To study the cost effective production of Multi-walled Carbon Nanotubes (MWCNTs) through Electric Arc Discharge (EAD) method and their purification

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Abstract---Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology encompassing electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials. In this research the MWCNTs were produced using Electric Arc Discharge (EAD) method. Graphite electrodes of high purity were sublimated in gaseous and liquid mediums by arcing at very high current but low voltage. The obtained yield contained lots of impurities which need to be removed. The as-prepared samples were processed through physical route in which the samples were heat treated at high temperature and chemical route in which samples were treated with a mixture of acids to get a purified product. The purified CNTs were then characterized using SEM and XRD techniques.

Keywords: Carbon Nanotubes, Electric Arc Discharge, Graphite electrodes, SEM, XRD

I. INTRODUCTION

Nanotubes were first observed by Iijima in 1991 in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100 A that was intended to produce fullerenes [1]. However the first macroscopic production of carbon nanotubes was made in 1992 by two researchers at NEC's Fundamental Research Laboratory [2].

These Nanotubes are members of the “fullerene” structural family and their name is derived from “graphene” which are long, hollow structure with the walls formed by one-atom-thick sheets of carbon. These sheets are rolled at specific and discrete ("chiral") angles. Nanotubes are categorized as single-walled nanotubes (SWNTs) having close to 1 nm diameter and multi-walled nanotubes (MWNTs) having several nm diameter.

There are 3 major processes for the production of CNTs:

- Arc Discharge
- Laser Ablation
- Chemical Vapor Deposition

The yield for arc discharge method is up to 30% by weight and it produces both single- and multi-walled nanotubes with lengths of up to 50 micrometers with few structural defects [3]. The laser ablation method yields around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature. However, it is more expensive than either arc discharge or chemical vapor deposition [3]. CVD is the most widely used method for the production of carbon nanotubes [4].

The MWCNTs that are produced have high impurity content and thus need to be purified. There are 2 routes for the CNT purification:

- Physical route
- Chemical route

In the physical route, the MWCNTs undergo heat treatment at high temperature for a certain amount of time. In the chemical route, the MWCNTs are treated with a mixture of acids. In both the cases the purification criteria is that the MWCNTs are relatively inert and non-reactive as compared to the impurities.

II. (A)EXPERIMENTATION

The experimentation was divided into two categories (i) gaseous and (ii) liquid medium

A. *Gaseous Medium:*

For the gaseous medium, Button Furnace setup (shown in the figure below) was used for the experimentation.

Figure 1 Button Furnace Setup for gas medium experimentation

The CNTs were produced using the electric arc discharge method in the gas medium using button furnace. Two graphite electrodes having diameter of 6mm and 12mm were chosen for the arcing process. One rod was taken as the cathode and the other rod acted as the anode. A high current of 70 Amps was passed through the rods with a low voltage value of 25 Volts in a vacuum environment. At such a high current value the rods sublimate together.

The two electrodes were manually brought into contact with each other to allow the current to flow through and then they were manually retracted to terminate the operation. Under these experimental conditions the anode sublimated onto the cathode in the form of a carbonaceous deposit. The arcing time was 10-20 seconds.

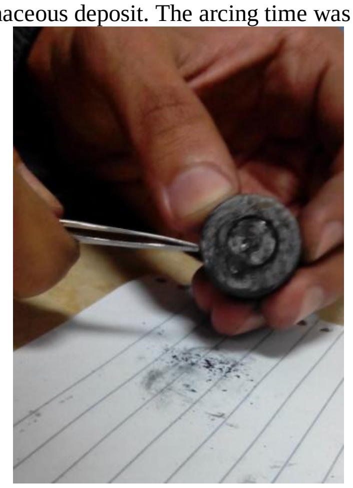


Figure 2 Graphite sample after gaseous medium arcing process

The graphite cathode was removed from the furnace and the carbon soot deposited on its surface was scraped off for characterization.

The above mentioned experiment was repeated for 50 Amps current value also.

