SRI LANKAN GRAPHITE MAKING THE SPACE ELEVATOR POSSIBLE

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Abstract: A metal catalyst free, low cost process of manufacturing carbon nanotubes (CNT) using Sri Lankan graphite as anode and cathode, in the absence of external cooling, in an inert gas atmosphere is presented in this paper. The CNT yield has been analyzed using High Resolution Transmission Electron Microscopy (HRTEM), Scanning Electron Microscopy (SEM) and Raman spectroscopy.

Keywords: Arc Discharge, Carbon Nanotubes, Graphite

1 Introduction

Graphite is one of the allotropes of carbon and it is an electrical conductor. Carbon nanotubes 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.

Vein graphite, also known as crystalline vein graphite, Sri Lankan graphite, or Ceylon graphite is a naturally occurring form of solid carbon deposited from a fluid phase, 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 graphite based products that are used mainly in the electrical applications. However, possibilities of utilizing them in the construction industry are also being looked at and one exciting opportunity is the space elevator concept discussed in "Fountains of Paradise" by Arthur C. Clarke [1].

In the recent past, several methods, such as chemical vapour deposition, arc discharge and laser ablation have been explored to produce CNTs of different characteristics. In the standard process of making carbon nanotubes using electric arc discharge method (Aternating Current or Direct Current), a controlled pressure and inert environment are maintained within the chamber [2]. The parameters such as duration of the electric arc and the discharging current are varied to produce multi walled carbon nanotubes (MWCNT) of various characteristics [3,4]. The process consists of an electric arc generator whose positive terminal is connected to the anode, which supplies the carbon source to make the nanotubes and the negative terminal is connected to the cathode on which the nanotubes are produced and deposited. In the standard arc discharge process, the anode is composed of flake graphite, either in rigid solid state or in powder state whereas the cathode contains either flake graphite or other carbon source. This process produces MWCNT while the cathode has to be modified by adding a small quantity of a transition metal such as iron, nickel or cobalt in order to result in Single Walled Carbon Nanotubes (SWCNT). In the conventional process cathode is water cooled [5,6]. This adds complexity and cost to the process. In addition, it might become necessary to modify the cathode to facilitate this cooling process. As a result, in the standard procedure the SWCNTs are always contaminated with metal particles which require subsequent purification using a chemical or a physical process. Attention must be paid to careful purification without damaging the nanotubes. However, this is a practically difficult and time consuming task.

As SWCNTs are also more expensive to make (SWCNTs cost about $ 500/g and MWCNTs cost about $ 5/g) and the economics of scale may not change until there is a large-scale market and a large scale production capability for SWCNTs. For these reasons, MWCNTs are widely used in applications such as composite materials than its SWCNT counterpart [7].

Hence, it is justified that there exists a growing need for a simple, low-cost method of manufacturing high-quality, CNTs that eliminates the need for extensive cleaning and purification of the CNT product. The objective of this paper is to describe a catalyst free low cost manufacturing process of CNTs from vein graphite using electric arc discharge method, in the absence of external cooling.

2 Experimental

2.1 Apparatus

For the purpose of DC electric arc discharging, a conventional DC power supply working as a current source together with sufficient cable ratings were used. The arcing was done inside a chamber whose interior was purged and filled with argon gas to provide an inert environment, hence to avoid possible firing and oxidation. Figure 1 shows the block diagram of the apparatus designed, fabricated and used for the production of CNT.

