# OPTICAL PLASMA CONTROL DURING ARC CARBON NANOTUBE GROWTH

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## ABSTRACT

To improve nanotube production, we developed a novel optical control technique, based of the shape of the visible plasma zone created between the anode and the cathode in the direct current (DC) arc process. For a given inert gas, we adjust the anode to cathode distance (ACD) in order to obtain strong visible vortices around the cathode. This enhance anode vaporization, which improve nanotubes formation. In light of our experimental results, we focus our discussion on the relationship between plasma parameters and nanotube growth. Plasma temperature control during arc process is achieved using argon, helium and their mixtures as a buffer gases. The variation of the gas mixture from pure argon to pure helium changes plasma temperature. As a consequence, the microscopic characteristics of nanotubes as diameter distribution is changed moving from smaller values for argon to higher diameters for helium. We also observe a dependence of the macroscopic characteristics of the final products as Brunauer-Emmett-Teller (BET) surface area.

**Keywords**: carbon, nanotubes, diameter, BET, control

## INTRODUCTION

The interest on single-walled carbon nanotubes (SWCNTs) has been stimulated by the properties and potential applications of these novel one-dimensional objects (ref. 1). Currently, there is an important challenge to understand the growth mechanism and to control the structure of the produced nanotubes. For the arc process, the plasma temperature distribution is an intimate component of SWCNTs synthesis (ref. 2). This parameter controls species production and condensation, hence nanotube growth and morphology. To control this parameter the majority of laboratory scale arc reactors use a water cooling system. Plasma temperature control is accomplished by one of the following methods: 1) changing the plasma conditions by varying the electric current and/or 2) varying the anode to cathode distance (ACD) to maintain a constant voltage. These methods do not allow active control on the plasma temperature, independently of plasma parameters. An alternative approach was developed in our recent work (ref. 3), which consists of varying the conductance of the gap between the electrodes, using an argon-helium mixture as the inert background gas. Unfortunately, the yield of nanotubes was found to be much higher with helium than with argon. To improve nanotube production independently of the used inert gas, we developed an optical control technique based on the shape of the visible plasma zone. For a given inert gas composition, we adjust the gap distance in order to obtain a strong visible vortices at the edge of the cathode. These vortices are suspected to ensure a maximal mass flux of carbon and catalyst species from the plasma zone to the cold cathode region, and to enhance the nanotube growth. In the present work we have achieved a set of experiments with different argon-helium mixtures as inert gases. In addition, the morphology and the structure of SWCNTs were analyzed using Raman spectroscopy to determine diameter distribution, and Brunauer-Emmett-Teller (BET) surface analysis to estimate the surface area of as produced nanotubes.

## EXPERIMENTAL

SWCNTs were prepared by conventional electric arc discharge method. The reactor consists of a water-cooled reaction chamber, in which has been introduced an anode, made of pure graphite: Alfa Ultra carbon rod, 6 mm in diameter and 150 mm length. The cathode is also made in high polished graphite. Nickel and yttrium, were introduced as catalysts in a drilled hole inside the anode of 3 mm diameter and 100 mm length. Finally the anode, including the outer graphite shell, consists of 94.8 % atom. carbon, 4.2 % atom. nickel and 1 % atom. yttrium. In the present work we have achieved a set of six experiments with different argon-helium mixtures used as inert gases under controlled pressure (ref. 3). Optimum nanotube yield was found at a pressure of 660 mbar for pure helium and 100 mbar for pure argon. Varying the percentage of helium from 0 to 100 with a step of 20 %, the pressure was arbitrarily fitted using a linear fit between 100 mbar and 660 mbar. The thermal conductivity of the mixture depends on the relative concentration of the two gases. The thermal conductivity of argon is about eight times smaller than of the helium. Varying the relative concentration of the two gases influences the temperature gradient between the plasma and the cathode. This affects the condensation of atomic carbon and metal catalysts, hence the nanotube diameter distribution.

The electric parameters of all the experiments were maintained at a direct current of 100 A to create the arc discharge. In the beginning the plasma is ignited by contact between the electrodes, which increases the temperature of the contact point until evaporation of the anode material. When the discharge runs, the plasma is observed through the quartz window of the reaction chamber, and a magnified image of the luminescent plasma is projected on a screen, using lens. The anode is moved back until vortices appear between the growing deposit on the cathode and the burning anode. The gap distance between the electrodes is maintained by moving the anode toward the cathode. The high temperature near the anode and the high energy densities in the plasma ensure a total vaporization of the anode material, while the water cooled cathode leads to high quench rates and to nanotube formation. The experimental results indicate that the carbon nanotubes are generated on the front-end surface of the deposit. The quench process is complex and uncontrolled but we usually obtain various products: soot on the reactor walls, web-like structures between the cathode and the chamber walls, a deposit on the cathode's edge, and a rubber-like collaret around this deposit.

