Theoretical investigation of chirality control in single walled carbon nanotube growth

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THEORETICAL INVESTIGATION OF CHIRALITY
CONTROL IN SINGLE WALLED CARBON NANOTUBE
GROWTH**

WANG QIANG

School of Chemical and Biomedical Engineering

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List of Abbreviations

Å	Angstrom
a.u.	atomic unit
BLYP	Becker-Lee-Yang-Parr
B3LYP	Becker's three-Parameter-Lee-Yang-Parr
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
DFT	Density Functional Theory
DOS	Density of States
ELF	Electron Localization Function
eV	electron Volt
fcc	face-centered cubic
GGA	Generalized Gradient Approximation
hcp	hexagonal close-packed
HEG	Homogenous Electron Gases
HF	Hartree-Fock
HiPCo	High Pressure Co
IRC	Intrinsic Reaction Coordinate
LDA	Local Density Approximation
MCM-41	Mobil Composition of Matter 41
MD	Molecular Dynamic
MWCNT	Multi Walled Carbon Nanotube
NEB	Nudge Elastic Band

oss	octahedral subsurface site
PAW	Projector Augmented Wave
PBE	Perden-Burke-Ernzerhof
PEP	Potential Energy Profiles
PES	Potential Energy Surface
RE	Relative Energy
REBO	Reactive Empirical Bond Order
SCF	Self-Consistent Field
SWCNT	Single Walled Carbon Nanotube
TEM	Transmission Electron Microscope
TS	Transition State
tss	tetrahedral subsurface site
VLS	Vapor-Liquid-Solid
XC	Exchange-Correlation
ZPVE	Zero Point Vibrational Energy

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Abstracts**Theoretical investigation of chirality control in single walled carbon
nanotube growth**

Wang Qiang

Nanyang Technological University

2011

The present thesis focuses on theoretical investigation of chirality control in single walled carbon nanotube (SWCNT) growth. Chirality controlled growth of SWCNTs is an essential prerequisite for their many potential applications. The experimental studies have found similar chirality selectivity toward higher chiral angle SWCNTs, in particular small diameter nanotubes such as (6,5) and (7,5). Also, experimental observations show that SWCNT chirality selectivity might be determined by the dynamic interplay between metal catalyst clusters and carbon caps/networks sprouted on metal cluster surfaces. In current work, two main factors on SWCNT chirality selectivity are studied theoretically: (1) the growth and chirality change mechanism for a series of higher chiral angle caps/tubes; (2) the nature of interaction between metal clusters and growing carbon structures in chirality selective growth for the higher chiral angle SWCNTs. Especially, potential energy surface (PES) was using to explore growth and chirality change mechanism for a series of the higher chiral angle SWCNTs. Two competitive reaction paths, i.e. chirality change induced by single C atom and nanotube growth through C₂ dimer addition, are identified. It is found that the direct adsorptions of C or C₂ on growing cap/tube edges have no energy barrier. Moreover, the incorporations of adsorbed C or C₂ also display low energy barriers, indicating

SWCNT growth and chirality change are thermodynamically and kinetically feasible under catalyst-free growth conditions. In addition, the concentrations of C and C₂ in experimental environment would play a critical role in the chirality selective SWCNT synthesis. Furthermore, the growths of zigzag (9,0), armchair (5,5), and near-armchair (6,5) nanotubes on a Ni₅₅ cluster are investigated. During the SWCNT nucleation, atomic carbon is a key intermediate interacting with transition metal clusters according to my studies on the initial carbon adsorptions on four Ni clusters (Ni₁₃, Ni₁₅, Ni₃₈, and Ni₅₅). It is also revealed that charges are transferred obviously from the metal atoms to the growing end edges of Caps/tubes during the SWCNT growth, which enhance the reactivity of the carbon atoms at end-edge. Different chiral end-edges exhibit distinct reaction active sites. Armchair (5,5) has five identical double-carbon active sites, while zigzag (9,0) has nine single-carbon active sites. (6,5) has a kink site with the highest reaction activity. These finding revealed that near-armchair nanotubes possess one or more reactive kink sites, which might lead to the preferential growth of near-armchair chiral caps/tubes. The structures of metal clusters strongly correlate with SWCNT growth sites through charge transfer (or redistribution). Overall, the simulation work in this thesis implied potential opportunities exist in achieving the chirality selective growth of SWCNTs by: (1) controlling the ratios of single C atoms and C₂ dimers at different growth stages; (2) engineering charge transfer, which could be achieved by proper design of catalytic cluster with definite composition and morphology.

Chapter 1

Introduction

Carbon nanotubes (CNTs) are cylinders rolled by carbon graphite layers. They are categorized as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), depending on the number of graphite layers in their walls. The experimental observation of MWCNTs was reported by Iijima et al. in 1991.¹ SWCNTs were synthesized by Iijima et al.² and Bethune et al.³ in 1993. These pioneer studies directly trigger the birth of CNT nanoscience and nanotechnology. Since then, CNTs have attracted intensive studies due to their special physical and chemical properties, and wide range of potential applications,^{4,5} including field effect transistors,⁶⁻¹¹ electron transistors,^{12,13} atomic force microscope tips,¹⁴ field emitters,^{15,16} and chemical sensors.¹⁷⁻²⁰

The properties of SWCNTs strongly depend on their geometrical structures, such as diameter, length, and chirality. Particularly, SWCNTs have unique chiral structures, which are identified as their chiral index (n,m). SWCNTs with well-defined chiral structures are desired for their potential applications. However, current synthesis methods result in SWCNT samples with a broad distribution in chiral structures. The present thesis focuses on theoretical investigation of chirality selectivity in SWCNT synthesis. By evaluating factors, which influence chirality selectivity at an atomic level, I aim to provide better insights on SWCNT growth reaction mechanism. Eventually, such knowledge may help researchers to achieve chirality selectivity in SWCNT synthesis for various applications.

1.1 Structure and property of SWCNTs

1.1.1 Chiral structure of SWCNTs

Ideal SWCNTs are seamless carbon cylinders with one atomic-layer thick wall, and the tips of SWCNTs are sealed with hemi-fullerene caps of matching diameter. Geometrically, the (n,m) structure of SWCNT can be considered as a perfect graphene sheet rolled into a cylinder at a specific direction,^{21, 22} as illustrated by the chiral index (n,m) in Fig. 1.1. Graphene has a hexagonal planar structure. Rolling up the graphene sheet in different directions would yield nanotubes with different symmetries, which induces different electronic structures in nanotubes. Following the established notation²³ in Fig. 1.1, if one point is set as an origin point (0,0) on the graphene sheet, other points on the graphene sheet (the center of each hexagon where a carbon atom locates) can be identified by a pair of integers (n,m) ($0 \leq |m| \leq n$), correspondingly. The rolling direction from the origin point toward any other points on the graphene sheet can be defined by a chiral vector, $C_h = n\mathbf{a}_1 + m\mathbf{a}_2$, where $(\mathbf{a}_1, \mathbf{a}_2)$ is a pair of lattice unit vectors of the graphene sheet. θ is considered as the chiral angle for the (n,m) nanotube. The chiral angle (θ) ranges from 0° to 30° due to the six fold symmetry of the graphene sheet. On the basis of their chiral angles, SWCNTs can be divided into 3 types: one is armchair nanotube when $n = m$, denoted as (n,n) with $\theta = 0^\circ$; the second is zigzag nanotube when $m = 0$, denoted as (n,0) with $\theta = 30^\circ$; The third is chiral nanotube when $n \neq m$, denoted as (n,m) with $0^\circ < \theta < 30^\circ$. Since the structure of SWCNTs can be exclusively specified by chiral vectors, the integer pair (n,m) is used to identify SWCNTs. The length of the base vector is $a = 2.49 \text{ \AA}$ on the graphene sheet, the lattice unit vectors are written as:

$$\mathbf{a}_1 = \frac{a}{2}(\sqrt{3}, 1), \quad \mathbf{a}_2 = \frac{a}{2}(\sqrt{3}, -1) \dots\dots\dots(1.1)$$

the length of chiral vector is

$$C_h = a\sqrt{n^2 + m^2 + nm} \dots\dots\dots(1.2)$$

the diameter of the SWCNT is

$$d_t = \frac{a}{\pi}\sqrt{n^2 + m^2 + nm} \dots\dots\dots(1.3)$$

and the chiral angle can be expressed as

$$\theta = \cos^{-1}\left(\frac{2n+m}{2\sqrt{n^2+m^2+nm}}\right) \dots\dots\dots(1.4)$$

In short, the chiral index (n,m) can exclusively specify the structure of SWCNTs and derive their geometric parameters, such as diameter, chiral angle, and so on. Ideally, there are no restrictions on the diameter and length of SWCNTs. However, most experimental studies show that the diameter of SWCNTs mainly ranges from ~0.4 to 3 nm, while the length of SWCNTs can be in millimeters. Theoretical calculations have attributed this to the fact that a flattened two-layer carbon ribbon compressed from a SWCNT is thermodynamically more favorable than keeping tubular structure if its diameter exceeds ~2.5 nm.²⁴⁻²⁶ The length of SWCNTs is apparently only restricted by their synthesis conditions, such as thermal gradients, residence time in reactors, and so on.

Figure 1.1 Chiral structures of SWCNTs

1.1.2 Chirality dependent SWCNT properties

The geometrical structure of SWCNTs strongly affects their electrical, mechanical, optical, chemical, and thermal properties. SWCNTs exhibit unique metallic or semiconducting behaviors, which are not found in many other one-dimensional nanomaterials. For a given (n,m) SWCNT, if its chiral index satisfies the condition that $n - m = 3j$, where j is integer, then, it is metallic (labeled in grey in Fig. 1.1). SWCNTs, having either $n - m = 3j + 1$ or $3j + 2$, are semiconductors (labeled in white in Fig. 1.1). Theoretically, SWCNTs should have a 1:2 ratio between metallic and semiconducting nanotubes.²⁷ Metallic SWCNTs are excellent conductors, which can carry an electric current density more than 1000 times greater than that by metal-conductors, such as silver and copper.²⁸ Semiconducting SWCNTs possess varied band gaps ranging between 0.4 ~ 0.7 eV. The band gap is inversely proportional to their diameters.²⁹ The property diversity among different (n,m) SWCNTs hinders many potential electronic applications, where either pure metallic or semiconducting SWCNTs with particular band gaps are desired. In addition, SWCNTs have excellent thermal and mechanical properties. Their thermal conductivities are extremely high along their axis (400-5800 W/m · K).³⁰ The Young's modulus and tensile strength of SWCNTs can be as high as ~1 TPa and ~20 GPa respectively,³¹ which exceed those of stainless steels in a few folds. Their thermal and mechanical properties are also chirality dependent. Meanwhile, the current synthesis has not yet been capable of selectively producing SWCNTs with a single chiral structure. Therefore, synthesis of SWCNTs with well-defined chiral structures is desired.

1.2 SWCNT synthesis

1.2.1 SWCNT synthesis methods

Currently, SWCNT synthesis methods include: arc discharge,^{2, 3, 32} laser ablation,³³⁻³⁵ and chemical vapor deposition (CVD).³⁶⁻³⁹ Many efforts have been devoted to develop these methods for scalable and controllable production of SWCNTs.

The arc discharge method was initially used to produce fullerene. It was the method used by Iijima et al. in 1991.¹ Usually, carbon vapors are generated by arc discharge between two carbon electrodes which contain metal catalysts. CNTs would self-assemble on metal catalyst clusters when carbon vapor condenses. By adjusting gas pressure and catalyst, SWCNTs with certain diameter control can be obtained. Laser ablation was developed by Richard Smalley at Rice University.⁴⁰ In a laser ablation process, a graphite target was vaporized by a pulsed laser in a high temperature reactor while an inert gas flows into the reactor. A water-cooled surface may be incorporated in the reactor. CNTs are formed on the cooler surfaces, when the carbon vapor condenses. A composite of metal catalyst particles and graphite was used to synthesize SWCNTs.³³ The diameter of SWCNTs can be adjusted by reaction temperature. CVD is a widely used method to grow SWCNTs in bulk or on various surfaces, which provides a convenient way for further electronic device fabrications.⁴¹ The method is achieved by decomposing gaseous carbon precursors, such as CH₄, CO, and C₂H₂, into reactive atomic carbon in a high temperature furnace, and sometimes assisted by plasma to enhance the generation of atomic carbon at a low temperature.⁴² Then, the atomic carbon species would interact with catalyst particles. Under the appropriate synthesis conditions, SWCNTs may form following the mechanism described in Section 1.4. CVD synthesis of SWCNTs usually includes two steps. The first step is to prepare suitable catalysts. Commonly used catalysts include Ni, Fe and Co nanoparticles.

Catalyst preparation is critical to the nanotube synthesis because the structure of SWCNTs depends on of the structure of catalyst particles. The second step is to synthesize SWCNTs from catalysts in a carbon rich gaseous environment.

Comparing three synthesis methods, it is difficult to control SWCNT structures by arc discharge and laser ablation, even though these two techniques can produce high quality SWCNTs. In contrast, CVD has some advantages including: (1) Chiral structure of SWCNTs can be modified by adjusting synthesis parameters in CVD (such as catalysts, carbon precursors, and synthesis conditions). (2) SWCNT structures can be assembled (vertically or horizontally aligned) on planar substrates. (3) It is feasible to scale up CVD process for industrial scale productions. Thus, CVD has been intensively studied in order to achieve better SWCNT structure control.

1.2.2 Chirality selective SWCNT synthesis

Many experimental studies have been carried out to selectively synthesize SWCNTs in term of diameter, length, and chirality. Here, a brief overview of the chirality selective synthesis of SWCNTs is given. The first effective chirality selective synthesis was reported by Resasco *et al.* using a Co and Mo bimetallic catalyst and CO as feedstock, which results in SWCNTs with a narrow distribution on the (6,5) and (7,5) accounted for 57% of the semiconducting tubes.⁴³ Then, Maruyama *et al.* showed that a similar narrow chirality distribution can be obtained using Fe/Co catalyst through low temperature alcohol growth.⁴⁴ They also found that a high selectivity to the higher chiral angle tubes close to armchair tubes existed and this tendency was more pronounced for smaller diameter tubes.⁴⁴ At the meantime, a new catalyst, Co incorporated MCM-41 (Co-MCM-41), was developed and shows high selectivity toward (7,5) tubes.⁴⁵⁻⁴⁸ The efficient control of Co species using

MCM-41 template has produced as-synthesized SWCNTs with the narrowest chirality distribution reported so far.⁴⁹ More recently, Dai *et al.* demonstrated that Fe and Ru bimetallic catalyst can afford SWCNT growth with narrow chirality distribution in methane CVD.⁵⁰ At 600 °C, they can produce predominantly (6,5) tubes. At 850 °C, the dominant species are (8,4), (7,6), and (7,5). Despite these noticeable selectivity reported, It is still limited to achieve selective synthesis of desired (n,m) SWCNTs. All reports show similar selectivity toward higher chiral angle tubes, in particular small diameter tubes such as (6,5) and (7,5). No effective selectivity toward other chiral tubes has been reported so far, especially larger diameter tubes with smaller band gaps which would be more promising to construct high performance transistors.⁵¹

Figure 1.2 SWNTs with narrow chirality distribution obtained on Co-MCM-41 catalyst. Right: 2-D PLE intensity map as a function of excitation and emission wavelength for dispersed Co-MCM-41 SWNT sample in D₂O. Inserted transmission electron microscope (TEM) image shows the uniform pore structure of Co-MCM-41. Left: chirality maps of aqueous suspensions of Co-MCM-41 (green hexagons) and HiPco SWNTs (enclosed by solid red line). Left part is reproduced from ref.⁴⁹ with permission from ACS.

1.3 Synthesis parameters related to chirality selectivity

SWCNT synthesis is a sensitive heterogeneous catalytic process which involves various physical and chemical reactions affecting the formation of SWCNTs. It involves carbon precursor decomposition, active carbon atoms nucleation on the catalyst particles, initial carbon network or cap formation, continuous growth of cap/nanotube structures, and termination of nanotube growth. In order to understand chirality selectivity, it is necessary to identify parameters, which play important roles in chirality selective synthesis. Three factors are often found to be important in SWCNT synthesis, including catalyst particle, carbon precursor, and temperature.

Figure 1.3 Influencing factors of chirality selectivity. TEM images are reproduced from ref.⁵² with permission from ACS.

1.3.1 Catalyst particles

Catalyst particles play a key role in the synthesis of SWCNTs. Their roles include: (1) assisting carbon precursor decomposition, (2) serving as seeds to organize carbon atom into carbon network or cap structures, (3) continually supplying carbon atoms into growing

SWCNTs, and (4) terminating SWCNT growth. Three aspects of catalyst particles, including composition, structure/size, and catalyst-substrate interaction, strongly influence the chirality selective synthesis of SWCNTs.

Currently, more than 20 metal (Cu, Ag, Au, Pd, Pt, Cr, Mn, Mo, Mg, Al, and Sn) and their combinations,^{53, 54} non-metals,^{50, 55-58} metal-oxides (Al₂O₃, MgO, SiO₂, and zirconia),^{50, 55-67} semiconductor particles (Si and SiC), and diamond^{57, 58, 65, 67, 68} have been found capable of catalyzing SWCNT growth. The most effective catalysts are transition metals, the iron-group (Fe,^{69, 70} Co,^{47, 48} and Ni,^{71, 72}) in particular. Their high activity has been attributed to their good carbon solubility and active hydrocarbon decomposition on their surface. Moreover, bimetallic catalysts,^{50, 73, 74} such as Fe-Co,^{44, 75-77} Ni-Co,⁷⁸ Fe-Mo,³⁸ and Co-Mo,^{43, 79} show better chirality selectivity than other catalysts.

The structure and size of catalyst particles are also important for chirality selectivity.^{53, 80-82} It is found that the diameter of SWCNTs is correlated with the diameter of catalyst particles.^{53, 78, 80-84} For CVD synthesis of SWCNTs, active catalyst particles are generally in the range 1~10 nm.^{53, 83} For such small nanoparticles, the structure and size of nanoparticles determine not only their physical properties but also their chemical activity. For example, with the shrinking of nanoparticles, their melting point decreases, while the solubility of carbon increases.⁸⁵

Furthermore, many metal nanoparticles are supported on various substrates. Catalyst nanoparticles may physically adsorb on substrates or be trapped inside pores by Van der Waals or electrostatic forces. They may also form strong chemical bonds with substrates, which could involve charge transfers between each other. Depending on the interaction strength between catalyst nanoparticles and substrates, SWCNTs can be synthesized through either root-growth^{84, 86} or tip-growth^{87, 88} as described in the mechanism section later. Hereby,

the choice of substrates would directly affect the size, structure, and activity of catalyst particles, which affect the chirality selective synthesis of SWCNTs.^{89, 90}

1.3.2 Carbon precursors

In CVD synthesis, carbon precursors supply active carbon atoms for SWCNT synthesis. Different carbon precursors have different chemical properties, thus different decomposition rates and interactions with catalyst particles. Resasco *et al.* reported that CH₄ is less chirality selectivity than CO at 800 °C on Co-Mo catalyst. They explained that this is because H₂, as a byproduct of CH₄, can increase the rate of reduction and aggregation of Co clusters, as well as restrain the carbon species nucleation on the surface of the catalyst particles by decreasing the carbon surface fugacity.⁸⁹ More recently, Liu *et al.* reported a highly selective synthesis of semiconducting tubes using a mixture of methanol and ethanol.⁹¹ They emphasized that the metallic SWCNTs can be selectively etched by the OH radical from methanol because they have smaller ionization potential than semiconducting SWCNTs.⁹¹ Researchers also has compared the chirality selectivity of four representative carbon precursors including CO, ethanol, methanol and C₂H₂ on Co-Mo catalyst.⁹² Narrow chirality distribution of SWCNTs can be achieved under vacuumed ethanol and methanol or high-pressure CO predominately in the same higher chiral-angle region. Furthermore, the different dominant chiralities, (6,5), (7,5), and (7,6), can be enriched from the selective synthesis of SWCNT samples.⁹³ Under higher CO pressure, the higher concentration of active carbon atoms may lead to faster growth of SWCNT, which results in smaller diameter tubes like (6,5) and (8,3).

1.3.3 Temperature

Temperature is a predominate parameter which influences almost every aspects of SWCNT synthesis. High synthesis temperature is required to decompose carbon precursors.

Higher temperature usually leads to faster carbon precursor decomposition rate, more aggressive nanoparticle nucleation, and less defects in SWCNTs. In general, a fast nanoparticle nucleation under high synthesis temperature would result in SWCNTs with a broad diameter distribution, having much wider chirality distribution. SWCNTs with narrow chirality distribution have been produced at temperatures around 600–650 °C in alcohol growth on Co/Fe catalyst⁴⁴ and CH₄ growth on Fe-Ru catalyst⁵⁰. The synthesis temperature window is shifted up to 700–800 °C with good selectivity toward (6,5) and (7,5) nanotubes in CO decomposition on Co-Mo catalyst and Co-MCM-41. This temperature up-shift may be attributed to a better control of Co nanoparticles using these two catalysts.^{43, 48} Even so, when synthesis temperature is further increased to 850–900 °C, a narrow chirality distribution disappears because of the increase in metal particle size.^{48, 94}

1.4 SWCNT growth mechanism

Although SWCNTs have been intensively studied in the past 20 years, there are still no reliable growth mechanisms available to provide a clear guideline to achieve the chirality selective synthesis. Here, SWCNT growth mechanisms based on current experimental studies are described.^{52, 95}

As illustrated in Fig. 1.4, various proposed mechanisms may be classified according to the different interaction scenarios among three basic components in SWCNT growth: carbon, metal particle and substrate. Depending on the interaction strength between carbon and metal particle, one mechanism is the vapor-liquid-solid (VLS) growth mechanism originated from the growth of carbon fibres.⁹⁶ This mechanism assumes the catalytic decomposition of gaseous hydrocarbons on the catalyst particle surface. Following the release of hydrogen, carbon atoms then dissolve into liquid metal particles. After supersaturation of carbon atoms

in liquid metal particles, excess carbon atoms would precipitate on metal particle surface with subsequent formation of carbon networks or cap structures. Finally, these carbon structures grow into SWCNTs on metal particles by incorporating more carbon atoms. The VLS model has been relatively successfully applied for SWCNT growth at high temperatures (laser ablation or arc-discharge methods).^{86, 97, 98} However, one question often being raised to challenge the VLS growth mechanism is whether metal particles are really liquid at the relative lower SWCNT growth temperature (e.g. CVD about 600-1000 °C). Such a situation becomes more complication, and requires further investigations.⁹⁹⁻¹⁰¹

Figure 1.4 Different growth mechanisms and their correlations with interactions among carbon, metal and substrates.