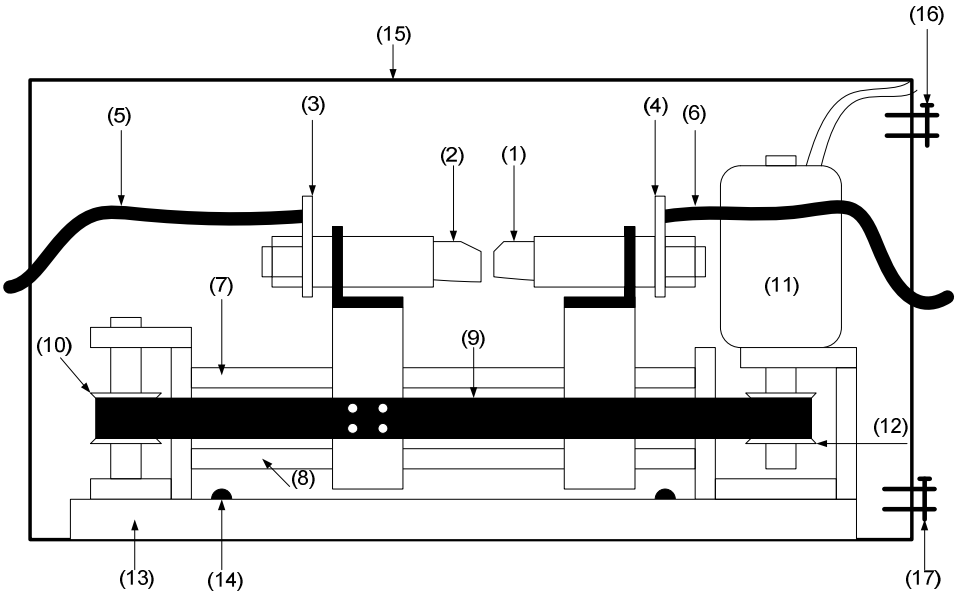

Fig. 1: Block diagram of the apparatus used in the laboratory for CNT production.

The setup shown in Figure 1 contains electrodes comprising a vein graphite cathode (1) and a vein graphite anode (2). Attached to cathode and anode are circular hollow clamps (3) and (4); and jumper cables (5) and (6). Clamp (3) is connected to the positive terminal and clamp (4) is connected to the grounding terminal of a DC arc discharge power source. This discharge power source which is not shown in the diagram can supply 400 A at 100 V. The anode assembly ((2), (3) and (5)) and cathode assembly ((1), (4) and (6)) are connected to the smooth stainless steel guides ((7) and (8)). These smooth stainless steel guides effectively provide for the cathode and anode assemblies to traverse linearly. The two assemblies are connected to a belt drive (9) which is traversed between the two pullies ((10) and (12)). A DC servo motor (11) connects the driving pully (12) and the other pully (10). The anode and cathode assemblies, their guides and the driving mechanisms are mounted securely to a steel frame (13), which is fastened (14) to the vessel (15) to avoid any undesired motion. The gas inlet valve (16) is used to supply Argon (Ar) gas to the vessel, while the outlet valve (17) is used to remove air using a vacuum pump (not shown) and to purge the vessel with argon gas.

2.2 Manufacturing process

The production process of CNT by using DC electric arc discharge method is described in steps as follows:

1. Two vein graphite pieces as received from the mine, are fixed firmly to the anode and the cathode. A linear motion, to bring the electrodes together to initiate the arc and then to separate, the anode and cathode is achieved using a geared mechanism driven by a belt. The entire system is kept inside a 315 l vessel, where there is a window to exchange the electrodes.
2. The vessel window is then closed.
3. The 315 l closed system vessel, in which the manufacturing is carried out, is purged (the pressure inside the vessel drops to -100 mmH_2O) using a vacuum pump.

4. Inert gas argon (Ar) is pumped in to the vessel until the dropped pressure reaches atmospheric pressure.
5. The above two steps are repeated three times to make sure that no active gas remains inside the vessel.
6. The DC power supply is switched on and the electrodes are moved such that the vein graphite pieces connected as anode and cathode come closer and touch each other. The electric arc is initiated at this point.
7. Once the arc is established in two to three seconds, the electrodes have to be moved apart by about 1 mm to 1.5 mm and the plasma is allowed to grow. After about 10 s from the arc initiation, the gap between the vein graphite pieces may be further increased by 1 mm to 2 mm, so that sufficient room exists for the vaporized carbon from the anode to get deposited on the vein graphite pieces of the cathode.
8. The electrodes are allowed cool naturally in the same inert gas vessel. The carbon nanotubes formed from vein graphite by the arc discharge method is allowed to cool naturally by a gradual temperature gradient towards ambient temperature. There is no rapid cooling like in other arc discharge methods. Once the temperature drops to room temperature, the carbon nanotubes formed on the cathode, which will appear as a dark ash colored circle of about 5 mm diameter surrounded by a fully black colored ring, have to be scratched and separated from the electrode.