Pictures of the plasma have been taken through the video camera and using the recorded film we can determine the distance between the electrodes in every moment of the experience. A data acquisition system, composed of a power and harmonics clamp and a multimeter connected to a PC, allows recording the variations respectively of the intensity of the current, and of the difference of the potential. Nanotube diameter was determined using Raman spectroscopy using spectrophotometer Jobin Yvon T64000. Spectra have been recorded at room temperature in ambient air with an argon laser at 514.5 nm. Surface analyses was accomplished with a BET COULTER SA 3100 instrument using nitrogen gas in order to determine the BET surface areas as well as the pore size distributions. The method consists of one-hour gas evacuation at 393 K and of determination of the pore volume introducing helium gas, followed by adsorption of nitrogen at temperature of liquid nitrogen (77 K).

## RESULTS AND DISCUSSION

### Plasma characteristics

In the present work, we have achieved the set of six experiments with different argon-helium mixtures as discussed above. The plasma characteristics are reported only of pure argon plasma but are reproducible for all the experiments. The conditions of the synthesis of nanotubes namely ACD were modified in order to improve the yield of nanotubes. This parameter was not maintained constant as suggested in refs. 4,5, but varied to establish a visible vortices around the cathode. These vortices are visible probably because of the presence of small particles of carbon acting as markers in the stream.

During all the experiments, we distinguished qualitatively two operative regimes concerning the shape and the color of the plasma.

1) The first is the stable regime, during which the arc flame is uniform, in a blue-green color, and does not change its shape and brightness (figure 1a, 1b). We adjust manually the distance between electrodes, until the appearance of the vortices (figure 1c, 1d). We found in our geometry that when we use argon as inert gas, the optimal distance between the electrodes, encouraging the formation of vortices is between 15 to 17 mm.

2) The second regime is not desirable, the vortices do not appear; the color of the arc flame is blue-purple and the brightness is weaker (figure 2a, 2b). This regime is unfavorable for the synthesis of nanotubes. It appears when the anode is very near (ACD = 1 to 7 mm) or when it is very far from the cathode, (ACD greater than 18 mm). If we continue to move away the anode from the cathode the arc extinct.

