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Production of Carbon Nanotubes Using Vein Graphite

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***Abstract*—Carbon nanotubes (CNT) are produced from a rare variety of natural vein graphite (VG) distinctive to Sri Lanka using electric arc discharge. Electric arc-discharge produces both single walled and multi walled nanotubes. The products are characterized using high resolution electron microscopy and Raman spectroscopy for verification and validation.**

Keywords—CNT, vein graphite, arc discharge, SWCNT

I. Introduction

Carbon nanotubes (CNT) are long, thin cylinders of carbon, with diameters as small as 1 nm and the length ranging from a few nanometers to a few tens or hundreds of microns. A CNT may be thought of as a sheet of graphite or a hexagonal lattice of carbon, rolled into a cylinder. A CNT may have a single cylindrical wall (SWCNT), or it may have multiple walls (MWCNT), giving it the appearance of cylinders inside other cylinders [1]. A SWCNT has only a single atomic layer, whereas a MWCNT may contain, for example, from 100 to 1,000 atomic layers. SWCNTs tend to be stronger and more flexible than their multi-walled counterparts. SWCNTs are also, better electrical conductors and find uses in electrical connectors in micro devices such as integrated circuits or in semiconductor chips used in the electronics industry. Their unique structural and electronic properties make them attractive for applications in nanoelectronics [2]. Depending on their chirality SWCNTs are either metallic or semiconducting. Uses of CNTs include antennas at optical frequencies, probes for scanning probe microscopy such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), and reinforcements for polymer composites [3,4].

CNTs can be made starting from microcrystalline amorphous carbon or highly crystalline flake graphite or vein graphite. However, the end product depends on the choice of carbon type, the process followed and the conditions applied during the process [6, 7, 10]. Vein graphite, also known as crystalline vein graphite, Sri Lankan graphite, or Ceylon graphite, is a naturally occurring form of pyrolytic carbon (solid carbon deposited from a fluid phase). Vein graphite has a morphology that ranges from flake-like for fine particles, needle or acicular for medium sized particles, and grains or lumps for very coarse particles. As the name implies, this form of graphite occurs as a vein mineral. Vein graphite has the highest "degree of crystalline" perfection of all conventional graphite materials. As a result of its high degree of crystallinity, vein graphite is utilized extensively in "formed" graphite products that are used in electrical applications. Many of the highest quality electrical motor brushes and other current carrying carbons are based on formulations using vein graphite.

To the best of the knowledge of the authors, this rare form of Ceylon vein graphite has not been investigated systematically for its chemical or physical properties or for its readiness, as a precursor to synthesis of nanomaterials. It is important to gather information on high quality isolated vein graphite crystallites because nanomaterials synthesized using it may inherit properties deriving from its distinctive nature of origin. In this paper, we discuss topographical and other information gathered from CNTs produced using this largely unexplored rare form of Ceylon vein graphite. The unique process deployed in producing CNTs using Ceylon vein graphite by electric arc discharge requires no external means to cool the graphite cathode and still produces both single walled and multi walled nanotubes.

II. Material and Methodology

For DC electric arc-discharging, a conventional DC power supply working as a current source together with sufficient cable ratings was used. The arc-discharge was carried out inside a chamber which was purged and filled with argon prior to the experiments. The inert atmosphere in the chamber generated by argon avoids the possible firing and oxidation of graphite.

Figure 1 shows the block diagram of the apparatus designed, fabricated and used for the production of CNT. In producing CNTs two vein graphite rods with equal dimensions were

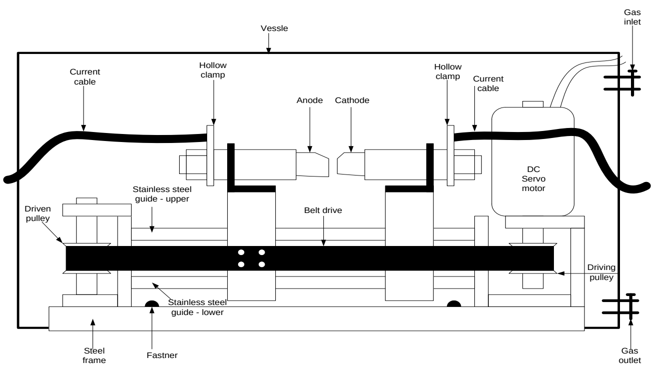

Figure 1: Block diagram of the apparatus used in the laboratory for CNT production

fixed firmly to the anode and the cathode. A linear motion, designed to bring the electrodes together to initiate the arc and then to separate, of the anode and cathode is achieved using a geared mechanism driven by a belt.

