Carbon Nanotube Synthesis via the Catalytic CVD Method: A Review on the Effect of Reaction Parameters

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Abstract: This review covers the results obtained in carbon nanotube synthesis by chemical vapor deposition. Parameters such as catalysts, supports, carbon precursors, reaction time, temperature and gas flow rates that are used in the production of carbon nanotubes are discussed throughout the text. Purification of the synthesized carbon nanotubes and methods utilized for cost reduction were also explored.

Keywords: Carbon nanotube, synthesis, CVD, catalyst, support material, carbon source

INTRODUCTION

Carbon nanotubes were discovered in 1991 (1). Intensive research activities to improve the synthesis methods and conditions, quality and productivity of the carbon nanotubes (2, 3) reached to rewarding conclusions. Due to their high strength, stiffness, and electrical conductivity, carbon nanotubes are designated as one of the most attractive materials for reinforcing the material in composites and nanoelectronic applications (4–7). Utilization for hydrogen and methane adsorption seem to be other important features for carbon nanotubes (8, 9).

The formation mechanism of carbon nanotubes was investigated by Peigney et al. (10). Formed nanotubes are categorized mainly as single-walled nanotubes

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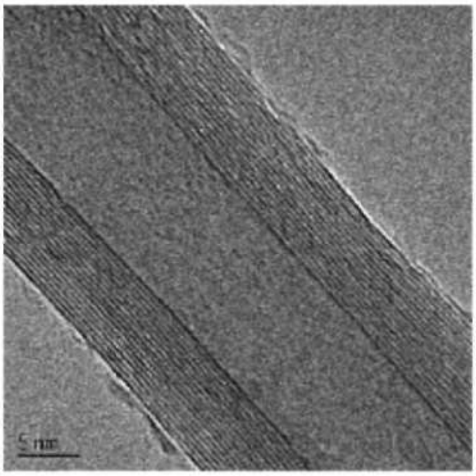

Figure 1. HRTEM image of a multi-walled carbon nanotube (11).

(SWNT) and multi-walled nanotubes (MWNT). Some electron microscopy images of SWNT and MWNT are shown in Figures 1–5.

Since SWNTs are one-dimensional quantum wires that are considered as unique materials, with one-atom wall thickness and tens of atoms in the circumference at which every atom being on the surface of the tube. Theoretical and experimental elastic modulus and tensile strength of these materials are in the range of 1000 and tens of GPa, respectively. Wong et al. (16) showed that the elastic modulus of the produced carbon nanotubes is in the TPa level (1 TPa (17), 1.25 TPa (18)), which is higher than any other known material. Moreover, due to their high aspect ratio, low density and electrical properties, (19–21) SWNTs are the subject of intense research until their discovery (22).

Also bundling characteristics of the nanotubes may be important in terms of the properties of the carbon nanotubes (23). Electrochemical actuators (24)

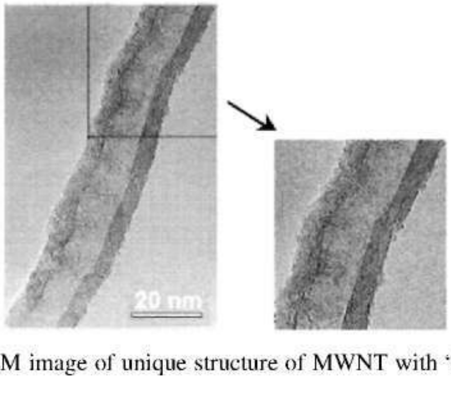

Figure 2. HRTEM image of unique structure of MWNT with "hairy core" (12).

