

Synthesis of Narrow Diameter Multiwalled Carbon Nanotubes (MWNTs) By Catalytic Chemical Vapor Deposition For Mechanical Reinforcement Applications

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ABSTRACT

Strong and versatile carbon nanotubes (CNTs) are finding new applications in improving conventional polymer-based fibers. Nanotube-reinforced composites could ultimately provide the foundation for a new class of strong and lightweight fibers with properties such as electrical and thermal conductivity unavailable in current fibers. A recent research has discovered that the best type of nanotube for polymer composite reinforcement is the small diameter multiwalled nanotubes (MWNTs). One serious weakness of all current techniques for preparing MWNTs is that they produce a wide range of tube sizes and structures, which could be a drawback in areas where specific tube structures are needed. Here, a catalytic technique has been developed that has the ability to define the diameter of bulk multiwalled carbon nanotubes grown. The method involved catalytic decomposition of methane over the catalyst at 950°C in a chemical vapor deposition (CVD) system. It includes pre-treatment of iron, nickel and cobalt catalyst with NH₃ gas as the key step to vary the size of catalyst used for the growth and subsequently defined the diameter of CNTs produced. Structural characterizations including scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), thermo gravimetric analysis and Raman spectroscopy conducted on CNTs grown on three different catalysts, namely iron, cobalt and nickel have indicated that the size and type of catalyst used affects their sizes and crystallinity. With this technique, narrow diameter bulk multiwalled carbon nanotubes in the range of 19 to 38 nm has been produced. It is believed that with this diameter-controlled synthesis, bulk CNTs of certain range of diameter can be produced to fulfill the requirement needed for mechanical reinforcement of polymer composites.

Keywords: multiwalled carbon nanotubes, catalyst, chemical vapor deposition, mechanical reinforcement, synthesis.

1 INTRODUCTION

In the last decade, the cylindrical molecule of carbon known as carbon nanotube has become the focus of intense research due to its unique properties such as remarkably high tensile strength, high resilience, electronic properties spanning from metallic to semiconducting, able to sustain high current densities and high thermal conductor. These distinctive characteristics are found to be the result of the molecular structure of nanotube, which comes in tabular form with various diameters. Its electronic property changes from metal to semiconductor depending on helicity and diameter. The diameter also affects its mechanical properties resulting in applications ranging from microscopy tip [1] to structural composite [2]. Thus development of the synthesis that has the ability to control the structural properties namely the diameter and chirality would be required in order to give a significant impact to certain application.

Recently [3], it was discovered that smaller diameter, multiwalled type nanotubes seem to provide better mechanical reinforcement of polymer composites indicating that reinforcement depends strongly on total surface area, which emphasize the importance of interfacial stress transfer. One serious weakness of all current techniques for preparing multiwalled nanotubes is that they produce a wide range of tube sizes and structures, which could be of disadvantage in areas where specific tube structures are needed such as in mechanical reinforcement of polymer composite. Past studies have shown that nanotubes with defined structures can be achieved by the creative use of catalysts. It has been reported [4, 5, 6] that the size of the growth catalyst can define the diameter of the CVD-grown nanotubes. Thus, the objective of this research effort is to develop appropriate catalytic methodology to produce nanotubes with defined structures, specifically reasonably narrow diameter, which is the prerequisite for fabrication of high strength composite materials.

2 EXPERIMENTAL

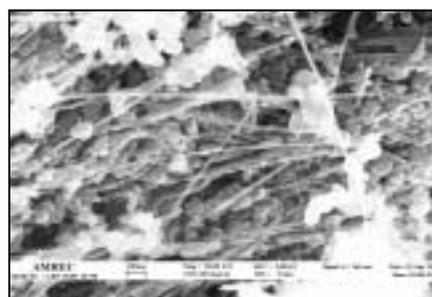
The catalytic decomposition of methane over the catalyst was carried out in a chemical vapor deposition system. Catalytic particles of iron, nickel and cobalt were prepared [7] and pretreated by etching with NH_3 gas to further reduce the active metal particles to nano-size. This is the key step in the synthesis that can determine the size of nanotubes. As a direct effect of particle size of the catalyst on the growth of CNTs, the diameters were expected to be in the order of $\text{Fe} > \text{Co} > \text{Ni}$. However the overall effect comes from the duration and flow rate of ammonia pretreatment prior to the growth of nanotubes. Thus longer period and higher gas flow rate of ammonia pretreatment would result in much smaller catalyst particles consequently produce much smaller nanotubes. The catalytic deposition of carbon on well-dispersed metal catalysts was carried out in the methane atmosphere at a flow rate of 40 sccm at 950°C . The raw products were then given heat and acid treatment to purify them into a fine black powder. The samples were examined using field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) operating at 200 kV. Sample preparation for TEM observation involved dispersion using ultrasonic method. For thermo gravimetric analysis (TGA), a small amount of sample was subjected to heat treatment from room temperature to 800°C with heating rate of 10°C per minute under the air ambient. Characterization with Raman microscopy involved irradiation with 514 nm and 633 nm laser excitation at low power.

