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PREPARATION AND CHARACTERIZATION OF MULTI-WALLED CARBON NANO TUBES BY LIQUID ARC-DISCHARGE METHOD

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Abstract- The paper reports the preparation and characterization of multiwall carbon nanotubes (MWCNT). The nanotubes have been synthesized by an electric arc discharge performed in deionised water using graphite electrodes. The method involves the application of a magnetic field which enhances the yield of carbon nano tubes. The carbon nanotubes (CNT) have been produced under varying conditions of voltages and currents using different refluxing media. Transmission Electron microscopy (TEM) observations reveal the morphological details of the nanotubes while Raman Spectroscopy has been performed for their structural characterization.

Keywords: A. Arc discharge; B Carbon nanotubes; C. Electron microscopy; D. Raman spectroscopy

I. INTRODUCTION

One of the major developments in the field of nanotechnology is the discovery of Carbon Nanotubes by Iijima in 1991[1]. Carbon nanotubes are members of the fullerene family (allotrope of carbon) which have long hollow cylindrical structures with the walls formed by thick layer of carbon atoms and are formed by rolling of graphene sheets. There are two types of carbon nanotubes:

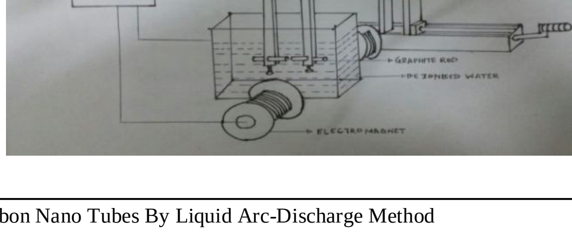
Single walled carbon nanotubes (SWCNT)-which involve single layer of graphene rolled into a cylinder. Multi walled carbon tubes (MWCNT) which consists of multilayer graphene sheets are rolled over one another in form of nested cylinders held by van der Waal forces. MWCNT are thermally more stable than SWCNT due to the increase in number of walls [2]
The extraordinary thermal, mechanical, electrical and storage properties of CNT created a gold rush amongst scholars and researchers leading to its widespread applications in various fields.

Due to the highly wettable surface area, conductivity and flexibility of CNT, they are used in supercapacitors which find attractive applications in consumer electronics and also as an alternative power source. CNT can also be used as an ultra-strong carbon-nanotube reinforced adhesive for structural applications. The new generation of solar cells utilize CNT because of their small in diameter which is easily compatible with the properties of organic solar cells. The rolling of graphene results in number of chiralities but the best semiconducting properties are obtained at a particular chirality. Their unique sizes, surface area and adsorption properties gives them application in water purifiers and cleaning filters for many industrial processes. Ceramic materials reinforced with carbon nanotubes are tougher than conventional ceramics. High aspect ratio of CNTs is very favorable for field emission. The potential applications of CNT include hydrogen storage, space elevators and artificial muscles.
There are three important methods to prepare high quality CNT, namely laser ablation, arc discharge, and chemical vapour deposition (CVD) amongst which the arc discharge method is the most cost effective. .The work deals with the preparation of MWCNT by arc discharge method and their characterisation by TEM and their structural investigation by Raman spectroscopy.

II. EXPERIMENTAL

Arc discharge method was developed by Ebbesen and Ajayan[3] at NEC Japan. The medium used in the experiment was deionised water instead of an inert gas as it reduces the amount of debris in the soot and is more economical [4].

1.1 Preparation of CNT- Two graphite rods with purity of 85.1% are taken and immersed in a glass vessel containing deionised water. Electromagnets are placed perpendicularly across both sides of the electrodes to produce a uniform magnetic field. The magnetic field provides initial Lorentz force to the ionized carbon atoms produced during the arc discharge thus providing the possibility of giving a curvature and enhancing tubular formation compared to parallel sheets.



A transformer converts the moderate voltage and moderate current electricity from the utility mains into a high current and low voltage supply. The sparking between the graphite electrodes, placed 1-2 mm apart, produces graphene, which is one atomic distance thick sheet of carbon [5]. The rolling of graphene results in the formation of carbon nano tubes which is enhanced by the use of electromagnets. The arc discharge results in the formation of soot which contains CNT and possibly amorphous carbon [6]. The soot collected is refluxed with nitric acid which oxidises the CNT and impurities. However, the damage to CNT is less than the damage to the impurities. Then, the CNT are suspended in ethanol and sonicated in order to agitate the particles. Ethanol is used since it has a high density and the CNT particles form a suspension which can be recovered easily.

2.2 Characterization-The size and morphology of as prepared CNT were observed by TEM on H7500. Raman spectra were recorded using IR550 with a laser of 500 mu and power of 40 mW.

