A NOVEL TECHNIQUE FOR PURIFICATION AND SEGREGATION OF CNTS FOR NANO-SCALE THIN FILM STUDIES

Dr. Tulin Mangir, Juan Chaves, Sindy Chaves.
California State University Long Beach
Long Beach, California, 90840-8303
{temangir@csulb.edu,jchaves@csulb.edu}

Abstract:

Since Carbon Nanotubes (CNT) were discovered in the early 90's a whole new research field have evolved. CNTs have many properties that make them desirable for nano-scale electronics. One area that is receiving increasing attention is the nano-scale thin films. Recently, graphene has been suggested as a thin film candidate for nano-electronics. Our work is focusing on other techniques to realize thin films of CNTs using bacteria.
In this work we describe a technique to purify and segregate CNTs from the iron impurities to use the CNTs for thin films. After much research into a proper and repeatable cleaning process we have developed a new method of using bacteria to remove impurities from CNT's. Our methods specifically apply to CNTs obtained by the use of HiPCo method of manufacturing the CNTs. However, we think the method can be extended to other cases.
We expect this approach will lead to finding novel conductors, structures and thin films for future nano-engineered devices that could be investigated further for use in nano-scale electronics, implants and bio-materials.

Introduction:

Carbon Nano Tubes (CNTs) have many properties that make them desirable for nano-scale electronics. One area that is receiving increasing attention is the nano-scale thin films. Developing new approaches for thin film fabrication techniques is an indispensable part of electronics and material sciences. The use of CNT as core material open a whole new dimension in the field of computing and technology that will lead to terahertz and higher speeds in future computers. Recently, graphene has been suggested as a thin film candidate for nano-electronics. Our work is focusing on other techniques to realize thin films of CNTs using bacteria.

***This work is supported by an ARO Research Grant #W911NF0510497.**

In this work we describe a technique to purify and segregate CNTs from the iron impurities to be used for thin films
Our observations have implications in both bio and nano materials. In the bio field our observations may suggest a way to stop further cell division of unwanted cells. On the nano material side we have a way of depositing purified CNT films [1].
Our planned research in this area includes the study of properties of the films for nanostructure applications and electronic fabrication of nanostructures.
We now describe a set of experiments for depositing films of CNTs on Si and other substrates.

NSTI-Nanotech 2007, www.nsti.org, ISBN 1420061828 Vol. 1, 2007

Experiment 1:

The Single Walled Carbon Nano Tubes (SWCNT) used in this research were obtained from Carbon Nanotechnologies Inc. (HiPCo SWCNT's). This material is synthesized by chemical vapor deposition from carbon mono-oxide using iron as a catalyst.

One of the techniques that was originally used for the production of thin films was through the Langmuir-Blodgett (LB) process. In this process pure SWCNT are dispersed in a chloroform solution of SWCNT and then spread on a surface of purified water. Then using either horizontal lifting or vertical dipping the LB film is transfered to a substrate for the electrical analysis [2]. Hence, one of the biggest problems was the purification of the SWCNT's from the iron contamination, deposited at the time of production, in order to use the material for the creation of thin films for electronic applications.

The first technique use to clean the CNT's was thru a chemical process, were the material was oxidized in wet air at 350° C for 12 h. After the furnace CNT's were stirred in a high concentration (35%) of Hydrochloric Acid (HCl) and centrifuged for 10 min. After the centrifugation the HCl was removed and the CNT's were washed with purified water, methanol, and ethyl ether and then dried [3].

Once the chemical process was finished a solid mass (rock like) of CNT's was left making virtually impossible to obtain individual SWCNT to work in the manufacturing process of thin films.

Experiment 2:

The second process investigated to remove the Fe contaminants from the CNT's was using a regular household microwave. This particular method was developed by the University of Trieste in Italy in the department of Pharmaceutical Sciences [4]. In this particular process microwaves penetrate the carbon cocoon in which the Fe is encapsulated. The microwaves and the oxygen present in the chamber accelerate the process of oxidation making the FeO_3 break the carbon cocoon and emerged to the surface. After the process the FeO_3 was removed thru a rinse process with purified water and methanol. After the process about 60% to 75% of the original 50mg of material was lost. A further analysis using Raman Spectroscopy show the amount of minerals lost in the purification process (see table 1).

This process of microwave purification was very cost effective and simple. However, it damaged any usable SWCNTs after the process due to violent nature of the oxidation and rupture of the Fe from the carbon cocoon. During the microwave cycle of 5 sec. the material actually explodes inside the microwave chamber affecting good SWCNT's.

	Ti	**Fe**	**Sr**	**Ba**	**Pr**
CNT Raw	3048	68347	291	8376	47
CNT Purified	1226	36681	91	44	26
Percentage Loss	60%	46%	69%	99%	45%

Table 1: Main elements percentage loss after microwave purification process (data given in particles per mg out of 12mg).

After the experiment deeper consideration was taken in using this process for purification.

