FROM ZERO-DIMENSIONAL TO 2-DIMENSIONAL CARBON NANOMATERIALS - part I: TYPES OF CNs

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Abstract: *In recent years, many theoretical and experimental studies have been carried out to develop one of the most interesting aspects of the science and nanotechnology which is called carbon-related nanomaterials. In this review paper are presented some of the most important developments in the synthesis, properties, and applications of low-dimensional carbon nanomaterials. The synthesis techniques are used to produce specific kinds of low-dimensional carbon nanomaterials such as zero-dimensional CNs (including fullerene, carbon-encapsulated metal nanoparticles, nanodiamond, and onion-like carbons), one-dimensional carbon nanomaterials (including carbon nanofibers and carbon nanotubes), and two-dimensional carbon nanomaterials (including graphene and carbon nanowalls).*

Keywords: graphene, carbon nanomaterials (CNs), synthesis techniques.

1. INTRODUCTION

Low-dimensional carbon nanomaterials can be divided into categories of different dimensionality ranging from zero-dimensional (0-D) to one-dimensional (1-D) and two-dimensional (2-D) depending on their nanoscale range (<100 nm) in different spatial directions. The representatives in family of low-dimensional carbon nanomaterials focus on fullerene, onion-like carbon, carbon-encapsulated metal nanoparticles, nanodiamond (0-D), carbon nanofibers, carbon nanotubes (1-D), graphene, and carbon nanowall (2-D) (fig.1[1]).

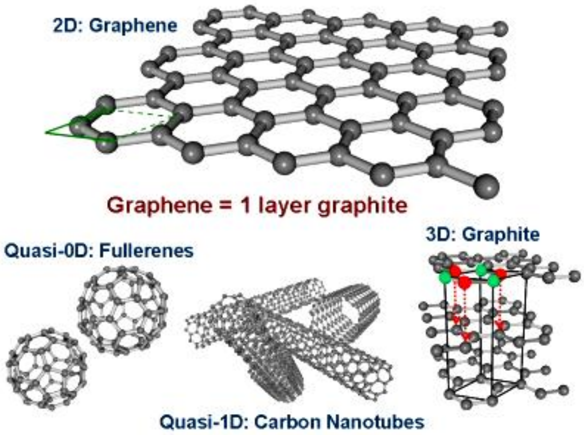

Figure 1. *Different forms of carbon nanomaterials [1]*

In the past decade, by using nanotechnology and carbon-based nanomaterials, the world might be able to see an industrial revolution surpassing any one before. This new technology could end the world's hunger, make affordable goods, have massive implications for medical breakthroughs, and unfortunately also be used in military applications. The latest research results and developments, hopefully may lead more researchers to address the area and look forward to more research results.

2. TYPES OF CNs

The types and structure description of carbon nanomaterials is as follows:

2.1. Zero-Dimensional Carbon Nanomaterials (0-DCNs)

2.1.1. Fullerene

Fullerenes are spherical, caged molecules with carbon atoms located at the corner of a polyhedral structure consisting of pentagons and hexagons. A spherical fullerene looks like a soccer ball and is often called “buckyball.” Fullerenes were named after Richard Buckminster Fuller, an architect known for the design of geodesic domes which resemble spherical fullerenes in appearance. In fact, fullerenes were discovered as an unexpected surprise during laser spectroscopy experiments in 1985, by researchers at Rice University. As mentioned in the Nobel Prize records, the 1996 Nobel Prize in chemistry was awarded jointly to Robert F. Curl, Jr., Richard E. Smalley, and Sir Harold W. Kroto “for their discovery of fullerenes”. The first method of production of fullerenes, by Kroto et al. in 1985 [2] used laser vaporization of carbon in an inert atmosphere in which microscopic amounts of fullerenes were produced.

2.1.2. Carbon-Encapsulated Metal Nanoparticles (CEMNPs)

Carbon-encapsulated metal (magnetic) nanoparticles (CEMNPs) represent a new class of Zero-dimensional carbon-metal composite nanomaterials. It is the shape of core-shell structure on the nanoscale. The polyhedral metallic core is entirely encapsulated by the multilayer-graphitized carbon shell. So, the carbon layers isolate the particles magnetically from external environment and protect them against corrosion and magnetic coupling between individual particles.

Since the first report on LaC_2 encapsulated within nanoscale polyhedral carbon particles in a carbon arc synthesized by Ruoff et al. [3] in 1993, carbon-encapsulated metal nanoparticles have received considerable attention because of their novel structures and obvious technological promise. Scientist have succeeded in encapsulating various materials into a hollow graphitic cage by arc discharge method. Saito [4] reported that 13 rare earth metals and iron-group metals were wrapped in graphitic carbon in 1995. In summary, CEMNPs can be synthesized by a variety of techniques such as arc discharge method, tungsten arc techniques, high-temperature heat treatments, the mechanical milling, cocarbonization, pulsed laser irradiation, and high-current pulsed arcs system.