The entire system was kept inside the chamber, where there is a window to exchange the electrodes. The vessel window was then closed and the system was evacuated (the pressure inside the vessel drops to -100 mm H_2O) using a vacuum pump. The inert gas argon was pumped into the vessel after the chamber was fully evacuated until the pressure in the chamber reaches atmospheric pressure. The above process was repeated three times to make sure that no active gas remained inside the vessel.

Then, the DC power supply was switched on and the electrodes were moved from opposite directions slowly until the vein graphite pieces connected to anode and cathode touch each other.

The electric arc was initiated at this point. Once the arc was established in two to three seconds, the electrodes were moved apart by about 1 - 1.5 mm to allow the arc to grow. After about 10 s from the initial arc the gap between the graphite electrodes was further increased by 1 -2 mm, in order to allow vaporized carbon from the anode to be deposited on the cathode. Then, the electrodes were allowed to cool naturally in the same inert gas atmosphere. Once the temperature dropped to room temperature, the carbon nanotubes formed on the cathode, appeared as a dark ash coloured circle of about 5 mm diameter surrounded by a fully black coloured ring, were scraped and separated from the electrodes and purified.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were carried out using Hitachi SU 6600 scanning electron microscope. Transmission electron microscopy imaging was done using JEOL 2010F UHR TEM/STEM transmission electron microscope. The microscope was operated at 200 keV, corresponding to an electron wavelength of 0.00251 nm. Raman spectra were recorded using Bruker Vertex 80 coupled with FT- Ram module (RAM II) FTIR Spectrophotometer in a range from 30 to 1600 cm^{-1}. Calcium fluoride (CaF_2) beam splitter and RT - InGaAs detector was employed for the analysis.

III. Results and Tables

The figures 2 through 5 show SEM images and EDX results of flake and vein graphite samples extracted in Sri Lanka. The quantitative descriptions of the contents of the samples are given in Tables 1 and 2 respectively. The SEM images indicate that vein graphite and flake graphite although structurally similar, morphologically they are different.

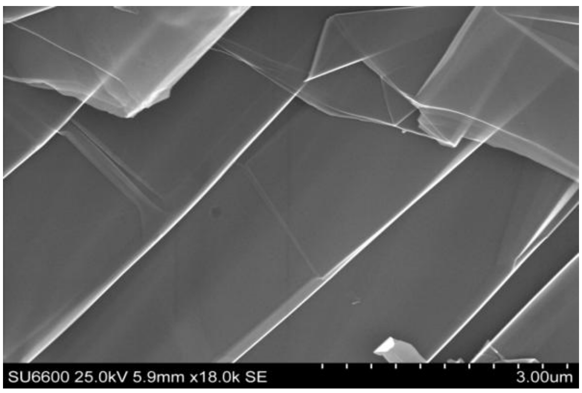

Figure 2: SEM image of flake graphite obtained from Sri Lanka

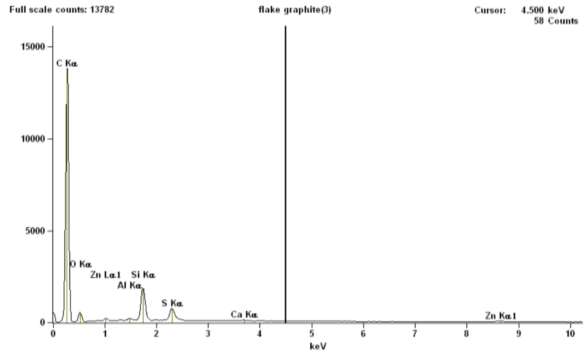

Figure 3: Energy dispersive X-ray analysis plot of flake graphite

During the arc-discharge, the carbon in the cathode undergoes a phase change from crystalline phase to amorphous phase and produce carbon nanoparticles. These carbon nanoparticles act as precursors (seeds) to the formation and growth of CNTs which comprises SWCNTs [3].

