Chapter 1 Introduction

1-1 Introduction to carbon nanotube (CNTs)

The carbon materials are found in various forms such as diamond, graphite, amorphous carbon, carbon fiber, diamond-like carbon (DLC) and polymer carbon. In past decade, the new carbon nanostructures were discovered, one is the Fullerenes (C_{60}), and another is the Carbon nanotube (CNT). The C_{60} which synthesized on the laser ablation method were discovered by R. F. Curl, H. W. Kroto and R. E. Smally in 1985 [Kroto-85-162]. The structure of C_{60} was consisted of sixty carbon atoms which arranged in pentagons and hexagons with spheroid shape as like the soccer ball as shown in Fig.1-1. The CNTs which synthesized by the arc-discharge method were discovered by S. Iijima in 1991 [Iijima-91-56]. The structure of CNT can be seen as the graphite sheet rolled into a seamless tube and was capped at each end by half-spherical fullerene structure.

Depending on the chirality of CNT can form armchair, zigzag or chiral type of CNTs. Furthermore, the CNT can divide into two categories: one is single-walled CNT (SWCNT); another is multi-walled CNT (MWCNT), which are corresponding to the number of graphene layers consisted of the CNT. The HRTEM images of SWCNT (only one graphene layer) and MWCNT (contained 2 to 5 graphene layers) are shown in Fig. 1-2 (a) to (e). Many morphologies of CNT also were discovered as like vertical aligned, helical, bamboo-like, Y-shaped CNTs or T-shaped CNTs…etc which are depending on its process parameters and methods. The different criterions were also proposed to elucidate growth mechanism of CNTs. However, the practical growth mechanisms of CNTs are still not well understood.

Recently the CNTs can be synthesized by many methods such as laser ablation, arc-discharge, microwave plasma chemical vapor deposition (MPCVD), electron cyclotron resonances chemical vapor deposition (ECRCVD) and thermal CVD. Although many methods can synthesize the CNTs, but how to produce high throughput, high quality and, high reproducible CNTs is still need more research and develop in the feature.

The CNTs are gained a greater interest to the scientific and industrial communities due to their excellent physical and chemical properties such as mechanical properties, thermal conductivity, chemical stability, electron properties, and field emission (FE) properties….etc. Nowadays many applications of CNT were researched and developed such as field-emission display (FED), electron transistor, hydrogen storage, biosensors, atomic force microscopy (AFM) tips, composite materials…etc. Hence, the applications of CNTs are expected to raise next industrial evolution. The Table 1-1 shows the time line of CNT [http://www.pa.msu.edu].

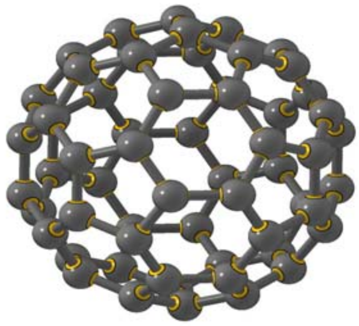


Fig.1-1 Schematic diagram of C_{60} structure

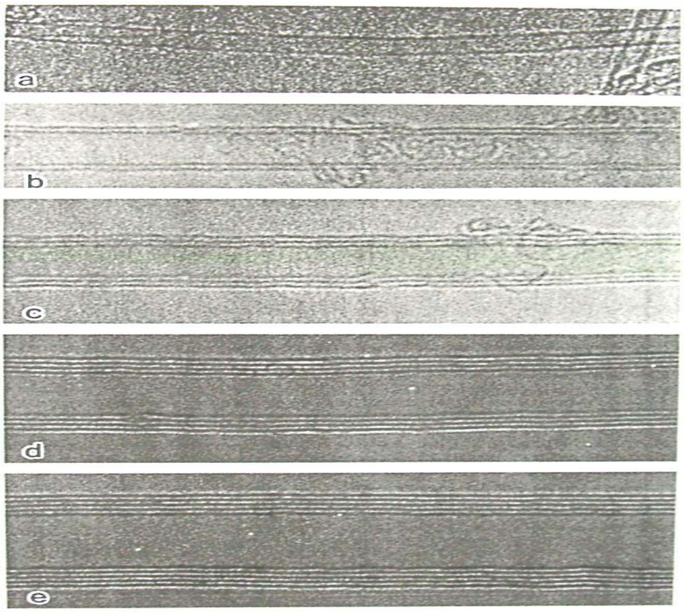


Fig.1-2 HRTEM images of carbon nanotubes with increasing numbers of concentric tubes-one to five layers seen in (a) to (e), respectively [Ebbesen-97-115].

