

## CCVD SYNTHESIS OF CARBON NANOTUBES (CNTs) USING MgO AND CaCO<sub>3</sub> SUPPORTS

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### ABSTRACT

Carbon nanotubes or CNTs are graphene sheets that are rolled into nano-sized tubes. It has unique physical and electrical properties and has a lot of potential in research and practical applications. In this work, carbon nanotubes have been synthesized using catalytic chemical vapor deposition (CCVD) method. This method has been identified as one of the most promising methods for large-scale CNT production. The catalysts used are Fe/Co bimetallic catalysts on magnesium oxide and calcium carbonate supports. The carbon source used is the acetylene gas. The nanotubes produced by the CCVD method are then treated with nitric acid in order to remove impurities such as carbonaceous matter, catalyst particles and catalyst support. The as-produced and purified CNTs were analyzed with scanning electron microscope (SEM), field-emission SEM (FE-SEM) and energy dispersive X-ray analysis (EDAX). The analysis results show that Ca and Mg salts are able to become supports in successful CCVD synthesis with Fe/Co catalyst. It also proves that acid treatment is capable of removing the catalyst particles and catalyst support from the magnesium oxide and calcium carbonate-supported CNTs.

**Keywords:** carbon nanotubes (CNTs), CCVD, Ca and Mg salt supports, Fe/Co catalysts

### INTRODUCTION

CNTs are unique tubular structures with nanometer diameters and large length/diameter ratios (~ 1000). CNTs can be considered conceptually as a prototype one-dimensional (1D) quantum wire [1]. The fundamental building block of carbon nanotubes is the very long all-carbon cylindrical single-walled carbon nanotubes (SWNTs), one atom in wall thickness and tens of atoms around the circumference (typical diameter ~ 1.4 nm). A single-walled carbon nanotube can be described as a graphene sheet rolled into a seamless hollow cylindrical shape with a high degree of molecular perfection. A multi-walled carbon nanotube

consists of concentric cylinders with an interlayer spacing of 34 nm and a diameter of typically 10 – 20 nm. Since its discovery and successful synthesis by Iijima in 1991 [2], CNTs has been the focus of a virtual storm of research, both to better understand its unique properties and to harness its potential in commercial applications such as hydrogen storage, atomic force microscope probe, microelectronic transistor, electrical field emitter of flat panel display and scanning tunneling microscope tip have been stimulated tremendously. High-quality and well-aligned carbon nanotubes are essential to the potential applications in the field of microelectronic industries.

CCVD synthesis is carried out by pyrolysis of hydrocarbons using metal catalysts supported on inert materials with high surface area such as zeolites and aluminum oxide. This is potentially the most practical and cost-effective way of synthesizing CNTs on a large scale. However, this approach has a few drawbacks, namely the purity of the CNTs is quite low and the supports are quite difficult to remove due to its chemically stable nature. Therefore, suitable methods for purification of the as-synthesized CNTs have been researched [3-5]. This includes attempts to synthesize CNTs using supports that are more easily removed yet still retain a high surface area, such as Ca and Mg salts [6]. The present work involves the application of MgO and CaCO<sub>3</sub> salts as supports in a CCVD synthesis of CNTs with iron-cobalt catalysts, and the effectiveness of a simple acid-wash purification of its resulting CNTs.

## EXPERIMENTAL DETAILS

There are several steps involved in obtaining the desired CNT samples and analyzing them. The first step is the preparation of supported catalysts that will be used in the CCVD system. The second step is the synthesis of CNTs using the prepared catalysts in the custom-built CCVD system. The third step is purification of the CNT samples by acid washing and the last step is analyzing all the samples obtained (as-produced samples, purified samples).

### *Preparation of supported catalysts*

The MgO and CaCO<sub>3</sub> supports were dried in an oven at a temperature 110 °C for 24 hours. The acetate salts of Fe and Co were measured and used in the amount needed to achieve the desired weight ratio between the metals and the support and then dissolved in distilled water. When the support was mixed with the salts solution, a paste that absorbed the solution completely was formed. This paste was then dried in an oven at a temperature of 110 °C for 24 hours to remove all the water molecules. The resulting material was a dry, crusty paste which was ground

into powder with a mortar and pestle. Finally, the dried catalyst powder was put into waterproof and airtight sample bottle.