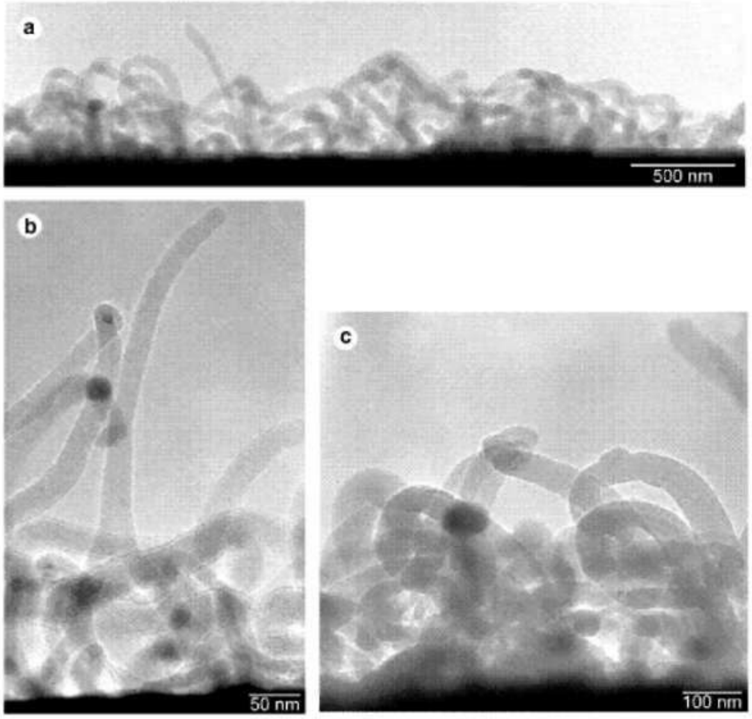

Figure 3. Cross-sectional TEM images of the SWNT sample. Image (a) illustrates the large cross-sectional area whereas images (b) and (c) show the magnification of the selected parts of image (a) (13).

and hydrogen storage (25) are designated as the important possible application areas for non-bundled carbon nanotubes.

In this review, catalyst and support material for the nanotube deposition, carbon precursor, synthesis temperature, atmosphere and reaction time, specific surface area of the resulting powder, and output ratio are discussed as the important parameters affecting the quality of the produced carbon nanotubes. Purification of the nanotubes and the synthesis cost are considered as the important industrial parameters. Also the effects of pretreatment of catalyst, hydrocarbon precursor, and ammonia as the environment gas are underlined. Most of the investigations on the carbon nanotube growth from chemical vapor deposition (CVD) carried out with either thermal CVD (26, 27) or microwave plasma CVD (28). The discussions are conducted in the light of the thermal CVD as the synthesis method, which is one of the most promising carbon nanotube production methods in terms of industrial production (29). The schematic of a typical thermal CVD set-up is shown in Figure 6.

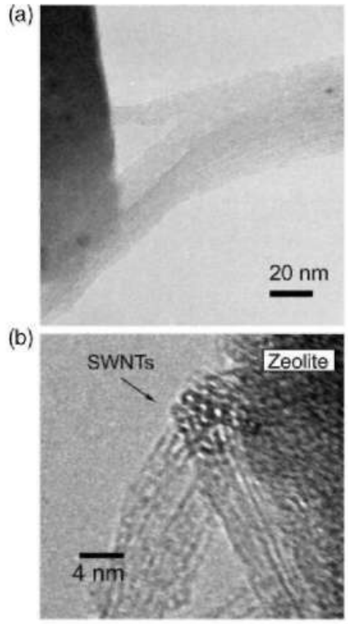

Figure 4. TEM (200 kV) image of "as grown" SWNTs by catalytic decomposition of C_{60} over Fe/Co mixture embedded in zeolite at 825°C. (a) Low-magnification image: zeolite particles are observed in left-hand side. (b) Higher magnification image of an upstanding bundle (14).

In principle, chemical vapor deposition is the catalytic decomposition of hydrocarbon or carbon monoxide feedstock with the aid of supported transition metal catalysts. The CVD method is believed as the most suitable carbon nanotube synthesis method in terms of product purity and large-scale production (30, 31).

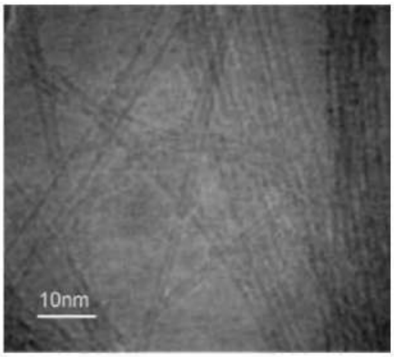

Figure 5. HRTEM image of the SWNTs prepared with benzene as carbon source (15).

