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Comparison of two methods of carbon nanotube synthesis: CVD and supercritical process (A review)

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ABSTRACT: A carbon nanotube (CNT) is a miniature cylindrical carbon structure that has hexagonal graphite molecules attached at the edges. Nanotubes look like a powder or black soot, but they're actually rolled-up sheets of graphene that form hollow strands with walls that are only one atom thick. Carbon nanotube has been one of the most actively explored materials in recent year(s) due to its unique properties and wide range of applications. Various methods have been adopted to produce CNT, including laser ablation, arc discharge and CVD process. Chemical vapor deposition (CVD) is parent to a family of processes whereby a solid material is deposited from a vapor by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface. The resulting solid material is in the form of a thin film, powder, or single crystal. Among these methods, the chemical vapor deposition method is a cheap and simple method. Supercritical fluids, particularly supercritical CO_2, have been used in various areas such as nanoparticle and CNT synthesis. In this paper the CNT synthesis methods based on CVD and using supercritical fluids were studied.

Keywords: *Carbon nanotube; CNT; CVD; Method; Nanotube; Supercritical.*

INTRODUCTION

Carbon nanotube (CNT) has been one of the most actively explored materials in recent year(s) due to its unique properties and wide range of applications. However, the large scale production of CNTs in an economic way is crucial for realizing these applications. Out of different techniques, catalytic chemical vapor depositions in fluidized bed and in inclined mobile bed reactors are the most promising techniques for the bulk production of CNT (Raji, *et al.*, 2011). CNTs have become one of the most famous nanomaterials and attracted a great deal of studies because of their novel and excellent properties and potential applications. The further development of these studies requires more precisely controlling of the features for as-grown CNTs, such as their lengths, diameters and chirality (Lee, *et al.*, 2002). CNTs as well as fullerenes are splendid gift brought to the Earth from the red giant carbon stars in the long-distant universe through the spectroscopy

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(Klinke, *et al.*, 2005). Moreover, those belong to new carbon allotropes of the microscopic scale with well-defined structures. In particular, CNTs are considered to be the materials appropriate to realize intriguing characteristics related to the microscopic system based on their size and physicochemical properties (Kims, *et al.*, 2005). CNT is the name of ultrathin carbon fiber with nanometer size diameter and micrometer-size length and was accidentally discovered by a Japanese scientist, Sumio Iijima, in the carbon cathode used for the arcdischarging process preparing small carbon clusters named by fullerenes (Sato and Sano, 2008). The structure of CNT consists of enrolled graphitic sheet, in a word, and can be classified into either multi-walled or single-walled CNT (MWCNT or SWCNT) depending on its preparation method (Pillay, *et al.*, 2009). It is understood that CNT is the material lying in-between fullerenes and graphite as a quite new member of carbon allotropes. Since the discovery of fullerenes, carbon nanostructures have attracted a great deal of interest. Numerous novel and exceptional properties have been observed or predicted for these pure carbon systems (Hu, *et al.*, 2009). From the large variety of members in the fullerene family, lately CNTs have focused the attention of the scientific and technological community. The basic structural unit of a CNT is a graphitic sheet rolled into a cylinder, while the tube tips are closed by hemispherical or polyhedral graphitic domes. These tubes present impressive aspect ratios from 100 to 1000, with diameters as small as a 1 nm and lengths ranging from microns to millimeters (Ye, *et al.*, 2004).

CNTs possess excellent properties for various applications such as the enhancement filler, supporting materials in catalysis and hydrogen storage materials. One of the most important applications is to use composites containing carbon nanotubes as structural materials. Therefore, the dispersion of CNTs in composites is crucial for the final properties of nanostructured materials because the poor dispersion typically results in the deteriorated mechanical and interfacial properties between carbon nanotubes and matrix (Klinke, *et al.*, 2005). For solving the problem occurring in CNTs/polymer composites and broadening the applications of carbon nanotubes, the functionalizing strategy is explored and developed continuously. Nowadays, the functionalization of carbon nanotubes by various methods is showing the paramount importance in many fields. The functionalizing strategy can be simply classified into covalent and non-covalent approaches. Compared with non-covalent (physical) approach, covalent approach can maintain the fruits of functionalization and show the promising future. In this study, the various method of CNT synthesis process was studied. The two main methods i.e. chemical vapor deposition (CVD) and the new method based supercritical fluid was investigated in details (Weber, *et al.*, 2009).

DEFINITION of CONFIGURATION OF TUBE

In order to examine the electronic structures of CNT it is necessary to first define the classification of structural configurations of CNT. The configuration of a CNT is constructed by enrolling a graphite sheet as illustrated in Fig. 1.