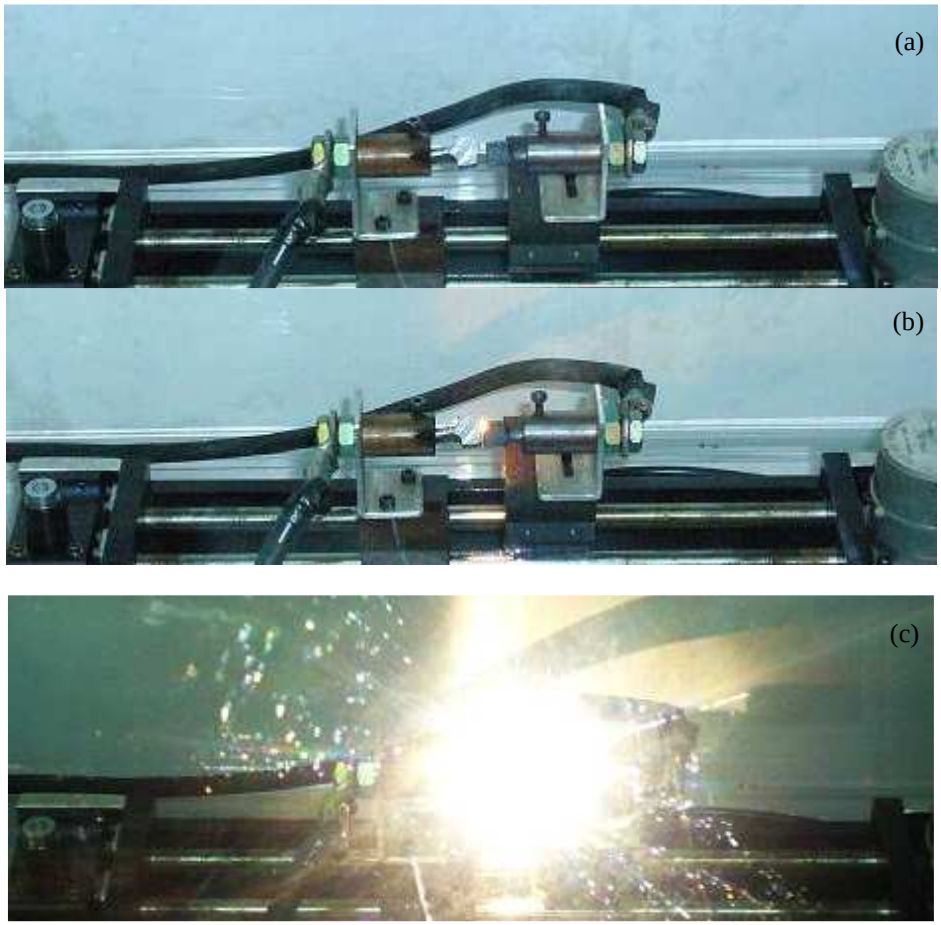

Fig. 2: CNT production by arc discharge – (a) prior to igniting, (b) arc initiation, (c) stabilized plasma.

2.3 Characterization

The particle size and the morphology of the synthesized samples were studied using a SEM, HITACHI SU6600 microscope at the Sri Lanka Institute of Nanotechnology, Sri Lanka. Further, the internal structure of the carbon nanotubes were studied using HRTEM using Jeol 2010F TEM/STEM microscope, where the microscope was operated at 200 keV, corresponding to an electron wavelength of 0.00251 nm. The objective lens had a spherical aberration coefficient of 0.47±0.01 mm and hence a resolution at optimum defocus of 0.19 nm in HRTEM. TEM samples were prepared scratching the surface of the substrate onto holey carbon-coated copper grids.