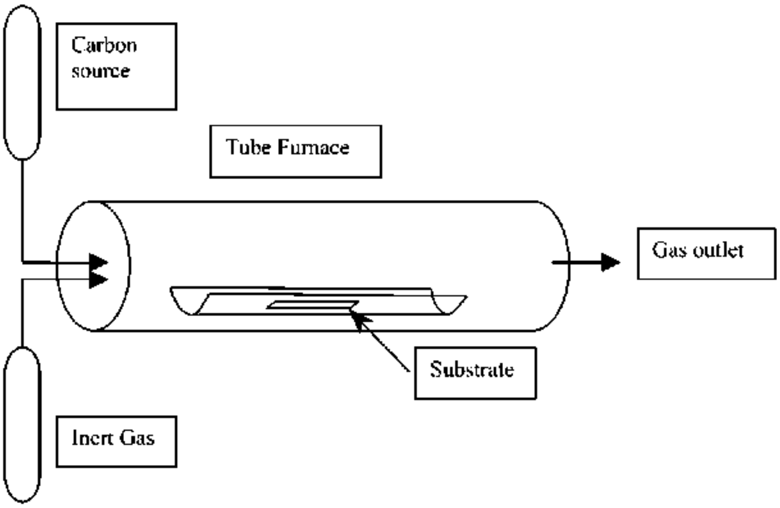

Figure 6. Schematic of a typical thermal CVD.

CATALYST

Most of carbon nanotube synthesis techniques require the introduction of catalyst in the form of gas particulates or as a solid support. The selection of a metallic catalyst may affect the growth and morphology of the nanotubes. Nagaraju et al. (32) compared catalytic activity of Fe, Co and Fe/Co supported on alumina or silica. They showed that a best yield of MWNTs resulted at 700°C on hydrated alumina prepared from aluminium isopropoxide and containing a mixture of Fe and Co in it. Seo et al. (33) compared the catalytic activity of Fe, Co, or Ni as the catalyst, and laser-treated vanadium plates having high surface area as the catalyst support in the decomposition of acetylene at 720°C under CVD conditions. Best-quality carbon nanotubes were obtained over the iron catalyst with high density and small diameter (10–15 nm) carbon nanotubes. Over nickel and cobalt catalysts, the carbon source was mainly converted to amorphous or fiber-like material (33). Lee et al. (34) showed that carbon nanotubes can be produced effectively with tungsten-based catalysts. The resulted carbon nanotubes were well-aligned, multi-walled structure and highly pure. Yokomichi et al. (35) studied on the effects of catalytic effects of several coatings with $M(NO_3)_n \cdot mH_2O$, where $M = Al$, Mg, Mn, Cu, Zn, Fe, Co, and Ni, in terms of yield of nanotube formation. The results showed that the yield of nanotube formation significantly depends on M and can be explained in terms of reducing tendency of the catalysts, as well as the size of the catalysts (35). Lee et al. (36) studied the effect of selected catalysts (nickel, iron and cobalt) on the synthesis of carbon nanotubes. The results revealed that respective nanotube growth rate is dependent on the catalyst type in the order of Ni > Co > Fe. Silica is used as the support material. Iron catalyst resulted in the best crystallinity of the nanotubes among the three catalyst (36). Carbon nanotubes that contain metal particles can be used for carbon nanotube source decomposition. Qian et al. (37) investigated the activity of such kind carbon nanotubes for methane decomposition. Their results showed that, with iron and molybdenum containing nanotubes, the conversion of methane increased steadily with temperature. The results were more promising than the experiments with nickel catalyst. C. Du and N. Pan (38) investigated growth of carbon nanotubes directly on nickel substrate. They studied nucleation and growth behaviour of nanotubes with respect to growth sites and reaction temperature. At lower synthesis temperatures nickel nanoparticles served as the nucleation sites, however at high temperatures grain boundaries and defective sites were the nucleation sites. Also, small amounts of iron nanoparticle deposition on nickel substrate resulted in an improvement of density of the carbon nanotubes (38). Paillet et al. (39) studied synthesis of SWNTs via discrete nickel nanoparticles and they showed some advantages for the physical property studies of carbon nanotubes with this synthesis route.

There are also studies on the performance of the non-metallic catalysts. Cho et al. (40) synthesized carbon nanotubes using dispersed magnetic fluids, instead of conventional metallic catalyst particles. Application of magnetic fluid of surfactant-coated magnetite nanoparticles by spin coating method on Si substrates resulted in successful growth of dense and aligned carbon nanotubes. Moreover, mixing the magnetic fluid in PVA renders a viscosity to the solution, provides uniform particles distribution without agglomeration and enable the control of the nanoparticle density on the substrate (40). Botti et al. (41) also reported carbon nanotube synthesis without metal catalyst addition. They fabricated carbon nanotubes and nanowires by using amorphous hydrogenetaed carbon nano-particles as precursor. In particular, depending on the process parameters they could obtain single-walled carbon nanotubes with mean diameter 1.2 nm and carbon nanowires with mean diameter 250 nm.