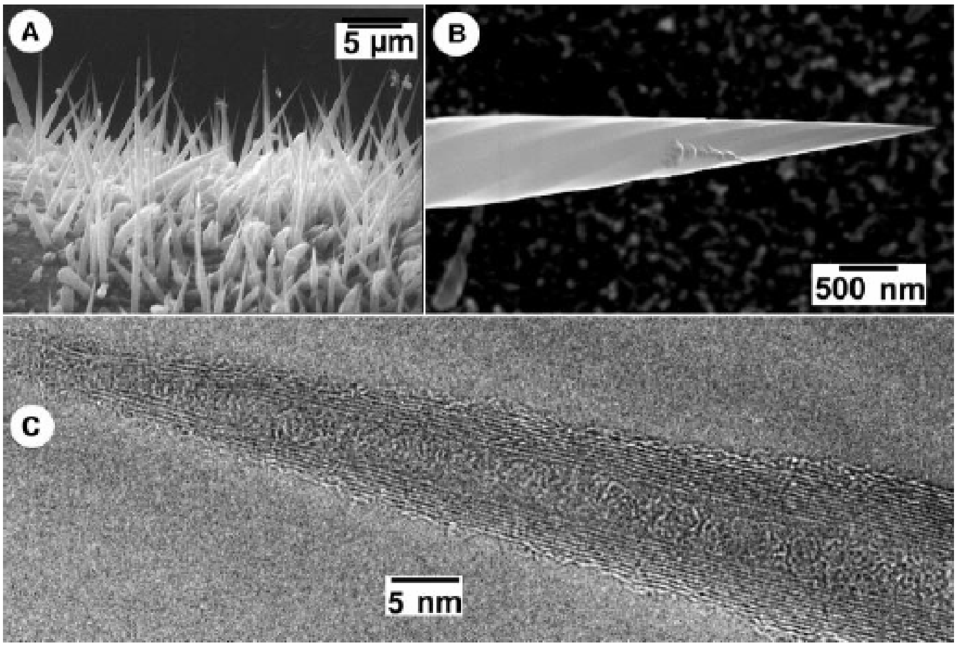
Table 1-1 Carbon nanotube-A time line

[http://www.pa.msu.edu]

