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Production of Multi-wall Carbon Nanotubes Starting from a Commercial Graphite Pencil using an Electric Arc Discharge in Aqueous Medium

Carbon nanotubes (CNTs) are studied because of their diverse applications in many fields, such as medicine, computing, physics, chemistry, and others. Therefore, it is crucial to develop techniques for producing a large volume of high-quality multi-wall carbon nanotubes (MWCNTs) with the best cost-to-benefit ratio. In this paper, we obtain MWCNTs via an arc-electric alternative route, which dispenses catalysts and sealed cameras using water as an insulating medium. This method is simple, cost-effective (starting from pieces of commercial graphite pencil), efficient, and highly reproducible. Since no catalysts are used, no purification post-treatment was necessary, leading to high-quality MWCNTs. This technique is very promising for industrial applications because a lot of high-quality MWCNTs could be easily produced in a short time.

Keywords: *Synthesis of MWCNT, electric arc discharge, commercial graphite pencil.*

1. INTRODUCTION

Nanotechnology has been the focus of research in several fields becoming a real revolution in science and technology. It is commercially used in products such as cosmetics, chips and building materials. As a definition, nanotechnology is understood as the manipulation of nanoscale structures in the order of atomic and molecular size. The nanoscale is defined as the billionth part of the meter (10^{-9}m) [1]. The manipulation in this order of magnitude has awakened a series of studies in the areas of health, computing, physics, chemistry, materials, among others. The primary motivation of research in nanotechnology is the development of new materials with specific properties that will improve the materials and substances existing in the micrometric and macrometric scale (as in [2, 3]). Theoretical and experimental studies of synthesis, purification, and characterization of nanostructures have been enhanced since these new nanomaterials do not always meet all the necessary specifications (mainly the degree of purity) for commercial applications [4-6]. Carbon nanotubes (CNTs) are structures formed by flat sheets of graphene that, at a particular temperature, become rolled into tubes with a nanometer-scale diameter [7, 8]. Depending on the synthesis method, it is possible to obtain single wall CNTs (SWCNTs), double wall CNTs (DWCNTs) and multiple walls (MWCNTs). The SWCNT is formed by a single coiled graphite layer (a graphene sheet), which may have its ends closed by halves of fullerenes or open, as represented in Figure 1.

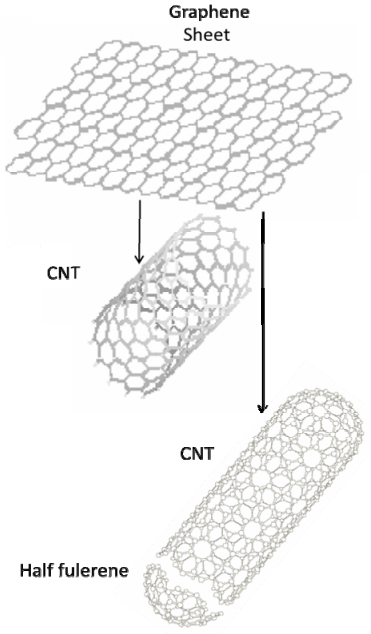

Figure 1. Schematic representation of a) a graphene sheet and b) a single wall CNT. Adapted from Iarrude, 2007 [7,8].

The carbon atoms in the SWCNTs form a hexagonal network, consisting of single and double bonds with sp2 hybridization. The MWCNTs (Figure 2) are formed by several SWCNTs in a coaxial-like structure. (Larrudé, 2007). CNTs have, in general, less than 100 nm in diameter and several micrometers in length. CNTs have a defined crystalline structure, as well as physical pro–perties characteristics of oriented crystals, such as high conductivity and mechanical resistance [8-10].

CNTs also present different chiralities depending on the synthesis method. They can show three different orientation; Armchair, ZigZag, and Chiral. The arm–chair CNTs have a metallic behavior, while the two

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others are semi metallic. The manipulation of CNTs has resulted in a series of studies in the areas of health, computing, physics, chemistry, and materials.

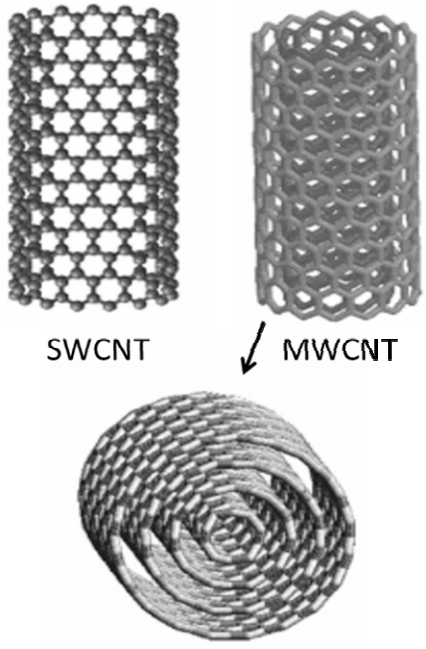

Figure 2. Schematic representation of a SWCNT and an MWCNT [11].