Gibbs-Thompson model predicts that the melting temperature of metal clusters decreases with their decreasing sizes.¹⁰² A few recent studies showed that the melting temperature of common used metals such as Ni, Fe and Co in the 1.1–1.6-nm-diameter range is at 600–800 °C. Furthermore, the melting temperature of metals, as well as the solubility of carbon, can be influenced by carbon concentration and substrate.¹⁰³⁻¹⁰⁵ All these results strongly support the feasibility of VLS growth mechanism. On the other hand, if metal

clusters do remain as solid crystalline particles, a yarmulke mechanism⁷⁸ suggests that carbon atoms would absorb on the surface of metal particles. Adsorbed carbon may agglomerate and form a carbon cap to lower the overall energy of the system. Adsorbed carbon atoms can continually diffuse on the surface of metal particles toward growing carbon caps. Subsequently, the cap can lift from the solid surface, forming a nanotube while incorporating more carbon atoms. Molecular dynamics simulations have demonstrated that such a mechanism is also feasible.¹⁰⁶⁻¹¹⁰ Between the above two mechanisms, some experimental and theoretical studies support the possibility of fluctuating metal particles or metal carbide crystals. Nanoparticles are neither purely liquid nor crystalline. Carbon atoms can be incorporated into nanoparticles, and cause dynamic reconstruction of nanoparticles.^{52, 109, 111}

Furthermore, according to the interaction strength between metal particle and substrate, there are two SWCNT growth models. One is the root growth model.^{84, 86} If metal particles have a strong interaction with a substrate, metal particles would be always anchored on the substrate during the entire growth process of SWCNTs. The other is the tip growth model.^{87, 88} Here, metal particles have a weak interaction with substrates so that metal clusters would leave substrates, and sit on the tip growing nanotubes detaching from substrates. Recent results also showed that the growth of SWCNTs from non-metal particles such as SiC and Si is also feasible.^{57, 65, 67}

As listed in Table 1, observations from various studies support different growth hypotheses discussed above. The diversity in TEM results may be originated from different reaction conditions employed. For instant, when the reaction temperature is relatively low; nanoparticles are more likely presented as crystalline structure. The difference in metal adhesion energies among Ni, Co and Fe may influence the possibility of carbide formation and carbon diffusion inside nanoparticles. In all TEM studies, the concentrations of atomic

carbons on the nanoparticle surface are very low due to the low carbon precursor pressure in TEM studies; and this could lead to different diffusion pathways compared to realistic SWCNT growth conditions. SWCNT growth mechanism could be differed when growth conditions are varied. It is possible that all proposed mechanisms can only be applied under a particular set of growth conditions.

In summary, the exact growth mechanism of SWCNTs is still unclear, and maybe more than one mechanism is involved during the synthesis process. The growth process roughly consists of four steps including: (1) SWCNT growth starts with the adsorption of free C atoms (or C₂ dimers) on metal nanoparticles. Free C atoms come from decomposition of gas-phase carbon precursors in CVD growth,^{112, 113} or evaporation of solid-phase carbon sources in laser ablation,^{36, 114} and arc discharge^{2, 32}. (2) This initial adsorption is followed by the diffusion of C on nanoparticle surfaces or into their interiors until C dissolution reaches a degree of saturation determined by the metal-metal and metal-substrate interaction; (3) Subsequently, individual C atoms staying on (or precipitating from) nanoparticles form graphitic fragments on particle surfaces followed by the further incorporation of C into growing C structures (graphitic fragments evolve into C caps, and then turn into SWCNTs). (4) Lastly, SWCNT growth stops due to some reasons. Several mechanisms have been proposed to explain the tube growth termination including: catalyst poisoning, diffusion limitations, and mechanical confinement.^{115, 116}

Table 1.1 *In situ* TEM observations of carbon nanotube growth

Ref.	Metal/ Size (nm)	Support	Carbon source	Pressure (mbar)	Temperature	Carbon nanostructure	Metal cluster structure	Metal-carbon interaction	growth mode /rate (nm/s)
¹¹⁷	Ni/ 5–20	MgAl ₂ O ₄	CH ₄	2	500–540	carbon nanofibres	crystalline reshaping	surface diffusion of C on Ni step edges	Tip /N.A.
¹¹⁸	Ni/ 1.5–3	SiO ₂	C ₂ H ₂	up to 0.13	480	MWCNTs or SWCNTs	melting re-crystalline	C cap matching with the facets on Ni particles	Root /6–9
¹¹⁹	Ni/ <6	MgO	C ₂ H ₂	5.3×10 ⁻⁶	650	SWCNTs	crystalline	surface diffusion of C	Root /0.011–0.31
¹²⁰	Fe, Co, FeCo or Ni	inside MWCNTs	inner wall of MWCNTs	high vacuum	600 under e-beam	SWCNTs MWCNTs	crystalline with carbide domains	bulk diffusion of C, tube attached to metal	Root /84
¹¹¹	Ni, Fe 5	SiO ₂	C ₂ H ₂	10	615	SWCNTs MWCNTs	fluctuating crystalline	lift-off of carbon caps, dynamic reshaping of metal	Root /N.A.
¹²¹	Ni 7–30	MgO	C ₂ H ₂	5.3×10 ⁻⁶	650	MWCNTs	crystalline	surface diffusion of C	Root and Tip /0.34
⁵²	Fe	SiO ₂	C ₂ H ₂	0.1	600	SWCNTs MWCNTs	Fe carbide, fluctuating	bulk diffusion of C in Fe carbide	Root /N.A.
¹²²	N.A.	inside MWCNTs	C from another tube	high vacuum	527–1527 under e-beam	SWCNTs	N.A.	directly incorporate into closed cap	N.A. /0.36

1.5 Theoretical studies on chirality selective SWCNT growth

Great efforts have been made on theoretical studies to investigate chirality selective SWCNT growth using both molecular dynamics (MD) simulations and static quantum chemical/first-principle calculations.

MD simulations have the advantage of spatio-temporal movement of atoms for nonequilibrium systems. Thus, MD simulations usually applied to investigate the entire SWCNT growing process in order to assist in the design of chirality selective synthesis of SWCNTs. Maruyama *et al.* performed a classical reactive empirical bond order (REBO)-based MD simulations to investigate the formation mechanism of SWCNT on nickel cluster.^{107, 123, 124} They proposed that the crystal orientation of metal clusters may play a critical factor for the determination of SWCNT chirality due to strong interaction between the growing carbon networks and metal clusters. Using the same REBO-based MD simulations, Ding *et al.* have investigated iron catalyzed nucleation and growth of SWCNTs¹²⁵ and the effect of catalyst cluster size on the structure of SWCNTs¹²⁶. Their results showed that SWCNTs can be grown from the iron-carbide particles at temperatures between 800 and 1400 K. SWCNTs nucleated from large iron clusters (> 20 atoms) have better tubular structures than those from smaller clusters. In addition, SWCNTs nucleated from large clusters have similar diameters with catalyst clusters. Recently, Morokuma *et al.* have simulated various stages of SWCNT nucleation, growth, and healing process using more accurate quantum mechanical MD technique based on a self-consistent-charge density-functional tight-binding methodology.¹²⁷⁻¹³¹ They proposed that SWCNT nucleation is the rate-limiting step during the entire SWCNT growing process,^{127, 128} and metal carbide is not essential prerequisite for the SWCNT nucleation and growth^{128, 129}. Additionally, they also

proposed chirality-controlled SWCNT growth can be achieved by controlling SWCNT healing using a slower carbon supply rate.¹³⁰

On the static quantum chemical/first-principle calculations side, the early theoretical explanations on the chirality selectivity are based on the carbon cap structure stability and the heat of formation energies.^{44, 132} In particular, Balbuena *et al.* extended the cap structure stability to the chirality dependent aromaticity and reactivity of different carbon caps.¹³³ Some differences are observed among chiral structures, which were used to justify the chirality selectivity observed in experimental studies. Adding the influence of metal surfaces, Reich *et al.* proposed that specific chiral caps could be favored by their epitaxial relationship to the solid catalyst surface.^{134, 135} It implies the possibility of chiral structure control through matching a SWCNT cap with a specific local crystalline lattice on metal surfaces. Balbuena *et al.* provided further studies on the interaction between carbon caps and small metal clusters, indicating that the interaction strengths are different among chiral species.^{136, 137} Reich *et al.* also suggested that once the chirality selectivity is determined during the cap nucleation stage, it would grow into a unique nanotube.^{134, 135} However, this argument is debatable, because some studies show that the chirality of SWCNTs can further change during the growth.^{138, 139} On the other hand, Ding *et al.* noticed that the strong adhesion between SWCNTs and the catalyst particles is necessary to support nanotube growth, and the dissociation energy may be chirality dependent.¹⁴⁰ The chirality selective growth can be possible if alloy metals with different adhesion strengths are used.¹⁴⁰ Furthermore, from the viewpoint of SWCNT growth rate, Ding *et al.* proposed a dislocation growth theory, in which nanotube growth rate is proportional to the chiral angle of the tube.¹⁴¹ A recent experimental study confirmed that a growing nanotube is rotating, which supports this dislocation growth theory.¹⁴² However,

Ding *et al.*¹⁴¹ also noted that the chirality selectivity induced by the carbon cap nucleation on metal surface cannot be ruled out.

1.6 Motivation and scope of this thesis

SWCNTs with specific chiral structures are desired for many potential applications. They may be obtained through two approaches: chirality selective synthesis or post-synthetic sorting. The post-synthetic sorting approach has several disadvantages: (1) Purification and functionalization may introduce defects on SWCNTs, which compromises their properties. (2) SWCNTs can be cut into short fragments by sonication or oxidation commonly used in sorting methods. (3) Some surfactants or polymers used in sorting process are difficult to be removed from SWCNT surfaces. (4) The very high cost of sorting processes also hinder wide spread applications of SWCNTs. In order to directly synthesize SWCNTs with desired chirality, a better understanding of their growth process is needed. This thesis focuses on the theoretical investigation of chirality selectivity in SWCNT synthesis.

As discussed in Section 1.2 and 1.3, experimental studies have found selectivity toward higher chiral angle small diameter SWCNTs, (6,5) and (7,5) in particular. The relative abundances of (n,m) SWCNTs change when different carbon precursors,⁹² pressures,⁹³ growth temperature,¹⁴³ and catalyst substrates are used.^{90, 94} These results suggest that the chirality of SWCNTs is determined during either chiral carbon cap nucleation or continuous elongation of nanotubes. The detailed chirality selection mechanisms remain unclear. It is intriguing to find out the detailed reaction pathways of chirality change and nanotube growth. It is useful to determine the reaction potential energy surface (PES) and activation energy of different reaction paths. It is also interesting to find out how different carbon species may

influence the chirality selection. Furthermore, can the growth of chiral SWCNTs be achieved under catalyst-free conditions?

On the other hand, previous experimental and theoretical studies have indicated that carbon cap nucleation on metal catalyst surface is important for chirality selectivity. The adsorption of C atoms on metal nanoparticles is the first step in carbon cap nucleation. There are a number of problems related to C adsorption which could be important for carbon cap formation: does the C adsorption depend on metal particle size and morphology? And whether adsorbed C atoms penetrate into metal particle or only stay on the particle outer surface?

Subsequently, C atoms adsorbed on the metal particles would evolve into different carbon structures, such as small carbon networks, carbon caps and carbon tubes. The dynamic and complex interactions between metal particles and growing carbon structures may play important roles in chirality selectivity. Thus, it is also useful to determine the adhesion energies and chemical potentials of growing carbon structures on metal nanoparticles. The reactivity of the interface between metal cluster and growing carbon structures may also influence the chirality selectivity.

Based on the above considerations, this thesis describes the theoretical study of chirality controlled SWCNT growth through two aspects: (1) the SWCNT growth and chirality change under catalyst-free conditions, and (2) interfacial interactions between metal particles and various growing carbon structures in catalytic growth of SWCNTs.

The background and literatures of experimental and theoretical studies on chirality controlled SWCNT growth are given in Chapter 1. Chapter 2 presents a brief overview of fundamentals on *ab initio* calculations and density functional theory. SWCNT growth and

chirality change under catalyst-free conditions is investigated in Chapter 3 by precise PES surveys using DFT calculations. Chapter 4 studied the atomic carbon adsorption on four Ni nanoclusters (Ni_{13} , Ni_{15} , Ni_{38} , and Ni_{55}). Chapter 5 investigated charge transfer between metal clusters and growing carbon structures including the various carbon networks, chiral carbon caps, and chiral nanotubes. Finally, Chapter 6 gives a summary of this thesis and outlooks for future studies.

1.7 Reference

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Chapter 2

Theoretical Background and Calculation Methodology

In this chapter, I will briefly introduce the theoretical background of computational methods relevant to this thesis.^{1, 2} I start with *ab initio* calculations presented in Sec. 2.1, followed by the Schrödinger equation and Born-Oppenheimer approximation in Sec. 2.2 and 2.3, respectively. The Hartree-Fock (HF) method as a typical classic *ab initio* method will be described in Sec. 2.4. The density functional theory (DFT) is a newly developed efficient *ab initio* method, which is presented in Sec. 2.5. I introduce two most commonly used approximations of exchange-correlation (XC) functionals used in DFT: the local density approximation (LDA) and the generalized gradient approximation (GGA). Finally, the calculation methods employed in this thesis are discussed in Sec. 2.6.

2.1 *Ab initio* calculations

Ab initio calculations in quantum chemistry/physics are simulation methods that predict physical and chemical properties of physical systems without any empirical and experimental parameters. When atomic number, type and positions of a physical system are provided, in principle, most of physical and chemical properties (optical, electronic, magnetic and mechanical) of the given system can be determined via *ab initio* calculations. Thus, *ab initio* calculations are often called as first principle calculations. With the continuous and rapid upgrades in computational capacity and the new developments in theoretical methodologies and techniques, *ab initio* calculations have been applied beyond traditional geometrical structure studies of bulk materials, defects, surface phenomena, clusters, and disordered systems,³ and they are now used in studying surface adsorption, catalysis activity, chemical

reaction kinetics and molecular dynamics. These calculation studies provide insights of new materials at atomic or even electron configuration and spin levels, and reveal the fundamental mechanisms behind various experimental findings.

DFT is one of the newly developed *ab initio* calculation methods, and widely used in physical, chemical, and biological research to explore the electronic structure of atoms, molecules,⁴ and the condensed-state solids.⁴⁻¹¹ It is very successful in describing ground state properties of many-electron systems.⁷ The main idea of DFT is to describe properties of a many-electron system by using its electron density as basic variable functions, which gives its name “density functional theory”. Generally speaking, DFT calculations can provide quite satisfactory predictions compared with experimental results.^{5, 6} At the same time, the DFT computation cost less compared with traditional computational methods such as HF theory and post-HF theory.

2.2 Schrödinger equation

Physical systems, such as atoms, molecules and condensed solids, consist of electrons and nuclei, which move in the force field generated by each other. The time-independent Schrödinger equation¹² of a physical system consisting of N electrons and K nuclei with the charges of Z_n takes the form:

$$H\psi = E\psi \quad (2.1)$$

with a wavefunction that looks like this:

$$\psi = \psi(\{r_i\}, \{R_k\}) \quad (2.2)$$

where r_i is the position of the electrons, R_k is the position of the nuclei, the index i refers to different electrons, k refers to different nuclei. The wavefunction depends on the positions of electrons and nuclei.

The Hamiltonian operator is as following:

$$H = -\frac{\hbar^2}{2M_k} \sum_k \nabla_k^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{k \neq l} \frac{Z_k Z_l}{|R_k - R_l|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} - \sum_{i,k} \frac{Z_k}{|r_i - R_k|} \quad (2.3)$$

The index i refers to different electrons, k refers to different nuclei, m_e is the mass of an electron, and M_k is the mass of different nuclei. Z_k is the atomic number of nucleus k . The Laplacian operators ∇_k^2 and ∇_i^2 involve differentiation with respect to the coordinates of the k th nucleus and the i th electron, respectively. The Hamiltonian operator can also be written as:

$$H = T_n + T_e + V_{nn} + V_{ee} + V_{en} \quad (2.4)$$

T_n and T_e are the kinetic energies of electrons and nuclei, respectively. V_{nn} , V_{ee} and V_{en} are the potential energies for nucleus-nucleus, electron-electron and electron-nucleus interactions, respectively. The Hamiltonian operator is complicated. In fact, if the number of electron and nucleus is not extremely small, it is impossible to solve the stationary Schrödinger equation for this Hamiltonian operator even on the fastest computer available today.

2.3 Born-Oppenheimer approximation

In order to solve the Schrödinger equation for a practical physical system, an approximation must be considered by separating degrees of freedom of the electrons and nuclei. Nuclei are much heavier than electrons (the mass of a proton or neutron is about 1835 times as large as that of an electron), so it is clear that electrons are moving much faster than nuclei. Thus, one may assume electrons in molecule are moving in the force field generated by stationary nuclei and other electrons. This separation of electron and nucleus motion is known as the Born-Oppenheimer approximation.¹³

To simplify the many-electron time-independent Schrödinger equation, the first step is to separate the motion of nuclei from these of electrons. As mentioned above, the total wavefunction is a function of both nuclear coordinates and electron coordinates, which can be written as:

$$\Psi_T = \Psi_T(\{r_i\}, \{R_k\}) = \Psi_e(\{r_i\}, \{R_k\}) \Psi_n(\{R_k\}) \quad (2.5)$$

Here, $\Psi_n(\{R_k\})$ is a nuclear wavefunction that only depends on the nuclear coordinates. $\Psi_e(\{r_i\}, \{R_k\})$ is an electron wavefunction that depends on both electron and nuclear coordinates.

Substituting Eq. (2.5) into Eq. (2.1), applying the separation of variables and end up with two different Schrödinger equations, one for the electrons:

$$H_e \Psi_e(\{r_i\}, \{R_k\}) = E_e \Psi_e(\{r_i\}, \{R_k\}) \quad (2.6)$$

H_e is an electronic Hamiltonian. The form of the electronic Hamiltonian can be written as:

$$\begin{aligned} H_e &= -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|r_i - r_j|} - \sum_{i,k}^{N,K} \frac{Z_k}{|r_i - R_k|} + \frac{1}{2} \sum_{k \neq l}^K \frac{Z_k Z_l}{|R_k - R_l|} \\ &= T_e + V_{ee} + V_{en} + V_{nn} \end{aligned} \quad (2.7)$$

The other is nuclear Schrödinger equation:

$$H_n \Psi_n(\{R_k\}) = E_n \Psi_n(\{R_k\}) \quad (2.8)$$

H_n is a nuclear Hamiltonian. The form of the nuclear Hamiltonian can be written as:

$$\begin{aligned} H_n &= -\frac{\hbar^2}{2M_k} \sum_k^K \nabla_k^2 + \langle \Psi_e(\{r_i\}, \{R_k\}) | T_e + V_{ee} + V_{en} + V_{nn} | \Psi_e(\{r_i\}, \{R_k\}) \rangle \\ &= -\frac{\hbar^2}{2M_k} \sum_k^K \nabla_k^2 + E_e(\{r_i\}, \{R_k\}) \\ &= T_n + E_e(\{r_i\}, \{R_k\}) \end{aligned} \quad (2.9)$$

The term in “< >” of the equation (2.9) represents the average field of all electrons that is experienced by the nuclei. Based on the Born-Oppenheimer approximation, the nuclei are assumed to be fixed, which means the nuclear coordinates $\{R_k\}$ are fixed within conformation of the molecule. $E_e(\{r_i\}, \{R_k\})$ is called the electronic energy, which is a function of the nuclear coordinates $\{R_k\}$ and electronic coordinates $\{r_i\}$. Thus, $E_e(\{r_i\}, \{R_k\})$ gives the potential energy surface for a given system. Therefore, the minimum of $E_e(\{r_i\}, \{R_k\})$ represents the ground state of the system, which is usually what one seeks in these calculations. E_n in the equation (2.8) is the total energy of the given system, including contributions from electronic energy, nuclear vibrations, and overall rotation and translation of the given system.

2.4 Hartree-Fock method: a typical classic *ab initio* method

As discussions in the former section, the electronic wavefunction and total energy of a given system can be obtained by solving electronic Schrödinger equation (2.6). However, Eq. (2.6) cannot be solved under the Born-Oppenheimer approximation alone because it is impossible to separate electronic coordinates from each other in the Eq. (2.6) for many-electron systems. In order to solve many-electron Schrödinger equations (2.6), the HF approximation is introduced, in which electrons are assumed to move under the average potential from nuclei and other electrons.