#### *Synthesis of CNTs*

In this work, carbon nanotubes were synthesized in a custom-built CCVD system, which incorporates a horizontal tube reactor furnace system. The supported catalysts were placed in a ceramic boat located in the middle of a reactor tube. The tube was then placed in the tube furnace in such a way that the boat containing the catalysts would be in the center of the heating element tube. Acetylene ( $C_2H_2$ ) and nitrogen ( $N_2$ ) were introduced into the tube reactor at a pre-determined flow rate. The  $N_2$  acts as a carrier gas for the carbon source gas  $C_2H_2$  and provides the inert condition for the system. The reaction was initiated at ambient pressure and temperature. The carrier gas was flowed into the system for about 15 minutes prior to heating to ensure that air was completely purged from the system. Then, the furnace was then heated up gradually until it reached the preset reaction temperature of 700 °C. Once this temperature was reached, the carbon source was flowed into the system to initiate the carbon deposition process. The reaction was continued for 30 minutes and then was cooled back gradually to room temperature. The carbon source gas flow was also stopped after 30 minutes. Once the system had reached ambient temperature, the carrier gas flow was stopped and the ceramic boat containing the carbon deposit was taken out of the reactor tube for analysis.

#### *Acid washing of CNTs*

In order to determine the viability of MgO and  $CaCO_3$  as supports in the production of CNTs that can be purified with acids, a simple acid washing was done to the CNT samples. The samples were immersed completely in a 5M nitric acid solution for 2 hours. Then, the samples were filtered out of the solution and dried for 24 hours. After the samples were completely dried, they were stored in a waterproof, airtight sample bottle.

#### *Characterization of CNTs*

Characterization of the samples obtained is important to ensure that meaningful data can be extracted from the experiments. In this work, the important information to be obtained is the effectiveness of MgO and  $CaCO_3$  as supports in CNT synthesis and the effectiveness of nitric acid in removing the metal and supports. Therefore, the characterization techniques chosen for this work are SEM (for confirming the existence of CNTs in the carbon deposits), EDAX (for analyzing the elemental composition of the samples) and FE-SEM (for the analysis of CNT morphology in greater magnification). From SEM and FE-SEM micrographs, the

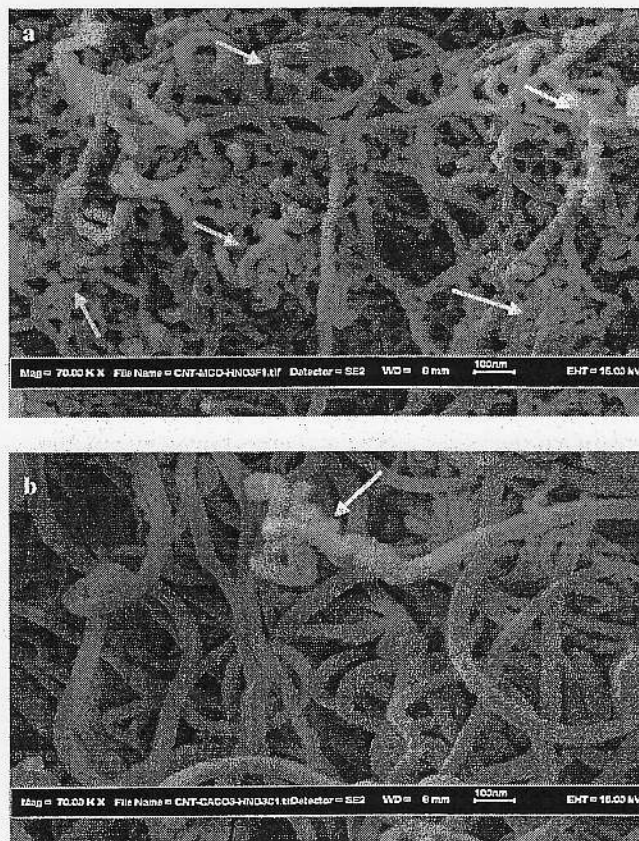
tubes and catalyst particles can be seen clearly at the appropriate magnification. Any surface defects can also be detected using this analysis. Since the EDAX analysis is done with the same instrument as the SEM microscope, it can be done at the same time as the SEM analysis. To initiate the EDAX analysis, different software was used on the computer interface. The software used for EDAX on SEM is the EDAX Control and for the FE-SEM is the INCA Material Analysis. The data obtained is the elemental species present on the surface of the sample, and presented in graph and table forms.

