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Single wall carbon nanotubes: Two ways of production

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Abstract

The electric arc discharge and the solar energy are two methods among a large number to produce single wall carbon nanotubes. They are based on the same process: sublimation of mixture of graphite and catalyst under an inert gas atmosphere. While the solar furnace is a small scale experiment, the electric arc discharge presents a better yield of production. Samples synthesized by both methods in the same conditions of gas pressure and catalysts are characterized by SEM, TEM and RAMAN spectroscopy.

Keywords: High temperature methods for material preparation, Electron Microscopy, Raman Spectroscopy, Fullerenes and derivatives

1. Introduction

Since their discovery [1], carbon nanotubes are of great interest from a fundamental point of view as well for future applications. They present a wide variety of fascinating electronic and mechanical properties. However, after several years of research, the large scale production of high purity carbon nanotubes is still a crucial problem and a better knowledge of the growth mechanisms must be necessary to improve the production. Two methods of production using either the electric arc discharge or high concentrated sun light to induce the vaporization of carbon under an inert gas atmosphere, are developed in our lab. In both cases, many experiments allowed the optimization of the process and hence improved the yield significantly [2, 3]. Here we report experimental conditions for the production of single wall carbon nanotubes (SWNTs) by the electric arc discharge and the solar energy and we discuss the results comparing the samples obtained with these two methods.

2. Description of the techniques

2.1 Electric arc discharge

The synthesis is performed in a water-cooled reaction chamber, first evacuated and then filled with an inert gas (helium, 660 mbar). Two graphite rods are used as electrodes: one is fixed while the other one can be moved by a translation mechanism. The mobile electrode (the anode) is drilled and filled with a mixture of powdered graphite and a couple of catalysts. The most used catalysts mixtures are Ni and Co, Co and Y or Ni and Y in various atomic percentages. Generally, the anode has a diameter smaller than the cathode and the holders of these electrodes are water-cooled. The anode is moved toward the cathode until the distance between them becomes small enough so that a current (100 A) passes through the electrodes creating a plasma between them. The average temperature in the interelectrode plasma region is extremely high (of the order of 4000 K) and allows the sublimation of graphite. As the anode is

consumed it is continuously translated to keep constant the distance between the rods and maintain the arc between them. Fluctuations of the plasma can be reduced by controlling the voltage (35 V) which is dependent on the distance between the rods. After around 10 min, we find four various kinds of product located in different parts of the reactor: (1) large quantities of rubbery soot on reactor walls; (2) web-like structures between the cathode and the chamber walls; (3) hard deposit at the cathode's end; (4) spongy collaret around the cathodic deposit.

As already known [2], the collaret contains the highest density of SWNTs. The best results are found for a mixture of 4.2 at.% Ni and 1 at.% Y.

2.2. Solar energy

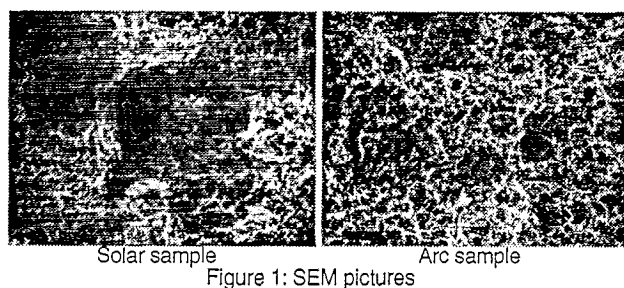
The solar route consists of a direct vaporization of a mixture of powdered graphite and catalysts, under argon atmosphere, with the same set-up as the one, previously described [3], used to produce fullerenes at small-scale. The advantage of the solar method is the use of light, like in laser ablation, to induce the vaporization of the target and the possibility to control each synthesis parameter independently. With the small furnace (2 kW) despite the numerous improvements to reduce the very intense thermal losses of graphite (conductivity and emissivity), the vaporization temperature remains in the range 2900-3000 K, and the small size of the focus limits the production. The pressure and the gas flow rate which dilute the atomic carbon vapor, prevent fast and disordered clustering of carbon atoms and we observe strong evolution of the structure of the tubes, varying these two parameters for the same mixture of graphite nickel and cobalt (2 at.% of each catalyst specie)

At low pressure (120 mb) we do not produce nanotubes. When the pressure reaches 250 mb, the samples contain large part of multi-wall nanotubes and we begin to find few small ropes of single wall nanotubes. In the pressure ranges 400-600 mb, we observe only bundles of single wall nanotubes. This small-scale experimental set-up limits the target size and yields a small amount of material