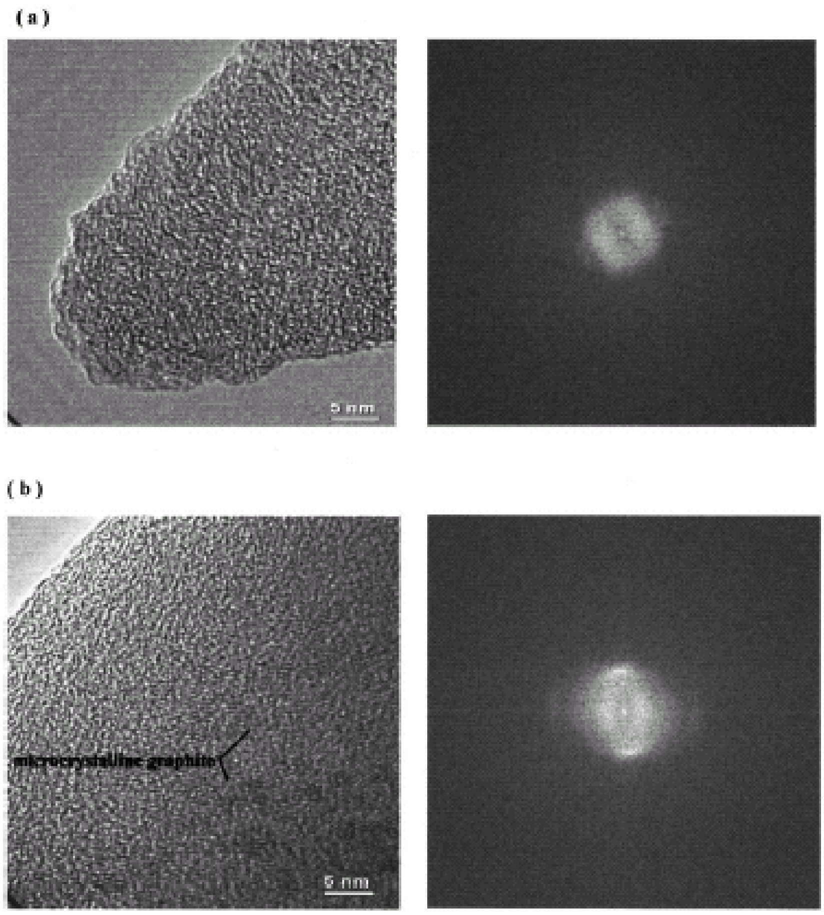
1991	**Discovery of multi-wall carbon nanotubes**
	["Helical microtubules of graphitic carbon", S. Iijima, Nature **354**, 56 (1991)]
1992	**Conductivity of carbon nanotubes**
	["Are fullerene tubules metallic?", J. W. Mintmire, B. I. Dunlap and C. T. White, Phys. Rev. Lett. **68**, 631 (1992) "New one-dimensional conductors - graphitic microtubules", N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992) "Electronic structure of graphene tubules based on C_{60}", R. Saito, M. Fujita, G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. B **46**, 1804 (1992)]
1993	**Structural rigidity of carbon nanotubes**
	["Structural Rigidity and Low Frequency Vibrational Modes of Long Carbon Tubules", G. Overney, W. Zhong, and D. Tománek, Z. Phys. D **27**, 93 (1993)]
1993	**Synthesis of single-wall nanotubes**
	["Single-shell carbon nanotubes of 1-nm diameter", S Iijima and T Ichihashi Nature, **363**, 603 (1993) "Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls", D S Bethune, C H Kiang, M S DeVries, G Gorman, R Savoy and R Beyers, Nature, **363**, 605 (1993)]
1995	**Nanotubes as field emitters**
	["Unraveling Nanotubes: Field Emission from an Atomic Wire", A.G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S.G. Kim, D. Tománek, P. Nordlander, D.T. Colbert, and R.E. Smalley, Science 269, 1550 (1995).]
1996	**Ropes of single-wall nanotubes**
	["Crystalline ropes of metallic carbon nanotubes", Andreas Thess, Roland Lee, Pavel Nikolaev, Hongjie Dai, Pierre Petit, Jerome Robert, Chunhui Xu, Young Hee Lee, Seong Gon Kim, Daniel T. Colbert, Gustavo Scuseria, David Tománek, John E. Fischer, and Richard E. Smalley, Science 273, 483 (1996).]
1997	**Quantum conductance of carbon nanotubes**
	[Individual single-wall carbon nanotubes as quantum wires", SJ Tans, M H Devoret, H Dai, A Thess, R E Smalley, L J Geerligs and C Dekker, Nature, **386**, 474 (1997).]
1998	**Chemical Vapor Deposition synthesis of aligned nanotube films**
	["Synthesis of large arrays of well-aligned carbon nanotubes on glass", Z F Ren et al., Science, **282**, 1105 (1998).]
1998	**Synthesis of nanotube peapods**
	["Encapsulated C_{60} in carbon nanotubes", B.W. Smith, M. Monthioux, and D.E. Luzzi, Nature **396**, 323 (1998).]
1999	**Hydrogen storage in nanotubes**
	["Hydrogen Storage in Single-Walled Carbon Nanotubes at Room Temperature" , C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, and M. S. Dresselhaus Science, **286**, 1127 (1999).]
2000	**Nanotubes as Ideal Thermal Conductors**
	["Unusually High Thermal Conductivity of Carbon Nanotubes", Savas Berber, Young-Kyun Kwon, and David Tománek, Phys. Rev. Lett. **84**, 4613 (2000).]
2000	**Macroscopically aligned nanotubes**
	["Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes" , Brigitte Vigolo, Alain Pénicaud, Claude Coulon, Cédric Sauder, René Pailler, Catherine Journet, Patrick Bernier, and Philippe Poulin, Science **290**, 1331 (2000).]
2001	**Integration of carbon nanotubes for logic circuits**
	["Engineering Carbon Nanotubes and Nanotube Circuits Using Electrical Breakdown", P.C. Collins, M.S. Arnold, and P. Avouris, Science **292**, 706 (2001).]
2001	**Intrinsic superconductivity of carbon nanotubes**
	[M. Kociak, A. Yu. Kasumov, S. Guéron, B. Reulet, I. I. Khodos, Yu. B. Gorbatov, V. T. Volkov, L. Vaccarini, and H. Bouchiat , Phys. Rev. Lett. **86**, 2416 (2001).]