B. Liquid Medium:

For the liquid medium, the experiment was conducted in an open beaker. The apparatus required for experimentation was:

- 5L pyrex beaker
- 5L de-ionized water
- 2 graphite electrodes having high purity
- High current, low voltage power supply (DC Welding Transformer)
- Connecting wires and clamps
- Safety goggles and gloves

The graphite electrodes were connected to the power supply using wires and clamps and were then immersed in the beaker containing the de-ionized water. A high current of 70 Amps was passed between the electrodes which again caused sublimation of one of the electrodes onto the other. The arcing time was set at 10-20 seconds.

Figure 3 Arcing in the liquid medium

The above mentioned experiment was repeated at a current value of 50 Amps.

Figure 4 As prepared MWCNTs

III. (B) PURIFICATION:

The as-prepared soot produced in the liquid medium was purified for characterization. Soot contains the CNTs (in small quantities) along with a lot of impurities like amorphous carbon and other nano-based structures which need to be reduced or removed from the soot inorder to get purified CNTs. After purification the soot has a significant weight loss because of the impurities being reduced and finally we are left with CNTs.

Both chemical and physical route were followed for the CNT purification.

The soot that was produced in the liquid medium was first of all centrifuged in-order to separate the soot material from the liquid medium.

After separation the soot was heated and dried at 100 ^{0}C in-order to remove water and moisture.

The soot was then divided into two samples.

Sample Name	Sample 1	Sample 2
Route followed	Physical Route Purification	Chemical Route Purification
Principle of the route	Heat Treatment at high temperature	Acid Treatment
Steps involved	Heat the sample at 450^{0}C for 10 min Then, Heat the sample at 500^{0}C for 20 min.	Prepare a 1:1 solution of 98% H_2SO_4 and 65% HNO_3 Mix the sample material in the acid mixture and leave for 2 hours to stand Wash the sample with de-ionized water and

		heat at 100^{0}C to remove moisture. Mix the sample in the acid mixture again and leave for 2 hours to stand Wash the sample with de-ionized water and heat at 100^{0}C to remove moisture.

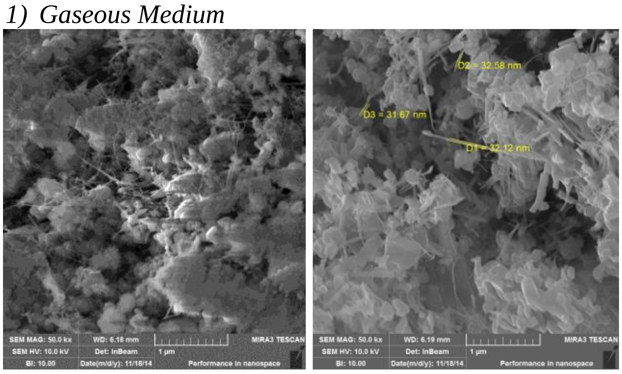
Table 1 Summary of Purification stages and steps involved

Figure 5 MWCNTs mixed in the Acid solution

IV. RESULTS ACHIEVED

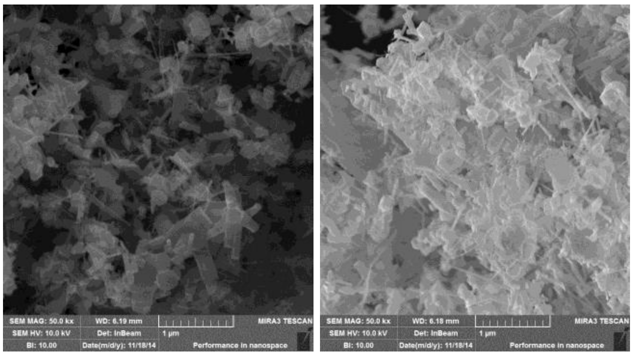
A. *Scanning Electron Microscopy (SEM) Images*

1) *Gaseous Medium*



(a) (b)

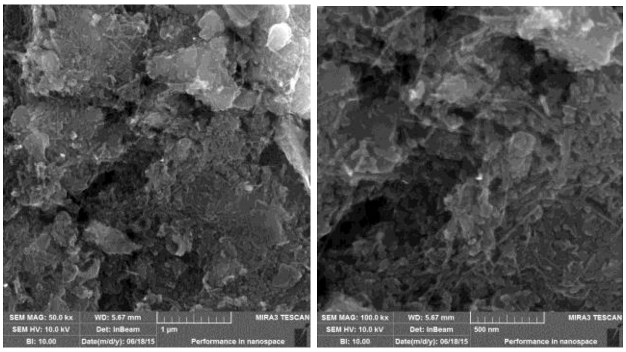
Figure 6 (a) and (b) As prepared MWCNTs without purification at 70 Amps