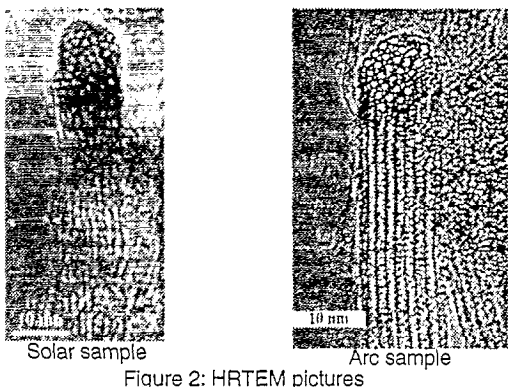
due to the low power of the solar furnace and the small size of the focus area. But the method can be scaled-up and studies are now in progress with the 1000 kW solar furnace of the Odeillo Institute [4].

3. Characterization and discussion

Samples were studied by Scanning Electron Microscopy (SEM JEOL JSM 6300F) and High Resolution Transmission Electron Microscopy (HRTEM JEOL 4000FX). SEM pictures observed with solar or with arc samples are very similar (figure 1). They show a large amount of entangled carbon filaments homogeneously distributed. These filaments are 10 to 20 nm in diameter and several micrometers long. The yield of these filaments appears to be of the order of 80% in the collaret of the arc method. For the solar samples, the density of undesired nanoparticles can widely change with the observed part.



HRTEM images of the solar or of the arc products are also very comparable (figure 2). They show that each of the filaments observed by SEM consists of aligned SWNTs organized into bundle-like crystallites. Sometimes, these bundles are oriented parallel to the electron beam in such a way that they are seen edge-on. They consist of large number of SWNTs (greater than 20), with uniform diameter, packed according to a triangular lattice.



We have also studied these samples by Raman Spectroscopy which is a powerful tool to determine the diameter and also the structure of carbon nanotubes. In the low frequency range, we observe the breathing mode, which are strongly dependent with the tube diameters. The more important peak, generally appears at 180 cm⁻¹ and corresponds to tube diameters around 1.3 nm but for the electric arc samples we can observe some other tubes with larger diameter (fig 3a). This is also the case for solar samples, but generally we observe a greater polydispersity in diameters depending both on the nature

of catalysts and sublimation temperature. The sublimation temperature seems to be a very important parameter which can influence the tube diameters whatever the method used.

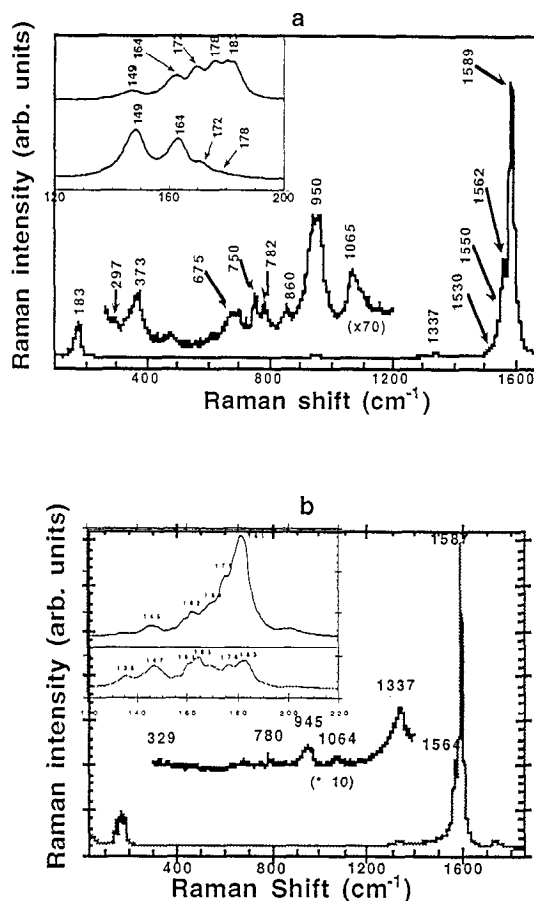


Figure 3: Raman spectra of SWNTs produced by the arc method (a) and by the solar energy (b). (Incident radiation $\lambda = 514.5$ nm)

4. Conclusion

We can produce bundles of SWNTs with various quantities depending on experimental conditions. Experiments using the same amounts of the same catalysts give very similar SEM and HRTEM pictures whatever the technique. However the electric arc discharge samples seem to be more homogeneous and this is certainly due to the more homogeneous plasma temperature. The sublimation temperature and the nature of the couple of catalysts seem to have greater influence than the technique itself for the nanotube production .

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