The HF method is a popular approximate variational method used to obtain the solution of the ground-state energy and wavefunction of a many-electron system.¹⁴ The HF method assumes that the wavefunction of many-electron system has the form of an anti-symmetrized product of one-electron wavefunctions (also called orbital), where the antisymmetrization is

necessary because of the fermion character of the electron. This means that the wavefunction of many-electron system can be approximately described by a single Slater determinant of N spin-orbitals. A set of N -coupled equations of the N spin orbitals can be derived by using the variational principle. Then, the HF energy and wavefunction of the system can be obtained via solving these N -coupled equations. The coupling between equations makes these N -coupled equations become non-linear in the orbital. Thus, the N -coupled equations must be solved using a non-linear method, such as the iterative self-consistent field (SCF) method. The details of the HF method are further elaborated below.

The solution of the many-electrons Schrödinger equation can be described as the form of a Slater determinant in the HF formalism. One way to construct the many-electrons wavefunction, $\Psi_e(\{r_i\}, \{R_k\})$, is from a single Slater determinant of N one-electron spin-orbitals:

$$\Psi_e(\{r_i\}, \{R_k\}) = \frac{1}{\sqrt{N!}} \det|\Psi_\mu(r)|, \quad \Psi_\mu(\{r_i\}) = \Psi(\{r_i\})\chi_a(s) \quad (2.10)$$

$\chi_a(s)$ is a spin function which satisfies:

$$\sum \chi_a^*(s)\chi_\beta(s) = \delta_{\alpha\beta} \quad (2.11)$$

with the sum over up and down spins, and the orbitals satisfy:

$$\int \Psi_i^*(\{r_i\})\Psi_j(\{r_i\})dr = \delta_{ij} \quad (2.12)$$

In both cases, δ is the standard Kronecker delta function.

The electronic energy of the many-electrons system of Eq. (2.6) can be rewritten by adopting the Dirac notation at such a determinantal wavefunction as following:

$$\begin{aligned}
E_e &= \langle \Psi_e(\{r_i\}, \{R_k\}) | H_e | \Psi_e(\{r_i\}, \{R_k\}) \rangle \\
&= \sum_{\lambda} \langle \lambda | T_e + V_{ee} + V_{en} + V_{nn} | \lambda \rangle \\
&= \sum_{\lambda} \langle \lambda | T_e | \lambda \rangle + \sum_{\lambda} \langle \lambda | V_{en} | \lambda \rangle + \sum_{\lambda} \langle \lambda | V_{nn} | \lambda \rangle + \frac{1}{2} \sum_{\lambda, \mu} \{ \langle \lambda \mu | V_{ee} | \lambda \mu \rangle - \langle \lambda \mu | V_{ee} | \mu \lambda \rangle \}
\end{aligned} \tag{2.13}$$

where the sums are over the occupied spin-orbitals. It should be noted that the fourth summation involves *four-centre* integrals. The electron density $\rho(r)$, the Hartree (E_H), exchange (E_X) and nuclei-nuclei (E_{nn}) energies are described below:

$$\rho(r_i) = \sum_{\lambda, s} |\Psi_{\lambda}(r_i, s)|^2 \tag{2.14}$$

$$E_H = \frac{1}{2} \sum_{\lambda, \mu} \langle \lambda \mu | V_{ee} | \lambda \mu \rangle = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \tag{2.15}$$

$$E_X = -\frac{1}{2} \sum_{\lambda, \mu} \langle \lambda \mu | V_{ee} | \mu \lambda \rangle = -\sum_{\lambda \mu} \sum_{S_1 S_2} \int \Psi_{\lambda}^*(r_i) \Psi_{\mu}^*(r_j) \frac{1}{|r_i - r_j|} \Psi_{\mu}(r_i) \Psi_{\lambda}(r_j) dr_i dr_j \tag{2.16}$$

$$E_{nn} = \sum_{\lambda} \langle \lambda | V_{nn} | \lambda \rangle = \frac{1}{2} \sum_{a \neq b} \frac{Z_a Z_b}{|R_a - R_b|} \tag{2.17}$$

Substituting these equations into Eq. (2.13), one arrives at the equation:

$$E_e = \sum_{\lambda, s} \int \Psi_{\lambda}^*(r, s) T_e \Psi_{\lambda}(r, s) dr + \int n(r) V_{en} dr + E_H + E_X + E_{nn} \tag{2.18}$$

The total energy (for a given set of nuclei), E_e , is then minimised subject to orthonormal $\Psi_{\lambda}(r, s)$ by introducing Lagrange multipliers $E_{\lambda \mu}$, giving the HF equations for each orbital λ :

$$\{T_e(r) + V_{en}(r) + V^H(r) + V_{\lambda}^X(r) - E_{\lambda}\} \Psi_{\lambda}(r, s) = \sum_{\mu \neq \lambda} E_{\lambda \mu} \Psi_{\mu}(r, s) \tag{2.19}$$

Here

$$V^H(r)\Psi_\lambda(r,s) = \frac{\partial E_H}{\partial \Psi_\lambda^*} = \int \frac{\rho(r_1)\Psi_\lambda(r,s)}{|r-r_1|} dr_1 \quad (2.20)$$

$$V_\lambda^X(r)\Psi_\lambda(r) = \frac{\partial E_X}{\partial \Psi_\lambda^*} = - \sum_{\mu \in S_1} \int \Psi_\mu^*(r_i)\Psi_\lambda(r_i) \frac{1}{|r-r_i|} \Psi_\mu(r) dr_i \quad (2.21)$$

are the Hartree and exchange potentials respectively, and the expression for the exchange involves a sum over occupied orbitals μ whose spin are the same as that of λ .

Next, one performs a unitary transformation on the Slater determinant to diagonalize $E_{\lambda\mu}$ reducing the right hand side of Eq. (2.19) to zero. The total energy can then be found by multiplying the HF equations (2.19) by $\Psi_\lambda^*(r)$, integrating over $\mathbf{r}$ and summing over λ and s , to give:

$$\begin{aligned} & - \sum_{\lambda,s} \int \Psi_\lambda^*(r) \frac{1}{2} \nabla^2 \Psi_\lambda(r) dr + \sum_{\lambda,s} \int \Psi_\lambda^*(r) V_{en}(r) \Psi_\lambda(r) dr \\ & + \sum_{\lambda,s} \int \Psi_\lambda^*(r) V^H(r) \Psi_\lambda(r) dr + \sum_{\lambda,s} \int \Psi_\lambda^*(r) V_\lambda^X(r) \Psi_\lambda(r) dr - \sum_{\lambda,s} E_\lambda = 0 \end{aligned} \quad (2.22)$$

Then, the first and second terms are the kinetic and the electron-nuclei interaction energies, respectively. The third and fourth terms are electron-electron interaction energies. The two terms involving the Hartree and exchange potentials are two times of the Hartree and exchange energies in real interactions, respectively. Therefore, it yields:

$$T_e + E_{en} + 2E_H + 2E_X - \sum_{\lambda} E_\lambda = 0 \quad (2.23)$$

Then, the total energy is found by removing the double counting and adding the ion-ion energy term:

$$E_{total} = \sum_{\lambda} E_\lambda - E_H - E_X + E_{nn} \quad (2.24)$$

As mentioned above, the HF equations can be solved through SCF method by making a sensible initial guess at the set of $\Psi_\lambda(r,s)$ and calculating the Hartree and exchange potentials. These output potentials are then fed back into the HF equations to calculate a new set of $\Psi_\lambda(r,s)$. This cycle is re-iterated until the input and output are sufficiently close. Usually, the initial guesses for the spin-orbitals are related to atomic orbitals.

In summary, there are four major simplifications made in the HF method. First, HF method completely neglected the relativistic effects. The momentum operator is non-relativistic completely. Second, the variational solution is a linear combination of finite basic functions. These basic functions are usually chosen to be orthogonal. These finite basis set is supposed to be approximately complete. Third, each energy eigenfunction can be described by a single Slater determinant, which is an antisymmetrized product of one-electron wavefunction (also called orbital). Forth, HF method applied the simple mean-field approximation. Thus, the effect of correlations between the opposite spin electrons are completely neglected, but the correlations between the parallel spin electrons are taken into account.

The HF method is a fast and reliable method for a wide range of atomic systems. However, a number of four-centre integrals are required for the exchange energy. This leads to a prohibitively heavy computational requirement for systems with more than a few atoms, and therefore the simulation of bulk solid systems is impractical. In order to apply the HF method to larger systems, a number of semi-empirical parameters have been developed to solve this problem.

2.5 Density functional theory

The above section has shown that the HF equations depend on the occupied electron orbitals, which results in a number of four-centre integral equations in a nonlocal way. It is difficult to apply HF nonlocal potentials in extended bulk solid systems. DFT methods can overcome this problem because the electronic orbitals resulted from DFT methods depend on the electron density rather than individual electron orbitals. This concept was initially proposed by Hohenberg,¹⁵ Kohn and Sham¹⁶.

2.5.1 The Hohenberg and Kohn theorems

The rigorous DFT theorem was first developed by Hohenberg and Kohn.¹⁵ The first Hohenberg and Kohn (HK) theorem shows that the ground-state electronic density $\rho(r)$ is sufficient to determine all ground state physical properties of a many-electron system. The use of electron density functions would reduce the many-electron problem of N electrons with $3N$ spatial coordinates to only 3 spatial coordinates. If two systems of electrons have the same ground-state density $\rho(r)$ and they are trapped in two different potentials $v_1(r)$ and $v_2(r)$, then it is necessary to have

$$v_1(r) - v_2(r) = \text{Const} \quad (2.25)$$

The Hamiltonian and its all derived properties are thus uniquely resolved by the ground state density $\rho(r)$. More importantly, the HK functional is defined as $F[\rho] = T[\rho] + U[\rho]$. It is a general functional of the electron density, which does not depend on any external potential explicitly. The second HK theorem defines energy functional $E_{(v,\rho)}[\rho]$ of a many-electron system as equation 2.26,

$$E_{(v,\rho)}[\rho] = F[\rho] + \int v(r)\rho(r) d^3r \quad (2.26)$$

The density functional can attain its minimal value if and only if the electron density $\rho(r)$ is the exact ground-state density of N electrons in the potential $v(r)$. Correspondingly, the ground state energy of this system is the minimal value of $E_{(v,\rho)}[\rho]$. $F[\rho]$ is a universal functional and independent of external potentials. Thereby, all the physical properties of a system can be obtained by minimising this functional $F[\rho]$.

The theorems by Hohenberg and Kohn simplify the many-electron problem to the many one-electron problems. However, one more problem remains to be solved: how to calculate the total energy with all these electron-electron interactions?

2.5.2 The Kohn and Sham equations

Subsequently, Kohn and Sham presented a way to solve the electron-electron interaction problem by replacing all interacting electrons with non-interacting quasi particles and making these quasi particles yield exactly the same electron density $\rho(r)$.¹⁶ They solved the problem by decomposing the functional to

$$F[\rho] = T_s[\rho(r)] + \frac{e^2}{2} \int dr dr' \frac{\rho(r)\rho(r')}{|r-r'|} + E_{xc}[\rho(r)] \quad (2.27)$$

where $T_s[\rho(r)]$ is the kinetic energy of non-interacting electrons that possess the same density as the real electron interacting system. The existence of such a non-interacting system is assumed, and still remains an open question for debates. The second term in the equation 2.27 is the Coulomb electronic repulsion. $E_{xc}[\rho(r)]$ is the remaining correction, and is known as the XC energy. The minimization of this functional under the constraint of a given number of particles leads to the single-particle Kohn-Sham equation:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff}(r) \right] \Psi_i(r) = \varepsilon_i \Psi_i(r) \quad (2.28)$$

$\Psi_i(r)$ is the single particle orbital, and $V_{eff}(r)$ is the quasi-particles induced potential that can be expressed as:¹⁷

$$V_{eff}(r) = V_{ext}(r) + \int \frac{\rho(r')}{|r - r'|} dr' + \frac{\delta E_{XC}[\rho(r)]}{\delta \rho(r)} \quad (2.29)$$

$$\rho(r) = \sum_{i=1}^N |\Psi_i(r)|^2 \quad (2.30)$$

These equations describe a system of non-interacting particles in an effective potential $V_{eff}(r)$ at zero temperature. The effective potential consists of the external potential $V_{ext}(r)$, the Hartree electrostatic interaction between electrons, and the XC potential $E_{XC}[\rho(r)]$. The system must be solved by the SCF method because the effective potential $V_{eff}(r)$ depends on the electron density $\rho(r)$, which is in turn determined by the sum over the N wave functions of the lowest energy. In practice, a guess for the electron density $\rho(r)$ is taken as a starting point, from which a set of wave functions are determined by solving the one-particle Kohn-Sham equation 2.28. A new electron density is thus obtained, and the process repeated until convergence is reached. When the self-consistent electron density is known, the ion can be optionally relaxed to their equilibrium positions. The Hellmann-Feynman theorem allows the forces exerted on the ion to be calculated and the relaxation determined.

2.5.3 The exchange-correlation functional approximations

2.5.3.1 The local density approximation

The XC potential, $E_{XC}[\rho(r)]$ in the equation 2.27, needs to be defined in order to solve the problem completely. This is a major issue with DFT. It can only be defined approximately because the energy functional $F[\rho]$ is not known generally. The most popular

and successful approximation was first suggested by Kohn and Sham¹⁶ in 1965 as the LDA. Kohn and Sham assumed that many crystal materials could be described as homogenous electron gas (HEG). Within HEG, the effect of correlation and exchange is localized. On the basis of this HEG approximation, for a spin-unpolarized system, the LDA for the total XC energy $E_{XC}[\rho(r)]$ can be written as:¹⁸

$$E_{XC}^{LDA}[\rho(r)] = \int \varepsilon_{XC}[\rho(r)] \rho(r) d^3r \quad (2.31)$$

where ε_{XC} is the XC energy density per particle in a HEG, and $\rho(r)$ is the density of the electron gas. The XC energy is decomposed into exchange and correlation terms, $E_{XC}[\rho(r)] = E_X[\rho(r)] + E_C[\rho(r)]$, so that separate expressions for $E_X[\rho(r)]$ and $E_C[\rho(r)]$ can be determined. The exchange energy, $E_X[\rho(r)]$, is very simple because the per volume exchange energy of the HEG is known.¹⁹

$$E_X^{LDA}[\rho(r)] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int \rho(r)^{4/3} d^3r \quad (2.32)$$

However, the situation of the correlation energy, $E_C[\rho(r)]$, is more complicated because the correlation energy of the HEG is not known. It is a many-electron problem to determine the correlation energy of homogeneous interacting electron system. The early expressions of the $E_C[\rho(r)]$ were built on the perturbation theory.^{20, 21} Nowadays, the modern expressions for $E_C[\rho(r)]$ are parametrization of these recent calculated data,²²⁻²⁴ which are applied in many DFT program packages. In addition, these functional can obtain almost identical results.

On the other hand, for a spin polarized system, DFT employs two spin-densities, $\rho_{\uparrow}(r)$ and $\rho_{\downarrow}(r)$ with $\rho(r) = \rho_{\uparrow}(r) + \rho_{\downarrow}(r)$, and the form of the local spin-density approximation (LSDA)²⁵ is

$$E_{XC}^{LSDA}[\rho_{\uparrow}, \rho_{\downarrow}] = \int \varepsilon_{XC}(\rho_{\uparrow}, \rho_{\downarrow}) \rho(r) d^3r \quad (2.33)$$

For spin-polarized systems, the exact spin-scaling to the exchange energy $E_X[\rho(r)]$ is also known as the spin-unpolarized functional:

$$E_X[\rho_{\uparrow}, \rho_{\downarrow}] = \frac{1}{2}(E_X[2\rho_{\uparrow}] + E_X[2\rho_{\downarrow}]) \quad (2.34)$$

But the further approximations to the correlation energy must be employed. The relative spin-polarization is introduced into the spin-dependence of the correlation energy density:

$$\zeta(r) = \frac{\rho_{\uparrow}(r) - \rho_{\downarrow}(r)}{\rho_{\uparrow}(r) + \rho_{\downarrow}(r)} \quad (2.35)$$

$\zeta = 0$ corresponds to the paramagnetic spin-unpolarized situation with equal $\uparrow$ and $\downarrow$ spin densities, whereas $\zeta = \pm 1$ corresponds to the ferromagnetic situation when one spin density vanishes. Thus, for a given values of the total density and relative polarization, The spin correlation energy density, $\varepsilon_C(\rho, \zeta)$, is further constructed by two variables, $\rho(r)$ and $\zeta(r)$. Several forms of the spin-polarized functional have been developed in conjunction with LDA correlation functional.^{22, 25}

The LDA for the XC energy $E_{XC}[\rho(r)]$ has been proved very successful, even when it is applied to different systems with the different electron gas. One of the reasons of this success of the LDA comes from systematic error cancellation. It is well known LDA typically overestimates exchange energy $E_X[\rho(r)]$ but it underestimates correlation energy $E_C[\rho(r)]$, which leads to unexpectedly good values of $E_{XC}[\rho(r)]$ ($E_{XC}[\rho(r)] = E_X[\rho(r)] + E_C[\rho(r)]$). This error cancellation is systematic, but not accidental, which attributed to the fact that for any density the XC hole of LDA satisfies the correct sum rule $\int \rho_{XC}^{LDA}(r, r') = -1$, which is only possible if integrated errors in ρ_X^{LDA} cancel with those of ρ_C^{LDA} . The LDA

has been widely applied in solid state physics calculations, including total energies and band structure. However, it is much less applied in quantum chemistry because it cannot obtain enough accurate quantitative results in the chemical bond of molecules.

It is worthwhile to recapitulate the conceptual structure of the LDA is introduced into practical DFT applications. Generally, such as atoms, molecules and solids, these real systems are interacting due to the electrons interact each other by the coulomb interaction. Actually, the electrons are also non-uniform because they are moving in spatially varying electric field generated by nuclei. In LDA approximation, the non-uniform many-electron problem is dealt with decomposing it into two simpler problems. The first step is the solution of a spatial uniform interacting problem yields the uniform XC energy. The second step is the solution of a spatial non-uniform non-interacting problem produces the particle density. Both steps are coupled with the local-density potential, which shows how the XC energy of the homogeneous interacting system introduces into the equations for the non-uniform non-interacting system.

2.5.3.2 The generalized gradient approximation

In the LDA, the knowledge of the electron density, $\rho(r)$, is exploited based on the HEG approximation. However, the real system is spatially inhomogeneous, which is a spatially varying electron density. Thereby, the variation rate of the electron density would be introduced into the functionals. The first was gradient expansion approximation (GEA). In GEA, The gradient correction calculation of the different forms, $|\nabla\rho(r)|$, $|\nabla\rho(r)|^2$, $\nabla^2\rho(r)$, were tried to systematically introduce into the LDA. The lowest order gradient correction for the exchange energy $E_X[\rho(r)]$ is one of the famous examples:

$$E_X[\rho(r)] \approx E_X^{\text{GEA}}[\rho(r)] = E_X^{\text{LDA}}[\rho(r)] - \frac{10q^2}{432\pi(3\pi^2)^{1/3}} \int \frac{|\nabla\rho(r)|^2}{\rho(r)^{4/3}} d^3r \quad (2.36)$$

On the right hand side, the second term is the lowest order gradient correction²⁶ to $E_X^{LDA}[\rho(r)]$. However, the introducing of lowest order gradient corrections scarcely ever improves the LDA, on the contrary, often even change for the worse. Moreover, higher order corrections are exceedingly difficult to calculate. In this situation, one further tries to more general functions of $\rho(r)$ and $\nabla\rho(r)$ replace power-series-like gradient expansions in the GEA, which avoid proceeding order by order. The general form of the XC functional is

$$E_{XC}^{GGA}[\rho(r)] = \int f[\rho(r), \nabla\rho(r)] d^3r \quad (2.37)$$

The general form has become known as GGA.²⁷ Similarly, a straightforward generalization of the GGAs for the spin-polarized systems can be written as

$$E_{XC}^{GGA}[\rho_\uparrow(r), \rho_\downarrow(r)] = \int f[\rho_\uparrow(r), \rho_\downarrow(r), \nabla\rho_\uparrow(r), \nabla\rho_\downarrow(r)] d^3r \quad (2.38)$$

The various GGAs mainly differ in the choice of the different functionals $f[\rho(r), \nabla\rho(r)]$, because there is no unique way to add gradients to a function. Thereby, the various GGAs become much more different from each other than the different LDAs. The LDAs have only one type of correct expression for $E_{XC}^{hom}[\rho(r)]$ and the various parameterizations, which is only different ways of writing it. The different GGAs can be obtained by the different construction methods of the functional $f[\rho(r), \nabla\rho(r)]$ obtained. In quantum chemistry, GGAs tend to fit parameters to test different selected molecules, While, GGAs mainly focus on improving exact constraints in physics.

