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Research Article

Surface analysis of catalytically grown carbon nanotubes (CNTS)

Imaekhai Lawrence

Author Email:oboscos@yahoo.com

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Abstract

This paper presents our recent success in synthesizing carbon nanotubes in powder form. The method adopted involved thermal chemical vapour deposition (CVD) using catalysts such as nickel (Ni, cobalt (Co) and iron (Fe). Measurements on the diameter of carbon nanotubes (CNTs) have been conducted using surface analysis software on the image derived from scanning electron microscopy (SEM). It was observed that the average diameter of CNTs follows the order of Fe> Co> Ni. This outcome is attributed to the effect of the particle size of the catalyst, which is in the same order before the synthesis. The morphologies of CNTs are almost the same regardless of the catalyst used. However, on closer examination, CNTs grown from Fe exhibit a fairly straight structure compared to the ones grown from Ni and Co where curled and even some helical nanotubes have been identified. Results obtained imply that the structure and size of CNTs can be determined by the selection of the catalyst.

Key words: Catalysts, chemical vapour deposition (CVD), carbon nanotubes (CNTs), scanning electron microscopy (SEM).

INTRODUCTION

The work here focused on synthesising carbon nanotubes, which are considered to be the most promising materials and anticipated to create an enormous impact on future nanotechnology. Their unique structural and electronic properties (Jacobson et al., 1997; Dekker et al., 1999) have generated huge interest for use in a wide range of potential nano devices (Tans et al., 1998; Martel et al., 1998; Soh et al., 1999).

Since the discovery of carbon nanotubes in 1991, various methods of production such as laser vaporization (Thess et al., 1996), pyrolysis (Sen et al., 1997; Terrones et al., 1997), plasma-enhanced (Ren et al., 1998; Ma et al., 1999), arc discharge (Bethune et al., 1993), and chemical vapor deposition (CVD) (Li et al., 1996; Fan et al., 1999) have been investigated. Recently, the CVD method has drawn a lot of attention because of its versatile advantages namely variety in products and hydrocarbon sources, adequacy for synthesis of high quality materials, simplicity of apparatus and mass production.

The objective of this research work was to develop the right procedures for growing nanotubes by thermal CVD. The effect of Fe, Co, and Ni catalysts on CNTs was also investigated. CNTs were grown on three different catalyst particles under the same conditions. It is predicted that the particle size of the catalyst is one of the factors determining the diameter of the CNTs produced. Despite tremendous progress on the fundamental work on the growth and structure of catalytically grown nanotubes, not much has been reported on the actual effect of catalysts on the structure and size of nanotubes produced.

METHODOLOGY

Experimental procedures

The first procedure in the synthesis of CNTs using thermal CVD involved preparing three different catalytic metal particles, iron, nickel and cobalt in nano size. A new method of preparing nano size catalytic particles to grow powder form CNTs has been developed. The catalytic metal powder was first weighed and then etched in diluted hydrofluoric acid (HF). The next step of rinsing with deionized water will remove HF solution from the residue. Once completely removed, the residue was left to dry in the oven. The residue was then mixed thoroughly in ethanol by supersonic dispersion and several drops were spread on the wafer before drying out in the oven. This technique of using ethanol droplets will ensure an even spread of catalytic particles on the substrate wafer and to prevent agglomeration from occurring. Finally, the wafer was loaded on a quartz boat and inserted into a CVD reaction tube, ready for growing CNTs.

Initially, Argon (Ar) gas was allowed to flow at the flow rate of 200 sccm into the reactor to prevent oxidation of the catalytic particles while increasing the temperature. When the reaction temperature reached 950°C, the flow of Ar gas was stopped and replaced by ammonia (NH_3) gas at the flow rate of 200 sccm for 5 h. This pretreatment with NH_3 gas prior to the synthesis process is to reduce the catalyst particles to nanometer sized particles, after the formation of nanosized catalyst particles, CNTs were grown on these etched catalytic particles in the methane (CH_4) atmosphere flowed in at 40 sccm for an hour at 950°C. When the growth of CNTs was completed and temperature was cooled down to 150°C, the quartz boat was retrieved from the reaction tube and left to cool to room temperature. The powder sample of CNTs produced was washed by diluted hydrochloric acid (HCl) solution in order to dissolve catalytic particles. The remaining sample of CNTs was washed and cleaned with deionised water and then dried in the oven. Surface analysis on CNT's grown on Fe, Co, and Ni catalyst particles was conducted using a scanning electron microscopy (SEM). SEM sample preparation involved coating the sample on conductive carbon tape with metallic film.

RESULTS AND DISCUSSION

From SEM micrographs, clear images of the tubes were chosen and their diameters were determined using surface analysis software of Carl Zeiss AxioVision 3.1. The value obtained ranges from 31 to 38 nm.

There is CNTs on grown Co particles. The values of diameter obtained are in the range of 23 to 26 nm. With CNTs grown on Ni particles, the values are slightly smaller, about 19 to 24 nm. These results are summarized in Table 1.