To produce CNTs, the most common methods are: chemical vapor deposition (CVD) [12], combustion [13], laser ablation [14], and electric arc [15, 16]. The CVD method produces CNTs based on the deposition of carbon precursor gases, while the combustion method is based on the combustion of carbon precursor gases. The production of CNTs by laser ablation and electric arc methods come from the sublimation of carbon atoms from a solid precursor, often mineral graphite. The electric arc method consists of an electric discharge generated by two carbon electrodes in a steel chamber containing an inert gas (usually helium) [17,18,19]. The electrodes (cathode and anode) are kept at a relatively short distance from each other (about 1 mm), generating plasma between them. The plasma temperature between the electrodes is extremely high (3000-4000°C) [20]. The precursor is sublimated at the positive electrode (anode), and the nanomaterials that form are deposited at the negative electrode (cathode) and on the chamber walls. The electric arc method in an aqueous medium is a variation of the conventional electric arc method. This process is simpler because it dispenses with the need for a sealed chamber, vacuum, and gas flow [21]. Water acts as an insulating medium and keeps the system cool.

Over the years, several theoretical and experimental studies of CNT synthesis and purification have been conducted. Most of these synthesis techniques do not achieve the minimum standards, especially concerning nanostructure purity [22–25]. Most of these methods (CVD, Combustion, HiPco, and others) use metal catalysts, leading to post-synthesis purification processes [26, 27]. These methods increase the production costs, and because of the use of strong acids, they directly affect the CNT structure, resulting in high rates of defective CNT products [28]. In this paper, we describe the production of MWCNTs using the electric arc technique in an aqueous medium. Commercial grap–hite pencils were used as a carbon precursor, which dispensed with the need for catalysts.

2. MATERIALS AND METHODS

2.1 Synthesis of MWCNTs

The reactor used in this work is divided into three parts: Mechanical; Electrical and Software. The mechanical part is understood by the support structures, tongs, and motors. The electronics are composed of a controller interface (control board). The software part has the responsibility of managing the system. A picture of the arc electric discharge system indicating all the com–ponents is presented in Figure 3.

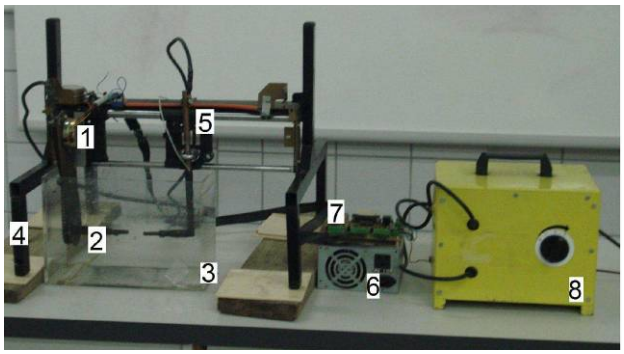

Figure 3. Picture of the arc electric discharge system. The numbers identify the components described in the text.

The numbers in Figure 3 indicate the components of the electric arc reactor used in this work for the MWCNTs production, where: (1) Stepper motor used to rotate the anode electrode (left electrode); (2) Tweezers for attaching graphite electrodes; (3) Acrylic tank (water tank); (4) Iron support used to support the other parts of the reactor; (5) Stem where the cathode electrode (right electrode) slides approaching the anode electrode (which is fixed); (6) Power supply of the control board; (7) Control board, which manages the system; (8) Electric source of alternating current for the formation of plasma (soldering machine).

Figure 4a shows, schematically, the MWCNT synthesis by an electric arc discharge in aqueous medium proposed in this work. A commercial graphite pencil (6B) from Faber-Castell was used as carbon precursor (Figure 4b).

According to previous thermogravimetric analyses, these graphite pencils are composed of 51% graphite and 49% amorphous carbon and polymeric structures.