2.1.3. Nanodiamond (ND)

As is well known, diamond is one of the carbon allotropes as graphite. Graphite is the most stable form of carbon at ambient pressure. Spherical and truncated octahedron diamond with predominant sp3-bonded carbon is one of the hardest materials known to date and is often regarded as the king of all gemstone and top-drawer materials because of its excellent scientific qualities in hardness, chemical corrosiveness, thermal expansion and conductivity, electrical insulation, and biocompatibility. On the other hand, nanodiamond (ND) is a cubic structural diamond. It possesses diamond structure and diamond properties. The average size is mere 5 nm in diameter. In the wide sense of the word, “nanodiamond” contains a variety of diamond-based materials at the nanoscale (the length scale of approximately 1–100 nm) including pure-phase diamond films, diamond particles, and their structural assemblies.

Several synthesis methods have been developed to synthesize laboratory-produced nanodiamonds. There are two main methods for fabrication of nanodiamond: transformation of graphite under high temperature and high pressure and detonation of the carbon explosive materials.

In 1955, Bundy et al. [5] realized the 30-year dream of many scientists in which diamond can be transformed from graphite, as they successfully reported the synthesis of diamond using a high-temperature and high-pressure process. However, the synthesis of diamond by the detonation of explosives with a negative oxygen balance in a steel container under vacuum condition was reported in the 1980s [6]. There are also some related literatures in recent reports shown two mentioned methods [7]. Explosive detonation is still widely used; however, the process of the detonator explosion is extremely fast and very complex. Moreover, there are some disadvantages observed in detonation method. In fact, the fraction of surface to bulk atom and oxygen, hydrogen, and nitrogen content in the nanodiamond resulting from after- purification process are difficult to remove.

As an interesting matter, most previous researches on detonation synthesis have been done at military or commercial plants; thus several reports are available for the scientific community. Therefore, the best method is to develop new techniques to the synthesis of well-dispersed and pure nanodiamonds. Recently, more researches also about the aspects of low energy, low cost, easily controlled, few byproducts, controlled-sized, and large scale have been reported in related literatures, such as microwave plasma chemical vapor deposition [8], hot filament chemical vapor deposition, pulse laser ablation [9], electron irradiation [10], and high-energy X-ray diffraction [11].

2.1.4. Onion-Like Carbons (OLCs)

Ugarte [12] in 1992 reported that carbon soot particles and tubular graphitic structures were radiated by intense electron-beam and reorganized into quasispherical particles. Subsequently, Harris and Tsang [13] in 1997 studied the structure of two typical nongraphitizing carbons by heat treatment. They observed the fullerene-like structure close to carbon nanoparticles. Then, a new model for nongraphitizing carbons was proposed which was different with the other representatives of the carbon family graphite, fullerenes, and nanotubes. The onion-like carbons (OLCs) have the three to eight closed graphitic shell structures with the hollow core. The outer diameters are in the range of 20–100 nm. The polyhedral nanoparticles exhibited a well aligned concentric and high degree of symmetry structure. Quasispherical shape, nanometer size, and surface specificity of OLCs have attracted enormous attention. Several routes were developed from synthesis of carbon onions including arc discharge, high-electron irradiation, chemical vapor deposition, radio frequency plasma and high-dose carbon ion implantation into metals, and thermal annealing of diamond nanoparticles [14]. The current researches on OLCs are limited because of unmanageable reaction, many byproducts, complex equipments, and high cost. At present, the most OLCs were synthesized using vacuum annealing of nanodiamond at fixed temperatures [15].

2.2. One-Dimensional Carbon Nanomaterials (1-DCNs)

2.2.1. Carbon Nanofibers

Carbon nanofibers (CNFs) are composed of stacked and curved graphene layers from a quasi-one-dimensional (1D) filament. CNFs have cylindrical or conical nanostructures. Their diameters vary from a few to hundred nanometers, while lengths range from less than a micrometer to millimeters. According to the angle between graphene layers and fiber axis, the morphological structure is often divided into plate CNFs, ribbon-like CNFs, herringbone CNFs [16].CNFs known as filamentous carbon have been known for a long time [17]. However, the synthesis of filamentous carbons did not evoke great interest of scientists in those early years until the discovery of carbon nanotubes by Iijima in 1991. Generally, CNFs can be synthesized through the traditional vapor growth method, cocatalyst deoxidization process, catalytic combustion technique, plasma-enhanced chemical vapor deposition, hot filament-assisted sputtering, ultrasonic spray pyrolysis, and ion beam irradiation.