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Table 1. Diameter measurement of CNTs grown on Fe, Co and Ni catalysts using thermal CVD at 950°C

Catalyst type	Diameter distribution (nm)	Average diameter (nm)	structure
Fe	31-38	35	fairly straight with some curled nanotubes
Co	23-26	25	Curled nanotubes with some helical ones
Ni	19-24	21	A lot of curled nanotubes

The results indicated that CNTs grown on Fe catalyst have larger diameters compared to the ones on Co and Ni. Similar order in the size of CNTs grown catalytically on the same catalyst particles has been reported by Lee et al. (2002). This can be explained by the size effect of catalyst particles on the CNT growth. It is believed that the size of catalyst particles is in the order of Fe> Co> Ni before CNT growth. Lee et al. (2002) has also reported the highest growth rate with Ni particles because being the smallest particles, the rate of adsorption of carbon at the growth sites is faster, resulting in a faster growth rate.

It appears that the morphologies of CNTs on all catalyst particles are almost the same. However, closer inspection of the images showed a distinction between CNTs on different catalyst particles. Nanotubes grown on Fe particles seem to have fairly straight structure whereas a lot of curled ones can be observed on CNT images grown on Ni. Some helical tubes can even be identified amongst the curled ones grown on Co. Similarly shaped nanotubes have been reported by Bernaerts et al. (1995).

Detailed model on curled and helical nanotubes is given by Amelinckx et al. (1994). The growth of these nanotubes is discussed in terms of a locus of active sites around the periphery of the catalytic particle, and growth velocity vectors. In the simplest case, the locus sites is circular and the extrusion velocity is constant, producing a straight tube propagating at a constant rate as can be seen in some of the tubes grown on Fe catalyst particles. In reality, the locus active sites may not be circular, which introduces some complexity in the shape of the tubes. It has been shown that a catalytic activity, which varies around the ellipse, will produce helical growths.

CONCLUSION

In this work, the right procedures have been developed to grow carbon nanotubes catalytically in powder form using thermal CVD. The effect of suing different catalyst particles on the size and shape of CNTs has also been investigated. It was found that the particle size of the catalyst which is in the order of Fe> Co> Ni produced CNTs with diameters in the same order. The size effect of catalyst particle is concluded to be the main factor determining the diameter of CNTs grown. Structurally, CNTs grown on Fe are fairly straight whereas CNTs grown on Ni and Co reveals some curled and even helical shaped tubes.

References

Amelinckx A , Zhang X B, Bernerts D, Zhang X F, Ivanov V, Nagy J B (1994). Science 265: Pp 635.

Bernaerts D, Zhang X B, Zhang X F, Amelinckx S, Van Tendeloo G, Van Landuyt J, Ivanov V , Nagy J B (1995 Philos.mag.A. 71:Pp 605.

Bethune D S, Kiang C H, DeVries M S, Gorman G , Savoy R, Vasquez J, Beyers R (1993) *Nature 363:* pp 605.

Dekker C (1999). Phys. Today, 52:22-28.

Fan S, Chapline M G, Franklin N R, Tombler T W, Cassel A M, Dai H (1999). *Science* 283 Pp 512.

Lee C J, Kim Park J, Yu J A (2002) *Chemical Phys. Lett.,* 360 Pp 250-255.

Li W Z, Xie S S, Qain Chang B H, Zou B S, Zhou R A, Wang G (1996). *Science* 274. Pp 1701.

Ma X, Wang E G, Zhou W, Jefferson D A, Chen J, Deng S, Xu N, Yuan J (1999). *Appl. Phys. Lett.* 75:pp3105.

Martel R, Schidmtj T, Shea H R, Hertel T, Avouris P (1998). *Appl. Phys. Lett.,* 73: pp 2447-2449.

Ren Z F, Huang Z P , Xu J W, Wang J H, Bush P, Siegal M P, Provencio P N (1998). *Science* 282:Pp1105.

Sen R, Govindaraj A , Rao C N R (1997). Chem. Phys. Lett. 267: Pp 276.

Soh H, Morpugo A, Kong J, Marcus C, Quate C, Dai H (1999). *Appl. Phys. Lett., 75.*

Tans S, Verschuren A, Dekker C (1998). *Nature,* 393:Pp49-52

Terrones M , Grobert N, Olivares J, Zhang J P, Terrones H, Kordatos K W K, Hare J P, Townsend P D, Prassides A K, Cheetham A K, Kroto H W (1997). Nature 388:Pp52.

Thess A, Lees R, Nikolaev P, Dai H, Petit P, Robert J, Xu C, Lee Y H, Kim S G, Rinzler A G, Colbert D T, Scuseria G E, Tomanek D, Fisher J E, Smalley R E (1996). Science 273:Pp 483.

Yacobson B I, Smalley R E (1997). *An. Sci,* 85: Pp324-337.