3 RESULTS AND DISCUSSION

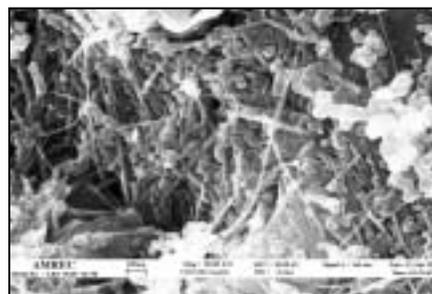
Figure 1 is a typical image of unpurified product showing the presence of contaminants such as nanoparticles and graphitic debris. In early work of synthesizing carbon nanotubes, removing these contaminants has proved to be difficult and many methods have been tested before some highly effective methods [8, 9] can be made available. Realising that nanoparticles with their defect rich structures could be easily oxidized much more readily than the relatively perfect nanotubes, subjecting raw nanotube samples to a range of oxidizing treatment would allow preferential removal of nanoparticles. In addition to large amount of amorphous carbon, the soot that contains nanotubes also have metal particles, often coated with carbon. Here, the raw sample was heated at 300°C in air for several hours in order to oxidize the amorphous carbon and to remove the graphitic covering the metal particles. Finally the remaining soot was treated with concentrated acid in order to dissolve the metal particles.

Examination of the SEM image of the pure product of nanotubes grown on Fe, Ni and Co catalyst (Figure 2) indicated that most contaminants had been removed, although some filled and empty nanoparticles remained. With the use of surface analysis software, diameter

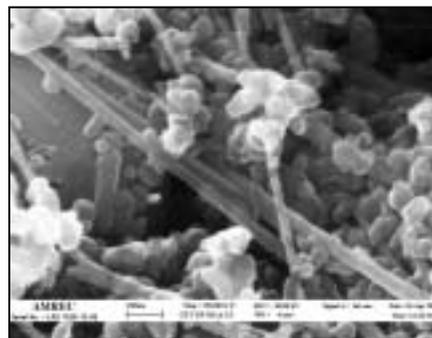
distributions of nanotubes grown on all three catalysts were determined from the SEM images.



(a)

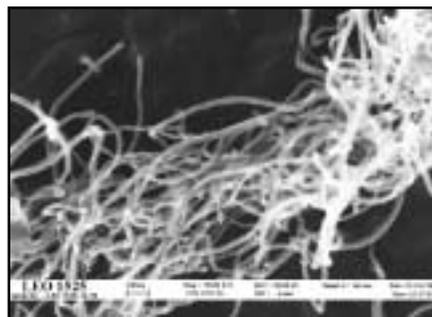


(b)

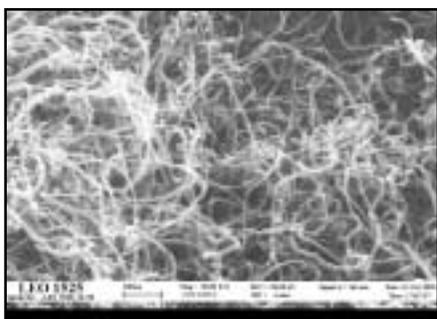


(c)

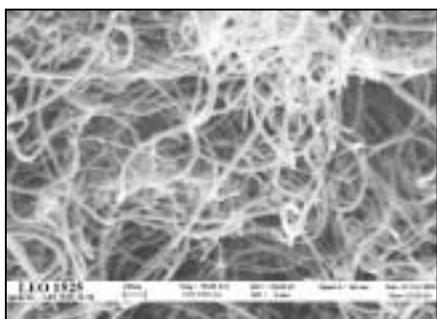
Figure 1: Unpurified bulk CNTs grown on (a) Fe, (b) Co and (c) Ni catalyst.



(a)



(b)



(c)

Figure 2: SEM image of MWNTs grown on (a) Fe (b) Ni and (c) Co catalyst.

Nanotubes grown on Fe (31-38 nm) are found to have the largest size distribution compared to the ones on Co (23-26 nm) and Ni (19-24 nm). Lee *et al* 2002 [10] had reported similar trend of the size of nanotubes. This was explained by the size effect of catalyst particles on the growth of CNTs where before the growth, the size distribution of the catalysts is in the order of Fe > Co > Ni. Unlike Lee, size distribution of nanotubes obtained here are much smaller, believed to be due to the longer period and higher gas flow rate of ammonia pretreatment prior to the growth of nanotubes, resulting in much smaller catalyst particles.