## RESULTS AND DISCUSSIONS

The main aim of this work is to determine whether the CNT synthesis is successful using the selected supports ( $\text{CaCO}_3$  and  $\text{MgO}$ ), and to gauge the effectiveness of the acid washing to remove the metal catalyst and supports. To that end, analysis result from SEM and EDAX will prove useful.

### *SEM analysis*

Figure 1 show the SEM micrographs of samples after acid washing. These micrographs indicate that there are indeed CNTs deposited on the surface. The CNTs produced with Fe/Co-MgO catalyst (Figure 1a) shows CNTs produced are of similar lengths, diameter and density, with bundling occurring in several locations. The bundles are believed to occur because of the van der Waals interaction between the walls of the nanotubes [7]. The growth of CNTs on the support was prolific, with large bundles of CNTs growing out of support granules and smaller group of CNTs growing from other surfaces of the support. The diameters of the CNTs are also quite small, ranging between 15 to 20 nm. Upon closer inspection, the outer walls of the nanotubes are found to be covered with bumps emanating from inside the tubes, as indicated by the arrows. This is caused by the carbonaceous matter that forms as a by-product of acid treatment [8]. The CNTs from Fe/Co- $\text{CaCO}_3$  catalyst, on the other hand, shows long and uniformly sized tubes in great density, covering most of the surface. The micrograph of the sample in Figure 1b reveals that the same bumps that are observed in the other treated CNTs are also evident here, but in fewer quantities than others. This indicates a higher purity of CNTs. With more refining of the purification technique, a highly pure CNT sample can be isolated. The diameter of the tubes is estimated to be around 20 to 30 nm. These results show that  $\text{MgO}$  and  $\text{CaCO}_3$  are suitable supports for CNT synthesis.



**Figure 1:** FE-SEM micrograph of CNTs produced by CCVD on Fe/Co supported on: (a) MgO; (b) CaCO<sub>3</sub>. Arrows indicate bumps on CNTs

#### *EDAX analysis*

Table I shows the elemental composition of CNTs for all supports before and after the acid treatment, which are obtained via EDAX. As can be seen from the table, the treatment with acid managed to remove almost all of the Fe and Co particles in the CNTs. Moreover, the acid treatment was able to remove almost all of the CaCO<sub>3</sub> and MgO supports from the CNTs. This proves that a significant amount of impurities (in the form of metal catalysts and MgO/CaCO<sub>3</sub> supports) can be removed easily with a simple acid wash method.

**Table 1:** Elemental composition of CNTs before and after acid treatment

Sample	Elemental composition (wt %)								
	C	Si	Al	Mg	Ca	O	Fe	Co	Others*
Fe/Co-MgO CNTs BEFORE acid wash	44.05	-	-	24.52	-	18.72	6.65	6.05	-
Fe/Co-MgO CNTs AFTER acid wash	66.69	-	-	7.06	-	26.25	-	-	-
Fe/Co-CaCO <sub>3</sub> CNTs BEFORE acid wash	27.56	-	-	-	40.97	29.21	0.51	1.75	-
Fe/Co-CaCO <sub>3</sub> CNTs AFTER acid wash	88.93	-	-	-	10.26	0.81	-	-	-

### CONCLUSIONS

This work has demonstrated the feasibility of using MgO and CaCO<sub>3</sub> as supports in large-scale CCVD synthesis of CNTs and its advantage in the purification of CNTs. Both supports influence the CNTs properties in slightly different ways, with MgO-based CNTs smaller in diameter but with bumpy walls, and CaCO<sub>3</sub>-based CNTs slightly larger in diameter but with smoother walls. However, both supports gives CNTs which are smaller in diameter compared with other supports used previously. They are also vastly easier to remove from the CNT samples. This can pave a way to a simple, cost-effective purification of as produced CNTs which should prove invaluable in any attempts of CNTs mass-production in the future.

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