Table 1: Quantitative results for flake graphite (live time: 30 s., acceleration voltage: 25.0 kV, take off angle: 25°C)

Element	Net counts	Weight %	Atomic %
C K	82958±296	93.8	96.5
O K	971±108	2.9	2.2
Al K	671±71	0.1	0.04
Si K	15276±188	1.9	0.8
S K	7433±194	0.9	0.4
Ca K	859±69	0.1	0.04
Zn K	1062±73	0.3	0.08

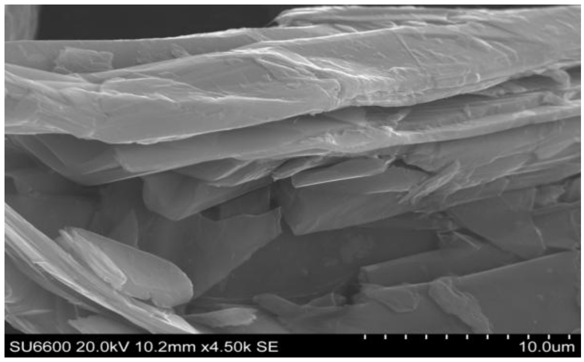

Figure 4: SEM image of vein graphite obtained from Sri Lanka used for CNT production

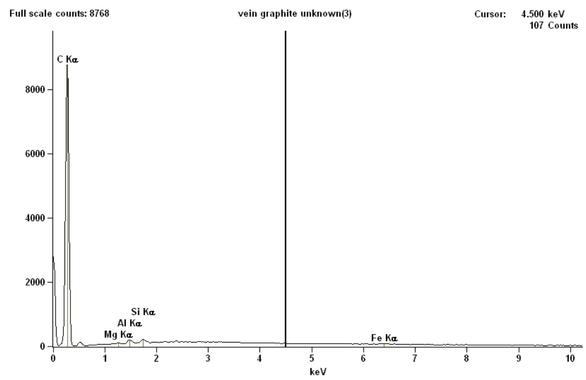

Figure 5: Energy dispersive X-ray analysis plot of vein graphite

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SEM images of the vein graphite cathode taken at intermediate stages of the process at various arc discharge times are shown in Figures 6, 7, 8 and 9.

Figure 5 shows the SEM image of the vein graphite that was attached to the cathode prior to arc discharge, and Figure 6 shows

Table 2: Quantitative results for vein graphite (live time: 30 s, acceleration voltage: 25.0 kV, take off angle: 25 °C)

Element	Net counts	Weight %	Atomic %
C K	60389±239	98.9	99.6
Mg K	368±49	0.1	0.06
Al K	1014±60	0.3	0.1
Si K	969±68	0.2	0.1
Fe K	748±84	0.5	0.14

the SEM image of the vein graphite cathode after 10 s of arc discharge time. Here the formation of carbon nano particles can clearly be seen, which at a later stage, provide the nuclei for the growth of CNT.

As seen from Figure 6 to Figure 8, it is clear that CNTs start to grow from carbon nanoparticles and continue to extend using evaporated carbon from the anode using the energy of the arc. The straight line structures seen in many places of the Figure 7 are carbon nanotubes. Still the carbon nano particles exist because the arcing time is only 25 s, which is below the optimum value. Optimum yield of CNTs was obtained when arc discharge was carried out for 30 s.

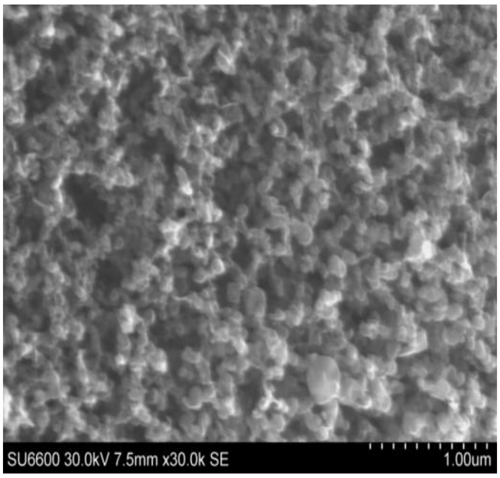

Figure 6: SEM image of vein graphite cathode after 10 s arcing at 40 A.