It is demonstrated that the structure of the nanotubes obtained strongly depends on the catalytic particle size and chemical composition (42). Ding et al. (43) synthesized carbon nanotubes with the Ni-Ni_3P film as the catalyst. Resulting products were 90% carbon nanofibers showing either curved or straight shapes. 10% of the products were carbon nanotubes with very small diameters of around 10 nm. When nanocrystalline Ni-Ni_3P was used as the catalyst, most of the pysolysis products were carbon nanotubes (about 95%) with diameters less than 100 nm. Cross-junctions of carbon nanotubes grown with a certain mechanism were also observed (43).

Widely used catalyst materials in carbon nanotube synthesis are cobalt (32, 44, 45), iron (32, 46, 47), titanium (47), nickel (3, 48), a couple of zeolites and combinations of these metals and/or oxides (3, 49, 50, 51).

CATALYST PREPARATION AND DISTRIBUTION

There are large numbers of catalyst preparation routes in carbon nanotube synthesis via CVD method. Patterning of catalytic islands on the substrate material is one way of catalyst preparation; Kong et al. described experimental details and used several catalysts and substrate materials in this work (52). There are also some other techniques that have been used to prepare carbon nanotubes or graphite nanofibers supported catalysts such as incipient wetness impregnation (53–55), ion-exchange (56), sol-gel technique (57), and organometallic grafting (58).

Different types of catalysts are produced by impregnation (33). This method consists of repeated dipping of porous support pellets into a solution containing a desired catalytic agent. The agent must be applied uniformly in a predetermined quantity to a preset depth of penetration. This is especially true for noble metals catalysts. The liquid penetration into the pellets is hindered by air trapped in the pellets pores. Obviously, large surface area of the catalyst (i.e., smaller the powder size) affect the amount of the produced carbon nanotubes in a positive manner.

Another factor that may influence the productivity of the catalyst material is the dispersion level of the catalyst material. Large particles and aggregates instead of fine and well dispersed particles may be inactive for nanotube growth (2). Well-dispersed catalyst systems may result a narrower size distribution of the synthesized nanotubes (59).

SUPPORT MATERIAL

It has been found that a single metal and mixture of metals supported on oxides, clays or zeolites have great contribution in terms of catalytic activity to nanotube synthesis (60–63). Dispersion and stabilization of the metallic catalyst materials can also be performed by using a number of oxides and mixed oxides (64). It is well known that the catalytic properties of the catalyst-support material combination strongly depend on the interaction between catalyst and the support material (32). Zhu et al. (65) used Fe and Co salts as the catalyst on mesoporous silica. They suggested that mesoporous silica might play a templating role in guiding the initial nanotube growth. They pointed also catalyst/support ratio. When both Fe and Co were present in the catalyst/support ratio range between 1.5% and 3%, abundant double-walled carbon nanotubes could be synthesized. When the catalyst/support ratio was 6%, most of the products were MWNTs. They concluded that Fe plays a major role in the catalytic CVD process, and Co might play a co-catalyst role in their process (65). It is well known that current CVD method has limited catalyst productivity for SWNTs, although it is the most promising nanotube synthesis method for large-scale nanotube production. Su et al. (2) improved the CVD method for SWNT preparation and achieved high-quiality SWNTs, greater than 200% the weight of the catalyst. They attributed their improvement to the strong interactions between the aerogel support and the Fe/Mo catalyst as well as the high surface area of the support (2). Hernadi et al. (66) investigated catalytic growth of carbon nanotubes from the point of view of reaction mechanism. Several catalyst supports such as silica gel, zeolites and alumina with different pore diameter was tested in acetylene decomposition. They proved that only catalyst particles deposit on the external surfaces of porous support could take part in the catalytic carbon nanotube formation. Gournis et al. (67) synthesized carbon nanotubes by catalytic decomposition of acetylene over iron-catalyst centers supported on montmorillonite surfaces by ion-exchange. Carbon nanotubes rooted on the clay layers and exhibited various relative orientations and many bridged different clay platelets. The clay in the carbon-modified solid maintains its exchange properties. Ward et al. (68) investigated several substrates to determine the effect of substrate on the growth of single walled carbon nanotubes on thin metallic films. It was found to be the ideal substrate for SWNT growth was a spun-on alumina film with the iron catalyst.

