Chapter 1

Introduction

It was known as a substance in prehistory through its recognition as an element came much later, being the culmination of several experiment in the eighteenth century.[1] Carbon is a Group 14 element. Carbon is distributed very widely in nature. It is found in abundance in the sun, stars, comets, and atmospheres of most planets. The atmosphere of Mars contains 96 % CO_2. As shown in Figure 1.1[2], carbon, at the head of the Group 14, forms so many compounds that it has its own branch of organic and inorganic chemistry. Carbon is found free in nature in three allotropic forms: amorphous,[3] graphite,[4] and diamond.[4] More recently, a new form of carbon, buckminsterfullerene,[5] with formula C_{60} is formed in the treatment of graphite by lasers and is now commercially available in small quantities. This new form of carbon is the subject of great interest in research laboratories today.

Amorphous carbon (*a*-C) refers to a highly disordered network of carbon atoms that predominantly have sp^2 bonding, with perhaps 10 % sp^3 bonds and almost no sp^1 bonds. Although *a*-C has no long-range order, some short-range order is present, as could be observed by study of the radial distribution function. The carbon bonding and the hydrogen content are most influential in characterizing the short-range order, which may exist on a length scale of ~10 Å. Thus, the sp^2 bonded carbons of *a*-C may cluster into tiny warped layered regions, and likewise the sp^3 bonded carbons may also cluster and segregate, as may the hydrogen impurities which are very effective in passivity the dangling bonds.[3]

Graphite consists of planar sheets of sp^2 hybridized carbon atoms in a hexagonal network and it is thermodynamically the most stable form at normal temperature and pressures. Electrons are free to move from one carbon atom to another through a delocalized π-network formed by the overlap of unhybridized *p*-obitals on each carbon atom. Because of the electron delocalization, graphite is a black, lustrous, electrically conducting solid and is utilized as

electrodes in electrochemical cells and batteries.[4]

Diamond is the hardest and least perishable of all minerals, and these qualities, coupled with its brilliant sparkle, which derives from its transparency and high refractive index, make it the most prized of gemstones. Diamond structure is probably the most-thoroughly investigated of all crystallographic structures. The ideal diamond structure has two distinct carbon sites and has the characteristic property that every carbon atom is surrounded by four other carbon atoms at the corners of a regular tetrahedron with a cube edge. The central carbon atom is bonded to these four neighbors by strong covalent sp^3 bonds. Because of the special properties, it is used as single-point tools for engraving or cutting, and for surgical knives, bearings and wire dies, as well as for industrial abrasives for grinding and polishing. Other uses are as thermistors and radiation detectors, and as optical window for lasers, etc.[4]

One of the most exciting and challenging developments in recent chemistry has been the synthesis and characterization of many new, soluble, molecular modifications of carbon. The new allotropes form an extensive series of poly hedral cluster molecules, C_n (n even), comprising fused pentagonal and hexagonal rings of C atoms. The first member to be characterized was C_{60} which features 12 pentagons separated by 20 fused hexagons. It has full icosahedral symmetry and was given the name buckminsterfullerene in honor of the architect R. Buckminster Fuller whose buildings popularized the geodesic dome, which uses the same tectonic.[5]

Carbon has a variety of common uses. It is widely used commercially because of their special electrical, thermal, chemical, and mechanical properties which arise from their special structure and bounding of carbon atoms. Carbons are, for example, used for electrodes for arc furnaces, for reduction reactions in other furnaces, especially for steel making. Also, exploiting the good high-temperature properties of carbon are applications to furnace linings, to use as casting molds, heating elements, and heat exchangers, as well as many other applications in high-temperature process equipment.
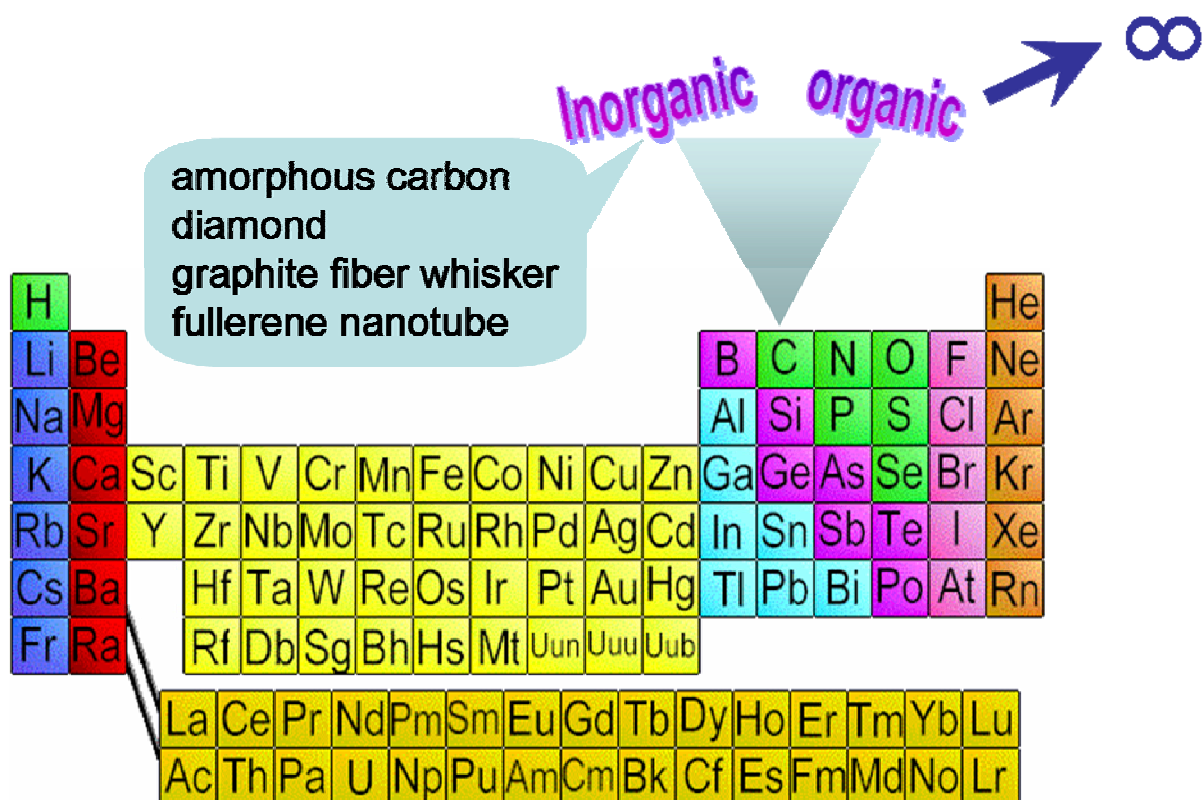
Figure 1.1 The variety of carbon.[2]