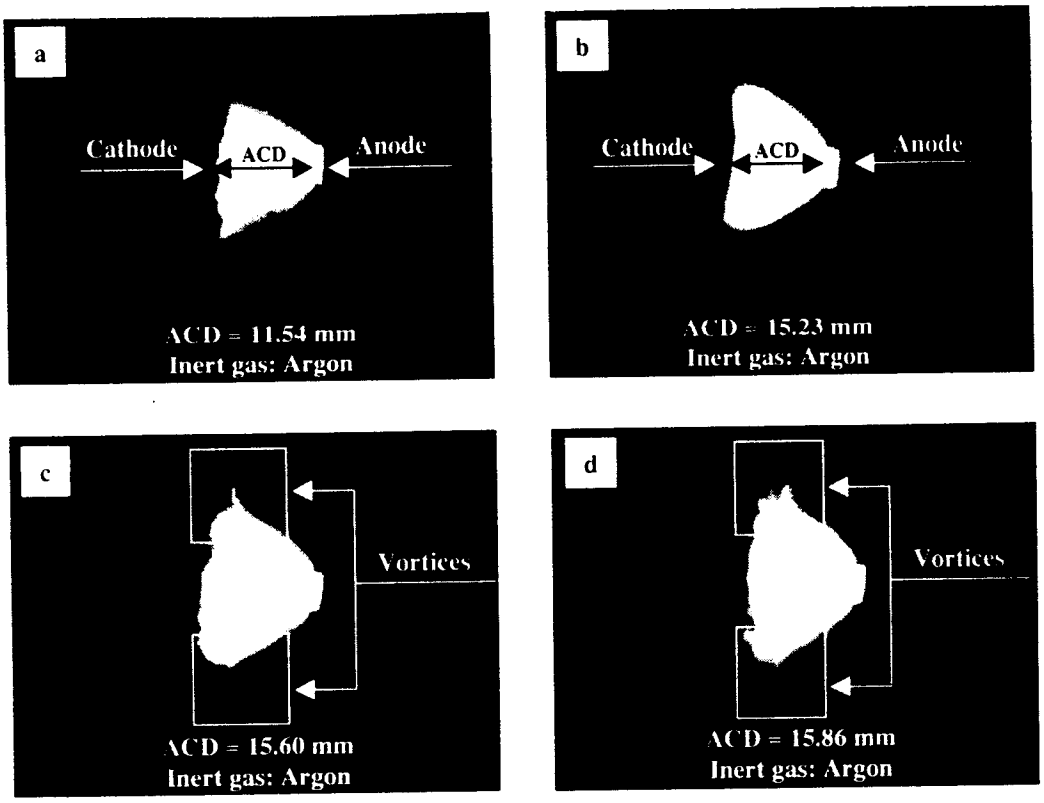


**Figure 1. Development of vortices in argon plasma (Pressure = 100 mbar, Current = 100 A). The streamlines are curved outside the plane of symmetry.**

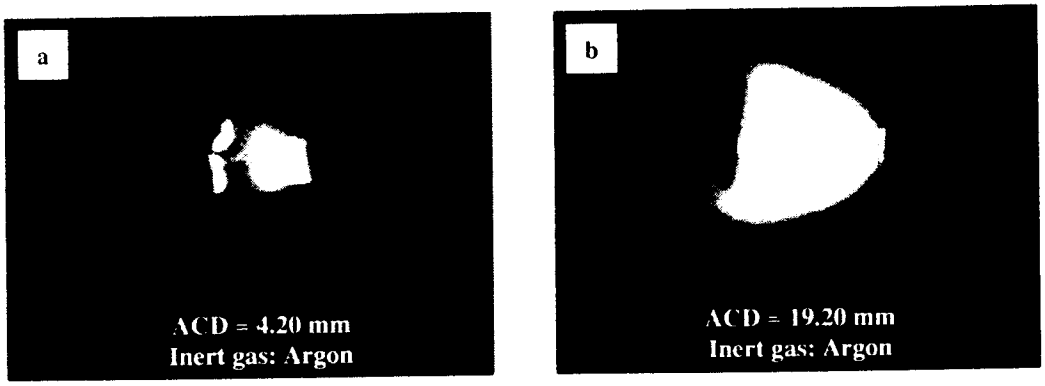


**Figure 2. Pictures of the non-desirable regime. The vortices do not appear**

Finally, the effect of the control of the ACD on the yield of nanotubes is reported on figure 3. From this figure we can conclude that optimal ACD giving vortices improve significantly the yield of collaret, compared with ACD giving a constant voltage (U = 40 V). For some mixtures namely 0 % and 40 % argon, the deposition of webs on the quartz window makes ACD control difficult and explain the decrease of the mass of collaret. For pure argon the yield is improved by a factor 3.5.

Our first experimental results demonstrate clearly the efficiency of ACD control technique for different inert atmospheres. This new design provides a means to improve nanotube yield but also to control gradient temperature in the arc independently of plasma conditions *i.e.* current and voltage. This increases the repeatability of experiments for various process conditions. It also provides the opportunity to control the morphology of nanotubes. Indeed, since the thermal conductivity of the argon-helium mixture is affected by the relative concentration of the two gases, we expect that control of thermal transfer and hence condensation of atomic carbon and metals between the plasma and the vicinity of the cathode can control nanotube diameter in arc process. This result implies that single-layer tubules nucleate and grow on a metal particle with different sizes depending on the quenching rate in the plasma and suggests that temperature and carbon and metal densities affect the diameter distribution.

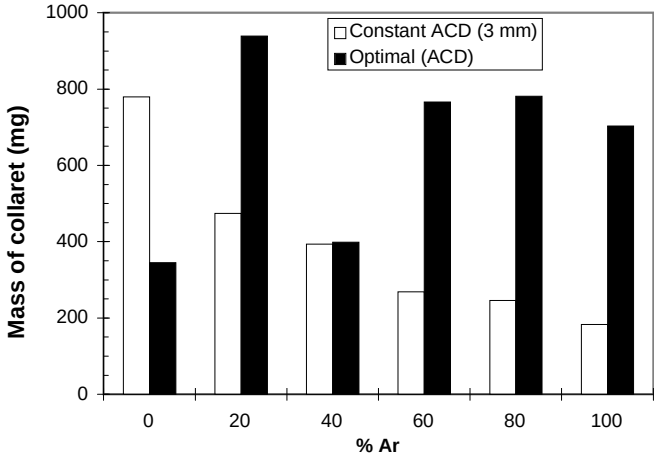


**Figure 3. Effect of the anode to cathode distance on collaret mass collected in the cathode using following parameters: burned anode length 100 mm and current I=100 A. ACD was maintained constant at 3 mm. ■ ACD was varied to obtain vortices.**

Microscopic characteristics: nanotube diameter

For each sample, we have recorded spectra on at least ten different points to get the best view of all the sample. Two main regions of the Raman spectrum can be attributed to SWCNTs: 1) the high frequency (1500-1600 $cm^{-1}$) and 2) the low frequency (100-250 $cm^{-1}$) ranges. In figure 4a, we can see the overall spectrum and in figure 4b, the low frequency range has been scaled up to better observe the breathing modes of nanotubes.