The presence of SWCNT were confirmed using Raman spectroscopy using Nd:YAG laser beam excitation Bruker, Vertex 80 spectrometer, with a laser beam wavelength 1064 nm, at the Sri Lanka Institute of Nanotechnology, Sri Lanka.

3 Results and discussion

The characteristics of the CNTs produced by the above discussed arc discharge method, were studied specifically using SEM, HRTEM and Raman spectroscopy.

Figure 3a shows a SEM image taken on an as mined raw vein graphite, where the vein structure can be observed as opposed to the structure of flake graphite as shown in the Figure 3b.

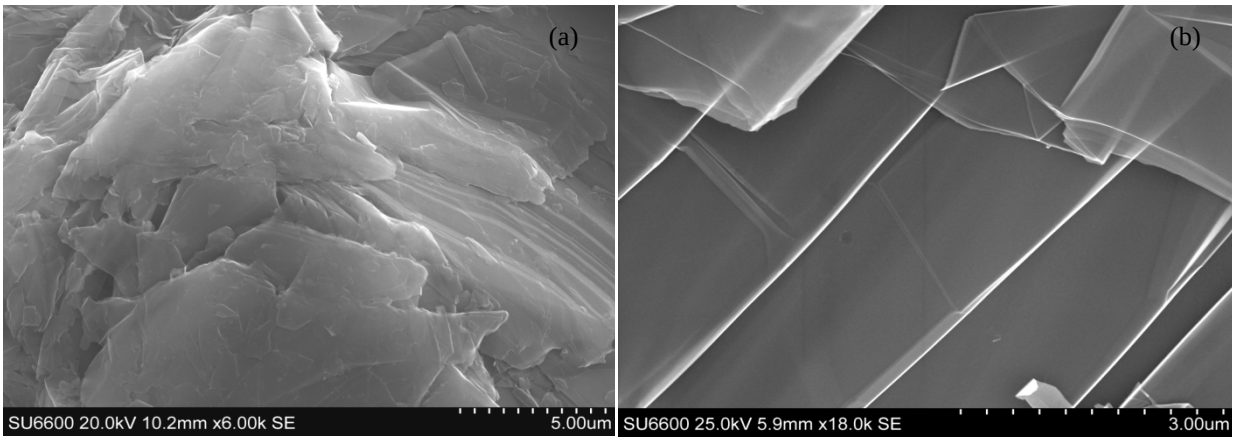

Fig. 3: SEM images of (a) – Vein graphite, (b) – Flake graphite

Figure 4 is an SEM image of an as produced CNT sample, where nests of long straight nanotubes can be observed. As evidenced by the transmission electron microscopic analysis shown in the Figure 5, the carbon soot obtained by arc discharge method contains a mixture of high quality SWCNT with uniform diameter of about 5 nm, MWCNT of with a diameter of 10 nm and carbon nano particles with an average diameter of 15 nm.