That is, any tube configuration can be generated by superimposing the hexagon at the original point (denoted by O) to a hexagon indicated by (a, b) defined by a chiral vector R = M + by, where x and y are the primitive vectors whose lengths are both equal to 1.74 dC- C with dC - C indicating the C - C bond length. The tube generated by such a chiral vector (a, 6) is called tube (a, b) in most of the literatures and, hence, we also use this notation in this chapter. The sector-range expressed by $0 \leq \theta \leq \pi/6$ is enough for the generation of any tubes except the enantiomer tube (b, a).

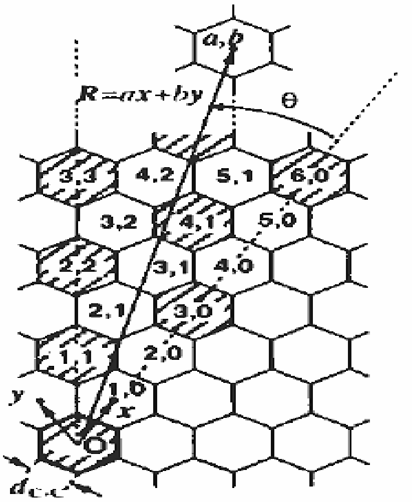

Fig. 1. Schematic representation of generation of tubes (a, b). Note a ≥ b. Hexagons with chiral vectors satisfying 2a + b = 3N in condition I are shadowed (Ye, et al., 2004).

Note that, however, definition of θ often depends on each researcher. The diameter D of tubes (a, b) and the conformation angle θ with equal dC - C are given by (Ye, *et al.*, 2004):

$$D = \frac{\sqrt{3}dc - c}{\pi}\sqrt{a^2 + b^2 + 2ab} \tag{1}$$

$$\theta = \arccos\left(\frac{2a + b}{2\sqrt{a^2 + b^2 + 2ab}}\right) \tag{2}$$

The tubes (a, a) and (a, 0) are generated from hexagons with θ = π/6 and 0, respectively. These tubes become non-helical and are called, respectively, armchair and zigzag structures. Other condition (0 < θ < π/6) generates the tube (a, b) of helical structures.

SYNTHESIS METHODS of CNT

CHEMICAL VAPOR DEPOSITION (CVD)

Chemical vapor deposition (CVD) is a versatile process applied to produce high-purity, high-performance solid materials by a chemical reaction of vapor-phase precursors. In typical CVD, a heated substrate is exposed to one or more volatile precursors, which decompose near or on the surface of substrate to form a solid deposit. As a result of reaction that takes place, volatile by-products are also released (Ye, *et al.*, 2004). The chemical reactions of precursor species occur both in the gas phase and also in the solid phase; surface of deposition. In general, CVD reactions are thermodynamically endothermic and hence energy has to be supplied to the reactor. Early example of using CVD is for the electron industry to produce ultraclean silicon, semiconductors and other electronic components. Traditionally, reactions were promoted or initiated by heat (thermal CVD) (Helfgen, *et al.*, 2000). However, elevated temperatures for deposition put some restrictions on the desired type of substrates to be coated, which is not favorable. The high temperature also leads to stresses in the film deposited on materials and causes mechanical instabilities in it. One way of reducing growth temperatures is to use plasma-assisted or plasma-enhanced CVD (PECVD). In this technique, electrical energy rather than thermal energy is used to initiate reactions and deposition can occur at low temperatures, even close to ambient. The ability of PECVD to achieve low temperatures deposition is often critical in manufacturing of semiconductors and organic coatings. Although PECVD usually allows lower temperature deposition than thermal CVD, it has some drawbacks (Raji, *et al.*, 2011). For example, the plasma bombardment of a surface often causes damage of the catalyst substrate and hence the growing film. PECVD has also strong process dependency on several parameters such as power and frequency of the source, gas pressure, reagent flow rate, reactor geometry, etc. Other methods of introducing energy to the CVD process are Laser Enhanced CVD (LECVD) also called photo-assisted CVD (PCVD) (Lee, *et al.*, 2000). In this type of CVD, laser is used to enhance the surface reactions. Two processes simultaneously occur, pyro lytic process, in which substrate is heated to enhance reactions, and photolytic process by use of Ultra Violate (UV) radiation in which molecules of gas phase is dissociated to enhance reactivity. Other types of CVD are atomic layer deposition (ALD) and the specialist version atomic layer epitaxial (ALE) however most of these techniques are too expensive and are rarely utilized (Pillay, *et al.*, 2009). Various methods have been adopted to produce carbon nanotubes, including laser ablation, arc discharge and CVD process. Among these methods, the chemical vapor deposition method is a cheap and simple method, and hence it is of interest to investigate this method through experimental studies and theoretical modeling, in order to optimize the technique. Carbon nanotube synthesis by CVD is essentially a two-step process, consisting of a catalyst preparation step followed by the actual synthesis of the nanotubes. Carbon nanotubes will be formed if proper parameters are maintained in the process. The important influencing parameters in carbon nanotube formation are the synthesis temperature, pressure, reaction time, volumetric flow rates of the precursor, catalyst and the supporting material (Ye, *et al.*, 2004).