(a) (b)

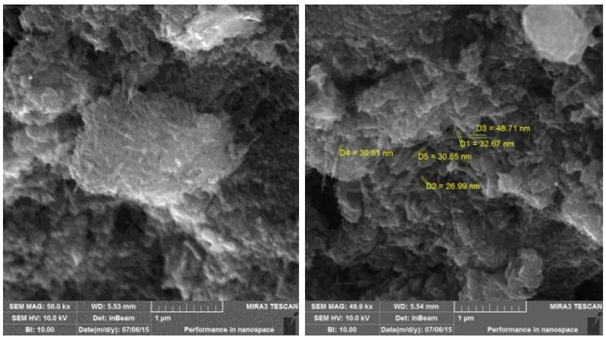
Figure 7 (a) and (b) As prepared MWCNTs without purification at 50 Amps

2) *Liquid Medium*



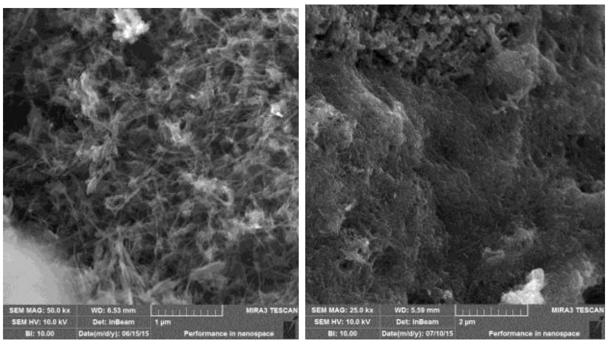
(a) 50 Amps (b) 70 Amps

Figure 8 (a) and (b) As prepared MWCNTs without purification



(a) 50 Amps (b) 70 Amps

Figure 9 (a) and (b) Physical Route purification (Heat Treatment at 500 ^{0}C)



(a) 50 Amps (b) 70 Amps

Figure 10 Chemical Route purification (Acid Treatment)