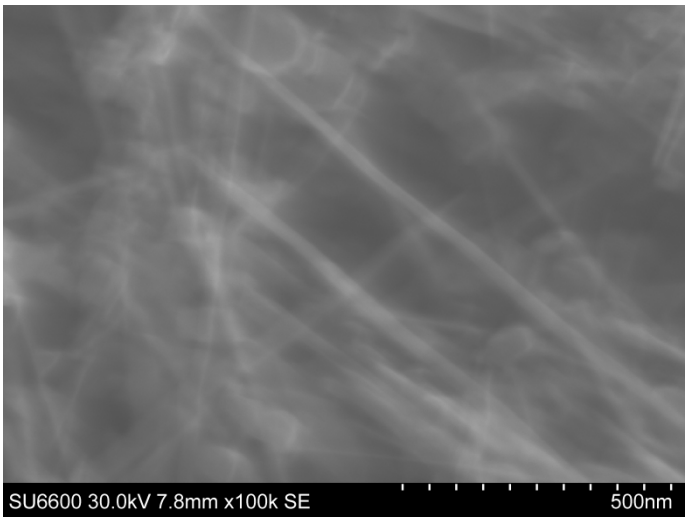

Fig. 4: SEM image of the produced CNTs

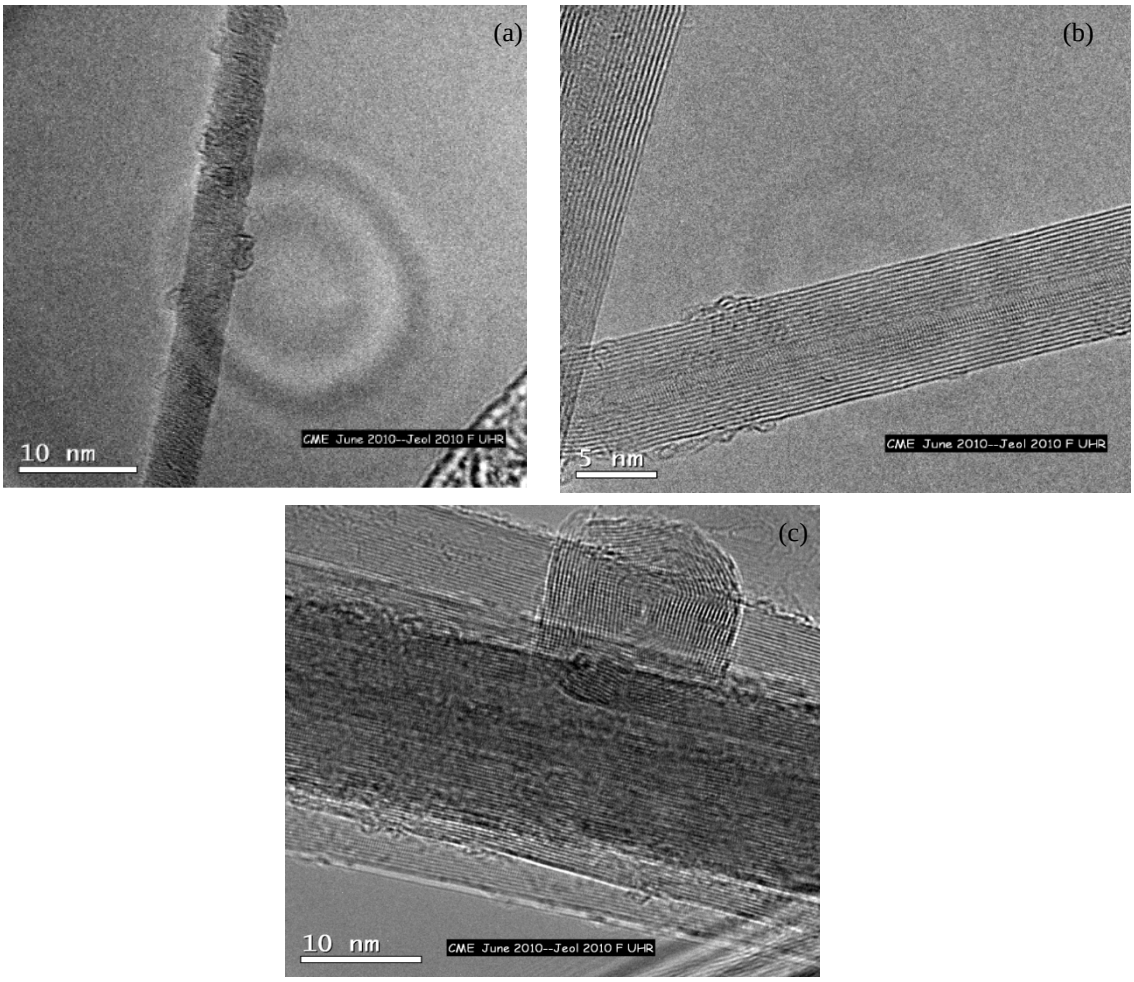

Fig. 5: TEM images of the as produced soot: (a) SWCNT of diameter about 5nm, (b) MWCNT of diameter about 10 nm and (c) Carbon nano onion of average diameter 15 nm.