The plastic around the graphite pencils was removed. The exposed graphite (95 mm long, 8 mm in diameter, and 8 g) was fixed to the cathode and anode. The system was submerged in Milli-Q water (18.2 μS/cm) while avoiding interaction with the atmosphere. A continuous current of 80 A was applied while the cat–hode and anode were slowly separated to a distance of approximately 1 mm. At this point, the applied current generated plasma (Figure 4c) between the electrodes, reaching temperatures of around 3000-4000°C. This led to sublimation of the carbon precursor (anode). The cathode was not affected during this process. The synthesis took around 5 min.

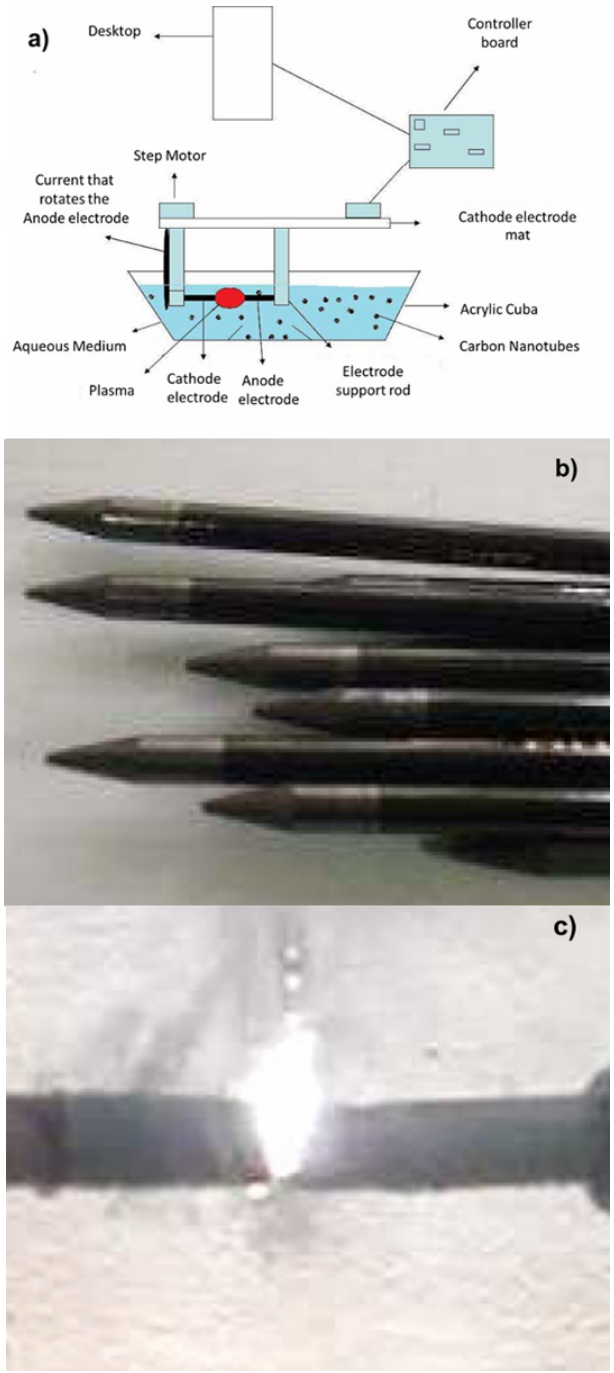

Figure 4. a) Scheme of MWCNT synthesis using an electric arc discharge in an aqueous medium. b) Image of the 6B graphite pencils used as a carbon precursor and c) the plasma generated at 80 A.

The product was vacuum filtered to separate it from the water and then thermally treated at 500°C to remove amorphous carbon. These processes took about 40 min. The complete MWCNT synthesis took 45 min.

2.2 Chemical and structural characterization

The sample was analyzed by Raman spectroscopy in a Renishaw inVia Spectrometer at 25 °C, in a range of 0 to 2500 cm^{-1} with a 532 nm laser. The Raman spectroscopy was preferred respect to other methods (as infrared [29, 30]) since its large application on graphite. The morphology was characterized by scanning electron microscopy (SEM) in a JEOL microscope (JSM 6060) with a maximum operational tension of 30kV and a nominal resolution of 3.5 nm. The applied tension was 10 to 20 kV.

Transmission electron microscopy (TEM) was performed on a JEOL microscope (JEM 1200 EXII model). This equipment operates between 80kV and 100kV, with a punctual resolution of 0.45 nm and line resolution of 0.2 nm. The magnification range was from 5,000x to 500,000x.