Sinha et al. (44) stated that the strength of the catalyst–support material and the type of support material may determine the conditions of metal free carbon nanotubes or carbon nanotubes filled with metal particles. Thus, the proper choice of catalyst material for a support material (or vice versa) is important in carbon nanotube synthesis. For example, Nagaraju et al. (32) investigated the effectiveness of different catalyst materials, namely iron, cobalt, and iron-cobalt, on the alumina and silica substrates. Some examples for proper catalyst–support material pairs are tabulated in Table 1. As a new approach, Higashi et al. (69) synthesized thick carbon nanotubes (80–130 nm) on Pd-loaded diamond catalyst.

Ortega-Cervantes et al. (70) synthesized carbon nanotubes on different substrate materials; quartz, conductive glass, porous alumina and nickel plates, using Fe and Co catalysts and ethanol as the carbon source. Successive nanotube growths were achieved on conducting glass, nickel plates and porous alumina substrates. Nickel plate and porous alumina substrates revealed SWNTs, whereas conducting glass substrate revealed MWNTs (70). Another approach was synthesizing carbon nanotubes using commercial Al_2O_3 pellets with some nickel concentrations (71). Different nickel content in alumina gave different results in terms of nanotube growth behaviour (71).

The catalyst–support material pair is critical also in terms of the synthesized SWNTs. The choice of the catalyst and support material may be a determining factor in the SWNT synthesis (72, 73).

The separation of carbon nanotubes from the support material at the end of the experiment is also an important factor. Separation and purification of carbon nanotubes may require treatments, which may damage the carbon nanotube material (74). It is essential to use a proper support material that can be soluble in a solution where carbon nanotubes are not soluble (44).

Table 1. Some examples of catalyst–support material pairs

Carbon nanotube synthesis method	Catalyst	Support material	Reference
CVD	Co	AlPO-5	(44)
CVD	Fe/Mo	Al_2O_3 aerogel	(2)
CVD	Co/V	Y-type zeolite	(49)
CVD	Co/Fe	Y-type zeolite	(49)
CVD	Fe	SiO_2/Si	(48)
CVD	Fe/Co	$CaCO_3$	(45)
CVD	Ni	Ti/Soda-lime glass	(75)
CVD	Co	MgO	(76)
CVD	Co/Fe	MgO	(77)
CVD	Fe/Co	Y-type zeolite	(31)
CVD	Ni	Si	(78)
CVD	Fe_3O_4	Si	(78)
CVD	Fe	Quartz	(79)
CVD	Fe/Co	Y-type zeolite	(23)
CVD	Fe	Graphite fiber	(80)

CARBON PRECURSOR AND OTHER FACTORS

The precursor for carbon nanotubes is fed into the system in the gaseous state at some specific conditions. To avoid oxidation of the carbon, the chamber is kept free of oxygen during the production process. Generally continuous inert gas flow is supplied to the reaction chamber. Nitrogen and argon are the most extensively used inert gases.

Reaction time and temperature, and gas flow rates of carbon source and inert gas are also important factors to optimize the carbon nanotube synthesis conditions and product quality (70). These parameters are adjusted so that the experimental conditions are optimized. Synthesized carbon nanotube / used catalyst weight ratio, and the weight ratio of the synthesized carbon nanotube to carbon nanotube after purification (e.g., removal of undesired amorphous carbon) are important indications of the quality of the produced carbon nanotubes.

It is reported that lower synthesis temperatures than optimum synthesis temperature result in lower carbon nanotube yield in the product (44). It is also reported that the reaction temperature plays an important role in the alignment properties and diameter of the synthesized nanotubes (79). Generally, carbon nanotube growth temperature (or reaction temperature) used is between 550°C and 1000°C, and the reaction temperature may vary according to the catalyst-support material pair. Zhu et al. (80) synthesized carbon nanotubes on graphite fibers by thermal CVD. They showed that carbon nanotubes can only be grown in a limited temperature range. At low growth temperatures, only a carbon layer is formed on the fiber surface. However, at high temperatures, the diffusion rate of iron particles into carbon fibers was enhanced and the nanotube growth possibility reduced. Li et al. (81) synthesized carbon nanotubes with nanocrystalline Ni/metallic oxide catalyst from decomposition of methane. When the reaction temperature is higher than 1000 K, carbon nanotubes can be obtained. At lower temperatures, formation of carbon fibers is observed. Gulino et al. (82) used ethane as carbon precursor over Fe/Al_2O_3 catalyst in large scale synthesis of carbon nanotubes. They showed that ethane is an effective carbon source to produce high-yield MWNTs. In their experiments, optimum reaction temperature was 660°C, and above 750°C amorphous soot and carbon nanoparticle were observed (82).