2.2.2. Carbon Nanotubes (CNT)

Carbon nanotubes are rolledup into tubular structures by sp2-bonded graphite sheets with nanometer diameter and large length ratio. The nanotubes may consist of two different types of carbon nanotubes. Namely, singlewall nanotubes (SWNTs) made of single layers of graphene cylinders with typical diameter of the order of 1.4 nm and the multiwall nanotubes (MWNTs) made of 4–24 concentric cylinders of graphene layers with adjacent shells separation of 0.34 nm and a diameter typically of the order 10–20 nm. Nowadays, carbon nanotubes are still mainly synthesized by the arc-discharge, laser-ablation (vaporization), and chemical vapor decomposition (CVD) method.

The MWNTs were first observed which deposited on the negative electrode during the direct current arc-discharge of two graphite electrodes for preparation of fullerenes in an argon-filled vessel by Iijima in 1991 [18]. Vast amount of reviews on carbon nanotubes have been discussed in the recent literature in detail, including the synthesis and growth mechanisms of CNT [19].

2.3. Two-Dimensional Carbon Nanomaterials (2-DCNs)

2.3.1. Graphene

Graphene, one-atom-thick planar sheet of sp2-bonded carbon atoms, is arranged densely in a two-dimensional hexagonal honeycomb crystal lattice. There are three extremely strong σ bonds in-plane result in the mechanical stability of the carbon sheet, π orbitals perpendicular to the plane interactions between graphene and a substrate or between graphene layers are responsible for the electron conduction. It is the basic building block of (0-D) fullerenes, (1-D) carbon nanotubes, and (3-D) graphite.

Diamond and graphit have been known for centuries, and the recently discovered fullerenes and nanotubes also have been studied in the last two decades. For a long time, graphene was only considered as theoretical concept. Until 2004, [20] a physicists group led by Andre Geim and Kostya Novoselov from Manchester University, UK used mechanical exfoliation approach to obtain graphene. The discovery of isolated graphene monolayer has attracted wide attention to investigate the properties of this new yet ancient two-dimensional carbon nanomaterial due to its exceptional electronic and mechanical properties [21]. More and more simple methods were searched for the growth of graphene. Several typical methods have been developed and will be presented in part II of the paper.

2.3.2. Carbon Nanowalls

Carbon nanowalls (CNWs) consist of vertical aligned graphene sheets standing on the substrates, form two-dimensional wall structure with large surface areas and sharp edges. The thickness of CNWs ranges from a few nm to a few tens nm. So far, research groups have explored different synthesis methods of CNWs based on plasma-enhanced chemical vapor deposition techniques. The main approaches are as follows: 1-Microwave plasma-enhanced chemical vapor deposition (MWPECVD); 2-Radio-frequency plasma-enhanced chemical vapor deposition (RFPECVD) (RF inductively coupled plasma (ICP) and RF capacitively coupled plasma (CCP); 3-Hot-wire chemical vapor deposition (HWCVD); 4-Electron beam excited plasma-enhanced chemical vapor deposition (EBEPECVD).

For the first time, carbon nanowalls were accidentally discovered during the growth of carbon nanotubes by Wu et al. [22] using MWPECVD. In the experiment, the NiFe-catalyzed substrate (Si, SiO_2/Si, sapphire) was preheated to about 650–700°C in hydrogen plasma; the mixtures of CH4 and H2 were utilized as flow gases. The well-controlled MWPECVD synthesis process induced further studies to search more flexible control of the growth of CNWs, which aided to understand the mechanisms of CNWs growth and solving unwanted byproduct owing to the use of metal catalyst particles.

Recently, some groups have prepared CNWs without catalysts, using RFPECVD, assisted by a hydrogen atom injection. Shiji et al. [23] synthesized carbon nanowalls on a Si substrate without catalysts using capacitively coupled RFPECVD by H atom injection. The grown samples employed fluorocarbon/hydrogen mixtures, used C2F6, CF4, CH4, and CHF3 as the carbon source gas, and heated a substrate temperature of 500°C.

3. CONCLUSIONS

As described in this paper, the unique structure and properties of low-dimensional carbon nanomaterials as the advanced materials have led them to have a strong and important potential role in various scientific fields and engineering such as nanoscale electronic devices, field emission displays, diodes, transistors, sensors, composite polymers, artificial muscles, mechanical reinforcements, capacitors, and hydrogen storage. For example, carbon nanobuds are the recently produced materials from two previously known allotropes of carbon nanotubes and fullerenes. These fullerene-like “buds” have found the unique properties of both fullerenes and CNTs which have many applications as good field emitters as well as their role to improve the mechanical properties of composites. As another example, the application of CNTs to develop the biofuel products is being noticeably growing.

As the definition of the low-dimensional carbon nanomaterial, these materials also cover a wide range of carbon-related nanostructures such as nanodiamonds, fibers, cones, scrolls, whiskers, and graphite polyhedral crystals. In fact, there are expectable outlooks for the use of these materials in the fields of molecular electronics, sensoring, nanoelectromechanic devices, field-emission displays, energy storage, and composite materials, as well as their growing applications in medical science, health, and daily life.

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