1-2 Introduction to Carbon nanocones (CNCs)

The carbon nanocones (CNCs) can be considered the nanoscale conical carbon-based material. In other words, it was consisted of graphene layers and amorphous carbon mixture in conical shape. The conical carbon-based materials have numerous structures and composition have synthesized and reported such as amorphous carbon nanocone [Jang-01-1682; Tsai-02-1821; Huang-03-6796], diamond nanocone [Jan-99-772], diamond-like carbon nanocone [Lin-01-126], cone-like carbon nanofiber [Merkulov-01-1178], tubular graphite CNC [Zhang-03-472; Hayashi-04-2886], as-grown amorphous coated Si tips [Bai-03-185], amorphous carbon nitride tips [Liu-00-304], SiC-capped nanotips [Lo-03-1420], and self-embedded nanocrystalline chromium carbides on polycrystalline CNCs [Tasi-03-4337]. The different structures and compositions of CNCs were synthesized under different process conditions and methods. Typically, Figs.1-3 show the SEM and HRTEM images of the tubular graphite cones [Zhang-03-472]. It indicates CNC was consisted of ordered graphene layers with inner channel in conical form. In contrary, Figs.1-4 (a) and (b) show the HRTEM image of amorphous carbon nanocones [Tasi-02-1281]. Due to CNC is carbon-based material and presented small radius with ultra sharp apex angle thus it was predicted having excellent FE properties. Moreover, the cone-shape structure also provides higher mechanical and thermal stability than a narrow cylinder. Hence, the CNCs have potential not only as FE device but as a rigid tip for scanning probe microscopy. The nanofabrication methods of CNCs include thermal CVD, PECVD, MPCVD and ECRCVD as like grown CNTs. However, the nanofabrication of CNCs shows lower temperature process than CNTs, it implies the synthesis of CNCs is compatible with integrated circuit (IC) process. Though many growth mechanisms of CNCs are proposed, however, the practical growth mechanisms of CNTs are still not well understood. Nevertheless, according to the literatures, it indicated the CNCs prefer grown on the applied bias assisted plasma methods. It implies may be CNCs was produced by the competition of the deposition and ion etching.



Figs. 1-3 (a) and (b) are SEM images of CNCs (c) HRTEM images of CNC [Zhang-03-472]



Figs.1-4 HRTEM images and Fourier filtering transformation (FFT) of amorphous CNC (a) the end section and (b) lateral section of an individual CNC ,where show the nanocrystalline graphite embedded in lateral section of CNC [Tasi-02-1281]

1-3 Motivation of this research

Recently carbon nanotubes (CNTs) and carbon nanocones (CNCs) are gained a greater attention in application of field emission (FE) devices due to their morphologies with high aspect ratio in nanoscale. In order to obtain the practical application of FE devices, how to manipulate the nanofabrication of carbon nanostructure and their FE properties are important topics needed to study and develop. According to the literature reviews, the field emission properties of these carbon nanostructures are affected by their tube diameters, orientation, morphologies, bonding structure, number density and adhesion between the substrate. Here the microwave plasma chemical vapor deposition (MPCVD) system is employed to synthesize carbon nanostructures in this experiment. All the effect factors of field emission for carbon nanostructures are corresponding to the deposited process parameters such as plasma pretreatment, species of precursor gases, precursor gases ratio, bias applied, deposition time and deposition temperature. Hence, by manipulating process parameters on MPCVD method to synthesize high aspect ratio, carbon-based nanostructures for gaining better FE properties are the purposes of experimental motivation.