Today, the essence of nanoscale science, engineering, and nanotechnology are the ability to work at the atomic, molecular and macromolecular levels in order to create materials, devices and systems with fundamentally new properties and functions. Compared to the bulk materials, the ultrafine specimens reveal the remarkable quantum effect, including electrical, optical, and magnetic properties that are in principle tunable by varying the diameter and chirality, to give the research with a new life. Building blocks are atoms and molecules, or their assemblies such as nanoparticles, nanolayers, nanowires and nanotubes.[6] The relative arrangement of the elementary blocks of matter into their assemblies leads to new properties and functions even for the same chemical composition.

Nanosized materials have been obtained by "top-down" methods, e.g. by the mechanical milling of bulk materials. Another strategy is the "bottom-up" methods for the preparation of nano-scaled materials. The strategy employs molecular precursors as the building blocks to

form solid materials through chemical bond formation. Chemical vapor deposition (CVD) is a good technology of producing nano-scaled materials in microchip fabricated.

A similar type of graphitic needlelike structure, first discovered[7] on the cathode surfaces in a carbon arc discharge apparatus that was designed to produce C_{60} and other fullerenes, was given the name carbon nanotubes (CNT) because of it nanometer size and tubular morphology. And there have been many reports[8] on the fabricated and physical properties of carbon nanotubes. Numerous methods to grow CNT have been developed, such as arc-discharge, laser ablation and CVD.[9-11] In the above methods, large quantities of CNT can be fabricated by either arc discharge or thermal decomposition of hydrocarbon vapor. Many potential applications have been proposed for CNT, including conductive and high-strength composites; energy storage and energy conversion devices; sensors; field emission displays and radiation sources; hydrogen storage media; and nanometer-sized semiconductor devices, probes, and interconnects.

There have been many reports about anodic aluminum oxide (AAO) membrane template-assisted growth of CNT and coaxial structure from hydrocarbons by CVD and related technologies.[6-18] By applying different template thickness and pore sizes, the length and diameter of the CNT can be manipulated effectively. A free-standing array of aligned CNT can be fabricated after the removal of the template. In addition, most of the reported cases show the need of transition metal catalysts or high energy reaction steps (see Table 1.1).

Table 1.1 Summary of fabrication methods of CNT and coaxial structure.

Method	Hydrocarbon Source	Flow Rate (sccm)	Temperature (K)	Catalyst	Reaction Time (h)	Ref.
polymerization	Polyacrylonitrile	—	473/873[*]	—	0.5	12
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thermal CVD	C_3H_6 (2.5 %) in N_2	200	1073/3073[*]	—	1	14
thermal CVD	C_3H_6 (2.5 %) in N_2	200	1073/3073[*]	—	1,6,12	15
thermal CVD	C_2H_4	10	1173	—	1/6	16
thermal CVD	C_3H_6 (2.5 %) in N_2	200	1073	—	1,6,12	17
thermal CVD	C_2H_2 (10 %) in N_2	50	973	—	2/3	18
thermal CVD	C_2H_4	20	943	—	5.5	19
CVD	C_2H_2 (10 %) in N_2	200	973	Co	15	20
CVD	C_2H_2, H_2, N_2 (2%/2%/96%)	100	973 – 1073	Co	1	21
CVD	C_2H_2, N_2	—	973	Co	—	22
PECVD	C_2H_2 (25%) in N_2	15 – 125	373 – 423 (dc 0 to - 450 V)	—	1/12	23
PECVD	C_2H_2, NH_3	—	823	Co	1/4	24
polymerization	Polyacrylonitrile	—	273	—	3	25
CVD	Propylene (1.2 %) in N_2; acetonotrile (4.2 %)	1000/500	1073	—	2/5	26

[*] annealing temperature.

Recently, one-dimensional (1D) structures with nanometer diameter, such as nanowires, nanorods, and nanotubes, have been synthesized in various methods for their special application. Many potential applications have been proposed for CNT,[27] including conductive and high-strength composites; energy storage and energy conversion devices; and nanometer-sized semiconductor devices, probes, and interconnects. Some of these applications are now realized in products. Others are demonstrated in early to advanced devices, and one, hydrogen storage, is clouded by controversy. Nanotube cost, polydispersity in nanotube type and limitation in processing and assembly methods are important barriers for some applications of single-walled nanotubes.

In this dissertation we present several methods employing bottom-up concept relied on the chemical reduction reaction. The preparation, characterization of the products and the

investigation of the reaction pathway are discussed.

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