3. RESULTS

The Raman spectrum revealed the MWCNT characteristics of the D, G, and G' bands at 1,342 cm^{-1}, 1,572 cm^{-1}, and 2,738 cm^{-1}, respectively [31, 32] (Figure 5). The G' band indicates the degree of purity for the MWCNTs. The higher the G' band intensity compared to the D and G bands, the higher the MWCNT purity, which translated to less amorphous carbon and defects [31]. MWCNT quality and quantity were also measured using the (I_D/I_G) ratio. This ratio is related to the carbon graphitization degree [33]. The lower the ratio, the higher the graphitization degree and the higher the quality and quantity of CNTs present in the sample [32]. The MWCNTs we synthesized had a ratio of 0.243 I_D/I_G, indicating an elevated graphitization degree and, consequently, the formation of high-quality CNTs [24].

Next, 2 g of MWCNTs were produced using the synthesis method we developed, resulting in about 25% of the production yield. The MWCNTs displayed high quality with just a few structural defects (Figures 6 and 7). The yield was calculated based on the mass balance. The anode electrode (carbon precursor) had a mass of 8 g, around 51% of the precursor was graphite (about 4 g), and the remainder was composed of structure-sustaining polymers and amorphous carbon. For the production of CNTs using the electric arc, only the pure graphite portion was used [34]. Graphite has high conductivity, facilitating the sublimation of the carbon atoms [35]. Electrodes with high conductivity generate higher temperatures in the plasma, leading to elevated carbon sublimation rates.

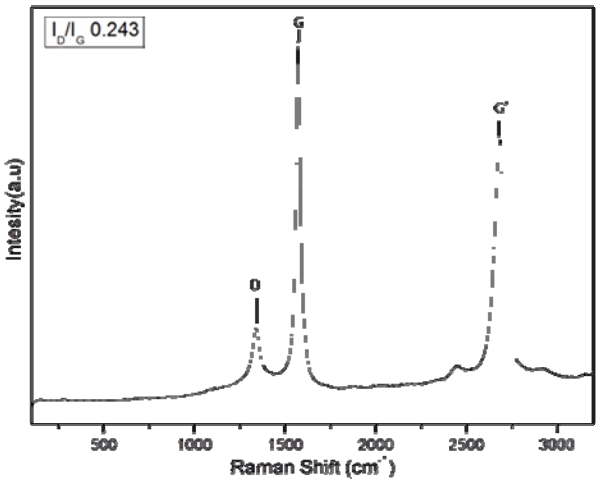

Figure 5. Raman spectrum of the synthesized MWCNTs.

The higher the quantity of sublimated atoms, the greater the quantity and quality of the MWCNTs produced. Polymeric amorphous and/or carbonaceous

structures exhibit low conductivity, which hampers the sublimation of carbon [35]. It is, therefore, possible that only about 51% of the pencil was ultimately used in the MWCNT synthesis. Although about 50% of this pre–cursor can be used, the cost-benefit ratio is still high concerning mineral graphite precursors (99% purity) because these have a high cost (about one hundred times more expensive than the method described here) [36].

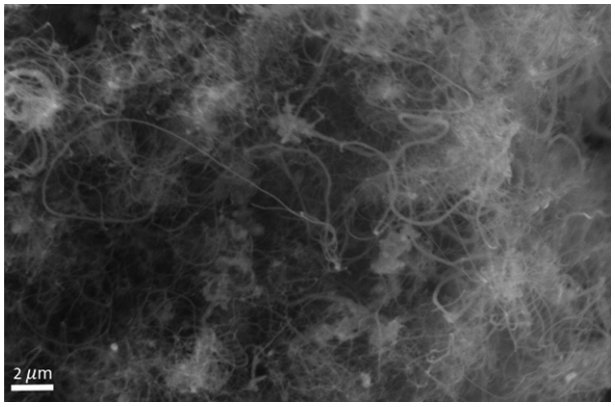

Figure 6. SEM image of the synthesized MWCNTs.