2.6 Calculation methods employed in the current thesis

As discussed above, there are a number of different functionals used in DFT simulations. The accuracy of these functionals varies with the studied molecules, materials

systems and properties. Recently, Kurth *et. al.*²⁸ and Adamo *et. al.*²⁹ have summarised the performance of these functionals by calculating a number of molecules and materials properties. Some functionals relevant to my work are tabulated in Table 2.1, including the LDA functional, GGA functionals, BLYP (denoted the Becke's exchange functional (1988)³⁰ combined with the correlation functional (1988)³¹ of Lee, Yang and Parr) and PBE (denoted the functional³² proposed by Perdew, Burke and Ernzerhof in 1996), and the hybrid functional of B3LYP (denoted the combination of the three-parameter Becke's gradient-corrected hybrid exchange functional³³ called "B3" with the LYP correlation functional). The LDA functionals overestimated atomisation energies with relative errors in the range of 20~30% as shown in Table 2.1. The GGA functionals yield significant improvements than LDA functional in atomisation energies. LDA usually underestimates the lattice parameters of bulk structures with the relative error of ~5%.^{28, 29, 34} While, GGA-PBE functional is relatively accurate compared the LDA and GGA-BLYP functionals for the lattice parameters of bulk crystals, in particular for the surface structures and adsorbate-surface interactions of transition metals.³⁵ However, for molecular systems, the hybrid functional, B3LYP, is somewhat more accurate than the GGA-PBE functional with the smallest absolute errors comparing to the experimental observations. Generally, LDA works better for the system with an electron structure close to a HEG, and not suitable for single atom or molecule systems.³⁶ However, GGAs seem to get significant improvements, and give reliable results both in chemistry and physics. The most popular and reliable GGA does indeed outperform LDA for many chemical systems.³⁷ The more detailed discussion about the different GGAs and their performance can be found in references³⁸ and textbooks.^{10, 39}

Table 2.1 Atomization energies -- the mean relative error (MRE) for 20 molecules²⁸ and the mean absolute error (MAE) in kcal/mol for 148 molecules²⁹; Structures -- MRE. in the unit cell volumes of 12 crystals²⁸ and MAE in the bond lengths of 23 molecules²⁹; Bulk Modulus -- MRE in the bulk moduli of 12 crystals²⁸.

Family	Mnemonic	Dependencies	Atomisation Energies		Structures		Bulk Modulus
			MRE	MAE(max)	MRE	MAE(max)	MRE
Local	LDA	ρ	22%	-	5%	-	19%
GGA	BLYP	$\nabla\rho$	5%	-	8%	-	22%
GGA	PBE	$\nabla\rho$	7%	17(51)	4%	0.011(0.064)	10%
Hybrid	B3LYP	$ \nabla\rho , \rho$	-	3(20)	-	0.007(0.062)	-

Based on the above discussion, the hybrid B3LYP functional may be a proper option for the molecular systems in chemical applications. B3LYP can yield more reliable results in geometry structures, bonding energies and reaction transition states than other functionals. Recently, Polestshuk *et. al.* reported a very detailed study on the comparative analysis of a series of multi-configurational methods such as multiconfigurational quasidegenerate perturbation theory and complete active space self-consistent field, as well as a group of single-configurational methods including Moller-Plesset second-order perturbation theory and B3LYP and PBE.⁴⁰ They found that B3LYP offers the best representation and outperforms other functionals. Thus, for the isolated pure carbon cap systems in Chapter 3, the selection of the hybrid B3LYP as an exchange correlation functional, 6-31G as Gaussian basis set, and Gaussian03 as a program package is reasonably accurate for optimizing the geometries of the isomers, intermediates and transition states. Meanwhile, it is also further

used to perform intrinsic reaction (IRC) coordinate calculations to confirm whether the transition states are connected to the right reaction intermediates or not.

For the complex heterogeneous catalyst systems, such as SWCNT growth on metal catalyst particles, the majority of the DFT calculations were performed using the VASP^{41, 42} with a plane-wave basis set. The projector augmented wave method is used to describe the interactions between an atomic core and electrons.^{43, 44} The exchange correlation energy was approximated by the Perdew-Wang functional (PW91)⁴⁵ with a plane-wave energy cutoff of 400 eV. These methods and computational parameters have been successfully used in the SWCNT-metal systems in previous studies.⁴⁶⁻⁴⁹ In order to verify the results obtained by VASP, a few calculations were implemented using the PBE exchange correlation functional for comparison. For example, the exchange part of PBE functional is similar to the Becke formula (1986), and its correlation part is close to the PW functional (1986). The PBE can obtain essentially the same reliable results, and it is more robust in those systems with rapidly varying electron density. PBE is also frequently used in various DFT calculations, which is recommended for studies of molecules interacting with metal surface.³² Therefore, for the SWCNT-Ni₅₅ coupling systems in Chapter 4 and 5, PBE has been chosen as an XC functional using to calculate interaction between metal clusters and various growing carbon structures including carbon species, carbon networks, chiral carbon caps and chiral nanotubes. More details of computational methods were given in simulation models of every Chapter.

Lastly, it is worth noting that most DFT studies, at the current stage, are primary ‘static’ calculations which intrinsically refer to zero Kelvin. In this study, I have not considered the temperature effect due to the time and computation constraints. High temperature implies the high kinetic energies of reactants, which could enhance SWCNT growth rates. The effect of

temperature on chirality selective SWCNT synthesis is very complex. I cannot tell the benefit of bringing in this complex problem without solving it in the current work. This may be my work in the next stage of research.

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Chapter 3

The Mechanism of SWCNT Growth and Chirality Selection Induced by Carbon Atom and Dimer Addition

Carbon species, such as single C atom and C₂ dimer, can be generated from decomposition of gaseous carbon precursors or evaporation of solid carbon sources. The direct interaction between carbon species and growing carbon nanotube structures is common in various SWCNT synthesis processes. An intriguing perspective is whether such direct interactions can induce (n,m) selectivity, especially under catalyst-free conditions. If SWCNT chirality can be manipulated through exposing small carbon caps to different carbon species, this may provide an alternative route toward (n,m) selective growth without worrying about the complex interactions between carbon caps and nanoparticles. As such, a detailed atomic level understanding of how the caps evolve upon interacting with carbon species is essential in the quest for chirality-controlled growth. To address this, precise *ab initio* calculations of potential energy surfaces (PESs) and activation energies of various reaction paths are required.

In this chapter, a mechanism for aforementioned SWCNT growth and chirality selection induced by single C atom and C₂ dimer addition is demonstrated based on abounding DFT calculation results. The armchair carbon cap (5,5) is selected as a starting point because some high chiral angle SWCNTs of (6,5), (7,5), (8,5) and (9,5) can be evolved from it. This family of high chiral angle tubes is most commonly found in chiral-selective SWCNT synthesis.¹⁻³ Both singlet and triplet PESs of single C atom and C₂ dimers reacting with the caps $(n,5)$ where $(n = 5, 6, 7, 8 \text{ and } 9)$ and the structures of the intermediates and

transition states in each growth step were presented. Finally, the possible roles of nanoparticles in SWCNT synthesis and feasible means to achieve the chirality controlled SWCNT growth are proposed.

3.1 Computational details

The carbon cap structures are given in Fig. 3.1, and the calculations were carried out using Gaussian03 program package.⁴ The geometries of these chiral caps, intermediates and transition states were fully optimized at B3LYP/6-31G level followed by harmonic vibrational frequency calculations to confirm their stationary points. Meanwhile, intrinsic reaction coordinate (IRC) calculations at B3LYP/6-31G level were performed to confirm whether the transition states are connected to the right reaction intermediates or not.⁵ Zero-point vibrational energies (ZPVE) were included in all given energies.

Each cap consists of six pentagons and a number of hexagons, similar as a half fullerene.^{6, 7} The matching cap of each specific chiral SWCNT can be uniquely constructed by arranging the position of these six pentagons and some hexagons according to the isolated pentagon rule.^{6, 8} (5,5) and (6,5) have only one cap obeying the isolated pentagon rule. Cap (5,5) can be constructed by adding five additional pentagons along the directions of arrows. Other chiral caps of (6,5), (7,5), (8,5) and (9,5) are built from the (5,5) cap by moving one or several pentagons outward along the arrows using the graphical modeling technique.⁸ These caps can grow into the corresponding SWCNTs with the specific (*n,m*) structure via the continuous addition of C₂ radicals, as long as no defects are included in the structures.^{7, 9-11}

3.2 Geometric structures thermodynamic stabilities of chiral caps

All optimized chiral caps are depicted in Fig. 3.1 and the relative energies at different spin states are given in Table 3.1. It is found that the ground spin states of the caps are different. For example, the ground state of the cap (5,5) is singlet which is more stable than its triplet and quintet states by 0.56 and 1.13 eV, respectively. While, the ground states of the caps (6,5), (7,5) and (8,5) are triplet; and their energies are 0.56, 0.53 and 0.46 eV lower than their quintet states, respectively. Uniquely, the cap (9,5) has a quintet ground state, and its energy is lower than its triplet, septet and singlet states by 0.53, 0.78 and 3.36 eV, respectively. The high spin multiplicity (triplet or quintet) found for the near-armchair ($n,5$) caps where ($n = 6, 7, 8$ and 9) suggests that those caps have higher possibility to react with carbon species with unpaired electron states, such as C_2 dimers.¹²

Figure 3.1 Geometric structures of selected caps with several chiralities fulfill the isolated pentagon rule.^{6, 8} The arrows denote the location of five pentagons for the cap (5,5) and the direction for moving pentagons outward.

To compare the stabilities of different caps, the energy per C atom relative to the cap (5,5) are listed in Table 3.2. The energies of the near-armchair caps ($n,5$) where ($n = 6, 7, 8$ and 9) are lower than that of the armchair cap (5,5) within the range of 0.31 to 0.36 eV per C atom. This agrees with the previous works by Balbuena *et al.* that the near-armchair caps are more stable compared with the armchair caps.¹⁰⁻¹² Furthermore, the energy per C atom increases monotonically as the chiral angle decreases from the near-armchair cap (6,5) to (9,5), indicating that the near-armchair caps with larger chiral angles are more stable. It has been generally speculated that a stable cap is more likely leading to the continuous growth to be nanotubes.^{7, 9-16} However, the complex interaction between the carbon caps and nanoparticles make it tremendously difficult for researchers to either theoretically elucidate the SWCNT growth processes^{17, 18} or experimentally achieve highly (n,m) selective growth. In this chapter, I focused on the evolution of carbon caps upon reacting with carbon species under catalyst-free conditions.

Table 3.1 The energies of the various caps at different spin multiplicities: the total energy (a.u.), zero-point vibrational energy (ZPVE) (kcal/mol) at B3LYP/6-31G, and the relative energies (RE) (eV) (inclusion of the ZPVE).

Cap	Cap55			Cap65			Cap75(46)		
Multiplicity	Total	ZPVE	RE	Total	ZPVE	RE	Total	ZPVE	RE
Singlet	-1141.8848	105.37	0.00	-1637.2519	157.21	0.59	-1751.4093	166.63	1.55
Triplet	-1141.8642	105.23	0.56	-1637.2735	156.86	0.00	-1751.4663	167.17	0.00
Quintet	-1141.8434	105.08	1.13	-1637.2528	156.99	0.56	-1751.4465	166.05	0.53
Cap	Cap85			Cap95					
Singlet	-1865.5647	175.85	2.51	-1979.7366	185.05	3.36			
Triplet	-1865.6577	177.07	0.00	-1979.8418	188.41	0.53			
Quintet	-1865.6411	177.62	0.46	-1979.8611	187.73	0.00			
Septet				-1979.8325	187.63	0.78			

Table 3.2 The ground state energies per C atom of different caps and their relative energy per C atom with respect to the cap (5,5).

Cap	Chiral angle ($^{\circ}$)	Energy/C atom (eV/C atom)	Relative energies (eV)
(5,5)	30.00	-1035.59	0.00
(6,5)	27.00	-1035.95	-0.36
(7,5)	24.50	-1035.93	-0.34
(8,5)	22.41	-1035.91	-0.32
(9,5)	20.63	-1035.90	-0.31

3.3 Chirality change and growth mechanism of SWCNTs

Figure 3.2 Schematic reaction paths of chirality change and nanotube growth via addition of C atoms or C₂ dimers for selected chiral caps. The vertical arrows indicate the cap growth processes leading to corresponding SWCNTs. The horizontal arrows represent the possible chirality change paths induced by individual C atoms.

There are two possible competitive reaction pathways at the initial growth stage starting from the (5,5) cap: single C atom incorporation which results in chirality change, and the tube growth by adding C₂ dimers (Fig. 3.2). In the former pathway, C atoms continuously adsorb on the pentagon edges followed by the pentagon edge reconstruction to form a hexagon edge, resulting in the configuration of other chiral caps (along the horizontal direction in Fig. 3.2). Meanwhile, along the tube growth pathway, C₂ dimers are continuously added to the pentagon carbon edges. The caps will eventually evolve into the corresponding SWCNTs (along the downward direction in Fig. 3.2). Therefore, the C atom and C₂ dimer ratio and their concentrations are critical in such chirality and growth competition. The complete chirality change and tube growth pathways for (*n*,5) tubes where (*n* = 5, 6, 7, 8 and 9) are illustrated in Fig. 3.2.

To uncover the reaction mechanism and elucidate the growth process in detail, the structures of intermediates and transition states are further optimized. Activation energies of PESs are also calculated. Here, both singlet and triplet PESs of each reaction step are considered, as well as their intermediates and transition states. The complete PESs for all chirality changes induced by C atoms and the tube growth by adding C₂ dimers are given in Figs. A3.1 and A3.2 respectively in Appendix A.

In order to have a straightforward image of the reactive aforementioned competitive reaction paths, I extract the initial steps of the reaction path for one type of (*n*,*m*) tubes ((6,5) tubes) among all the calculated results to illustrate the reaction PES details in Fig. 3.3. In general, the path includes the following subsequent steps: (1) A single carbon atom is adsorbed on the pentagon edges of the (5,5) cap (^{1,3}Cap55-C). (2) A transition state (^{1,3}TsCap55-C/Int65) can be found between the ^{1,3}Cap55-C and newly formed (3)

intermediate ($^{1,3}\text{Int65}$). (4) Then, the C_2 dimer is adsorbed on the pentagon edges of the intermediate $^{1,3}\text{Int65}$ ($^{1,3}\text{Int65-C}_2$) to overcome (5) a transition state ($^{1,3}\text{TsInt65-C}_2/\text{Int65+C}_2$) barrier and form $^{1,3}\text{Int65-C}_2$ and ($^{1,3}\text{Int65+C}_2$) intermediates. Finally, (6) when more C_2 dimers are incorporated into the growing cap, a (6,5) carbon nanotube is formed. To substantially support each step reaction in Fig. 3.2, all the energy, structure details of the intermediates and transition states of the singlet and triplet PESs are provided in Tables A3.1, A3.2 and Figs. A3.3, A3.4 in Appendix A.

Step (1) and Step (4) in the PESs show that there are no energy barriers for either single C atom or C_2 dimer adsorbing on the pentagon edges of the caps, which is validated by the PES scans. In Step (1), one single C atom tends to attach on the side of the pentagon edge (the $\text{C}=\text{C}$ double bond), forming a trigon-pentagon pair intermediate. All (n,m) caps except the $^3\text{Cap55-C}$ cap under investigation have the similar C atom adsorption process as that in Step (1) (see Fig. A3.1 in Appendix A).

For all the caps, the adsorption energies of a single C atom at the singlet PES are higher than those at the triplet PES by 1.78 to 2.64 eV (Fig. A3.1 in Appendix A). Moreover, the adsorption energies increase with the cap diameters. The “Int95” has the largest adsorption energies of -9.56 and -7.11 eV at the singlet and triplet PESs, respectively (note that a large negative value indicates a more stable structure). This cap diameter dependent adsorption energy implies that it is easier for single C atoms to adsorb on larger diameter caps. In addition, as illustrated in Step (4), a C_2 dimer prefers attaching to one carbon of the pentagon edge, and forms a C_2 side chain. The adsorption energies of C_2 dimers are -5.70 to -6.18 eV and -5.41 to -6.45 eV at singlet and triplet PESs (Fig. A3.2 in Appendix), respectively. The “Int95” has the largest adsorption energies of -11.89 (singlet) and -7.12 (triplet) eV. Overall,

the adsorption energies of C_2 dimers are smaller than those of a single C atom by 0.72 to 2.15 eV.

Figure 3.3 Schematic potential energy surfaces of singlet (black) and triplet (red) along the reaction “Path 2” shown in Fig. 3.2 at the B3LYP/6-31G level. (a) A single C atom induces the chirality change reaction. The relative energy of $^1\text{Cap55/C}$ is set to zero as a reference point for corresponding species. (b) The C_2 dimer addition growth reaction. The relative energy of $^1\text{Int65/C}_2$ is set to zero as a reference point for corresponding species.

Step (2) illustrates the transition state from the trigon-pentagon pair structure in Step (1) to the hexagonal ring reaction intermediate in Step (3). A total of 20 reaction intermediates

for various (n,m) caps connected by 10 transition states were identified (Table A3.1 and Fig. A3.3 in Appendix A). Based on the calculated energy barriers, it is easy to convert from a trigon-pentagon pair structure to a hexagonal ring reaction intermediate along the chirality change reaction path induced by adding single C atoms. Interestingly, the reaction energy barriers are different among various (n,m) structures (Fig. A3.1 in Appendix A). The energy barriers for $^3\text{Int65-C}$ and $^3\text{Int75-C}$ are almost zero at 0.02 and 0.03 eV, respectively; while the energy barriers for $^3\text{Cap55-C}$, $^3\text{Int85-C}$ and $^3\text{Int95-C}$ are 0.31, 0.56 and 0.97 eV, respectively. Furthermore, the energy barriers in singlet PESs are slightly higher than those in their triplet PESs. For example, the energy barriers for $^1\text{Int65-C}$ and $^1\text{Int75-C}$ are 0.97 and 0.61 eV, respectively. Therefore, the relatively low energy barriers of those transition states suggest that the formation of the reaction intermediates with hexagonal ring structures is thermodynamically and kinetically favorable.

The transition state of C_2 induced tube growth is displayed as Step (5). The growth is a close-ring reaction by incorporating C_2 side chains (the structure shown in Step (4)) into a new hexagonal ring. A total of 20 intermediates for various (n,m) caps connected by 10 transition states on the tube growth reaction pathways were identified (Table A3.2 and Fig. A3.4 in Appendix A). All energy barriers are lower than 0.42 eV (Fig. A3.2 in Appendix A), implying an easy transformation from an adsorbed C_2 side chain to a new hexagonal ring. Similar to the chirality change reaction induced by single C atoms, the triplet PESs of tube growth reaction paths are more favorable than the singlet PESs.

Along the nanotube growth path, an armchair (6,5) cap can grow by continuously adding five C_2 dimers to the edge of $^{1,3}\text{Int65}+\text{C}_2$ intermediate. The (6,5) cap formation process is illustrated in Fig. 3.4a, following Step (6) in Fig. 3.3b. Each C_2 dimer addition step

Figure 3.4 Schematic potential energy surfaces of the (6,5) cap formation and (6,5) tube growth processes along the reaction “Path 2” shown in Fig. 3.2 at the B3LYP/6-31G level, Singlet (black) and triplet (red). (a) the (6,5) cap formation. (b) (6,5) tube growth by continuous addition of C_2 dimers to the edge of the (6,5) cap.

shown in Fig. 3.4a has a similar adsorption feature as that in Step (4) and close-ring reaction process as that in Step (5). The addition would continue until a new hexagonal ring is formed. Similar energy changes of about -8.32 to -10.04 eV are found in the first five C_2 addition steps. Nevertheless, the last C_2 addition step has a lower energy than the first five steps at -6.98 (singlet) and -6.16 (triplet) eV. It could be due to the reconstruction of the carbon cap to form a new pentagonal ring in the last step. Once the (6,5) chiral cap is formed, this (6,5) cap

is able to continuously grow into the corresponding (6,5) chiral tube by adding more C_2 dimers, as long as no defects are included in the growing carbon structure.

Fig. 3.4b illustrates the sequential growth process of a (6,5) chiral tube by continuously adding 6 C_2 dimers to the edge of (6,5) cap. Each C_2 radical addition step would repeat the similar process as the process illustrated in Step (4) to Step (6). The energy changes of adding C_2 in six steps are about -7.00 to -9.42 eV. Altogether, 11 C_2 (the number equals to $n+m$ for a specific (n,m) tube) are needed to grow one complete ring along the tube edge.

3.4 The role of catalyst nanoparticles

The DFT calculations illustrate the detailed steps on how adding a single C atom induces the chirality change and how the incorporation of C_2 dimers grows the tube with the near-armchair chirality ($n,5$) caps where ($n = 6, 7, 8$ and 9) derived from a (5,5) cap. Some general information can be derived from these calculations: firstly, I show that the adsorption of C atom or C_2 dimer on growing carbon structures has no energy barrier. Secondly, the incorporation of adsorbed C atom or C_2 dimer displays relatively low energy barriers. (Fig. A3.1 and A3.2 in Appendix A). Thirdly, the (n,m) nanotube growth will continue from specific (n,m) caps through C_2 radical addition as long as no defects are introduced in the growing carbon structure.

Instead, there are several roles for catalysts in catalyzed SWCNT growth, note that the catalysts may include both metal and non-metal nanoparticles. The first role is to facilitate the atomization of carbon precursor to produce single C atoms or C_2 dimers necessary for the tube growth with certain chirality evolution. This role is evident for metal nanoparticles, while further experimental evidences are still required to verify the same role for non-metal

nanoparticles. In some cases, plasma has been utilized to enhance the atomization of carbon precursor in chemical vapor deposition,^{16, 19} which results in SWCNT growth at low temperatures. Nevertheless, the thermal decomposition of carbon precursor gas can also occur at a high enough reaction temperature in the absence of catalyst, resulting in sufficient single C atoms or C₂ dimers for either chirality change or nanotube growth reaction. As a result, catalyst is not necessarily required for the atomization of carbon precursors.