Also the variations in the optimum gas (carbon source) flow rate and inert gas flow rate result in the decrease in the carbon nanotube yield. Most widely used carbon precursors are acetylene (44, 49), methane (2, 80), ethanol (23, 70), 2-propanol (23), ethylene (83), and toluene (79). The type of the carbon source is essential. Recently, Qiu et al. (84) showed that coal gas is an effective carbon source to synthesize single-walled carbon nanotubes with ferrocene catalyst by chemical vapor deposition method. Pradhan and Sharon (85) studied on carbon nanotube synthesis with kerosene, which consist of many small- and long-chain aliphatic and aromatic compounds, as the carbon source. Nickel and iron catalysts facilitated straight and coiled nanotube growth. With increasing pyrolysis temperature, nanobead formation were observed.

Most widely used inert gases are argon and nitrogen with a flow rate of around 100 ml/min. Sometimes inert gas is changed with hydrogen gas to reduce the oxygen content in the reaction environment (80). The flow rate of carbon source gas is generally between 10 and 30 ml per minute. Inert gas flow rate and exposure time is larger than the carbon source gas. The typical reaction time is around 60 minutes, but the reaction time also depends on the desired carbon nanotube amount. Interestingly, different support material does not require different carbon gas and inert gas flow rates (44). Similarly, deviations of the optimum reaction time for the specific synthesis suffer from the quality of the final product (44).

Formation of amorphous carbon is an important factor affecting the quality of the final product. The formed amorphous carbon film decreases considerably the diffusion rate of carbon source gas to the catalyst (2).

PURIFICATION OF CARBON NANOTUBES

The synthesized carbon nanotubes may contain large amount of impurities such as amorphous carbon, multishell carbon nanocapsules, and metal particles. The removal of these impurities is important in terms of the purity of the final product and the hurdles in the characterization stages.

There are several carbon nanotube purification methods (86–90). One of the efficient one is oxidation in air at temperatures around 750°C (86).

Oxidation period is highly important to prevent burning off of the pure nanotubes. Liquid-phase oxidation using $KMnO_4/H_2SO_4$ solution is another purification method (87). Extremely pure carbon nanotubes can be obtained by this method, but the final nanotubes may be severely damaged. Graphite intercalation is another purification method, and the results showed that the resistance to bromination of carbon nanotubes was smaller than the carbon nanoparticles (88).

Hou et al. (91) derived an efficient technique for purification stage. They improved a multi-step purification process which could remove undesired impurities with an improved yield. The first step of the purification process is ultrasonic and heat-treatment of the raw material to obtain a well-dispersed nanotube structure. Following treatment was immersing in the bromine water at 90°C for 3 hours, and than heated at 520°C in air for 45 minutes. To remove the metal particles at room temperature, the residual powder is immersed in 5 molar hydrochloric acid. The effect of bromination was investigated by repeating the purification steps without applying bromination step. It was understood that bromination is an important stage in carbon nanotube purification, and the bromination mechanism of purification of multi-walled carbon nanotubes was investigated.