III. RESULTS AND DISCUSSION

1.2 TEM ANALYSIS

Transmission Electron Microscopy images of the CNT prepared in these studies are shown in Figs. 1 (a, b, c, d). It's apparent that the CNT are not clearly visible in Fig.1 (a) and Fig.1 (c), which have been prepared at low discharge currents while the CNT are clearly visible in Fig.1 (b) and Fig.1 (d) which have been prepared using higher discharge currents. This is because at lower currents there is more coagulation of the amorphous carbon which overshadows the CNT

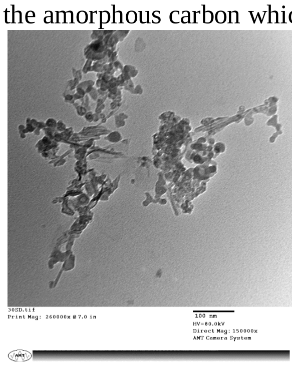


Fig. 1(a)

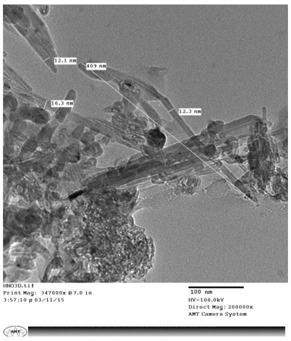


Fig. 1(b)

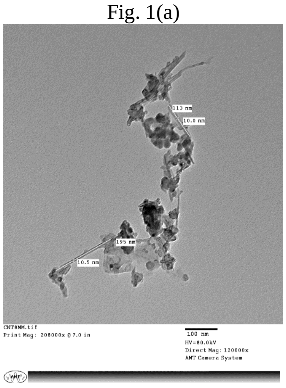


Fig. 1(c)

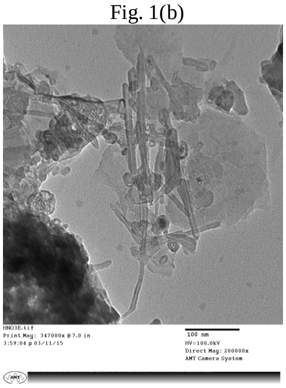


Fig. 1(d)

Fig. 1.TEM images of carbon nanotubes: (a) at 100 A and 30 V (b) at 150 A and 30 V (c) at 100 A and 40 V (d) at 150 A and 40 V

TEM images of CNT after refluxing in nitric acid and aqua regia media are presented in Fig. 2. It is seen that when CNT are refluxed in aqua regia, the CNT shrink in size and the yield is lesser. But on refluxing with nitric acid, the CNT formed are longer in length and more in amount as the coagulation in this case is lesser. This can also be attributed to the fact that nitric acid is a stronger oxidising agent which better oxidises the amorphous carbon [6].

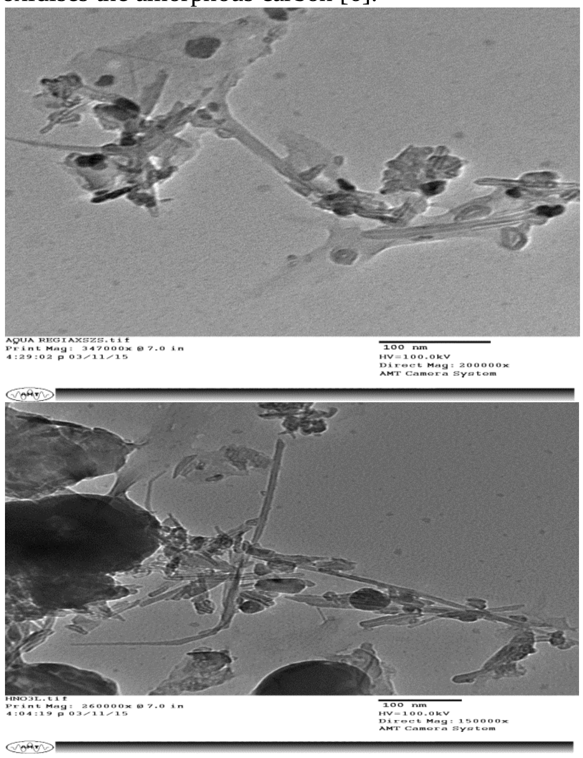


Fig. 2.TEM images of carbon nanotubes after refluxing with (a) Aqua regia (b) Nitric acid

TEM image Fig 3(b) reveals that before reflux some open tip as well as closed tip nanotubes were present but TEM image of CNT after refluxing as shown in Fig 3(a) indicates that after refluxing mainly closed tip nano tubes are obtained. This is because the oxidation of open structure of CNT is more prominent than the closed structure of CNT. [5]