The second role of catalyst is to prevent the spontaneous closure of growing nanotube free edges. Previous experimental results²⁰ and molecular dynamics simulations^{12, 17, 18, 21-23} have shown that the edge carbon atoms would move radically inward and arrange themselves in a structurally stable pentagonal configuration, resulting in a closed carbon cap. Inspecting all the singlet and triplet optimized structures found in this study (Fig. A3.3 and A3.4 in Appendix A), some defective tetragon configurations can be found on the large diameter intermediate caps, such as ¹Int85, ^{1,3}Int85-C, ^{1,3}Int95-C, ^{1,3}Int85-C₂, and ^{1,3}Int95-C₂ (highlighted in red color). Additions of dangling atoms/dimers (such as single C or C₂) on these carbon caps can generate high curvature strains on the edges. The high strains would lead to the shrinking of cap edges. With the addition of more C₂ dimers, the cap edge may eventually enclose and result in the formation of fullerene-like spherical carbon structures. Thus, the existence of nanoparticles may effectively prevent the cap enclosure of growing carbon structure in a fullerene-like manner and stabilize the dangling energy of cap/tube edges for the elongation of nanotubes at a fixed diameter. For this purpose, recent experimental findings²⁴⁻²⁸ have demonstrated that metal catalyst nanoparticles can be replaced by various non-metal nanoparticles.

The third role of catalyst nanoparticles is to assist the transformation of individual carbon species (such as C or C₂) into stable carbon caps, and to continuously deliver carbon species to the growing nanotubes. Our calculation results demonstrate that the direct adsorptions of C atom or C₂ dimer on growing carbon caps show no energy barrier. The incorporations of adsorbed C atom or C₂ dimer directly into growing carbon caps also display low energy barriers without the assistance of any catalysts. SWCNT growth and chirality change are thermodynamically and kinetically feasible under catalyst-free conditions. However, apart from activation energy barrier under catalyst-free conditions, catalyst nanoparticles are apparently influencing (n,m) selectivity towards specific carbon cap structures.^{1, 2, 13, 20} The details of how do carbon species adsorb, diffuse and organize on (or into) metal nanoparticles remain unclear. Moreover, whether or not non-metal nanoparticles involve in these processes also requires further verifications. I speculate that the functions of catalyst nanoparticles may be most critical for the initial carbon cap formation; further research is on-going on this topic in our lab.

3.5 Influence of carbon species concentration on (n,m) selectivity

From the aspect of chiral-selective SWCNT synthesis, the relatively low energy barriers (all are lower than 1.02 eV) among different reaction pathways bring challenges in manipulating the selectivity toward a particular (n,m) tube. In particular, the addition of single C atoms on larger diameter caps is more energetically favorable, which may result in more chirality changes. This suggests that it would be more feasible to achieve chirality control on small diameter SWCNTs over larger diameter ones. Our calculation results show that the energy barriers of nanotube growth reactions for (6,5) (“Path 2” in Fig. 3.2) and (7,5) tubes (“Path 3”) are smaller than those of (8,5) (“Path 4”) and (9,5) (“Path 5”). I predict that

the chiral-selective growth of SWCNTs is more likely to be achieved on (n,m) species with low energy barriers such as (6,5) and (7,5).

Considering the competition between the chirality change pathway and the tube growth pathway, because the initial adsorptions of either a single C atom or C₂ dimer on the pentagon edge of the carbon caps show no energy barriers, the concentrations of C atoms and C₂ dimers in the experimental environment would thus also play a strong role in the chiral-selective SWCNT synthesis. The existence of abundant single C atoms would facilitate the chirality change reaction path; while the presence of C₂ radicals can push forward the nanotube growth. The concentrations of C or C₂ species can be changed by many experimental reaction parameters, such as temperature, chemistry of carbon precursors, pressure, and plasma power,^{1, 3, 13, 20, 29-34} and may help explain the preferential growth of specific chiralities in previous experiments.

A recent study has investigated the time dependent concentration changes of C, C₂ and C₃ species during the decomposition of acetylene.³⁵ It shows that the C₂ and C₃ species are absent for the first 1 ms; both the C₂ and C₃ species appear in considerable amount in subsequent 10 ms; the C₂ and C₃ amounts increase proportionally with reaction time later on.³⁵ I propose a possible strategy for chirality selection would be delivering the C species at the early stage of SWCNT growth. Once the desired chiral caps are formed, it would be more efficient to promote the C₂ dimer addition growth reaction with the increase of C₂ amount in reaction environment. Therefore, the control of reaction conditions in a short time scale would be critical to achieve the (n,m) selective SWCNT growth.

3.6 Conclusion

In summary, I have presented a growth and chirality change mechanism for selected chiral nanotubes via precise PES survey using DFT calculations. The adsorptions of C atom or C₂ dimer on growing carbon structures show no energy barrier. The armchair (5,5) cap can evolve to near-armchair (n,5) where ($n = 6, 7, 8$ and 9) caps by changing its chirality and increasing its diameter. Both the single C induced chirality change and C₂ addition nanotube growth reaction processes have low energy barriers. The processes are more favorable via the triplet PES than the singlet PES. SWCNT growth and chirality change are thermodynamically and kinetically feasible under catalyst-free growth conditions. In addition to assist the initial carbon cap nucleation, nanoparticles may play roles in SWCNT growth by preventing the enclosure of the growing carbon structure in a fullerene-like manner and assist the elongation growth of nanotubes at a fixed diameter. Chiral-selective growth is additionally possible if the concentrations of single C atoms and C₂ radicals in the experimental environment can be precisely managed at different reaction stages.

3.7 Reference

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Chapter 4

Atomic Carbon Adsorption on Ni Nanoclusters

In previous chapter, Investigations of growth and chirality change mechanism of SWCNTs induced by C atom and C₂ dimer addition implied that the ratios/concentrations of delivering C atom and C₂ dimer would play a critical role in the chiral selective SWCNT synthesis. The ratios of delivering carbon species is directly related to the adsorptions and diffusions of carbon species on metal catalyst surface. Additionally, carbon species is a key intermediates interaction with metal catalyst clusters during the growth of SWCNTs. On basis of this motivation, this chapter investigates the initial carbon adsorption on four Ni nanoclusters, Ni₁₃, Ni₁₅, Ni₃₈, and Ni₅₅.

C species are generated from the decomposition/evaporation of gas/solid phase carbon precursors in different SWCNT synthesis methods.¹⁻⁶ It is generally accepted that the adsorption of C atoms (or C₂ dimers) on metal nanoparticles is an initial step in the SWCNT growth. Subsequently, the diffusion of adsorbed C atoms on/in metal clusters controls the SWCNT cap nucleation, eventually resulting in the growth of SWCNT s.⁷⁻⁹ The interaction between growing carbon structures and metal clusters would determine the SWCNT diameter^{10, 11} and chirality¹²⁻¹⁴. Adding to the complication, experimental studies also found that the dynamic reshaping of catalyst nanoparticles occurs during the SWCNT growth.¹⁵ SWCNT researchers are puzzled by a number of problems existing at the initial SWCNT growth step, the C atom adsorption on metal nanoparticles. The metal nanoparticles around one nanometer in diameter are specially important, because they are responsible to the SWCNTs structure control.¹⁶ It is intriguing to answer the following questions: (1) are there significant differences in the C atom adsorption energy on metal nanoparticles of different

sizes? (2) Would C atoms preferably adsorb on specific facets of a metal nanocluster? (3) Whether adsorbed C atoms can penetrate into metal clusters or merely stay on the cluster surface?

Previously, the adsorption of carbon on Ni surfaces has been studied theoretically to understand the catalytic hydrocarbon synthesis. In the early *ab initio* calculations, due to the limitation of computational capacity, fixed Ni cluster models arranged according to the geometry of low index Ni surfaces were employed.¹⁷⁻²⁰ Without considering the restructure of Ni atoms, the obtained absorption energy of C on these Ni surfaces are usually over predicted. Zhang *et al.* extended such a calculation to Ni periodic slabs of three low-index nickel surfaces.²¹ Furthermore, C adsorption on a Ni₃₈ cluster was also reported.²¹ Several other recent *ab initio* calculations studied the C adsorption and diffusion on the surface and in the subsurface of periodic slabs of Ni (111), Ni (100) and Ni bulk. Their results suggested that C can diffuse on Ni surfaces, as well as into the sub-surfaces before forming metal carbides.²²⁻²⁴ It would be interesting to evaluate whether the similar phenomena also happen on small Ni nanoparticles with the size of about one nanometer, which are the catalysts employed in SWCNT growth.

In this chapter, I revisited the adsorption of carbon atom on a series of Ni metal nanoclusters using density functional calculations to address the aforementioned three questions on C adsorption related to CNT growth. (1) Ni particle size effect. Experimental results found that a small change in catalyst particle diameter has significant impacts on the diameter and chirality of CNTs produced.¹⁰ (2) The role of Ni nanoparticle facets. A previous calculation has suggested that adsorption of C may be distinct on various facets of the Ni₃₈ cluster.²¹ In this study, we extended such calculations to nanoclusters of four different sizes.

(3) To answer the intriguing question: whether a C atom can enter the small nanocluster (sub-nano scale) or only preferentially adsorbs on the surface. A series of sub-nanometer Ni clusters were modeled. Adsorption sites on individual cluster facets, along with conceivable sub-surface adsorption sites were investigated. The adsorption energy, surface reconstruction and charge distribution induced by C adsorption were also compared. The possibility of C migrating into the bulk of nanocluster was also evaluated by studying the stability of C atoms at sub-surface sites. These results on the C adsorption will help to obtain a better understanding of the SWCNT growth mechanism.

4.1 Computational details

Four clusters, namely Ni₁₃, Ni₁₅, Ni₃₈, and Ni₅₅ (illustrated in Fig. 4.1), were modeled based on a simulated annealing study on the structure stability of Ni₂₋₅₅²⁵ and an electric dipole polarizability experimental study for Ni₁₂₋₅₈.²⁶ These clusters are also within the range of diameter found to be suitable for the SWCNT growth. Three types of high symmetry surface adsorption sites on clusters were investigated, including one fourfold hollow site of (100) facets (μ_4 -100), two threefold hollow fcc and hcp sites on (111) facets (μ_3 -fcc, μ_3 -hcp). At the same time, several subsurface sites in four clusters were also investigated. Here, we restrict our report to the most stable adsorption sites of C atom. In the current context, two types of cluster models were investigated including (1) Ni clusters were fixed at their optimized geometry and (2) Ni clusters were fully optimized with the adsorbate, which allows us to investigate the effect of C adsorption on the reconstruction of clusters. Due to the limitation of computational capacity, our initial intention is to evaluate whether there are significant differences in term of adsorption energies of C adsorption between the fixed

cluster models and the fully relaxed models. We speculated that if no noticeable differences are observed between two types of models, then the fixed cluster models could be considered for further studies, such as C diffusion and C cap formation on metal cluster surfaces. Fixed models require significant less computational time. Fig. 4.1 and 4.2 illustrate all the atomic C adsorption sites studied on Ni clusters. Furthermore, the activation barriers of surface-to-subsurface diffusion were determined by scanning the potential energy profiles (PEPs) along the lines which connect the local energy minima of C atoms adsorbed at the surface fcc sites and subsurface μ_6 -sub sites for Ni_{38} clusters (Fig. 4.3). For each sampling point, the nearest-neighbor Ni atoms of a C adsorbate were relaxed while the radial distance of the C atom and other Ni atoms were fixed. To validate the transition state found by the PEP method, a precise nudge elastic band (NEB) method was also applied to locate the transition-state (TS) structure of the surface-to-subsurface diffusion.²⁷

All computations were performed spin polarized, with Perdew-Burke-Ernzerhof (PBE) exchange correlation function²⁸ using the VASP code.^{29, 30} The interaction between an atomic core and electrons were described by the projector augmented wave method.^{31, 32} The plane-wave basis set energy cutoff was set to 400 eV. The periodic boundary conditions were implemented with at least 1 nm vacuum to preclude interactions between a cluster and its images (used cubic supercells with sides of 15 Å for the smaller Ni_{13} and Ni_{15} and 20 Å for the bigger Ni_{38} and Ni_{55} clusters). Considering the large size of present clusters, the reciprocal space integration was performed with a $1 \times 1 \times 1$ k-point mesh. Increasing the Brillouin zone sampling to $3 \times 3 \times 3$ k-point mesh for the Ni_{13} cluster system, the adsorption energies change less than 1 meV, indicating that the chosen k-point mesh is sufficient for our current purposes. Between spin-polarized and non-spin-polarized calculations on the Ni_{13}

system, we found that spin-polarized calculations bind C atoms more strongly by ~0.3 eV. Thus all computations were performed spin polarized for this work. In the current work, we did not further study the magnetization of Ni cluster as it could be considered as a weakly magnetic material at 0 K according to the work by Reddy *et al.*³³ All local minimums and transition states are verified by frequency analysis. To compare conveniently the average binding energies of the clusters chosen, the Ni₂ dimer was computed with a cubic supercell of size 15³ Å³, and Ni bulk was calculated using the optimized lattice constant. Charge distribution was calculated by Bader charge analysis.^{34, 35}

The average binding energy per Ni atom of four clusters is calculated according to Equation (1), where n is the number of Ni atoms per cluster.

$$E_b(\text{Ni}_n) = [nE(\text{Ni atom}) - E(\text{Ni}_n)] / n \quad (4.1)$$

From the total energy of C adsorbed clusters $E_{\text{tot}}(\text{C/Ni}_n)$, the total energy of pure clusters $E_{\text{tot}}(\text{Ni}_n)$, and the energy of free C atoms $E_{\text{tot}}(\text{C atom})$, binding energies per C atom E_b can be calculated according to Equation (2), where n is the number of Ni atoms per cluster.

$$E_b = E_{\text{tot}}(\text{Ni}_n) + E_{\text{tot}}(\text{C atom}) - E_{\text{tot}}(\text{C/Ni}_n) \quad (4.2)$$

4.2 Ni_n (n=13, 15, 38, and 55) Clusters

Fig 4.1 illustrates optimized structures of four Ni clusters. Ni₃₈ has a truncated octahedral geometry; Ni₁₅ has a hexagonal antiprism structure; Ni₁₃ and Ni₅₅ adopt an icosahedral geometry. Their geometries are similar to those from a previous report for the Pt_n (with n=13, 38 and 55) nanoclusters.³⁶ The calculated average binding energies and Ni-Ni bond lengths of these four clusters are listed in Table 4.1.

Ni_{13} has one atom at the center and the other 12 identical atoms on the spherical shell surface with a coordination number of 6. The distance between the spherical shell and the central atom is 2.32 Å. The surface bond length is 2.44 Å. Ni_{15} has three atoms along the symmetric axis. Similar to Ni_{13} , it has only one atom at the center, and all other Ni atoms are on the surface. Radial distribution analysis shows that there are two types of nonequivalent Ni atoms relating to the center atom. Their distances to the central atom are 2.22 and 2.51 Å, and their coordination numbers are 6 and 7, respectively. Thus, the bond lengths between two Ni atoms at the Ni_{15} surface are 2.29, 2.41, and 2.57 Å (Fig. 4.1B), which are in the range of the bond length values for bulk Ni (2.49 Å) and dimer Ni_2 (2.09 Å).

Radial distribution analysis shows that Ni atoms of the optimized structure of Ni_{38} can be classified into three types of nonequivalent atoms related to the center of Ni_{38} . The first group has 6 identical atoms in the most inner shell, and they have an octahedral arrangement. The distance from 6 identical atoms to the central point of the octahedral is 1.74 Å, and their bond lengths between two Ni atoms are 2.46 Å. The second group has 24 identical atoms lying at the vertexes of six (100) faces in the outer shell. They have a coordination number of 6, and are 3.81 Å to the cluster center (denoted as “edge atoms”). The third group contains 8 atoms of the outer shell. They lie at the center of the eight (111) faces. They have a coordination number of 9, and are 3.08 Å to the Ni_{38} cluster center (denoted as “center atom”) (Fig. 4.1C). The surface bond lengths are 2.40 to 2.42 Å between two surface atoms.

Based on the Ni_{13} icosahedral structure, the Ni_{55} is built by adding 30 atoms on the top of Ni_{13} “edge atoms” with a coordination of 8 (denoted as “edge atoms” for Ni_{55}), and additional 12 atoms on the top of vertex positions of Ni_{38} with a coordination number of 6 (denoted as “top atoms” for Ni_{55}). The “top atoms” are 4.65 Å away to the cluster center,

while the “edge atoms” are 4.07 Å to the cluster center. The surface bond lengths are 2.52 Å between two “edge atoms” and 2.45 Å two adjacent “top atom” and “edge atom” (illustrated in Fig. 4.1D). Furthermore, a Ni₅₅ sub-layer is 2.36 Å to the cluster center, suggesting this layer is slightly enlarged compared to the original Ni₁₃ clusters due to addition of surface atoms.

Figure 4.1 Ni clusters: (A) Ni₁₃, (B) Ni₁₅, (C) Ni₃₈, and (D) Ni₅₅. Surface adsorption sites are depicted on the models with Ni-Ni bond lengths showed in angstroms.

Results presented in Table 4.1 show that the average binding energies and average coordination numbers increase with the increase of Ni cluster size. The minimum Ni-Ni binding energy (3.22 eV for Ni₁₃) is higher than the binding energy of a Ni₂ dimer (2.23 eV), and the strongest Ni-Ni binding energy (3.92 eV for Ni₅₅) is lower than the cohesive

energy of the bulk Ni (4.08 eV). The average interatomic distance also increases with the increase of the Ni cluster size, varying between the bond distance of Ni₂ dimer (2.09 Å) and bulk Ni (2.49 Å). Our simulation results are also consistent with the structural data obtained from an extended X-ray absorption fine structure experiment³⁷.

Table 4.1 Calculated results of the average binding energy E_b (eV), the average coordination number Z^a , bond lengths to the central Ni atom $R_{\text{Ni-Cen}}$ (Å), and surface bond lengths $R_{\text{Ni-Ni}}$ (Å).

	Ni ₂	Ni ₁₃	Ni ₁₅	Ni ₃₈	Ni ₅₅	Ni-bulk
E_b	2.23	3.22	3.26	3.75	3.92	4.08
Z	1	5.5	5.7	7.2	7.7	12
$R_{\text{Ni-Cen}}$		2.32	2.22, 2.51	1.74, 3.08, 3.81	2.36, 4.65, 4.07	
$R_{\text{Ni-Ni}}$	2.09	2.44	2.29, 2.41, 2.57	2.40, 2.41, 2.42	2.45, 2.52	2.49

^a The average coordination number Z are calculated based on Ref.²⁶

4.3 C adsorption on Ni_n (n=13, 15, 38, and 55)

Table 4.2 summarizes our results of the C adsorption on Ni clusters. The adsorption energy, interatomic distance and charge distribution induced by C absorption on different sites were first studied using fixed Ni clusters as described in section 4.3.1. Next, the effect of Ni cluster relaxation on the C adsorption energies and bond lengths was further investigated using fully relaxed Ni clusters. Lastly, the stability of C atoms at subsurface sites of relaxed Ni clusters was investigated to evaluate the possibility of C penetration into the clusters.

4.3. 1 C adsorption on fixed Ni_n clusters

When C is adsorbed on Ni₁₃, only the hcp (μ_3 -hcp) adsorption site is stable with adsorption energy of 7.06 eV. Two stable threefold hollow adsorption sites are found on the Ni₁₅ instead, which consist of 3 Ni atoms with different coordination numbers (denoted as hcp1 and hcp2 in Fig. 4.1B). However, C adsorption energies of these two sites are similar, 7.19 eV and 7.16 eV at $^1\mu_3$ -hcp and $^2\mu_3$ -hcp, respectively. Three stable C adsorption sites are found on Ni₃₈ (Fig. 4.1C). One is the fourfold hollow site (μ_4 -100) on the (100) facet with a coordination of 4 Ni atoms. The others are two μ_3 -fcc and μ_3 -hcp sites on the (111) facet. C adsorption on the μ_4 -100 site has the highest adsorption energy at 7.82 eV. The adsorption energies on μ_3 -fcc and μ_3 -hcp sites are 6.98 and 6.95 eV, respectively. Our results on the Ni₃₈ cluster agree with previous reports that atomic C has no preference toward threefold hollow sites on transition metal surfaces, such as the Pd (111) surface^{38, 39} and Pd nanoclusters.⁴⁰ On the other hand, the higher C adsorption energy at the fourfold (μ_4 -100) site suggests that C would preferably adsorb on a higher coordination site of Ni surfaces. Furthermore, two stable adsorption sites are found on Ni₅₅. They are highly symmetric threefold hollow sites, μ_3 -fcc and μ_3 -hcp (Fig. 4.1D). C adsorbed on the μ_3 -fcc and μ_3 -hcp sites shows adsorption energies at 6.80 and 6.89 eV, respectively. The energy difference between μ_3 -fcc and μ_3 -hcp sites may be due to the local environment differences of these two sites. Shown in Fig. 4.1, Ni atoms forming the μ_3 -hcp site have a coordination number of 6, while Ni atoms forming the μ_3 -fcc site have a coordination number of 8. Overall, two trends can be derived from the investigation of C adsorption energies on fixed clusters. (1) C atoms prefer adsorbing on highly coordinated sites, such as μ_4 -100, μ_3 -hcp and μ_3 -fcc. (2) C adsorption is stronger on

smaller clusters. For example, the adsorption energies increase from 6.89 eV (Ni_{55}) to 7.19 eV (Ni_{15}) on the μ_3 -hcp site, and from 6.80 eV (Ni_{55}) to 6.98 eV (Ni_{38}) on the μ_3 -fcc site.