Raman spectroscopy is one of the most powerful tools that provide the information on unique characteristics of CNTs such as the phonon and electronic structure and the defects. In 2-D vein graphite the only first order Raman peak around 1582 cm^{-1} corresponding to E2g vibrations of SP^2 carbons, is observed while the other transverse out of plane modes are Raman inactive. Comparatively the G-band of the CNTs with a split into many features around 1580 cm^{-1} is observed unambiguously deciding the formation of a 1_D confinement of electronic and phonon states. Furthermore, in Raman spectra of CNTs particularly SWCNTs radial breathing modes (RBM) which are also corresponding to the first order Raman scattering are observed. These characteristic Raman bands are observed below 500 cm^{-1} in the Figure 5. This RBM is a unique phonon mode characteristic of CNTs thus providing direct evidence for the presence of SWCNTs in the product obtained by our catalyst free arc discharge method [8]. The RBM mode in our study, appears as multiple peaks suggesting the possibility of forming SWCNTs with different diameters, which is typical for arch discharge process. This RBM frequency is directly related to the diameter of SWCNTs through $\omega_{RBM}(cm^{-1})= 248\ cm^{-1}/ d_t$, where ω_{RBM} is the RBM frequency and d_t is the tube diameter in nanometers [9]. The SWCNT calculated according to this formula varies between 3 nm – 6 nm, which corroborate the diameters observed in TEM images.

In addition, the peak observed around 1330 cm^{-1} corresponds to the sp^2, the local vibration mode of the amorphous carbon. The ratio of the peak height at 1580 cm^{-1} to that at 1330 cm^{-1}reflects the weight ratio of SWCNT to MWCNT in the soot.

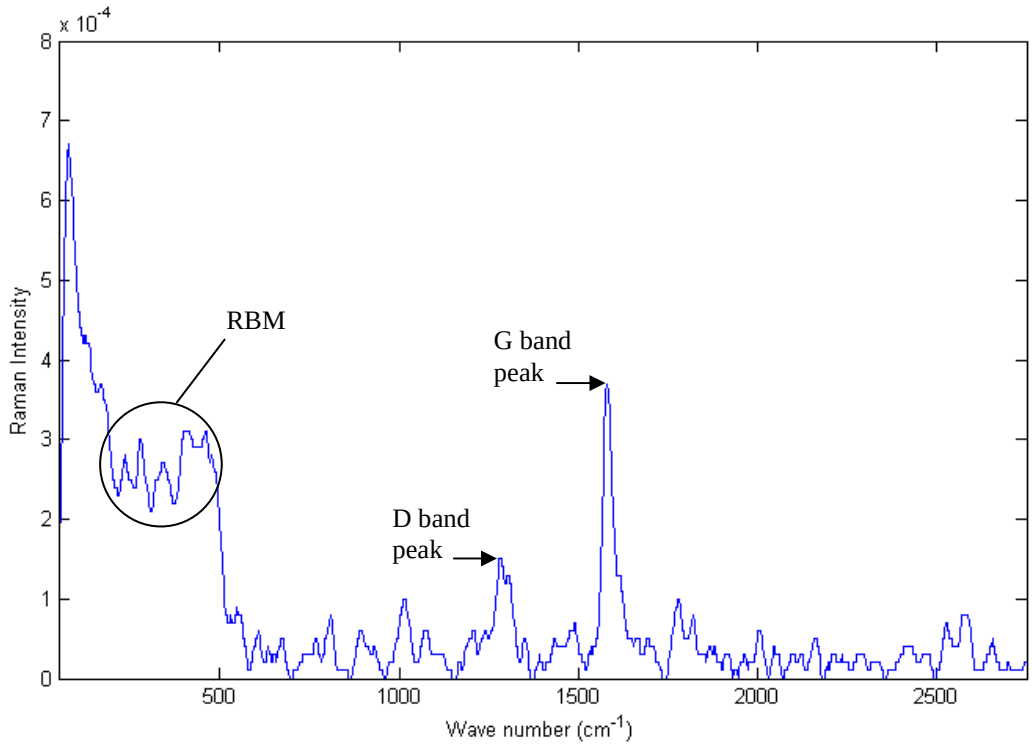

Fig. 6: Raman spectrum of the CNT sample produced by arc discharge method

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