The CVD process is assumed to be a non-isothermal and non-adiabatic process. In the analysis presented, a series arrangement of plug flow and batch reactors is assumed to model the reaction phase. This means that the CNT formation process has both space and time dependencies. It is also assumed that the CNT formation follows the VLS growth mechanism. The elementary reactions namely the acetylene decomposition, iron carbide formation and iron carbide decomposition as given by Eqs. (3)-(5) are assumed to take place individually at an instant of time, so that the heat transfer coefficient can be calculated in a simple manner. It is understood from the literature that the crude carbon nanotubes produced consist of catalytic and amorphous carbon impurities. Based on the assumed chemical reactions due to VLS growth, Eq. (5) below yields amorphous carbon and Eq. (5) yields pure carbon nanotubes (Raji, *et al.*, 2011):

$$C_2H_2(g) \rightarrow 2C(g) + H_2(g) \qquad (3)$$

$$2C(g) + 6\,Fe(s) \rightarrow 2Fe_3C(i) \qquad (4)$$

$$2Fe_3C(i) \rightarrow 3Fe_2(s) + 2\,C_{nanosized}(S) \qquad (5)$$

SUPERCRITICAL METHOD

Although SCF technology is in use from late 19th century as a tool to understand the natural mineralization, the actual impetus for this technology as a tool to process a wide range of materials began in 1980s. With the invention of Green Chemistry in the early 1990s, there was a surge in the popularity of SCF technology. Green Chemistry is important because supercritical fluids, particularly supercritical CO_2 (SC CO_2) and, to a more limited extent, SC H_2O are perceived as environmentally more acceptable replacements for the petroleum-based solvents, which are currently used in the world's chemical industries. The adverse effects of the residual solvents from both processing and environmental standpoints have been recognized. Hence the transitional processing techniques for pharmaceutical products have limited applications compared to the alternative techniques of material processing like SCF technology (Helfgen, *et al.*, 2000). In the last one decade SCF technology has witnessed a seminal growth in its application to process a variety of materials. SCF technology replaces organic solvents in a number of chemical processes, including nanoparticle fabrication, food processing (such as decaffeination of coffee beans), chemical manufacturing, extraction, dry cleaning, semiconductor wafer cleaning, polymer processing, recycling, waste treatment, organic decomposition, particles coating, etc. Especially for the nanomaterial fabrication for the advanced drug delivery and for drug formulation systems, SCF technology emerges out as an alternate to most of the existing techniques (Weber, *et al.*, 2002).

There are several variants in SCF technology like static supercritical fluid process (SSF), rapid expansion of supercritical solutions (RESS), particles from gas-saturated solutions (PGSS), gas anti-solvent process (GAS), precipitation from compressed anti-solvent (PCA), aerosol solvent extraction system (ASES), supercritical anti-solvent process (SAS), solution enhanced dispersion by supercritical fluids (SEDS), supercritical anti-solvent process with enhanced mass transfer (SAS-EM), depressurization of an expanded liquid organic solution (DELOS), supercritical assisted atomization (SAA), hydrothermal synthesis under supercritical conditions via flow reactor (HTSSF), hydrothermal synthesis under supercritical conditions via batch reactor (HTSSB), supercritical fluids drying (SCFD), supercritical fluid extraction emulsions (SFEE) (Vemavarapu, *et al.*, 2009). Here, some of these important processes of SCF technology in the first part and the supercritical hydrothermal synthesis method in the second part have been discussed in greater detail with a focus on materials being prepared in the authors' laboratories, for the purpose of biomedical applications. The SCFs of CO_2, propane, acetone, N_2O, trifluoromethane, chlorodifluoromethane, diethyl ether, water, CHF_3, CO_2+ethanol are frequently employed in nanomaterial fabrication. The solvent properties like critical parameters, solubility parameters, etc. for several commonly used solvents are available in the literature (Weber, *et al.*, 2002).

Several methods of CNT preparation have been proposed and can be classified in physical and chemical methods. Chemical methods seem to be more efficient in terms of yield and energy needed to control strictly the detailed components in the gas phase and a careful consideration of growth process in order to obtain super long and high-quality CNTs by a thermal CVD. Therefore, it is very important to understand the growth mechanism of CNTs. consumption, but, can produce lower quality carbon nanotubes. Carbon nanotubes production has also been proposed using SCF based processes (Lee, *et al.*, 2000). Chemical methods seem to be more efficient in terms of yield and energy consumption, but, can produce lower quality carbon nanotubes. Carbon nanotubes production has also been proposed using SCF based processes. Also, the yield of CVD process is low and it needs the presence of nanosized metal particles acting as catalyst and use similar growth mechanism in the gas phase in high temperature regime and vacuum or inert atmospheres (Hu, *et al.*, 2009). SCF technology routes may lead to a reproducible fabrication method of crystalline nanocarbons with a control over the tube structure and morphology. Yoshimura and group have done extensive work on the fabrication and stability of the CNTs under SCF conditions. They suggest that virtually any liquid, solid or gaseous carbon source can be used in the SCF synthesis. Through an appropriate tuning of the experimental conditions, they were able to obtain CNTs with a wide variance in tube structure (Ye, *et al.*, 2004).

