The effect of the changing temperature and catalyst on the growth of Carbon Nanotubes

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We have conducted two types of experiments in order to study the growth of carbon nanotubes synthesized through the method of chemical vapor deposition (CVD) of methane (CH_4). In the first experiment, the synthesis process will use MgO supported type catalyst of $FeCl_2/(NH_4)_2MoO_4$ with mass ratio Fe:Mo of 9:1 at the temperatures of 700^oC, 800 ^oC, 850 ^oC, 900 ^oC, and 1000 ^oC. In the second experiment, MgO supported type of $FeCl_2$ alone was used as catalyst with all the other parameters remaining the same. The objective is to observe and study the temperature dependence of nanotube growth, and specifically, whether or not the temperature would affect the diameter and the quality (smoothness) of the tubes. In addition, samples from the two experiments will be compared in order to find the effect of adding Molybdenum to the catalyst, making it bimetallic, on the growth of the tube.

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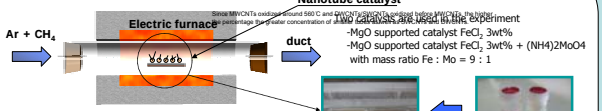
Introduction

Much research has gone into Carbon nanotubes (CNTs) in recent years. This is due to its excellent mechanical properties as well as extreme electrical and thermal conductivity resulted from its unique long, thin, cylindrical structure. These potentials allow it to be used in diversified fields such as aerospace, automobile, and construction materials applications. However, since the properties of CNTs depends greatly on its chilarity and diameter, different structure tubes are required for different applications. Furthermore, since chilarity has a closed relation to the diameter, by controlling the diameter we are able to control the chilarity of CNTs as well. Therefore methods of controlling the diameter are essentially required. In this study, we explored the effect of temperature and bimetallic catalyst on the growth of CNTs, in particular, the diameter and the quality (smoothness) of CNTs.

Experimental

Synthesis Method

Carbon Vapor Deposition (CVD)



Two catalysts are used in this experiment
-MgO supported catalyst $FeCl_2$ 3wt%
-MgO supported catalyst $FeCl_2$ 3wt% + $(NH_4)_2MoO_4$ with mass ratio Fe : Mo = 9 : 1

Synthesis conditions
Reaction Temperature : 800 C,850 C ,900 C,950 C,1000 C
Heating Period : 30 min.
Gas flow : Ar 0.3 L/min ; CH_4 300 ccm

Characterization Method

Raman Spectroscopy

Raman Spectroscopy-an analytical technique arising from the interactions of a species with electromagnetic radiation specifically to the scattering of radiation by sample.

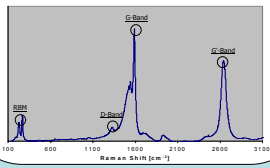
For the case of CNTs, the Raman spectrum generally appears to have 5 distinct peaks:

•**G-band** (1580~1600cm^{-1})- corresponds to the graphite-like bonds. The height of graph represents the concentration of the graphite bonds.

•**D-band** (1250~1350cm^{-1})-represents the defect of CNTs, the higher the peak is the more defected CNTs become.

•**Radial Breathing Modes (RBM)** (100~400cm^{-1})- corresponds to the radial motions of carbon atom and is proportional to the inverse diameter of CNTs.

•**G'-band** (2500~2700cm^{-1})- expected for most carbonaceous materials



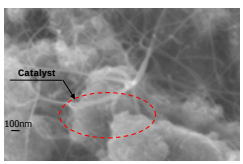
TG-Thermogavimetry

TG-measures the weight of the chosen material as a function of increasing temperature and/or time. TG is usually used both for determining the purity and rate of increasing in temperature of the chosen sample.

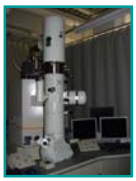
For the case of CNTs, the oxidation temperature of multi-walls nanotubes is around 560℃. The bigger the diameter and the greater the number of walls, the higher the oxidation temperature. This is due to the stability of the carbon-carbon bonds with in the CNTs structure.