B. X – Ray Diffraction Images

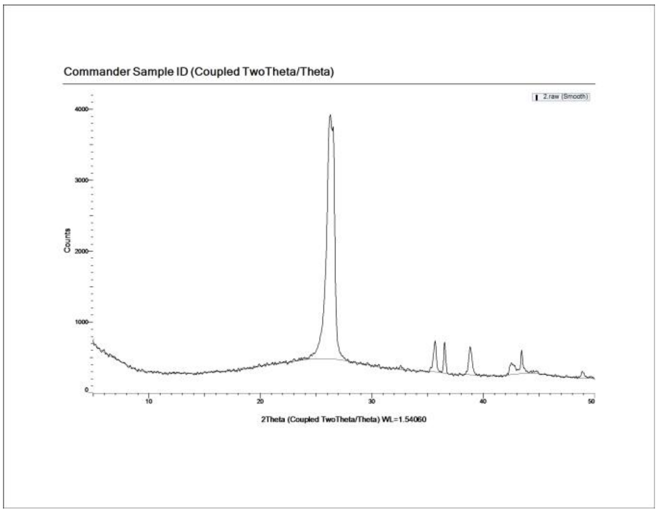


Figure 11 As prepared MWCNTs

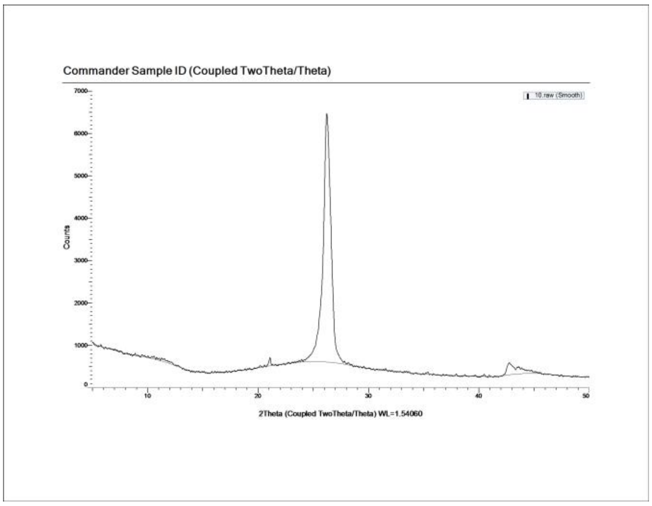


Figure 12 Chemical Route Purification (Acid Treatment)

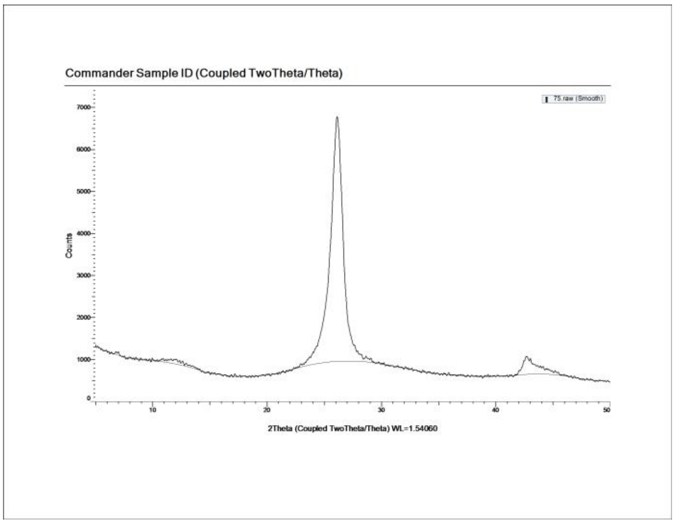


Figure 13 Physical Route Purification (Heat Treatment)

The peaks in the XRD graph confirms the presence of crystalline MWCNTs.

V. CONCLUSION

The CNTs were produced through the arc discharge method in gaseous and liquid medium. The button furnace provides a good environment for the process to take place but controlling the parameters is an issue. The electrode orientation is difficult to change due to the small area for arcing in the button furnace. If the arcing is done on a portion of the electrode where previously arcing has already been done that causes burn-out of the CNTs and produces a white surface on the electrode. Burn-out should always be avoided in the case of CNT fabrication. Once arcing has been done on a particular point on the electrode, next arcing should be done on a new point on the sample in-order to avoid the burn-out of CNTs. Another issue is the dissipation of the huge amount of heat that is produced due to the high values of currents, which is why the arcing time usually cannot be exceeded for more than 10-15 sec. Using a liquid medium for the production of CNTs using arc discharge has much better and improved results, because the arc can be maintained for a longer period of time because of the liquid medium which provides excellent heat dissipation. Liquid medium is also relatively cheap as compared to the gaseous medium.

VI. HOW IS IT COST EFFECTIVE

The electric arc discharge method in the liquid medium is more cost effective because of simple and easy use and no need for vacuum environment. In the gaseous medium, we require highly efficient button furnace which costs large amounts of money and requiring a vacuum environment adds to the cost. Whereas in the liquid medium we require power supply, a beaker, liquid water, some connecting wires and clamps along with high purity graphite electrodes. Hence liquid medium is more cost effective, time saving and relatively easy and simple to operate.

VII. FUTURE PROSPECTS

As of 2013, carbon nanotube production exceeded several thousand tons per year, used for applications in energy storage, automotive parts, boat hulls, sporting goods, water filters, thin-film electronics, coatings, actuators and electromagnetic shields.[5][6] CNT-related publications more than tripled in the prior decade, while rates of patent issuance also increased. Most output was of unorganized architecture. Organized CNT architectures such as "forests", yarns and regular sheets were produced in much smaller volumes.[5] CNTs have even been proposed as the tether for a purported space elevator.[7]Recently, several studies have highlighted the prospect of using carbon nanotubes as building blocks to fabricate three-dimensional macroscopic (>1mm in all three dimensions) all-carbon devices.

VIII. ACKNOWLEDMENTS

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