Purification stage for SWNTs is one of the most essential challenges. Strong et al. developed an easy and inexpensive method of purifying SWNTs (92). The method includes oxidative heat treatment and following acid washing. In the heat treatment stage metal catalyst (iron) was oxidized and acid washing was able to remove the oxidized catalyst (iron oxide) (95). Cheng et al. (93) developed a procedure for purifying SWNTs synthesized by the catalytic decomposition of hydrocarbons. The characterization results revealed that amorphous carbon, catalyst particles, vapor-grown carbon nanofibers and multi-walled carbon nanotubes were removed from the single-walled carbon nanotubes without damaging SWNTs. The yield of SWNTs were 40%, and the purity was about 95% after purification. Complete removal of metallic impurities (metal catalysts) SWNTs is a fairly important issue. Chattopadhyay et al. (94) applied a purification process including a sonication-mediated treatment of obtained SWNT soot in a one-to-one mixture of hydrofluoric and nitric acids (94). Billaud et al. (90) reported their purification process for SWNT synthesis as hot water treatment, partial oxidation at 700°C and following oxide dissolving by HCl. However, still small amounts of amorphous carbon and encapsulated metal particles were observed. They proposed that as one of the limiting factor of macroscopic physical studies of SWNTs. Removal of metal catalyst particles by heating the material above the evaporation temperature of the metal is also suggested as one purification stage (95). To remove surface oxygen from nanotube materials, high temperature annealing was suggested subsequent to oxidative purification (96). Andrews et al. (97) suggested also high temperature annealing, so called graphitization, is effective in removing both the catalyst particles as well as microstructural defects within the nanotube. Heat treatment of MWNTs at temperatures above 1800°C was found to be efficient method of removing residual metals, even for metal particles contained within the core of the MWNT. Chen et al. (98) proposed a three-step purification process of MWNTs produced by catalytic CVD method with Ni-Mg-O as catalysts. First two steps involve 3M HNO_3 treatment, and following 5M HCl treatment. These are found to be effective to remove metal and metal oxide. For the third step purification, burning of the nanotubes at 510°C, which was chosen as the optimum temperature to eliminate non-nanotube carbon materials. This temperature is consistent with the results obtained by Colomer et al. (99) which was 500°C as the optimum temperature. After purification, larger than 96% pure MWNTs were obtained without any damage. Biro et al. (100) applied wet and dry chemical purification for the removal of unwanted carbonaceous products and of the catalyst particles. Wet oxidation is found to be effective in achieving both goals and produces a relatively moderate damage of the outer wall of the nanotubes. The catalyst particles encapsulated in the central channel of the carbon nanotubes cannot be removed even if repeated treatments are applied.

PARAMETER CONTROL

To be able to control some parameters is essential in terms of the quality of the resulting nanotubes. Willems et al. (63) synthesized multi-walled carbon nanotubes with different catalysts and they showed that the outer diameter of the nanotubes can be controlled by choosing appropriate catalyst. Ci et al. (101) used ferrocene as the floating catalyst to synthesize single-walled carbon nanotubes. sublimed catalyst was carried by the flowing argon. They stated that control of SWNT growth in their experimental setup by adjusting the partial pressure of the carbon source, C_2H_2, and the reaction temperature. Wang et al. (102) concluded that metal catalyst film thickness, catalyst pattern size, deposition temperature and pressure of the carbon source are the important parameters which affect the carbon nanotube growth characteristics. Thinner and smaller catalyst patterns, at a lower carbon source gas pressure result in high quality and high yield nanotubes (102). Li et al. (103) synthesized carbon nanotubes on graphite foil. Stainless film is used as the catalyst material. After annealing the steel coated graphite film in hydrogen, initial stainless steel film go through phase segregation during annealing and form desired composition for the catalysization process. According to the results, catalyst particle size increases with increasing initial stainless steel film thickness. The effect of the catalyst particle size on the outer diameter of the carbon nanotubes are reported in the increasing order.

Controlling temperature and catalyst particle size are stated as important processes in diameter of the synthesized carbon nanotubes. Tang et al. (104) synthesized SWNTs by using Co/MgO catalyst from decomposition of methane. They showed that the addition of Mo to Co/MgO catalyst increases the yield and improve the quality of SWNTs. The generation rate of SWNTs could be raised at least 10 times and amorphous carbon formation was suppressed, but there is an optimum content of Mo and Co.

Therefore, they could control the realtive amount of SWNTs and MWNTs by adjusting the composition of the catalyst. Kitiyanan et al. (105) studied on SWNT synthesis by decompositon of CO on bimetallic Co–Mo catalyst. They found that the control of SWNT production could be done by adjusting Co:Mo ratio, operation temperature, and processing time. Kaatz et al. (106) synthesized carbon nanotubes from sputtered 4-nm-thick catalyst film on a tungsten-coated silicon substrate. Controlled growth of nanotubes is obtained with uniform diameters ranging from 5 to 350 nm. They showed that carbon nanotube diameters increase exponentially with temperature. Yoon et al. (107) synthesized SWNTs and MWNTs on silicon substrates. They could control synthesis of nanotubes by the catalyst and hydrocarbon species. Highly oriented MWNTs could be obtained by high carbon flux of acetylene gas on pure Co catalyst. SWNTs could be grown on Co–Mo catalysts by keeping a low carbon flux with methane gas.