Experiment 3:

Since the main purpose of our research is to create thin films for use in electronic applications we needed to find a simple way to purified CNT from the iron contaminants. Hence, we needed to have a more passive process for the purification that will prevent damage in SWCNTs to be used for creation of the thin films. That was why the use of a biological agent was so appealing to use for the purification process. After some research we found that one particular bacteria (Pseudomonas Aeuginosa) had the right characteristics for the cleaning task without affecting the condition of the CNTs, but eliminating some of the minerals in the process [5].
First about 5 to 10 mg of raw CNTs are mixed with an iron deficient nutrient for the pseudomonas. After incubating the pseudomonas for three days the bacteria is removed from the incubator and autoclaved to kill the agent. Once the bacteria are killed the sample is then cleaned with a rinse process of purified water and centrifuged to separate the biological mater from the CNT's. After the rinse the CNTs are analyzed under the SEM for characterization. Once the material is verified the CNTs then are suspended in a chloroform and water solution for the LB process to create the thin films.

Results:

The results obtained in this work are still preliminary. This is an ongoing research and what is shown in this work are recent findings of this purification method. The preliminary image results show some interesting characteristics of the process. In figure 1 we observed the interaction between the bacteria and the CNTs in raw state.

Figure 1: Pseudomonas and raw CNT material.

In this particular picture a red tint can be observed due to breaking of the Iron from the CNTs. It can also be observed the pseudomonas cluster around the area. Furthermore, in the next picture we tint the pseudomonas with a blue die and then we observed the same phenomenon of the red tint around the CNTs.

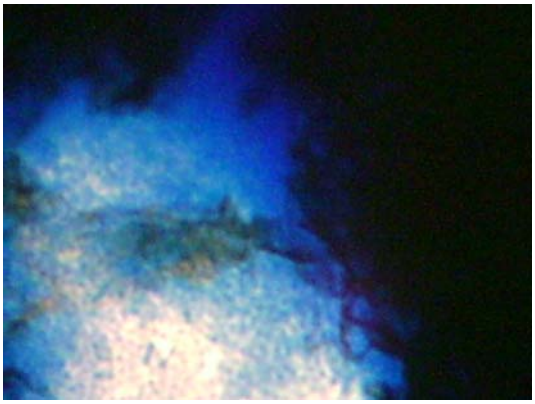

Figure 2: Pseudomonas in blue die.

The next set of figures show SEM images of samples taken from the previous images. The samples were coated with gold in order to preserve the biological part of the specimen.

NSTI-Nanotech 2007, www.nsti.org, ISBN 1420061828 Vol. 1, 2007

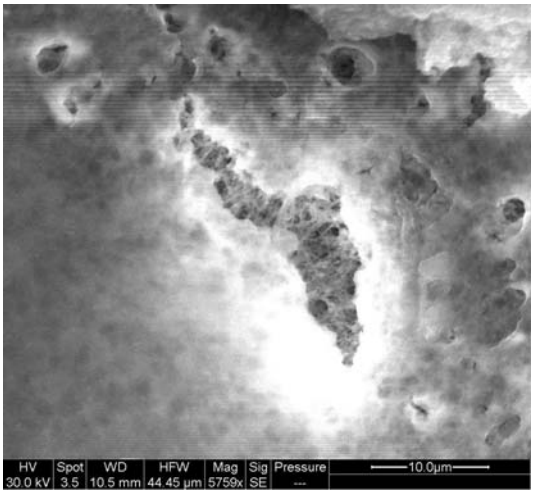

Figure 3: SEM image of pseudomonad after ingesting CNT's

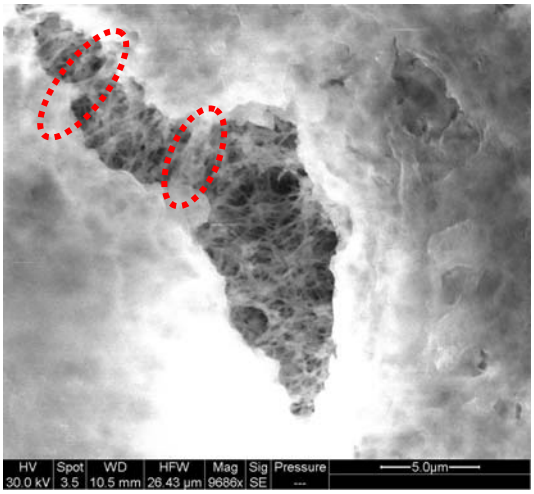

Figure 4: SEM image of pseudomonad after CNT ingestion.

In figure 3 pseudomonas, after ingesting raw CNTs, can be observed. This picture was taken after filtering the bacteria. In the SEM figure the bacteria changes its shape due to the CNTs now inside, leaving a thin shell supported only by the CNTs forming a film inside of it. Since one of the nutrients of Pseudomonas is iron, the bacteria started to look for the only supply of food available in its environment, the CNTs, which contain iron particles. Since the pseudomonas has iron receptors, those absorbed the CNT's in order to extract the iron from them.