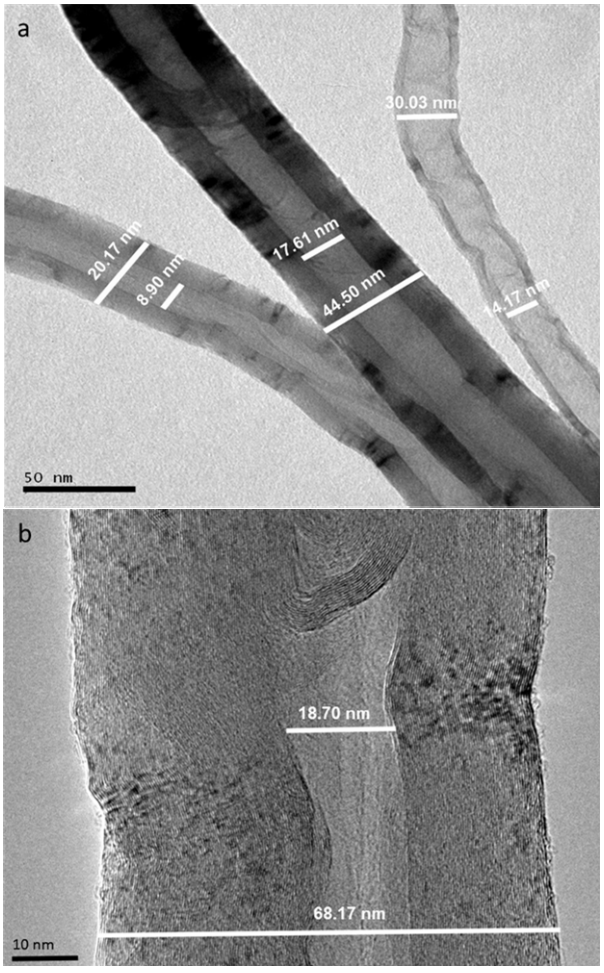

Figure 7. a) TEM images of MWCNTs. b) HRTEM of a single MWCNT with an internal diameter of 18.70 nm and an external diameter of 68.17 nm.

The 25% production yield is considered satisfactory when compared to other production techniques [26, 27]. With the exception of chemical vapor deposition (CVD), the other existing techniques take much more hours to produce the same quantity of MWCNTs (2 g). The method we developed takes 45 min. Besides, this synthesis technique does not require the use of catalysts, which are indispensable for CVD methods. A fast syn–thesis approach, which skips MWCNT purification stages, is very industrially feasible. It is possible to pro–duce large quantities of MWCNTs of high quality, avo–iding structural defects related to acid purification treatments [22, 23].

The TEM image (Figure 7a) shows some MWCNTs with an average internal diameter of 10 nm and an average external diameter of 30 nm. The HRTEM (Figure 7b) proved the existence of an MWCNT, which had an internal diameter of 18.70 nm and an external diameter of 68.17 nm. The nanotube structure was formed by more than 40 tubular walls.

The CNT sponge-like structure was composed of disorganized, tangled MWCNTs (Figure 7b). The MWCNTs had diameters ranging from 10-100 nm and lengths of approximately 10 μm.

4. CONCLUSIONS

The proposed synthesis method was effective for gene–rating mwcnts, and we successfully generated a large quantity of high-quality mwcnts. Also, this technique dispenses with purification treatments, as well as the use of catalysts. The system that applied the electric arc in aqu–eous medium did not require expensive furnaces, lasers, or vacuum chambers, considerably reducing the processing costs. The use of commercial pencils as precursors suggests that we can produce high-quality mwcnts while recycling discarded materials. Cumula–tively, the data presented in this paper makes this approach a useful, low-cost, large-scale technique for producing high-quality mwcnts in an environmentally conscious fashion.

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ПРОИЗВОДЊА ВИШЕСЛОЈНИХ УГЉЕНИЧ–НИХ НАНОЦЕВКИ ПОЛАЗЕЋИ ОД КОМЕР–ЦИЈАЛНИХ ГРАФИТНИХ ОЛОВАКА

КОРИШЋЕЊЕМ ПРАЖЊЕЊА ЕЛЕКТ–РИЧНОГ ЛУКА У ВОДЕНОЈ СРЕДИНИ

К. Кауфман, Р. Зампива, К. Бергман, А. Алвес, С. Мортари, А Павловић

Карбонске наноцеви (CNT) су проучаване због различитих примена у многим областима, као што су медицина, рачунарство, физика, хемија и друге. Због тога је кључно развити технике за производњу великог броја висококвалитетних вишезидних угље–ничних наноцеви (MVCNT) са најбољим односом трошкова и бенефита. У овом раду добијене су MVCNT-ови коришћењем правца електричног алт–ернативног лука, који користећи воду као изо–лациону средину остварује катализу. Овај метод је једноставан, исплатив (почев од комада комер–цијалне графитне оловке), ефикасан и високо репро–дуктибилан. Пошто се не користе катализатори, није потребан било који додатни третман пречишћа–вања, што је доводи до високо–квалитетних MVCNT. Ова техника је веома перспективна за индустријске примене, јер се за врло кратко време лако може произвести много висококвалитетних MVCNT.