SEM-Scanning electron Microscope

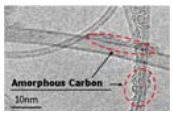
SEM-a type of microscope that can produce high-resolution images of the sample based on the use electrostatic and electromagnetic lenses to control the illumination and imaging of the specimen. Images taken by SEM have a 3-D appearance characteristic of the surface of the sample. (As shown below)



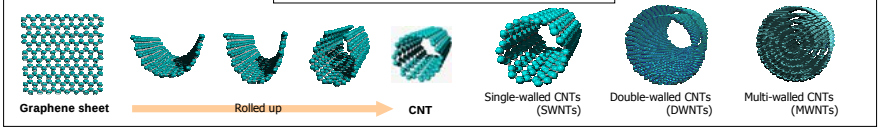
TEM-Transmission electron Microscope



TEM-another type of microscope that can produce high-resolution image is TEM. Unlike microscope pictures which take advantage of reflection of wavelengths off samples, TEM compiles images from signals of electrons traveling through the sample. This results in images produced having not the normal surface but the X-Ray-like characteristic

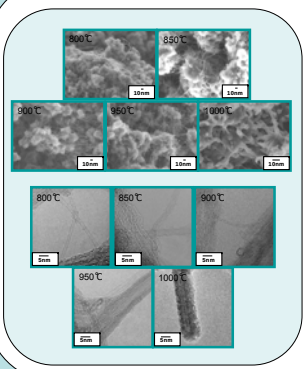


What is carbon nanotube (CNT) ?

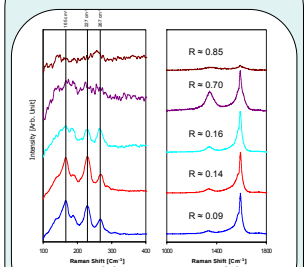


Results

MgO supported catalyst FeCl2 3wt% + (NH4)2MoO4

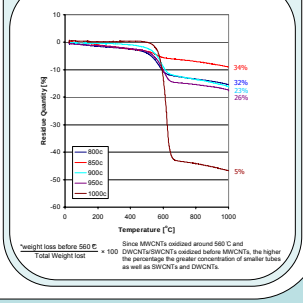


Raman Spectrum of Synthesized Samples



*R value is a way to define the quality of CNTs and is defined by equation R = Peak of D-Band/Peak of G-Band. The greater the R value the lower the quality of CNTs.

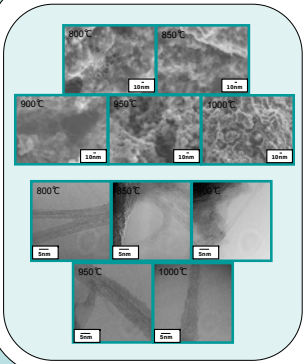
Thermal Process of Synthesized Samples



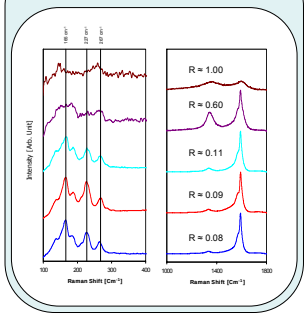
*weight loss before 560 ℃ / Total Weight lost × 100

Since MWCNTs oxidized around 560 C and DWCNTs/SWCNTs oxidized before MWCNTs, the higher the percentage the greater concentration of smaller tubes as well as SWCNTs and DWCNTs.

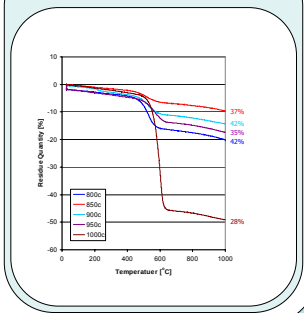
MgO supported catalyst FeCl2 3wt%



Raman Spectrum of Synthesized Samples



Thermal Process of Synthesized Samples



Conclusions

•Temperature during the synthesis process has an effect on the growth of CNTs as with higher temperature resulting CNTs to grow with more defects.
•Lower temperature favors the growth of smaller diameter CNTs as well as single and double walls CNTs.
•The effect of adding Mo to the catalyst on the growth of CNTs is undetectable.

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