Figure 4.2 Subsurface adsorption sites: (A) μ_4 -hol (Ni_{13}), (B) $^1\mu_4$ -hol (Ni_{15}), (C) $^2\mu_4$ -hol (Ni_{15}), (D) μ_6 -sub (Ni_{38}), (E) μ_4 -hol (Ni_{55}), and (F) μ_6 -sub (Ni_{55}). Subsurface adsorption sites are depicted on the models with Ni-Ni bond lengths showed in angstroms.

Table 4.2 Observables calculated for the adsorption of C atoms on threefold sites (μ_3 -fcc, μ_3 -hcp), fourfold sites (μ_4 -100), subsurface fourfold hollow sites (μ_4 -hol), and sixfold hollow sites (μ_6 -sub) on both fixed and fully relaxed Ni_n (with $n=13, 15, 38$ and 55) clusters. E : adsorption energy of C atoms; R_{C-Ni} : interatomic distances between an adsorbed C atom and its nearest-neighbor Ni atoms; R_{Ni-Ni} : interatomic distances between the two nearest-neighbor Ni atoms.

Sites		Ni_{13}		Ni_{15}		Ni_{38}		Ni_{55}	
		fixed	relaxed	fixed	relaxed	fixed	relaxed	fixed	relaxed
$E(\text{eV})$	μ_3 -fcc					6.98	7.17	6.80	6.94
	μ_3 -hcp	7.06	7.29	¹ 7.19, ² 7.16	7.37	6.95	7.25	6.89	7.09
	μ_4 -100					7.82	8.02		
	μ_4 -hol		7.44		¹ 8.17, ² 7.92				7.34
	μ_6 -sub						7.70		7.41
$R_{C-Ni}(\text{\AA})$	μ_3 -fcc					1.77, 1.78	1.76, 1.78	1.79	1.78
	μ_3 -hcp	1.77	1.76	¹ 1.76, ² 1.78	1.75, 1.77	1.77, 1.76	1.77, 1.75	1.77, 2.94	1.75, 1.76, 2.80
	μ_4 -100					1.83	1.83		
	μ_4 -hol		1.79, 1.88		1.82				1.76, 1.78, 1.94, 1.98
	μ_6 -sub						1.82, 2.08, 1.86		1.82, 1.92
$R_{Ni-Ni}(\text{\AA})$	μ_3 -fcc					2.40	2.52, 2.60	2.52	2.56
	μ_3 -hcp	2.44	2.61	¹ 2.29, ¹ 2.41, ² 2.29, ² 2.57	2.37, 2.59	2.41	2.62, 2.71	2.45, 2.52	2.65, 2.68
	μ_4 -100					2.42	2.54		
	μ_4 -hol		2.50		¹ 2.48, ¹ 2.56, ² 2.39, ² 2.56				2.55, 2.73
	μ_6 -sub						2.56, 2.68, 2.37, 3.42, 2.44		2.56, 2.52, 2.84

^{1,2} refers to different positions on the hcp site shown in Fig. 4.1

In addition to the adsorption energies, Table 4.2 also shows that the interatomic distances between adsorbed C atoms and their nearest-neighbor Ni atoms ($R_{\text{C-Ni}}$). It indicates that $R_{\text{C-Ni}}$ is 1.83 Å at the μ_4 -100 site. This agrees with previous experimental observations.⁴¹,⁴² Overall, the values of ($R_{\text{C-Ni}}$) have little variation among all adsorption sites on the fixed Ni clusters. Furthermore, the Bader charges of adsorbed C atoms were calculated. The charges of C atoms adsorbed on the μ_3 -fcc, μ_3 -hcp, and μ_4 -100 sites are about -0.78 e, -0.81 e, and -0.96 e, respectively. The negative values indicate that net charges are transferred from nearest-neighbor Ni atoms to the adsorbed C atoms. Unlike the significant differences observed on adsorption energies, the charges of adsorbed C atoms show little variation on four Ni clusters.

4.3.2 C adsorption on relaxed Ni_n clusters

Previously, fixed cluster models were commonly utilized due to the limitation of computational capacity.¹⁷⁻²⁰ In our fixed Ni cluster studies, cluster reconstructions upon the adsorption of C atoms were also neglected. Because experimental studies have suggested that metal cluster reconstruction could happen during CNT synthesis,¹⁵ the results obtained on fixed models may not be appropriate for investigating CNT growth mechanism. Thus, fully relaxed Ni cluster models were studied.

Two stable adsorption sites can be identified on a fully relaxed Ni_{13} cluster, in contrast to one stable site found on the fixed Ni_{13} cluster. One site is the μ_3 -hcp with similar geometric configuration as the μ_3 -hcp on the fixed cluster. The other is a new hollow site (μ_4 -hol) (see Fig. 4.2A). Our simulation results showed that a C atom adsorbed on a Ni-Ni bridge site can break the Ni-Ni surface bond to increase its coordination number from 3 to 4, resulting in the

reconstruction of Ni_{13} . Using single point calculation, we found that the energy required by the Ni_{13} cluster reconstruction is 0.64 eV. This energy may be compensated by the exothermic Ni-C bond formation, leading to a more stable adsorption complex with adsorption energy of -7.44 eV. This adsorption energy (at μ_4 -hol) is lower than that at the μ_3 -hcp site by 0.15 eV. Furthermore, energy of C adsorption at the μ_3 -hcp site on a fully relaxed Ni_{13} cluster is lower by ~ 0.2 eV, comparing to the adsorption energy at the μ_3 -hcp site on the fixed cluster. Three stable adsorption sites were found on the relaxed Ni_{15} cluster. One is at the μ_3 -hcp site. The other two are hollow sites $^1\mu_4$ -hol and $^2\mu_4$ -hol, and each hollow site is connected with four Ni atoms (Fig. 4.2B, C). Similar to the μ_4 -hol site on Ni_{13} , the two μ_4 -hol sites on Ni_{15} originate from the breakdown of Ni-Ni surface bonds (2.41 and 2.51 Å, respectively) upon C adsorption. C adsorption at the $^1\mu_4$ -hol site (8.17 eV) is the most favorable site among three adsorption sites on Ni_{15} . On the Ni_{38} cluster, three stable surface adsorption sites were found, including μ_4 -100, μ_3 -hcp and μ_3 -fcc. The C adsorption energies are 8.02 eV, 7.25 eV, and 7.17 eV, respectively. On the Ni_{55} cluster, two stable surface adsorption sites, μ_3 -fcc and μ_3 -hcp were found with adsorption energies of 6.94 and 7.09 eV, respectively. Furthermore, Table 4.2 also illustrates that the interatomic distances between an adsorbed C atom and its nearest-neighbor Ni atom becomes shorter on fully relaxed clusters compared to fixed clusters, in consistent with the stronger C-Ni bond formation. However, no significant differences were found on the Bader charges of adsorbed C atoms at different adsorption sites of relaxed clusters.

Overall, the C adsorption energies derived on fully relaxed clusters in this study are comparable with experimental results, such as Ni (100) (7.35 eV) and Ni (111) (6.94 eV), obtained on single crystal surface by measuring the heat of segregation and vaporization

through a thermodynamic cycle.⁴³⁻⁴⁵ Similar to the results obtained on fixed clusters, C adsorption energies are larger on smaller clusters and highly coordinated sites. More importantly, new C adsorption sites were identified on Ni clusters when cluster reconstruction upon C adsorption sites were identified on Ni clusters when cluster reconstruction upon C adsorption was considered. In fact, C adsorption energies on reconstructed sites are higher than those on other sites, suggesting reconstructed sites are more favorable adsorption sites. This finding highlights that some previous studies,^{14, 46} which investigated carbon diffusion or CNT cap formation on fixed metal clusters could be inadequate. Metal cluster reconstruction is an indispensable part toward a better understanding of CNT growth mechanism.

4.3.3 C adsorption at subsurface sites

An unsolved puzzle in CNT growth mechanism is whether adsorbed C atoms would enter the metal clusters or merely diffuse on the cluster surfaces. Our investigation on the relaxed Ni clusters suggests that surface Ni-Ni bonds can be broken upon C adsorption. Investigating the stability of C atoms at subsurface sites may help to elucidate this puzzle. For this purpose, the stability of a subsurface C atom in fully relaxed Ni₃₈ and Ni₅₅ clusters were studied.

We identified two interstitial sites in Ni₃₈: one is located at the subsurface octahedral site (denoted as μ_6 -sub); and the other is located at the center octahedral site (denoted as μ_6 -cen). Between these two subsurface sites, the μ_6 -sub is more stable on the relaxed Ni₃₈ cluster (Fig. 4.2D). The adsorption energy on μ_6 -sub site is 0.32 eV less than that of the most stable surface adsorption site (μ_4 -100). This may be due to the fact that a C atom at the μ_6 -sub

subsurface adsorption sites is located in a confined space. Two stable C subsurface adsorption sites, μ_4 -hol and μ_6 -sub sites were identified (shown in Fig. 4.2E and F, respectively) on the relaxed Ni_{55} cluster. C adsorption at the μ_6 -sub site has the highest adsorption energy of 7.41 eV among all subsurface and surface adsorption sites on Ni_{55} . The μ_4 -hol site is of comparable stability as the μ_6 -sub site, and its adsorption energy is only 0.07 eV lower than that of the μ_6 -sub site.

At the subsurface μ_6 -sub site, the interatomic distances between adsorbed C atoms and their nearest-neighbor Ni atoms ($R_{\text{C-Ni}}$) increase considerably (between 5 and 21%) compared to those at the surface sites. This interatomic distance expansion can be explained by the relief of the repulsive interaction between subsurface C atoms and their adjacent Ni atoms inside clusters⁴⁷. We have further investigated the local charge variation upon C adsorption. We found that C atoms adsorbed at subsurface adsorption sites with a coordination of six Ni atoms possess a charge of about -1.10 e, higher than the charge of C atoms at any surface sites. It suggests a stronger C-Ni interaction when C atoms locate at subsurface sites.

Our results indicated that C atoms located at subsurface sites of Ni clusters are more stable than those on the surface sites. The next step is to find out whether a C atom can migrate directly from the surface sites to the subsurface sites? The PEP method described in the methodology session was first applied to investigate this problem. The curve in Fig. 4.3 depicted the potential energy profiles for the diffusion of single C atom from the surface μ_3 -fcc sites to subsurface μ_6 -sub sites in the relaxed Ni_{38} cluster. The calculated activation barriers are 0.26 eV. To validate the transition state found by the PEP method, the precise NEB method was also applied to locate the transition-state structure for the surface-to-subsurface diffusion. The activation barrier (0.25 eV) by the NEB method is only less 0.01

eV than that obtained by the PEP method. In addition, the transition state geometric structures from the two methods are very similar. As illustrated in Fig. 4.3, the PEP method shows that the distances between the C atom and Ni atoms are 1.72 and 1.75 Å, while the NEB method indicates the distances are 1.75 and 1.93 Å. The adsorbed C atom at the surface threefold μ_3 -fcc site would break the longer Ni-Ni bond at one edge and interact with the forth Ni atom before it slips into the subsurface μ_6 -sub site. Recently, Zhu et al. reported that

Figure 4.3 Potential energy profiles from a fcc three-fold hollow surface site to a six-fold sub-surface site on a Ni₃₈. Local minima on the curves correspond to fcc three-fold hollow sites (on the right) and octahedral subsurface holes (on the left). R_{C-cen} : interatomic distances between an adsorbed C atom and Ni atoms at the center of clusters.

the activation barriers for C atom diffusion from surface threefold sites to subsurface sites are about 0.755 eV²³. Compared with their transition state structures found on the periodic (111) slab surface, Ni atoms near the adsorbed C atom have a coordination number of 9. However, on our Ni₃₈ cluster, Ni atoms adjacent to the carbon atom have smaller coordination numbers of 6 or 8. Thus, it is expected the C diffusion from the surface μ_3 -fcc site to the subsurface μ_6 -sub site on a Ni cluster would be easier than on a periodic slab. Vines et al. recently also reported a similar finding, that the C atom diffusion on Pb clusters from surface sites into tetrahedral subsurface sites is almost non-activated⁴⁸. They have proposed that this is due to the high mobility of low-coordinated Pb atoms at cluster edges. These results resolve our puzzle, and we conclude that it is thermodynamically and kinetically feasible for a C atom adsorbed on Ni cluster surface to migrate into the underlying interstitial subsurface positions. This finding also supports the previous speculation that C atoms may enter the metal nanoclusters during CNT growth.⁴⁹⁻⁵¹

4.4 Conclusion

This study systematically investigated the adsorption energies of atomic carbon on Ni clusters with various cluster sizes (Ni₁₃, Ni₁₅, Ni₃₈, and Ni₅₅). On both fixed and relaxed clusters, C atom prefers to adsorb at high coordination sites. μ_4 -100 was found to be the most stable adsorption site on fixed Ni clusters. The μ_3 -hcp and μ_3 -fcc sites are of comparable stability, but less favored than the μ_4 -100 site by ~0.8 eV. Taking cluster relaxation into account, new stable adsorption sites were found on the relaxed clusters. C atoms located at subsurface sites of Ni clusters are more stable than C atoms on the surface sites. Furthermore, the migration of surface C atom located on the threefold hollow site into the underlying

interstitial subsurface positions is thermodynamically and kinetically feasible. These results indicate that CNT growth would involve both surface and subsurface C atoms coupled with surface reconstruction of Ni nanoclusters. Our results highlight that C diffusion and CNT cap formation need to be investigated on relaxed clusters for a better understanding of CNT growth mechanism.

4.5 Reference

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Chapter 5

Charge Transfer between Metal Clusters and Growing Carbon Structures in Chirality-Controlled SWCNT Growth

The initial single C atom adsorptions and diffusions on different nickel nanoparticle (Ni_{13} , Ni_{15} , Ni_{38} , and Ni_{55}) have investigated in Chapter 4. In this chapter, I investigate continuously the interactions between Ni metal clusters and various growing carbon structures including other carbon species, carbon networks, chiral caps and chiral nanotubes in order to obtain some insights into chirality controlled SWCNT growth.

As aforementioned discussed in chapter 1, experimental results have shown that metal clusters, the most common catalysts used in synthesis, with various sizes, morphology, and composition may lead to preferential growth of a subset of chiral SWCNTs.¹⁻⁵ Metal clusters play important/key roles in catalyzing conversion of the carbon-containing feedstock, annealing defects of growing nanotubes, prevention of SWCNT closure, terminating of the edge dangling bonds and providing critical carbon density.⁶⁻⁹ Theoretical studies have suggested that the chirality selectivity could be related to the epitaxial matching between nanotube ends and metal catalyst surface atoms,¹⁰ the adhesion strength between nanotubes and catalyst clusters,¹¹ and chirality dependent growth rates obeying the dislocation theory¹². However, the detailed role of metal clusters in chirality-controlled SWCNT growth remains elusive.

Recent experimental results indicated that the interface between the carbon cap/tube end edge and metal/metal carbide clusters is active in SWCNT growth.¹³⁻¹⁵ Charge or

electron transfer is fundamental for explaining structural stability and reactivity of organometallic and metal cluster species.¹⁶ In general, charge transfer is the intrinsic mechanism behind many chemical reactions. It is a useful tool in understanding and predicting the structural change and chemical reactivity in organometallic chemistry. In this study, on the basis of *ab initio* calculations, I found that significant charge transfer or charge redistribution exists between growing carbon structures and metal clusters. The electronic charges transfer evidently from metal surface atoms to carbon atoms, resulting in negative charges accumulated on edge carbon atoms. In contrast, non-edge carbon atoms gain little charge. More importantly, I identified that distinct charge distribution patterns for different chiral SWCNTs at their interfaces with metal clusters. This chapter is to present our calculation results to highlight that growth sites may be controlled by metal clusters through charge transfer in chirality-controlled SWCNT synthesis.

5.1 Computational details

Spin polarized computations were performed with the Perdew-Burke-Ernzerhof (PBE) exchange correlation function¹⁷ using the VASP code.^{18, 19} The interaction between an atomic core and electrons was described by the projector augmented wave method.^{20, 21} The plane-wave basis set energy cutoff was set to 400 eV. Periodic boundary conditions were implemented with at least 1 nm vacuum to preclude interactions between a cluster and its images. Simulation boxes were $20 \times 20 \times C$ Å (where C is from 20 to 32 Å) for different calculated systems. The reciprocal space integration was performed with a $1 \times 1 \times 1$ k-point mesh for all calculated systems with discrete characters. The global transferred charge was

calculated by the atomic Bader charge analysis,²²⁻²⁴ and the electron distribution was determined by means of the electron localization function (ELF).^{25, 26}

The total adhesion energy of a carbon structure (C_n) on the Ni_{55} cluster was defined by the energy difference between the fully geometry-optimized $Ni_{55}-C_n$ complex and the corresponding separated Ni_{55} and C_n :

$$E_{T(C-Ni)} = E_{Ni_{55}-C_n} - (E_{Ni_{55}} + E_{C_n}) \quad (5.1)$$

The average cohesive energy of C–Ni per C atom of $Ni_{55}-C_n$ complexes was computed by means of dividing the total adhesion energy by the number of C atoms (n) adsorbed on the Ni_{55} cluster.

$$E_{C-Ni} = E_{T(C-Ni)} / n \quad (5.2)$$

The cohesive energy of C–C (E_{C-C}) of C_n on Ni_{55} was estimated by the following procedure: first, the final optimized geometry of the corresponding $Ni_{55}-C_n$ complex was fixed; then all Ni atoms were taken away; and lastly, a single point calculation was performed to obtain the energy (E_{C_n}) matching to the remaining C_n structure. E_{C-C} is calculated by the equation:

$$E_{C-C} = (nE_C - E_{C_n}) / n \quad (5.3)$$

where E_C is the energy of a free carbon atom at its ground state, 7.7 eV.²⁷

Chemical potential (μ) of the growing carbon structure (C_n) on Ni_{55} , which is the energy required to add one additional carbon atom during SWCNT growth, was defined as:

$$\mu = \frac{E_{Ni_{55}-C_n} - E_{Ni_{55}}}{n} - \mu_C \quad (5.4)$$

where $E_{Ni_{55}-C_n}$ and $E_{Ni_{55}}$ are the total energies of fully geometry-optimized complexes with and without C_n , respectively. n corresponds to the number of carbon atoms in C_n . The

reference chemical potential, μ_c , is the chemical potential of a free carbon atom at its ground state, 7.7 eV. The concept of chemical potential has previously been applied in SWCNT nucleation and growth studies.²⁷

5.2 Computational models

In this chapter, The growth of armchair (5,5), chiral (6,5) and zigzag (9,0) nanotubes on a relaxed Ni₅₅ cluster is investigated. The (5,5) nanotube was selected because a series of near-armchair nanotubes ((6,5), (7,5), (8,5), and (9,5)), which are most commonly found in chiral-selective SWCNT synthesis,¹⁻⁵ can all be derived from one (5,5) carbon cap.²⁸ The (6,5) nanotube was chosen as a representative chiral nanotube model. The (9,0) nanotube has a similar diameter as the (5,5) nanotube, while holding a different chiral angle. A high symmetrical icosahedral structure was adopted as an initial structure for the Ni₅₅ cluster, because of fact that this structure is a local geometry minimum in its size range. Besides, the Ni₅₅ cluster has a diameter comparable with that of the armchair (5,5), chiral (6,5), and zigzag (9,0) nanotubes. The Ni₅₅ cluster has also been often observed in experiments,^{29, 30} and is often used in theoretical studies of SWCNT growth.^{11, 31, 32} All structures, including carbon intermediates C_n, metal cluster Ni₅₅, and Ni₅₅-C_n complexes, are fully relaxed to optimize without any constraints.

On the basis of the nanotube root growth hypothesis,^{33, 34} SWCNT growth on the Ni₅₅ cluster can be classified into three stages as illustrated in Fig. 5.1: (1) early nucleation of carbon species (single carbon atom, C₂ dimer and C₃ chain); (2) formation of (5,5), (6,5) and (9,0) chiral caps from five- and six-membered carbon rings; and (3) continuous growth into (5,5), (6,5), and (9,0) nanotubes. During the initial nucleation stage, carbon species (C, C₂,

A: initial nucleation **B: formation of chiral caps**

C: growth of chiral nanotubes

Figure 5.1 Based on the root growth hypothesis, the catalytic growth of the armchair (5,5), chiral (6,5), and zigzag (9,0) SWCNTs on the Ni_{55} cluster can be classified into three stages: (A) initial nucleation of carbon species, such as single C atom, C_2 dimer and C_3 chain; (B) formation of (5,5), (6,5), and (9,0) chiral caps from five- and six-member carbon rings; and (C) continuous growth of (5,5), (6,5), and (9,0) nanotubes, which carbon caps depart from the Ni_{55} cluster with certain nanotube length.

and C_3) may adsorb on different sites of the Ni_{55} cluster. They include two stable fcc and hcp three-fold hollow surface sites and two corresponding interstitial subsurface sites: an octahedral (oss) site below the fcc site, and a tetrahedral (tss) site below the hcp site. The

detailed results of all possible sites for the adsorption of a single carbon atom on various Ni clusters have been discussed in the chapter 4. In this chapter, I extended our study to the nucleation of two or three isolated carbon atoms adsorbed on the Ni_{55} cluster, which results in the formation of C_2 dimer and C_3 chain. A few representative adsorption sites are shown in Fig. 5.1A. The carbon dimer and chain on the Ni_{55} cluster would further grow into larger carbon structures.