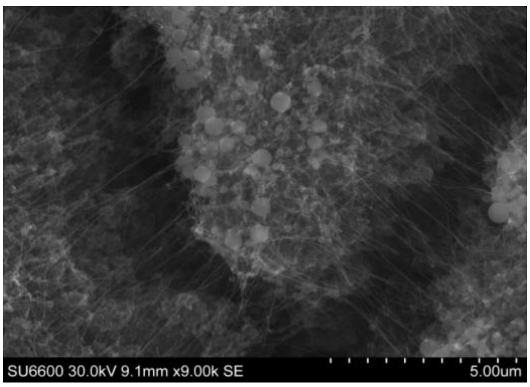

Figure 7: SEM image of the cathode cooled in inert atmosphere after 25 s of arcing.

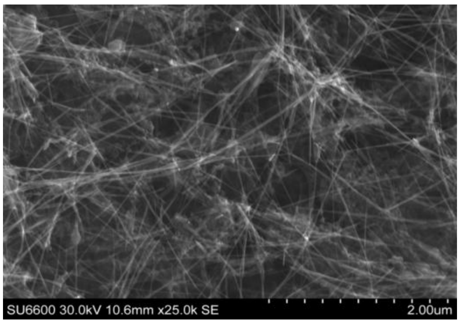

Figure 8: SEM image of the cathode cooled naturally in inert environment after 30 s of arcing.

Figure 9 shows the TEM image of arc discharged CNTs. The existence of transparent walls in TEM images is the best microscopic evidence to prove the presence of SWCNT. In the SWCNT soot, the only impurity has been amorphous carbon, which can be removed easily using physical methods. In addition, the existence of a residual breathing mode (RBM) below 500 cm^{-1} wave number is the best unique feature of SWCNT when Raman spectroscopy is carried out [23]. Figure 10 shows Raman spectroscopy results of ~~a~~ SWCNT sample produced in the above process. It clearly shows a RBM below 500 cm^{-1} which is the unique identity for SWCNT. Hence, it can be confirmed that the CNTs produced by arc discharge contains single wall carbon nanotubes. SWCNTs are produced here without the use of a catalyst. The D-band to G-band height ratio obtained in Raman spectrum is approximately 3:8.

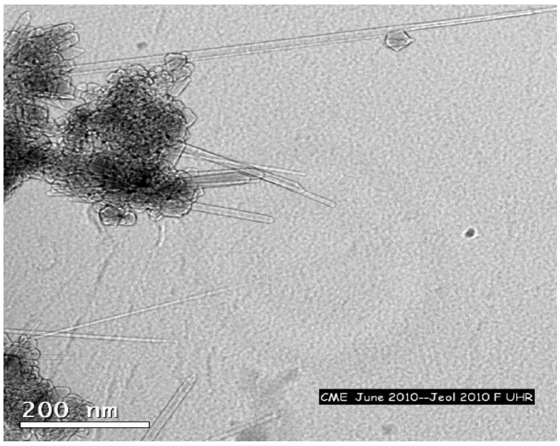

Figure 9: HRTEM image showing SWCNT produced.

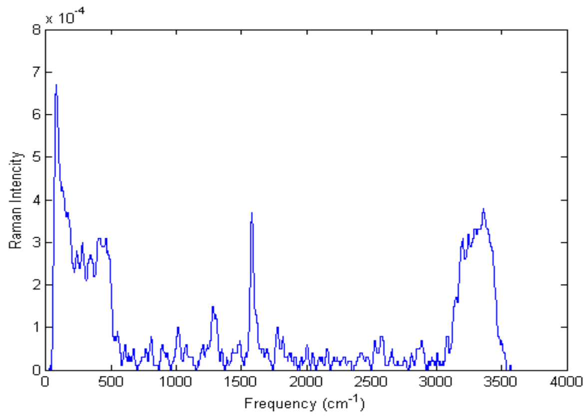

Figure 10: Raman spectroscopy results of the CNT sample

IV. Conclusion

We have succeeded in producing carbon nanotubes from a rare form of naturally occurring graphite for the first time. We also have been successful in characterizing CNTs, and observing and identifying the formation a special type of nanotubes, SWCNTs, in an arc discharge process without the use of a catalyst.

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