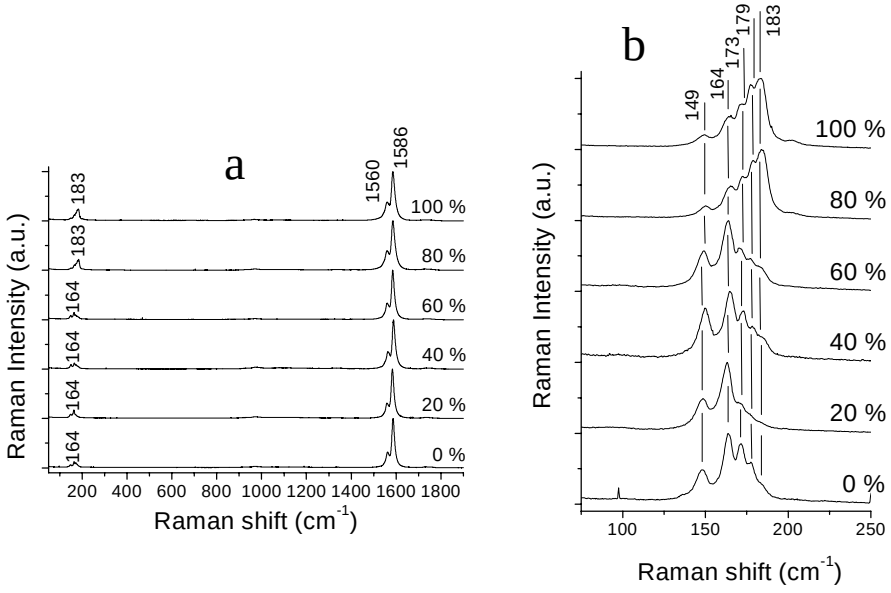


**Figure 4. (a) Overall Raman spectrum and (b) Radial breathing mode of the SWNT produced with various concentration of Ar in the inert atmosphere. The percentage of Ar is indicated on the rigth side.**

The relative intensity of these bands changes as the inert gas varies from pure helium to pure argon. To determine exactly the variation in the diameter distribution, we have fitted several lorentzian shapes (one shape per band) to the whole group of peaks assigned to the breathing mode. In this way, we have been able to get the proportion of each diameter for all recorded spectra. We can then calculate an average diameter distribution and an average diameter from all spectra obtained on the same sample. We assume that the diameter distribution and average diameter depend on the inert atmosphere condition. This dependence is given in the figure 4. Varying the gas from helium to argon changes average diameter to smaller values.

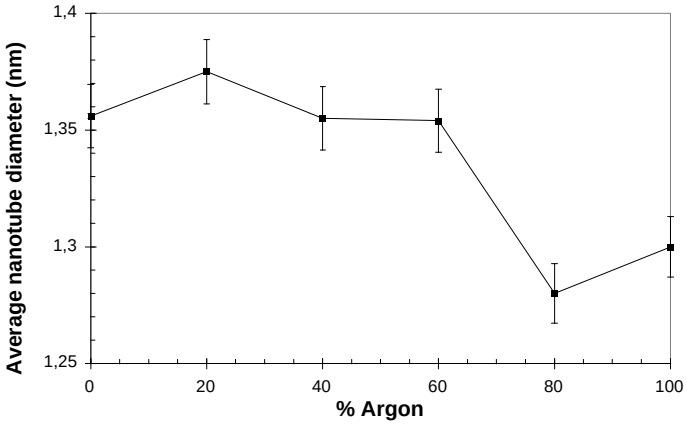


**Figure 5. Variation of the average nanotube diameter as determined by Raman spectroscopy with the argon percentage in the arc chamber obtained with I=100 A and optimal ACD giving vortices around the cathode.**