Delzeit et al. (108) deposited metal multilayer (i.e., Al and Ir) by ion beam sputtering on various substrated to control the density of SWNTs synthesized by CVD. Underlayers with 10–20 nm thickness, are found to be activate the substrates for SWNT growth with Fe as the catalyst. Adding Mo as co-catalyst gives increased production of SWNTs and the density could be controlled by changing the thickness of the metal layers.

REDUCTION OF THE SYNTHESIS COST

When the cost of carbon nanotube production comes into account, the first consideration is the synthesis method. As it is mentioned earlier, chemical vapor deposition is the most suitable low-cost mass production technique of carbon nanotubes. By this technique, gram quantities of single-walled carbon nanotubes could be obtained in 30 minutes (109). Moreover, it is reported that as an improvement to the CVD technique, in the hot-filament assisted CVD method, the efficiency of the single-wall carbon nanotube synthesis increased considerably indicating an easy system scale-up and reduction in production cost (23).

In large-scale production, the cost of carbon source also plays an important role in the final product cost. Compared to graphite, methane, and coal-derived hydrocarbons, coal is cheap and an abundant carbon source. Since carbon nanotube synthesis with coal as the carbon source is a newly appearing area, it needs further investigation and study. In economical base, the cost of different coal materials as the raw material is not the determining factor in the final product cost. The product yield and purity affect the product cost more than the raw material cost (110).

Another example for the cost reduction due to carbon source can be given as the usage of alcohol as the feedstock. It is reported that high purity carbon nanotube synthesis at lower temperatures is possible by alcohols, which allows high-purity products by low temperature synthesis (31). Decrease in the synthesis temperature obviously results in the final product cost.

Graphitization of carbon nanotubes offers a low-cost and commercially viable purification process by removing the residual metal catalyst in the nanotubes and reducing the defects in the nanotube structure (97).

EXTRA EFFECTS

Hydrogen plasma treatment is found to be a critical step to maintain the activity of catalyst prior the reaction with acetylene gas for the carbon nanorube growth (111).

In carbon nanotube synthesis with high-temperature decomposition of hydrocarbons, Li et al. (15) showed that thermodynamic properties and chemical structures of hydrocarbon precursors play important role on the morphology of the carbon deposits over catalyst. After the experiments with several hydrocarbons such as methane, hexane, cyclohexane, benzene, naphthalene and anthracene, for high-molecular weight hydrocarbons chemical structures play important role rather than thermodynamic properties in nanotube formation. Also, aromatic molecules such as benzene, naphthalene and anthracene tend to formation of single walled carbon nanotubes.

The role of ammonia as the environment gas was investigated as to obtain high density nucleation sites for carbon nanotube formation. This is achieved by ammonia by inhibiting generation of amorphous carbon in the initial stage of synthesis (112). Jung et al. (113) investigated the effect of ammonia environmental gas on the aligned carbon nanotube growth. The results of the compositional analysis of the catalyst surface showed that activated nitrogen atoms were generated by the decomposition of ammonia. They enhance formation of graphitic layer and improve separation kinetics of graphitic layer and catalyst. Also, without preptreatment of ammonia environment, the role of nitrogen appeared in different ways depending on the catalyst material. Juang et al. (114) investigated the role of ammonia on the carbon nanotube growth and it was considered to enhance the catalyst activity. Ammonia achieved this enhancement just by preventing the catalyst from passivization. Moreover, growth characteristics of nanotubes changes from spaghetti-like to vertically aligned when the growth condition was switched from low to high ammonia ratio.

CONCLUSIONS

Carbon nanotubes that were discovered in 1991 are designated as one of the most attractive materials for reinforcing the material in composites and nanoelectronic applications. Intensive research activities to improve the synthesis methods and conditions, quality and productivity of the carbon nanotubes reached to rewarding conclusions because of their high strength, stiffness, and electrical conductivity.

Nanotubes are categorized mainly as single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). SWNTs are one-dimensional quantum wires that are considered as unique materials, with one-atom wall thickness and tens of atoms in the circumference at which every atom being on the surface of the tube.

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Chemical vapor deposition is the most suitable low-cost mass production technique of carbon nanotubes. In large-scale production, the cost of carbon source also plays an important role in the final product cost. Compared to graphite, methane, and coal-derived hydrocarbons, coal is cheap and an abundant carbon source. Since carbon nanotube synthesis with coal as the carbon source is a newly appearing area, it needs further investigation and study.

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