During the formation of chiral caps and their sequential nanotube growth, it is impractical to calculate all possible $\text{Ni}_{55}\text{-C}_n$ complexes with different interaction interfaces between C_n and Ni_{55} . A series of representative intermediate structures for the growth of armchair (5,5), chiral (6,5) and zigzag (9,0) nanotubes on the Ni_{55} cluster were chosen as studying models. Following the formation of C_2 dimer and C_3 chain, graphitic fragments would evolve into complete carbon caps on the metal cluster by further incorporating C/C_2 . The two pathways, (a) $\rightarrow$ (c) (the top row of Fig. 5.1B) and (f) $\rightarrow$ (h) (the bottom row of Fig. 5.1B), illustrate the formation of the armchair (5,5) cap and the zigzag (9,0) cap, respectively. The (5,5) and (9,0) nanotube each has only one matching chiral cap, which can obey the isolated pentagon rule.^{35, 36} As illustrated on Fig. 5.1B (a) and (f), the (5,5) cap can be constructed starting from a five-membered carbon ring, while the (9,0) cap can be built from a six-membered carbon ring. Subsequently, 15 carbon atoms were added to the initial five-membered ring to form the intermediate cap fragment ($\text{Ni}_{55}\text{C}_{20}$) (see Fig. 5.1B (b)). Next, the complete (5,5) cap ($\text{Ni}_{55}\text{-(5,5) Cap}$) was created by joining five C_2 dimers (or 10 carbon atoms) to the intermediate cap fragment $\text{Ni}_{55}\text{C}_{20}$ (see Fig. 5.1B (b) to (c)). Similarly, the complete (9,0) cap ($\text{Ni}_{55}\text{-(9,0) Cap}$) can be constructed, as illustrated on Fig. 5.1B (g) and (h). The formation of (6,5) can be achieved through two paths: 11 carbon atoms can be added to

the $\text{Ni}_{55}\text{C}_{20}$ to form the intermediate cap fragment $\text{Ni}_{55}\text{C}_{31}$ (Fig. 5.1B (b) to (d)), followed by joining six C_2 dimers (or 12 carbon atoms) to have the complete (6,5) cap (Fig. 5.1B (d) to (e)); alternatively, the intermediate cap fragment $\text{Ni}_{55}\text{C}_{31}$ can also be formed by a single carbon atom addition to the complete (5,5) cap (Fig. 5.1B (c) to (d)).

It has been proposed that a (n,m) chiral carbon cap can sequentially grow into the corresponding SWCNT with the specific (n,m) structure by constant addition of carbon atoms.^{37, 38} In our previous study, I showed that the addition of C_2 dimers at the pentagon carbon edges of chiral carbon caps can lead to the continuous growth of nanotubes without chirality changes. Moreover, $n+m$ C_2 dimers (the number of a specific (n,m) tube) are needed to grow one complete ring along the tube edge.²⁸ Fig. 5.1C illustrates the proposed sequential step-by-step growth of the (5,5), (6,5), and (9,0) chiral caps on the Ni_{55} cluster. The pathway (i) $\rightarrow$ (l) (the top row of Fig. 5.1C) represents the growth from the complete (5,5) cap (Ni_{55} –(5,5) Cap) to a short (5,5) nanotube (Ni_{55} – C_{110}) by repeated addition of 10 C_2 dimers (or 20 carbon atoms) at the interface between the open edge of the (5,5) cap/nanotube and the Ni_{55} cluster. Similarly, the pathway (p) $\rightarrow$ (s) (the lower row of Fig. 5.1C) represents the growth of a (9,0) nanotube on the Ni_{55} cluster from Ni_{55} –Cap (9,0) (Fig. 5.1B (h)) to the short (9,0) nanotube (Fig. 5.1C (s)) by repeated addition of 9 C_2 dimers (or 18 carbon atoms) to the interface between the open edge of the (9,0) cap/nanotube and the Ni_{55} cluster. The middle row of Fig. 5.1C ((m) to (o)) shows the growth of (6,5) nanotube by repeated addition of 11 carbon atoms.

It should be noted that the models shown in Fig. 5.1 are only representative configurations for the growth of (5,5), (6,5), and (9,0) nanotubes. The actual growth process

may be less orderly, with numerous polyynes chains and incomplete carbon rings, which have been shown in recent molecular simulations.

5.3 Adhesion energy of C_n on Ni_{55}

The total adhesion energies of C_n structures on the Ni_{55} cluster for the armchair (5,5), chiral (6,5), and zigzag (9,0) nanotubes at different growth stages are shown in Fig. 5.2. They span from about 5 to 22 eV. The adhesion energies change significantly at the cap nucleation stages. It is generally considered that the nucleation and formation of chiral caps are critical in determining the chirality of SWCNTs.^{38,39} At initial nucleation step, small carbon species are key intermediates interacting with metal clusters. Single carbon atoms have stronger adsorption on surface hollow sites (6.94 eV/C for the fcc site and 7.09 eV/C for the hcp site), and they can penetrate into the Ni cluster (7.34 eV/C for the tetrahedral subsurface site (tss) and 7.41 eV/C for the octahedral subsurface site (oss)). The activation energy barrier is about 0.25 eV for an adsorbed surface carbon atom to migrate from the fcc hollow site to the underneath oss subsurface site.⁴⁰ However, I found that C_2 dimers and C_3 chains, as small elementary units for SWCNT growth, are unable to penetrate into the Ni_{55} cluster, and they can only adsorb on the cluster surface (7.06 eV/C for C_2 dimers and 5.75 eV/C for C_3 chains). This may be due to fact that their relative weak interaction with Ni atoms and strong covalent bonds among carbon atoms. These results suggest that carbon structure growth happens on the surface of metal clusters, even though single carbon atoms could initially penetrate into clusters.

In the following steps of chiral cap formation, small carbon species would first coalesce into five or six-membered carbon rings. The five-membered carbon ring, attached on the

surface of the Ni_{55} cluster (Fig. 5.1B (a)), has adhesion energy of 5.91 eV, which is 0.26 eV higher than that of the six-membered carbon ring attached on the same Ni_{55} cluster (Fig. 1B (f)). This agrees with recent results from a first-principles calculation⁴¹ and a molecular dynamics simulation,⁴² which suggests the preferential formation of five-membered carbon rings than six-membered carbon rings on metal clusters during the chiral cap formation. Subsequently, the intermediate cap fragment (Fig. 5.1B (b), $\text{Ni}_{55}\text{C}_{20}$) has a smaller adhesion energy of 5.56 eV. The strongest adhesion energy in the growth of (5,5) nanotube exists when a complete (5,5) end cap (Fig. 5.1B (c), Ni_{55} –(5,5) Cap) is formed. Similarly, in the growth of (9,0) nanotube, the adhesion energy is 4.59 eV for the creation of the intermediate cap fragment (Fig. 5.1B (g), $\text{Ni}_{55}\text{C}_{21}$). This is much lower compared to the adhesion energy of 20.82 eV, when the complete (9,0) cap (Fig. 5.1B (h), Ni_{55} –(9,0) Cap) is produced. For the (6,5) nanotube, the first few steps are the same as those of the (5,5) nanotubes. And the adhesion energy of the complete (6,5) cap (Fig. 5.1B (e)) is slightly smaller than that of the the intermediate cap fragment $\text{Ni}_{55}\text{C}_{31}$ (Fig. 5.1B (d)). It should be noted that complete caps have been lifted up from the Ni_{55} cluster surface, and only end edge carbon atoms of the caps are attached on the Ni_{55} cluster surface.

A chiral carbon cap can sequentially grow into the corresponding (n,m) SWCNT by continuous addition of C_2 dimers at the interface between the chiral cap/nanotube end and the Ni_{55} cluster. The growth energies of (5,5), (6,5), and (9,0) nanotubes differ maximum by only a couple of eV throughout the growth from the complete chiral caps. The (5,5), (6,5), and (9,0) nanotubes have adhesion energies of 17.00 ± 0.25 , 18.60 ± 0.15 and 21.70 ± 0.10 eV,

Figure 5.2 The total adhesion energies of C_n structures on the Ni_{55} cluster at different growth stages for the armchair (5,5), chiral (6,5), and zigzag (9,0) nanotubes. The carbon atom number corresponds to the carbon number in various carbon structures as illustrated in Fig. 5.1

respectively. The zigzag (9,0) nanotube has larger adhesion energies than those of armchair (5,5) and chiral (6,5) nanotubes. It has been proposed that the chirality selection in SWCNT growth could be influenced by the adhesion energy between growing nanotube structures and

metal clusters.¹¹ However, the optimal strengths required for SWCNT growth between carbon and carbon or between carbon and metal are still unclear. In order to gain a better understanding on their interaction strengths, in this study, I further investigated the evolution of C–C and C–Ni interactions throughout the nanotube growth.

5.4 Cohesive energies of C–C and C–Ni in $\text{Ni}_{55}\text{--C}_n$ complexes

Fig. 5.3 summarizes the cohesive energies of C–C and C–Ni interactions per carbon atom for the growing armchair (5,5), chiral (6,5), and zigzag (9,0) $\text{Ni}_{55}\text{--C}_n$ complexes. It shows that the changing trend of C–C interactions is opposite to that of C–Ni interactions. For various C_n structures, the cohesive energy of C–C per carbon atom is weaker at the beginning, and then, it increases rapidly with the expansion of C_n structures, until complete chiral caps are formed. Subsequently, the C–C interaction energy would only increase slightly to about 7.50 eV/C. For the (5,5), (6,5), and (9,0) nanotubes, once chiral caps are formed, there are no significant changes in their C–C interaction strengths with the elongation of nanotubes. On the opposite, the cohesive energy of C–Ni per carbon atom is very strong (about 7.20 eV/C) at the start. Then, it decrease rapidly until the formation of complete chiral caps on the Ni_{55} cluster surface. At last, the C–Ni interaction energy shows minimum changes with the nanotube growth. These results suggest that there is a competition among the interactions of C–C, C–Ni and Ni–Ni throughout the growth of SWCNTs. Their strengths would adjust continuously with the growth of C_n structures on metal clusters until reaching a dynamic equilibrium during the extension of nanotube length.

Figure 5.3 (A) the average C–C interaction energies per atom, and (B) the average C–Ni interaction energies per atom for the growing armchair (5,5), chiral (6,5), and zigzag (9,0) $\text{Ni}_{55}\text{--C}_n$ complexes. The number of carbon atoms corresponds to models illustrated in Fig. 5.1.

5.5 Chemical potential of C_n on Ni_{55}

The energy required to add one additional carbon atom to a C_n structure is defined as its chemical potential (μ). Fig. 5.4 show chemical potentials of various possible C_n structures

(illustrated in Fig. 5.1), which could appear in the process of growing (5,5), (6,5), and (9,0) nanotubes. Firstly, I investigated the growth of these C_n structures without metal clusters. Shown in Fig. 5.4 A, the chemical potentials of C_n structures decline rapidly until complete (5,5), (6,5), or (9,0) carbon caps are formed. Subsequently, they decrease gradually to zero with the increase of nanotube lengths. The result suggests that carbon atoms can spontaneously assemble into carbon caps leading to nanotube growth under catalyst-free condition. However, significant differences are observed when these C_n structures are grown on the Ni_{55} cluster. During initial nucleation, the adsorption of single carbon atoms on various surface sites of the Ni_{55} cluster (0.76 eV at fcc site and 0.61 eV at hcp site) has higher chemical potentials than the adsorption at subsurface sites (0.36 eV at oss site and 0.29 eV at tss site). Note that only the chemical potential at the subsurface oss site is shown on Fig. 5.4B. Moreover, chemical potentials of a C_2 dimer and a C_3 chain adsorbed on the Ni_{55} cluster surface sites are 0.68 and 0.73 eV, respectively, which are higher than that of single carbon atom at subsurface sites. These results imply that single carbon atom would rather penetrate into the Ni_{55} cluster than stay on the surface or form C_2/C_3 . This is consistent with our previous transition state calculation.⁴⁰ During the formation of chiral caps, the five-membered carbon ring has the highest chemical potential over all SWCNT growth stages at 1.53 eV. The six-membered carbon ring has the second highest chemical potential at 0.81 eV. The high chemical potentials of carbon rings have two implications: (1) considering the lower chemical potentials of $C/C_2/C_3$ species, it suggests that C species at low coverage on metal surface would not spontaneously assemble into carbon rings. The formation of five- and six-membered carbon rings requires a large surface coverage of carbon species with chemical potentials exceeding 1.53 eV or 0.81 eV, in agreement with a recent paper.²⁷

Figure 5.4 Chemical potentials of various carbon structures: (A) C_n without metal clusters, and (B) $Ni_{55}-C_n$ complexes of the (5,5), (6,5), and (9,0) nanotubes. The chemical potentials are expressed with respect to the chemical potential of a free carbon atom in its ground state. The number of carbon atoms corresponds to models illustrated in Fig. 5.1.

(2) Once these small carbon rings are formed under certain surface coverage of carbon species, they can spontaneously extend into larger carbon structures by incorporating more small carbon species, because chiral cap intermediates (C_{20} , C_{21} , and C_{22}) and complete (5,5), (6,5), and (9,0) chiral caps all have lower chemical potentials than those of carbon rings on the Ni_{55} cluster. During the growth of chiral nanotubes, the growing nanotubes have lower chemical potentials than small carbon species (under the red line indicated on Fig. 5.4 B), and their chemical potentials would decrease gradually to zero with the increase of nanotube length. It suggests that complete chiral carbon caps, attached on the metal cluster, would spontaneously grow into nanotubes by incorporating other carbon species adsorbed on the metal surface. Furthermore, the chemical potentials of all C_n structures attached on the metal cluster are lower than those of corresponding C_n structures in gas phase. This implies that the adsorption of C_n structures on metal clusters is energetically favored. It also suggests that there is a driving force from dissociation of carbon species in gas phase toward adsorption of carbon species on metal clusters and growth of carbon structures.

5.6 Charge transfer between C_n and Ni_{55}

Based on the above calculation results of the total adhesion energies (in section 5.3), cohesive energies of C-C (in section 5.4), and chemical potentials of C_n (in section 5.5) at different growth stages, I found that at the initial nucleation stage, small carbon species (e.g. C, C_2 , and C_3) have high adhesion energies per carbon atom on the Ni_{55} cluster. With the growth of carbon structures, the C–C cohesive energy becomes stronger, while the C–Ni interaction becomes weaker (see Fig. 5.3); meaning that it is energetically favorable for forming, lifting-up, and growing of carbon caps on metal cluster surface. As depicted in Fig. 5.4 B, the carbon ring formation requires a large surface coverage of carbon species on

metal surface due to the very high chemical potential barriers for incorporating additional carbon atoms at the early nucleation stages. Once these carbon rings are formed under certain carbon surface coverage, they can spontaneously extend into complete chiral caps. Small carbon species on Ni₅₅ with higher chemical potentials (red line in Fig. 5.4 B) provide a driving force for the continuous growth of SWCNTs. (see Fig. 5.4 B).

However, the growth energies of (5,5), (6,5), and (9,0) nanotubes differ by only a couple of eV. Considering the high growth temperature, it implies no strong preference for specific chirality on Ni₅₅. Based on energy calculations, a recent study suggested that free metal clusters are incapable of growing SWCNTs with desired chiralities, which is not in agreement with existing experimental results. I investigated charge transfer between C_n and Ni₅₅ to better understand hidden roles played by metal clusters. As rendered in Fig. 5.5, negative charges are transferred from Ni atoms to carbon atoms when carbon species are absorbed on Ni₅₅. Inspecting the interface of Ni₅₅–C_n complexes, I found that charges always accumulate on edge carbon atoms; on the contrary, non-edge carbon atoms have little charge (see Fig. 5.5). For Ni atoms of Ni₅₅, charge depletion is almost all from the carbon neighboring Ni atoms (+0.2 to +0.39 e, see Fig. 5.5). Other Ni atoms deplete no charges. These outcomes indicate that the charge transfer is short-ranged, and mainly occurs between outmost edge carbon atoms and their neighboring Ni atoms.

More importantly, I found that charge distributions at Ni₅₅–C_n interface exhibit specific patterns associated with nanotube chirality, as shown in Fig. 5.5C. For the armchair (5,5) cap/nanotube, charges (-0.31 to -0.38 e) mainly accumulate on five pairs of interval outmost edge carbon atoms (red, in Fig. 5.5C a, c); while the other edge carbon atoms (green), hardly possess any charge. In contrast, for the zigzag (9,0) cap/nanotube, charges are localized on

nine interval outmost edge carbon atoms (red, in Fig. 5.5C i, k); while other edge carbon atoms (green) do not possess any charge. For the chiral (6,5) cap/nanotube, charges mainly accumulate on three carbon atoms (a kink site, red) and four pairs of interval double-carbon atoms (armchair sites, red in Fig. 5.5C e, g); while other edge carbon atoms (green) are near neutral. Analogous phenomena are also noticed for other chiral caps/nanotubes in our ongoing works.

(A) Carbon species

(B) Carbon rings and intermediates

(C) Carbon caps and tubes

Figure 5.5 Charge distribution of (A) carbon species, (B) carbon rings and intermediates, (C) carbon caps and tubes on the Ni_{55} clusters. The carbon atom number corresponds to models illustrated in Fig. 5.1.

ELF plots further illustrate that charges are transferred evidently from neighboring Ni atoms to edge carbon atoms (see Fig. 5.6 b, d, f, h, j and l). Comparing with delocalized π -electrons at chiral cap/nanotube edges without metal clusters (see Fig. 5.6 a, c, e, g, i and k), the electrons between $\text{Ni}_{55}\text{-C}_n$ interfaces are localized at five pairs of interval identical edge carbon atoms of armchair (5,5) cap/nanotube and nine interval carbon atoms of zigzag (9,0) cap/nanotube. While electrons of the chiral (6,5) cap/nanotube are at a combination of three carbon atoms of kink site and four pairs of double-carbon atoms. The formation of C–Ni

bonds significantly disturbs delocalized π -conjugation at the edge of chiral carbon caps/nanotubes, leading to the loss of aromaticity.

Figure 5.6 ELF plots of edge carbon atoms: C_n without metal clusters: a. (5,5) cap, c. (5,5) nanotube (C_{110}), e. (6,5) cap, g. (6,5) nanotube (C_{109}), i. (9,0) cap, and k. (9,0) nanotube (C_{111}); and $Ni_{55}-C_n$ complexes: b. $Ni_{55}-(5,5)$ cap, d. $Ni_{55}-C_{110}$, f. $Ni_{55}-(6,5)$ cap, h. $Ni_{55}-C_{109}$, j. $Ni_{55}-(9,0)$ cap, and l. $Ni_{55}-C_{111}$.

5.7 Charge-transfer induced reactivity

In order to further understand charge transfer induced reactivity, the frontier electron density distribution analysis was performed to determine electron density of states (DOS) of edge carbon atoms. According to the frontier orbital theory, reaction sites with higher frontier electron density are more reactive.^{43, 44} I first compared the electronic DOS of ten outmost edge carbon atoms with other twenty inner carbon atoms of the (5,5) cap ($Ni_{55}-C_{30}$, Fig. 5.1B

Figure 5.7 DOS of edge carbon atoms: (A) ten outmost edge (blue solid line) and twenty inner (grey dotted line) carbon atoms of the armchair (5,5) cap in the Ni_{55} -(5,5) cap complex (Fig. 5.1B (c)); (B) five pairs of carbon atoms (red solid line, highlighted in red atoms in Fig. 5.1C (l),) and other five pairs of carbon atoms (green dotted line, highlighted in green atoms on Fig. 5.1C (l),) on an armchair (5,5) nanotube in the Ni_{55} - C_{110} complex (Fig. 5.1C (l)). The vertical lines indicate the Fermi level of the Ni_{55} -(5,5) Cap and the Ni_{55} - C_{110} complexes, respectively.

Figure 5.8 (a) Edges of (5,5), (6,5) and (9,0) SWCNTs. Electronic DOS for carbon atoms (b) at (5,5), (6,5), and (9,0) nanotube edges without metal clusters and (c) at interfaces between (5,5), (6,5), and (9,0) nanotubes and Ni_{55} cluster.

(c)) and the (5,5) nanotube ($\text{Ni}_{55}\text{-C}_{110}$, Fig. 5.1C (l)) adsorbed on Ni_{55} cluster. For both (5,5) cap and (5,5) nanotube, Fig. 5.7 indicates that outmost edge carbon atoms with negative charges have significant higher electron density near Fermi level than inner carbon atoms. It indicates that outmost edge carbon atoms with negative charges are more reactive than other carbon atoms. This finding agrees with previous published works.⁴⁵⁻⁴⁷ Outmost edge carbon atoms are likely reactive sites where SWCNTs continuously grow by incorporating more carbon atoms. Next, Electronic DOS of edge carbon atoms among (5,5), (6,5) and (9,0) nanotubes are compared. As illustrated in Fig. 5.8a, the edge of (5,5) nanotube has ten identical carbon atoms at five pairs of armchair sites; nine identical carbon atoms sit at zigzag

sites on the edge of (9,0) nanotube; and the edge of (6,5) nanotube has three carbon atoms at a kink site and eight carbon atoms at four pairs of armchair sites similar to the armchair sites of (5,5) nanotube. The electronic DOS of five representative edge carbon atoms (one from (5,5) nanotube, one from (9,0) nanotube, and three from kink site of (6,5) nanotube) are shown in Fig. 5.9. Comparing carbon atoms at the interface between nanotubes and Ni₅₅ (Fig. 5.9 B, D, and F) with at nanotube edges without metal clusters (Fig. 5.9 A, C, and E), I found that the electron density at frontier orbital region of edge carbon atoms has significantly increased due to charge transfer induced by Ni₅₅. Fig. 5.8b and c further highlight differences among three chiralities. For nanotube edges without metal clusters, carbon atoms on (9,0) nanotube show highest electron density at the frontier orbital region than carbon atoms on (5,5) and (6,5) nanotubes. This agrees with the previous work by Kumeda *et al.*, in which they suggested that zigzag nanotube grows easier than armchair nanotube in the absence of any catalyst.⁴⁵⁻⁴⁷ However, due to charge transfer induced by Ni₅₅, carbon atom (C₁) at the kink site of (6,5) nanotube actually processes highest electron density at the frontier orbital region than carbon atoms at both zigzag (9,0) and armchair (5,5) nanotube edges. According to the frontier orbital theory, it is expected that the kink site is more reactive than zigzag and armchair sites.