Macroscopic characteristics: BET surface area

The BET analysis of the as-produced nanotubes was achieved during this work and permits to measure the BET surface area. On the figure 6, we report the variation of the BET surface area of the collected collaret with the argon mole fraction in the inert gas obtained with the optimal ACD discussed above. On the figure 7 we report the corresponding isotherms of nitrogen on nanotubes. BET surface areas varies in the range of [200 – 450 $m^2/g$] and are less than the outer surface area of single nanotube (1300 $m^2/g$) as given by Ye *et al.* (ref. 6). This is a proof that the measured BET surface area is attributed to the outer surface of a nanotubes organized in bundles, or "ropes" of SWCNTs as discussed in ref. 6. Hence, the parameter controlling BET surface area must be the rope diameter. In spite the fact that the relationship between individual nanotube diameter and rope diameter is not yet fully understood, we can conclude that the macroscopic surface area of nanotubes is controlled by the argon-helium mixture gases. In our knowledge, the maximal value of BET surface area published in the literature never exceed 350 $m^2/g$. Further High Resolution Transmission Electron Microscopy (HRTEM) observations of our samples are needed to determine the number of individual nanotubes per rope and to better understand this result. In the present work, the maximal value of BET surface area is found with mixture of 80 % helium and 20 % argon, and it decrease increasing the argon percentage. In the most favorable case the BET surface is 440 $m^2/g$, which is bigger than the values reported in the ref. 6 (285 $m^2/g$).

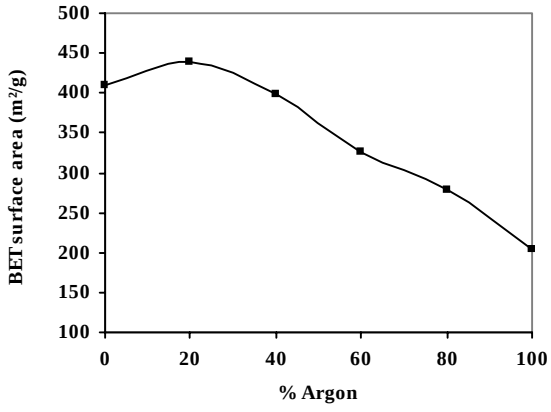


**Figure 6. Variation of the BET surface area of the collaret with the argon mole fraction.**

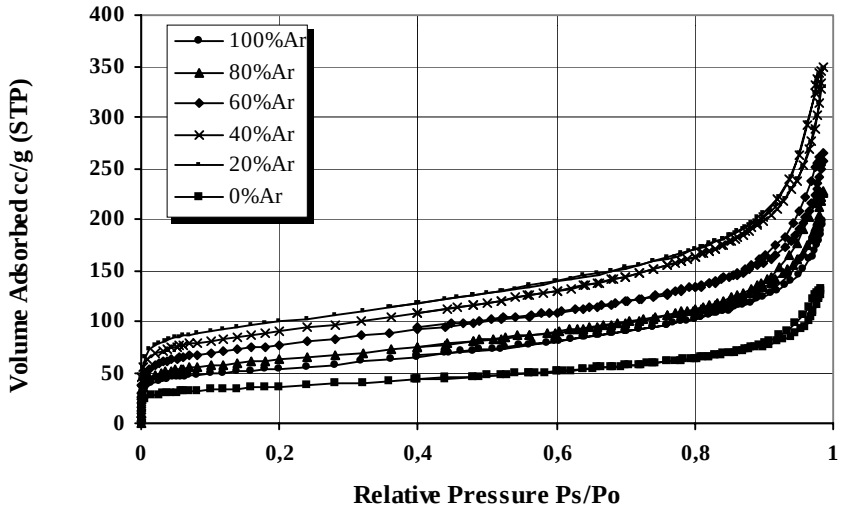


**Figure 7. Adsorption isotherms of nitrogen at 77 K on as prepared nanotubes at different argon mole fractions.**

## CONCLUSION

The mechanism of plasma control with a variable ACD and a variable thermal conductivity of the plasma is demonstrated in this paper and validated in DC arc process for specific SWCNTs synthesis. More precisely, it was demonstrated that varying the arc plasma parameters and basically the distance between the electrodes permits to work in optimal regime, with a strong vortices around the cathode, which increase significantly the nanotube yield. This suggests that controlling the argon-helium mixture and/or the ACD provide the opportunity to control simultaneously:

1) microscopic nanotube parameters as nanotube diameter in the range of 1.27 to 1.37 nm
2) macroscopic nanotube parameters as BET surface area in the range of 200 to 450 $m^2/g$.

This opens new horizons to investigate hydrogen adsorption in SWCNTs of different diameters.

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