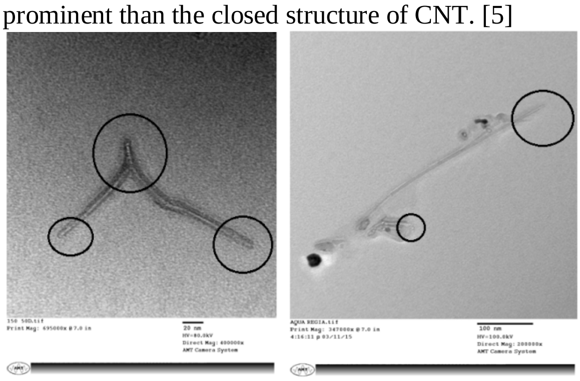


Fig 3.(a) Closed tip carbon nanotubes Fig 3.(b) Open tip cabon nanotubes

Percentage yield of CNT'S-

Table 1. The percentage yield of CNT'S under varying conditions of discharge currents and voltages

S.N O.	VOLTAGE (V)	CURRENT (A)	SOOT PRODUCED (EXPERIMENTAL)(Z)(g)	CNT PRODUCED (W)(g)	% YIELD OF CNT's
1	30	100	0.595	0.29	48.68
2	40	100	0.56	0.306	54.57
3	50	100	0.68	0.224	33.02
4	30	150	0.9441	0.3944	41.77
5	40	150	1.682	1.1727	69.72
6	50	150	1.201	0.7233	60.23
7	30	200	1.0674	0.6802	63.72

It is seen that at 100 amps discharge current, the percentage yield of CNT depends on the discharge voltage and is maximum at 40 V (54.57%). It is evident from Table.1 that the increase in discharge current results in the increase of percentage yield of CNT while the yield is optimised at a discharge voltage of 40 V.

It is also observed that at an applied voltage of 30 V, the arc is low in intensity and hardly gets ignited, so the deposited material mostly consists of amorphous carbon with very few nanotubes. Application of higher discharge voltages (40 V) produces very fine carbonaceous material dispersed in deionised water and contains considerable amount of CNT. At 40 V, the arc discharge is so intense that more carbon is lost as volatile matter; hence the amount of CNT formed is lesser.

3.2 RAMAN SPECTROSCOPY

Raman spectra (λ_{exc}=500mu) of the CNT is shown is Fig. 4. The prominent peaks of CNT under different conditions are recorded in Table 2, which correspond to the D-band and G-band.

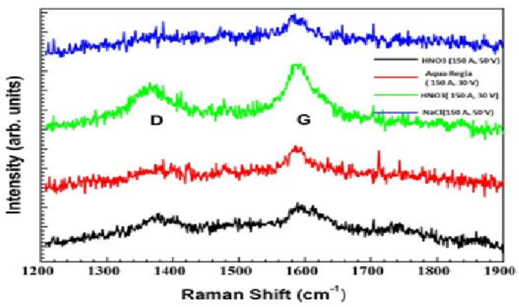


Fig.4. Raman spectroscopy of CNT

Table 2.Raman measurements of CNT

VOLTAGE (V)	MEDIUM OF PREPARATION	MEDIUM OF REFLUX	PEAK POSITION (cm^{-1}) D BAND	G BAND	RATIO (I_D/I_G)
50	NaCl	HNO3	1385.9	1585.6	1.14
50	Deionised water	HNO3	1383.5	1598.1	1.16
30	Deionised water	HNO3	1370.22	1591	1.16
30	Deionised water	Aqua Regia	1388.4	1588.6	1.14

Table 2 represents the different parameters affecting the Raman spectra of CNT.The G-band refers to planar vibrations of sp^2 carbon atoms [6]. It occurs due to the stretching of the C-C bond mainly in graphitic materials, and is common to all sp2 carbon systems. The D-band arises from a hybridized vibrational mode linked with graphene edges and indicates the existence of some disorder in its structure. This band is called the disorder band or the defect band and its intensity relative to that of the G-band is a measure of the quality of nanotubes. [7]The Raman shifts observed in the spectra are well consistent with the earlier reported results [8]. The appearance of D-band in Raman spectra indicates that the CNT have some characteristic defects due to unsaturated bonds which are produced during rolling of graphene at the time of synthesis. The peak positions of G-band and D-bands in the Raman spectra are also comparable to those reported in the literature [9]. The ratio of intensities of I_D and I_G indicates the quality and level of disorder in the graphene structure[10].

CONCLUSIONS

We have successfully prepared quality MWCNT by arc discharge method. TEM analysis shows that the internal diameter of CNT was found to vary between 2-3 nm and the external diameter between 4-10 nm..The diameter and the yield of CNT can be varied by varying the magnitude of the current and the voltage used for discharge as well as by the refluxing medium.

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