The continuous growth of SWCNT likely happens at edge reactive sites through incorporation of additional small carbon species. As shown in Fig. 5.5 and Fig. 5.6, the distribution of these reactive sites is chiral dependent. The more reactive kink site on chiral (6,5) would lead to preferential growth of (6,5) nanotubes over armchair (5,0) and zigzag (9,0) nanotubes. I hypothesize that these reactive sites are controlled by the structure of Ni₅₅. Further work is under way in our lab to understand how metal clusters manage different

reactive sites, which includes comparing charge transfer behaviors at the interfaces of various (n,m) nanotubes and Ni clusters, as well as nanotube growth on non-metal clusters as references.

Figure 5.9 Electronic DOS for five representative carbon atoms: A, C, E, at nanotube edges of (5,5), (6,5), and (9,0) nanotubes without metal clusters; and B, D, F, at interfaces between those nanotubes and Ni_{55} .

5.8 Conclusion

In conclusion, the growth energies of (5,5), (6,5), and (9,0) nanotubes differ by only a couple of eV, which is not significant considering the high growth temperature. However, charges are transferred from metal atoms to edge carbon atoms on the growing SWCNTs, which enhance the reactivity of edge carbon atoms. Different chiral nanotubes exhibit distinct reaction active sites. Armchair (5,5) nanotube has double-carbon active sites, while zigzag (9,0) nanotube has single-carbon active sites. Chiral (6,5) nanotube processes a more reactive kink site. These findings imply that the structure of catalytic metal clusters strongly correlate with chiral nanotube growth sites through charge transfer. Therefore, potential opportunities exist in enabling (n,m) selective growth by engineering charge transfer interactions, which could be achieved by appropriate design of catalytic clusters with definite composition and morphology.

5.9 Reference

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Chapter 6

Summary and Future Research

6.1 Summary

The discovery of SWCNTs directly triggered the birth of nanoscience and nanotechnology. Thereafter, intensive experimental and theoretical efforts have been dedicated to achieve the chirality selectivity in SWCNT synthesis. The present thesis focuses on theoretical investigation of chirality control in SWCNT growth. Two main factors on SWCNT chirality selectivity are explored: (1) the growth and chirality change mechanism for a series of higher chiral angle caps/tubes; (2) the nature of interaction between nickel clusters and growing carbon structures in chirality selective growth of the higher chiral angle SWCNTs.

A growth and chirality change mechanism of a series of higher chiral angle nanotubes has been investigated by the precise PES survey using DFT calculations. The adsorptions of C atom and C₂ dimer on growing carbon structures show no energy barrier. The armchair (5,5) cap can evolve to near-armchair (*n*,5) where (*n* = 6, 7, 8, and 9) caps by changing its chirality and increasing its diameter. Both the single C induced chirality change and C₂ addition nanotube growth reaction processes have low energy barriers. Their reaction processes are more favorable via the triplet PES than the singlet PES. SWCNT growth and chirality change are thermodynamically and kinetically feasible under catalyst-free growth conditions. In addition to assist the carbon cap nucleation, nanoparticles may play roles in SWCNT growth by preventing the enclosure of the growing carbon structure in a fullerene-like manner and assist the elongation growth of nanotubes at a fixed diameter. Chiral-

selective growth is additionally possible if the concentrations of single C atoms and C₂ dimers in the experimental environment can be precisely managed at different reaction stages.

Atomic carbon is a key intermediate interacting with transition metal clusters during the CNT growth. Therefore, the initial carbon adsorption on four Ni clusters (Ni₁₃, Ni₁₅, Ni₃₈, and Ni₅₅) was studied firstly. The results show carbon atoms preferentially adsorb on high-coordination sites, and carbon adsorption energies are larger on smaller Ni clusters. Ni cluster reconstruction plays an important role in creating more stable subsurface adsorption sites. The migration of adsorbed carbon atom on the surface threefold hollow site into the underlying interstitial subsurface positions is thermodynamically and kinetically feasible. The results indicate that the investigation of CNT growth mechanism should include both surface and subsurface carbon atoms, coupled with surface reconstruction of Ni clusters.

The growth of zigzag (9,0), armchair (5,5), and near-armchair (6,5) nanotubes on a Ni₅₅ cluster as representative models has been further investigated. Among these chiral nanotubes, the total adhesion energies between Ni₅₅ and growing carbon structures C_n, cohesive energies of C-C, and C-Ni, and chemical potentials of C_n have maximum difference of a couple of eV throughout SWCNT growth. Considering the high growth temperature, it implies no strong preference for the specific chirality on Ni₅₅ cluster. However, charge transfers are found evidently from the metal atoms closest interface to edge carbon atoms on growing SWCNTs, which enhance the reactivity of the carbon atoms at end-edge. Additionally, different chiral nanotubes exhibit distinct reaction active sites. Armchair (5,5) nanotube has double-carbon active sites, while zigzag (9,0) nanotube has single-carbon active sites. Near-armchair (6,5) nanotubes process one highest reactive kink sites. These findings imply that the structure of catalytic metal clusters strongly correlate with chiral nanotube

growth sites through charge transfer. Therefore, potential opportunities exist in enabling (n,m) selective growth by engineering charge transfer, which could be achieved by proper design of catalytic cluster with definite composition and morphology.

6.2 Proposed future works

As aforementioned discussed in chapter 1, experimental results have shown that the carbide or doping of metal catalyst clusters may lead to preferential growth of a subset of chiral SWCNTs.¹⁻⁵ Therefore, although I have obtained certain understandings on the interaction of the various chiral caps/tubes with pure metal particles in chirality selectivity of SWCNT growth, further works are needed to carry on from the following two directions:

6.2.1 Interaction between metal carbide clusters and various chiral caps/tubes

There are still many controversies about the growth mechanism of CNTs. An important one is whether metal carbide nanoparticles do exist prior to SWCNT nucleation. Pure Ni⁶ and Fe⁷ metal catalyst particles have been observed to grow SWCNTs. However, the existence of the metal carbides, such as Ni₃C⁸ and Fe₃C^{9, 10}, has also been reported in many experimental studies. Therefore, I propose that the growth of zigzag (9,0), armchair (5,5), and a series of near-armchair (n,5) where (n = 6, 7, 8, and 9) nanotubes on metallic carbide particles would be investigated continuously in order to obtain some insights into chirality selectivity in SWCNT synthesis.

Figure 6.1 The growth of various chiral nanotubes on metal carbide nanoparticles

Figure 6.2 The growth of various chiral nanotubes on core-shell bimetallic nanoparticles

6.2.2 Effect of transition-metal doping in chirality selective SWCNT growth

On the other hand, there are a larger number of reports about mixtures of the pure metals such as Fe-Co,¹¹⁻¹⁴ Ni-Co,¹⁵ Fe-Mo,¹⁶ Co-Mo^{17, 18} and other bimetallic catalysts¹⁹⁻²¹ in order to improve the nanotube yield and (n,m) selective growth. Particularly for the binary catalysts of Fe/Mo and Co/Mo, these bimetallic catalysts not only show a dramatic increase

in SWCNTs yield and (n,m) selectivity, but also require the lowering synthesis temperatures relative to corresponding pure metal catalysts. Recently, Chiang and Sankaran showed that chirality distribution in final SWCNT sample can be altered by precise tuning the composition of $\text{Ni}_x\text{Fe}_{1-x}$ nanocatalysts.⁵ Therefore, based on the present calculation results in this thesis, the interaction of various chiral caps/tubes with the bimetallic nanoparticles would be further investigated by the type of core-shell bimetallic alloy as illustrated in Fig. 6.2.

The growth of zigzag (9,0), armchair (5,5), and a series of near-armchair (6,5) nanotubes on bimetallic nanoparticles would continue to be selected as representative models in order to systematically study the nature of interaction between bimetallic particles and growing carbon structures including various carbon species, carbon networks, chiral cap and chiral nanotubes. Comparing interaction of the various chiral caps with pure metal nanoparticles, the affecting factors for the chirality selectivity in SWCNT growth would be evaluated from the following aspects:

- (1) Interaction energies between the various chiral caps and bimetallic particles.
- (2) Geometry deformation in interface between end-edge of various chair caps and bimetallic particles.
- (3) The electronic charge density redistributions and the electronic structure rearrangements for various chiral caps/tubes and bimetallic particles coupling systems.

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APPENDIX A

Figure A3.1 Schematic potential energy surfaces of singlet and triplet for single C atom induced chirality change reactions at the B3LYP/6-31G level.

Figure A3.2 Schematic potential energy surfaces of singlet (black) and triplet (red) for C₂ dimer addition growth reactions at the B3LYP/6-31G level.

Table A3.1 The energies of the various caps, intermediates and transition states during the chirality change reaction path at different spin multiplicities.

Table A3.2 The energies of the various caps, intermediates and transition states during the tube growth reaction path at different spin multiplicities.

Figure A3.3 Optimized geometries of singlet and triplet intermediates and transition states along the chirality change paths at B3LYP/6-31G level.

Figure A3.4 Optimized geometries of singlet and triplet intermediates and transition states along the nanotube growth paths at B3LYP/6-31G level.

Figure A3.1 Schematic potential energy surfaces (PESs) of singlet (black) and triplet (red) for single C atom induced chirality change reactions at the B3LYP/6-31G level. The relative energies of ¹Cap55/C, ¹Cap65/C, ¹Cap75/C, ¹Cap85/C, and ¹Cap95/C are set to zero as references for corresponding species. These singlet and triplet PESs correspond to the blue horizontal arrows indicating the possible chirality change reaction sections in Fig. 3.2 of the main text. (5, 5) armchair cap is chosen as a starting point and reaction along the pathways aforementioned from (5, 5) cap to near-armchair (n, 5) Caps (n = 6, 7, 8 and 9) shown in Fig. 3.2 of the main text. In the throughout discussions, the term “thermodynamical stability” is referring to the relative energy order. A cap or intermediate with low relative energy is considered to have high thermodynamical stability. On the other hand, kinetic stability is

judged by its conversion barrier. The lower conversion barrier the intermediate has, the higher the kinetic stability it possesses.

Figure A3.2 Schematic potential energy surfaces (PESs) of singlet (black) and triplet (red) for C₂ dimer addition growth reactions at the B3LYP/6-31G level. The relative energies of ¹Cap55/C₂, ¹Int65/C₂, ¹Int75/C₂, ¹Int85/C₂, and ¹Int95/C₂ are set to zero as references for corresponding species. These singlet and triplet PESs correspond to the black vertical arrows representing the specific (n, 5) caps (n = 5, 6, 7, 8, and 90 growth reaction sections in Fig. 3.2 of the main text.

Table A3.1 The energies of the various cap, intermediates and transition states during the chirality change reaction path at different spin multiplicities: the total energy (a.u.), zero-point vibrational energy (ZPVE) (kcal/mole), and the relative energies (RE) (in both kcal/mole and eV) (inclusion of the ZPVE). The relative energies of ¹Cap55/C, ¹Int65/C, ¹Int75/C, ¹Int85/C and ¹Int95/C are set to zero as references for corresponding species.

Species	Total	ZPVE (kcal/mole)	RE (kcal/mol)	RE (eV)
¹ Cap55/C	-1179.65897	105.37150	0.00	0.00
¹ Cap55-C	-1179.95335	108.22805	-181.86	-7.89
¹ TsCap55-C/Int65	-1179.91250	106.08112	-158.38	-6.87
¹ Int65	-1179.95983	107.94228	-186.22	-8.08
³ Cap55/C	-1179.70786	105.22648	-30.82	-1.34
³ Cap55-C	-1179.90376	107.05299	-151.92	-6.59
³ TsCap55-C/Int65	-1179.89108	106.15540	-144.87	-6.28
³ Int65	-1179.96483	107.05299	-190.25	-8.25
¹ Int65/C	-1217.73398	107.94228	0.00	0.00
¹ Int65-C	-1218.02707	110.74477	-181.12	-7.85
¹ TsInt65-C/Int75	-1217.98794	108.72062	-158.58	-6.88
¹ Int75	-1218.03356	110.39250	-185.54	-8.05
³ Int65/C	-1217.80850	107.05299	-47.65	-2.07
³ Int65-C	-1218.03368	110.40881	-185.60	-8.05
³ TsInt65-C/Int75	-1218.02893	107.88147	-185.14	-8.03
³ Int75	-1218.04124	109.52502	-191.22	-8.29
¹ Int75/C	-1255.80771	110.39250	0.00	0.00
¹ Int75-C	-1256.09934	113.03809	-180.35	-7.82
¹ TsInt75-C/Int85	-1256.07472	111.75871	-166.18	-7.21
¹ Int85	-1256.13449	114.80013	-200.65	-8.70
³ Int75/C	-1255.88490	109.52502	-49.30	-2.14
³ Int75-C	-1256.11130	112.29316	-188.61	-8.18
³ TsInt75-C/Int85	-1256.10939	111.74124	-187.95	-8.15
³ Int85	-1256.13668	113.32138	-203.50	-8.82
¹ Int85/C	-1293.90865	114.80013	0.00	0.00
¹ Int85-C	-1294.20574	117.60256	-183.63	-7.96
¹ TsInt85-C/Int95	-1294.19679	116.47176	-179.14	-7.77
¹ Int95	-1294.21003	115.82592	-188.10	-8.16
³ Int85/C	-1293.98035	113.32138	-46.47	-2.02
³ Int85-C	-1294.21269	116.88044	-188.71	-8.18
³ TsInt85-C/Int95	-1294.18995	115.60007	-175.72	-7.62
³ Int95	-1294.23909	116.32690	-205.83	-8.93

¹ Int95/C	-1331.98419	115.82592	0.00	0.00
¹ Int95-C	-1332.33848	122.97380	-220.55	-9.56
¹ TsInt95-C/graphite	-1332.29909	121.03582	-196.96	-8.54
¹ graphite	-1332.30294	118.49153	-197.35	-8.56
³ Int95/C	-1332.08275	116.32690	-61.35	-2.66
³ Int95-C	-1332.35350	122.22787	-225.35	-9.77
³ TsInt95-C/graphite	-1332.31542	120.86504	-202.82	-8.80
³ graphite	-1332.38732	119.53282	-249.26	-10.81
¹ C	-37.77415			
³ C	-37.84366			

Table A3.2 The energies of the various cap, intermediates and transition states during the tube growth reaction path at different spin multiplicities: the total energy (a.u.), zero-point vibrational energy (ZPVE) (kcal/mole), and the relative energies (RE) (in both kcal/mole and eV) (inclusion of the ZPVE). The relative energy of ¹Cap55/C₂, ¹Int65/C₂, ¹Int75/C₂, ¹Int85/C₂ and ¹Int95/C₂ are set to zero as references for corresponding species.

Species	Total	ZPVE (kcal/mole)	RE (kcal/mol)	RE (eV)
¹ Cap55/C ₂	-1217.74896	108.02003	0.00	0.00
¹ Cap55-C ₂	-1217.96397	110.19937	-132.74	-5.76
¹ TsCap55-C ₂ /Cap55+C ₂	-1217.95713	110.03787	-128.61	-5.58
¹ Cap55+C ₂	-1218.05038	111.54376	-185.62	-8.05
³ Cap55/ ³ C ₂	-1217.76045	107.58295	-7.65	-0.33
³ Cap55-C ₂	-1217.99268	110.80708	-150.15	-6.51
³ TsCap55-C ₂ /Cap55+C ₂	-1217.98514	110.81604	-145.41	-6.31
³ Cap55+C ₂	-1218.10062	113.43040	-215.26	-9.33
¹ Int65/C ₂	-1255.82397	110.59081	0.00	0.00
¹ Int65-C ₂	-1256.03671	112.60093	-131.48	-5.70
¹ TsInt65-C ₂ /Int65+C ₂	-1256.02857	112.43195	-126.55	-5.49
¹ Int65+C ₂	-1256.15666	116.12163	-203.23	-8.81
³ Int65/ ³ C ₂	-1255.86109	109.40946	-24.47	-1.06
³ Int65-C ₂	-1256.06594	113.25077	-149.18	-6.47
³ TsInt65-C ₂ /Int65+C ₂	-1256.06296	112.46986	-148.09	-6.42
³ Int65+C ₂	-1256.18574	116.50240	-221.10	-9.59
¹ Int75/C ₂	-1293.89770	113.04103	0.00	0.00
¹ Int75-C ₂	-1294.11481	115.04612	-134.23	-5.82

¹ TsInt75-C ₂ /Int75+C ₂	-1294.11407	115.05568	-133.76	-5.80
¹ Int75+C ₂	-1294.26613	118.86910	-225.37	-9.77
³ Int75/ ³ C ₂	-1293.93750	111.88149	-26.13	-1.13
³ Int75-C ₂	-1294.16422	115.81993	-164.47	-7.13
³ TsInt75-C ₂ /Int75+C ₂	-1294.17231	116.08306	-169.28	-7.34
³ Int75+C ₂	-1294.29891	119.80344	-245.00	-10.62
¹ Int85/C ₂	-1331.99864	117.44866	0.00	0.00
¹ Int85-C ₂	-1332.23004	120.10597	-142.47	-6.18
¹ TsInt85-C ₂ /Int85+C ₂	-1332.22241	119.87545	-137.91	-5.98
¹ Int85+C ₂	-1332.34592	121.43000	-213.82	-9.27
³ Int85/ ³ C ₂	-1332.03294	115.67785	-23.28	-1.01
³ Int85-C ₂	-1332.27697	119.95684	-172.05	-7.46
³ TsInt85-C ₂ /Int85+C ₂	-1332.26935	119.97926	-167.25	-7.25
³ Int85+C ₂	-1332.37994	122.43581	-234.15	-10.15
¹ Int95/C ₂	-1370.07417	211.825920	0.00	0.00
¹ Int95-C ₂	-1370.37372	125.51243	-274.28	-11.89
¹ TsInt95-C ₂ /Int95+C ₂	-1370.37596	125.51532	-275.69	-11.96
¹ Int95+C ₂	-1370.44458	124.39862	-319.86	-13.87
³ Int95/ ³ C ₂	-1370.13534	118.683370	-131.53	-5.70
³ Int95-C ₂	-1370.40756	125.48993	-295.54	-12.82
³ TsInt95-C ₂ /Int95+C ₂	-1370.38723	122.31290	-285.96	-12.40
³ Int95+C ₂	-1370.51212	125.570490	-361.07	-15.66
¹ C ₂	-75.86414	2.64853		
³ C ₂	-75.89626	2.35647		

Figure A3.3 Optimized geometries of singlet and triplet intermediates and transition states for single C atom induced chirality change reactions at B3LYP/6-31G level. Bond lengths are in angstroms, and angles are in degrees. The structure labels refer to the description in the main text.

Figure A3.3 continued

Figure A3.3 continued

Figure A3.3 continued

Figure A3.3 continued

Figure A3.4 Optimized geometries of singlet and triplet intermediates and transition states for C₂ dimer addition growth reactions. Bond lengths are in angstroms and angles in degrees. The structure labels refer to the description in the main text.

Figure A3.4 continued

Figure A3.4 continued

Figure A3.4 continued

Figure A3.4 continued

Figure A3.4 continued

$$D_{C1C2C3C4} = -14.38$$

 $^1\text{TsInt85-C}_2/\text{Int85+C}_2$

$$D_{C1C2C3C4} = -13.64$$

 $^3\text{TsInt85-C}_2/\text{Int85+C}_2$

$$D_{C1C2C3C4} = -13.53$$

 $^1\text{TsInt95-C}_2/\text{Int95+C}_2$

$$D_{C1C2C3C4} = -11.36$$

 $^3\text{TsInt95-C}_2/\text{Int95+C}_2$

APPENDIX B

List of related publications

- (1) **Wang, Qiang**; Ng, Man-Fai; Yang, Shuo-Wang; Yang, Yanhui; Chen, Yuan*; The Mechanism of Single-Walled Carbon Nanotube Growth and Chirality Selection Induced by Carbon Atom and Dimer Addition, *ACS Nano*, **2010**, 4(2) 939–946.
Highlighted on Agency for Science, Technology and Research of Singapore (A*STAR): <http://www.research.a-star.edu.sg/research/6181>
- (2) **Qiang Wang**; Kok Hwa Lim; Shuo-Wang Yang; Yanhui Yang; **Yuan Chen***; Atomic Carbon Adsorption on Ni Nanoclusters: A DFT Study, *Theoretical Chemistry Accounts*, **2011**, 128, 17-24.
- (3) **Wang, Qiang**; Yang, Shuo-Wang; Yang, Yanhui; Chan-Park, Mary; Chen, Yuan*; Charge Transfer between Metal Clusters and Growing Carbon Structures in Chirality-Controlled Single Walled Carbon Nanotube Growth, *Journal of Physical Chemistry Letters*, **2011**, 2, 1009–1014.
Highlighted on NPG (Nature Publishing Group) Asia material:
<http://www.natureasia.com/asia-materials/highlight.php?id=936>
- (4) Wei, Li; Wang, Bo; **Wang, Qiang**; Li, Lain-Jong; Yang, Yanhui; **Chen, Yuan***; Effect of centrifugation on the purity of single-walled carbon nanotubes from MCM-41 containing cobalt. *Journal of Physical Chemistry C* **2008**, 112, 17567–17575.