The experimental conditions used by this group are: T = 550 to 800 °C; P = up to 100 MPa. Also the stability of the CNTs has been studied extensively under SCF. The results show that the SWCNTs completely transform into MWCNTs and polyhedral nanoparticles. The opening and thinning of CNTs will be of interest for applications especially in the drug delivery systems. Such an attempt has been done by Pilley *et al.* (2009) for the first time using the sc H_2O in the presence and absence of oxygen to study the opening and thinning of MWCNTs. They have examined the influence of variation of pressure, temperature, and time on the opening and thinning of MWCNTs. The presence of oxygen contributed greatly to the thinning of the MWCNTs. There are no reports on the preparation of CNTs using a flow reactor and much of the work has been done using the batch type of reactors only. On the whole the fabrication of CNTs using SCF technology is an attractive field of research, and it has been reviewed in [11]. In recent years, CNT are encapsulated with a great variety of active complexes, biological molecules, functionalized surfaces based on polymers and CNTs for biomedical and optoelectronic applications. In that sense, the SCF technique offers special advantages for processing such advanced materials (Weber, *et al.*, 2002).

CONCLUSIONS

Carbon nanotubes (CNTs) are classified among the most promising novel materials due to their exceptional physical properties. Still, optimal fabrication of carbon nanotubes involves a number of challenges. Whatever be the fabrication method, a process optimization can be evolved only on the basis of a good theoretical model to predict the parametric influences on the final product. The work reported here investigates of the two main methods in CNT process, chemical vapor deposition (CVD) and supercritical technique. CVD process is costly, need high temperature and can produce lower quality carbon nanotubes. Processing materials in a SCF, especially in SC CO2, is a novel and emerging technology for preparing nanoparticles, nanowires, and thin solid films. The CNTs based on supercritical method have high quality and the supercritical process consume low energy.

REFERENCES

Helfgen, B., Türk, M., Schaber, K., (2000). Theoretical and experimental investigations of the micronization of organic solids by rapid expansion of supercritical solution. Powder Technol., 110: 22-28.

Hu, J., Chen, Ch., Zhu, X., Wang, X., (2009). Removal of chromium from aqueous solution by using oxidized multiwall carbon nanotubes". J Hazard Mater, 162: 1542-1550.

Kim, K., Kim, J., Jung, W. S., Bae, S. Y., Park, J., Choi, J., Choo, J., (2005). Investigation on the temperature-dependent growth rate of carbon nanotubes using chemical vapor deposition of ferrocene and acetylene. Chem. Phys. Lett., 401: 459-464.

Klinke, Ch., Bonard, J. M., Kern, K., (2005). Thermodynamic calculations on the catalytic growth of multiwall carbon nanotubes. Phys. Rev. B, 71: 1-7.

Lee, Y. T., Park, J., Choi, J. S., Ryu, H. Lee, H. J., (2002). Temperature-Dependent Growth of Vertically Aligned Carbon Nanotubes in the Range 800-1100 °C. J. Phys. Chem. B, 106 (31): 7614-7618.

Pillay, K., Cukrowska, E. M., Coville, N. J., (2009).

Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution. J Hazard Mater, 166: 1067-1075.

Raji, K., Thomas, Sh., Sobhan, C. B., (2011). A chemical kinetic model for chemical vapor deposition of carbon nanotubes. Appl. Surf. Sci., 257: 10562-10570.

Sato, H., Sano, M., (2008). Characteristics of ultrasonic dispersion of carbon nanotubes aided by antifoam. Colloids and Surfaces A: Physicochem. Eng. Aspects, 322: 103-107.

Vemavarapu, Ch., Mollan, M. J., Needham, Th. E., (2009). Coprecipitation of pharmaceutical actives and their structurally related additives by the RESS process. Powder Technol., 189: 444-453.

Weber, M., Russell, L. M., Debenedetti, P. G., (2002). Mathematical modeling of nucleation and growth of particles formed by the rapid expansion of a supercritical solution under subsonic conditions. J. Supercrit. Fluid, 23: 65-80.

Ye, M., Lin, Y., Wang, Ch., (2004). Supercritical fluid synthesis and characterization of catalytic metal nanoparticles on carbon nanotubes. J. Mater. Chem, 14: 908-918.

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