A typical high-resolution transmission electron microscopy (HRTEM) image of a nanotube is shown in Figure 3. Nanotubes grown on all three catalysts are found to be of multiwalled type with average spacing of 0.35 nm, agreeable with the values obtained by Kiang *et al* [11]. The determination of crystallinity using HRTEM images is based on the observation of the intricate arrangement of the walls of nanotube. CNTs grown on Fe showed the highest degree of crystalline perfection followed by that on Ni and Co catalyst.

This outcome is supported by the result of TGA and Raman spectroscopy. In thermo gravimetric analysis, CNTs with less crystalline structure will react preferentially with the oxidant and lose weight at a lower temperature compared to the more highly crystalline CNTs.

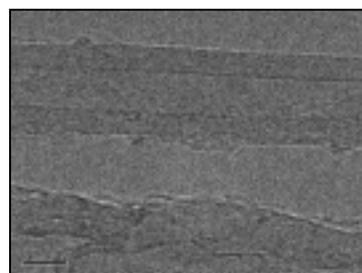
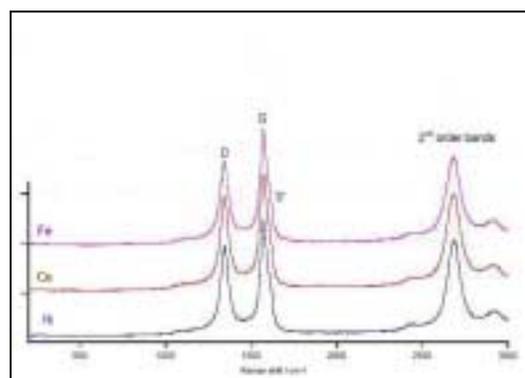
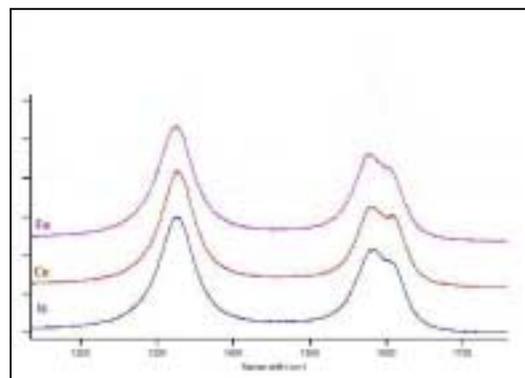


Figure 3: HRTEM image of MWNTs grown on Co catalyst.



(a)



(b)

Figure 4: Raman spectra of CNTs at (a) 514 nm and (b) 633 nm.

With Raman spectroscopy shown in Figure 4, both 514 and 633 nm laser excitation have produced the expected D band, G band, D' band and 2nd order Raman information. The crystallinity was determined using the ratio of D (disordered) band to G (graphitic) band. So the lower the ratio (I_D/I_G), the more crystalline the sample would be. According to Lee *et al* (2002), the growth rate of CNTs on the catalyst is of the order of Ni > Co > Fe. This lead to the

conclusion that the presence of more defective constituents in the bulk nanotubes of Co and Ni is due to their faster growth rates, giving lower crystallinity. Overall characteristics of nanotubes grown on Fe, Co and Ni are tabulated in Table 1. The above results imply that when grown catalytically, the size distribution of CNTs can be defined and their degree of crystalline perfection can be manipulated by the selection of the catalyst and the duration of the etching treatment prior to the growth.

Catalyst		Fe	Co	Ni
Diameter [nm]		31-38	23-26	19-24
High resolution TEM		Well-defined graphene layers	More defective structure	Short-range layers
TGA		Gasifies at 550°C	Gasifies at 470°C	Gasifies at 540°C
Raman I_D/I_G	514 nm	0.745	0.822	0.783
	633 nm	1.454	1.538	1.483

Table 1: Characteristics of bulk CNTs grown on Fe, Co and Ni catalyst.

4 CONCLUSION

Several researchers have reported a wide size distribution of nanotubes typically from 80 to 200 nm [10] depending on the catalyst used. Here, we have developed a method that includes etching of the catalytic particles using NH_3 gas prior to the growth in order to produce bulk multiwalled nanotubes. The parameters of the etching process such as duration and gas flow rate can determine the size of the catalysts, which in turn produce a corresponding size of nanotubes. By increasing the gas flow rate and duration of the etching process, a reasonably narrow diameter bulk carbon nanotubes in the range of 19 nm to 38 nm have been produced.

Thus by using this diameter-controlled synthesis, bulk CNTs of certain range of diameter can be produced to fulfill the requirement needed for further investigation of the optimum diameter in the search for most effective, high-strength nanotube reinforced polymer composites. It would also pave the way for more research in producing lightweight, high strength, thermally and electrically conducting materials.

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