Energy gap of 4Å single-walled carbon nanotubes (SWCNT) with different tube length: (a) armchair (3, 3), and (b) chiral (4, 2).

Figure 6-4. Frequency of radical breathing mode (RMB) of 4Å single-walled carbon nanotubes (SWCNT) with different tube length: (a) armchair (3, 3), and (b) chiral (4, 2).

Figure 7-1. Optimized structures of (a) armchair (5, 5) and (b) zigzag (8, 0) nanotubes with alternate Si and C atoms. Black and grey balls represent silicon and carbon atoms, respectively.

Figure 7-2. Sums of bond of angles $\sum\alpha$ and $\sum\beta$ vs the diameter of the SiCNTs.

Figure 7-3. Cohesive energy vs 10^3/diameter^2 for the SiCNTs.

Figure 7-4. Strain energy vs 10^3/diameter^2 for the SiCNTs.

Figure 7-5. Energy gap vs the diameter for the SiCNT.

Figure 8-1. Optimized structures of (a) armchair (5, 5) and (b) zigzag (8, 0) nanotubes with alternate Si and C atoms. Black and grey balls represent silicon and carbon atoms, respectively.

Figure 8-2. Sums of bond of angles $\sum\alpha$ and $\sum\beta$ Vs the diameter of the SiCNTs.

Figure 8-3. Cohesive energy vs 10^3/diameter^2 for the SiCNTs.

Figure 8-4. Strain energy vs 10^3/diameter^2 for the SiCNTs.

Figure 8-5. Energy gap vs the diameter for the SiCNTs.

List of Tables

Table 1-1. Band gap, E_g, as a function of radius R for $(n, 0)$ zigzag nanotubes. M denotes the metallic state. The first-row values were obtained within the GGA. The second and third rows give LDA results, while all the rest are tight binding (TB) results. The two rows are for two different TB parametrizations.

Table 2-1. Parameters of Slater-Kirkwood effective number of electrons N_α, static atomic polarizabilites P_α and the range of the overlap of two atoms R_0 for atoms C, O, H, F, S, P, Al, Cu, and Au.

Table 5-1. Various parameters of the fully optimized structures of fully hydrogenated armchair and zigzag carbon nanotubes.

Table 6-1. Calculated structural parameters for (5, 0), (3, 3) and (4, 2) tubes. R is the average diameter of nanotube. T is the length of translational vector along the tube axis, D1 is the average bond length “along” the tube axis, and D2 is that “around” the circumference of the tube. E is the calculated folding energies per carbon atom.