In figure 4, how the mitosis of the bacteria is stopped can be observed. This is caused by the amount of CNT ingested for the bacteria interfering in the cytokinesis process of the bacterial division. In the red circles how the division was blocked because of CNT can be observed. Hence, the implications in the bio realm may suggest a way to further stop cell division of unwanted cells.

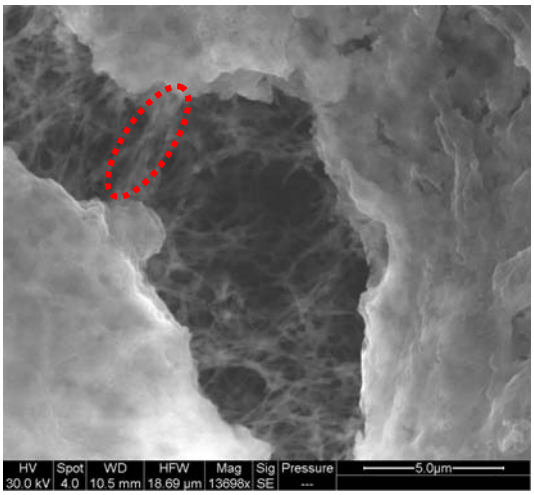

Figure 5: A closer look of block cell division

A closer look of the bacteria shell in figure 5 reveals the amount of CNT inside the bacteria and the blockage of the cytokinesis process for the CNT. As stated before this was a surprising finding of this approach creating thin films. Another issue is the fact of manipulation of the bacteria shell containing the thin film inside. This will be another part of the manipulation of the bacteria shell for handling of the CNT thin film created inside the bacteria.

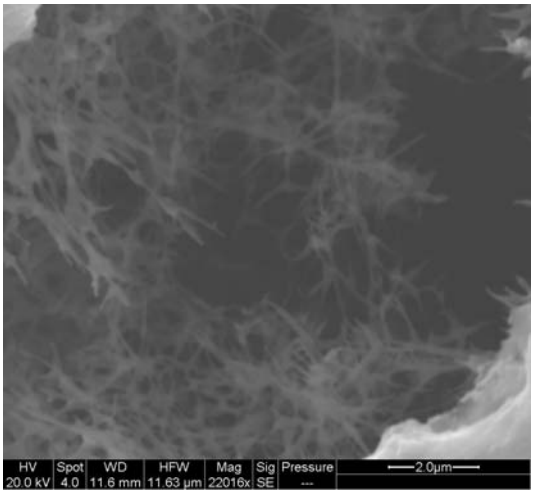

Figure 6: Closer look of CNT's inside the bacteria

In figure 6 we observed a much closer view of the CNT filaments inside the bacteria. Most of them are bundles of SWCNT probably cluster after the time of "ingestion" or absorption.

Conclusion:

As mentioned before, this is an ongoing research. As of today we are still resolving handling issues for the thin film creation. Although, our preliminary findings show great promise in the purification process of CNTs without damaging the structures and keeping the conducting characteristics that are necessary for the successful creation of thin films for electronics use [6]. The "passive" purification process also shows great promise not only in the electronics area but also the biological area. Hence, further testing is required and ongoing in order to perfect the process and use of the resulting material.

References:

[1] Minh Phuc Nguyen Dao. 2005. ***Suspended Langmuir-Blodgett Film for Surround* Gate Transistors. NNIN**: 26-27.

[2] KIM Yeji, et Al., 2003. **Langmuir-Blodgett films of single-wall carbon nanotubes: Layer-by-layer deposition and in-plane orientation of tubes**. *Japanese Journal ofApplied Physics* 42, no. 12 [December 10, 2003]: 7629-7634.

[3] Cheol-Min Yang, et Al. 2002. **Effect of Purification on Pore Structure of HiPco Single-Walled Carbon Nanotube Aggregates**. *Nano Letters* 2, no. 4 [March 7th, 2002]: 385-388.

[4] Ester Vázquez, Vasilios Georgakilas, and Maurizio Prato. 2002. **Microwave-assisted purification of HIPCO carbon nanotubes**. *Chemical Communications*, no. 20: 2308-2309.

[5] GREG SOMERVILLE, CAROLE ANN MIKORYAK, LARRY REITZER. February 1999. **Physiological Characterization of *Pseudomonas aeruginosa* during Exotoxin a Synthesis: Glutamate, Iron Limitation, and Aconitase Activity**. *JOURNAL OF BACTERIOLOGY* 181, no. 4: 1072-1078.

[6] Tae-Jin Park, Sarbajit Banerjee, Tirandai Hemraj-Bennya, and Stanislaus S. Wong. 2005. **Purification strategies and purity visualization techniques for single-walled carbon nanotubes**. *Journal of Materials Chemistry*, no. 16 [August 30th, 2005]: 141-154.