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CARBON SINGLE-WALL NANOTUBE GROWTH IN A VOLUMETRICALLY CONFINED ARC DISCHARGE SYSTEM

Kale J. Franz, Jeff L. Alleman, Kim M. Jones, Anne C. Dillon, Mike J. Heben

ABSTRACT

Carbon nanotubes hold significant promise for a vast number of materials applications due to their unique mechanical, electrical, and gas storage properties. Although carbon single-wall nanotubes (SWNTs) have been synthesized since 1993 by the arc discharge method, and numerous other synthesis methods have since been developed, no method has yet produced 100% pure carbon nanotubes. Instead, a significant amount of impurities—various carbon structures and metal catalysts—are present in the raw soot. While arc discharge was the first method for SWNT synthesis, it also produces more impure raw soot in comparison to the more recently developed laser vaporization, which has produced the purest raw soot to date but is much slower. Geometry and thermal gradient are appreciably different between traditional arc discharge systems and laser vaporization systems. We report that, by incorporating some characteristics inherent to a laser vaporization system into an arc discharge system, improvement in the yield of SWNT raw soot may be achieved. This is accomplished by confining the arc within a 50 mm diameter quartz tube, similar to laser vaporization. We find through transmission electron microscopy and Raman spectroscopy that SWNTs are made in significant numbers in this confined arc discharge system, comparable to laser vaporization synthesized material. Further study is, however, required to prove reproducibility and attain an exact value for the purity of the produced raw soot.

INTRODUCTION

Although significant progress has been made in enhancing the quality of raw carbon single-wall nanotube (SWNT) material synthesized by arc discharge [1], we hypothesize further improvements can be made. Substantial research has been conducted into the growth mechanisms of SWNTs synthesized in laser vaporization systems [2], which produce comparatively better raw SWNT material. We propose that, by applying characteristics found to be advantageous in laser vaporization to an arc discharge system, we can improve the quality of SWNTs produced by arc discharge.

Carbon nanotubes have been of significant interest since their discovery in 1991 [3] because of their unique electrical, mechanical, and gas storage properties. Discovered in the soot of an arc discharge apparatus designed to synthesize fullerenes or "bucky balls," the first carbon nanotubes were multi-wall. Single-wall nanotubes (SWNTs) were synthesized in 1993 by incorporating a metal catalyst [4,5]. Numerous methods have since been employed for the production of SWNTs [6,7,8].

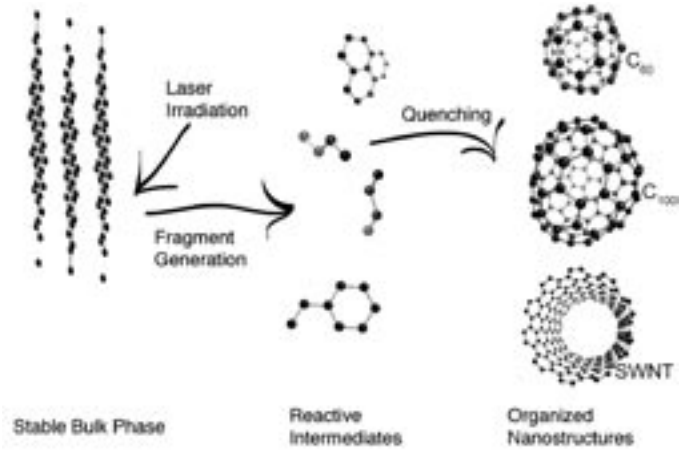

Figure 1. Carbon nanotube growth process.

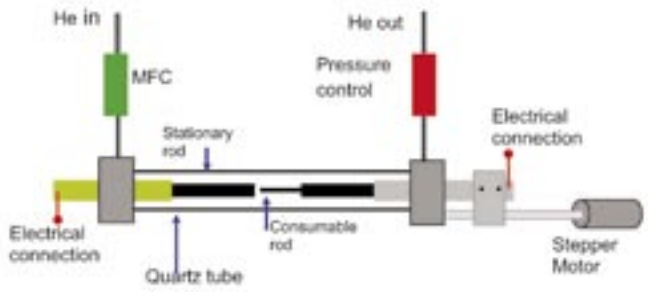

Figure 2. Arc-discharge apparatus.

Of the SWNT synthesis methods demonstrated to date, laser vaporization has produced the purest raw material; yields of 70-90 mass % SWNTs have been achieved [9]. The laser vaporization process of A. Thess et al. uses two Nd:YAG lasers to provide alternating 532 nm and 1024 nm pulses at 10 Hz, which vaporize a graphite target doped with 0.6 at. % Co and 0.6 at. % Ni. The process occurs in a 500 Torr Ar environment confined by a 56 mm quartz tube around which a clamshell furnace provides an ambient temperature of 1200 ºC. Purification further enhanced the quality of SWNT material up to 98 mass % [10].

Studies of SWNT laser vaporization growth suggest the following growth progression, as illustrated in Figure 1. Laser pulses rapidly heat and vaporize the graphite and metal catalyst of the target. A plume of vaporized carbon—consisting of reactive intermediates of less than 60 carbon atoms—flows from the target and cools. While the plume cools, the reactive intermediates coalesce into more stable structures. In the absence of a metal catalyst, C_{60} (bucky balls) and other spherical fullerenes are formed. When a metal catalyst is introduced, however, the catalyst facilitates the formation of single-wall carbon nanotubes.

There are significant differences between traditional arc discharge systems and laser vaporization systems, two of which are geometry and temperature profile. Laser vaporization is confined by a quartz tube ~50 mm in diameter, while the traditional arc discharge apparatus uses reaction a bell jar reaction chamber of much greater volume. The temperature of laser-vaporized carbon has been estimated at 3000-4000 K [11], and the plasma temperature of an arc discharge system is 4000 K [12]. However, ambient heating to 1200 ºC in laser systems may lead to significant differences in the temperature profiles of the two systems. The geometric and thermal properties of the laser system, which is proven to grow nanotubes of greater purity, may thus facilitate superior nanotube growth if applied to an arc discharge system.

MATERIALS AND METHODS

A diagram of the arc discharge apparatus is shown in Figure 2. An arc is struck between a stationary 19 x 305 mm graphite rod and a traveling 6.15 x 150 mm consumable graphite rod. A hole in the consumable rod is bored to a diameter of 4 mm and a depth of 100 mm, and then filled with a graphite powder doped with 0.6 at. % Co and 0.6 at. % Ni. The graphite powder has a particle diameter of 1 to 2 µm, CO a diameter of 1.6 µm, and Ni a diameter of 2.2 to 3.0 µm. A 50 x 760 mm quartz tube sealed at both ends provides enclosure for the arc. A roughing pump, mass flow controllers rated at 100 sccm and 500 sccm, and an MKS control system provide variable flow rates for the atmosphere within the system. A stepping motor with a minimum speed of 0.1 mm/min is used to advance the consumable rod. A 5 kVA AC power supply provides power for the arc.

Each run begins by evacuating the system to around 20 mTorr then backfilling with He to 500 Torr. A He flow rate of 100 to 500 sccm is established. The power supply is set to 20 V, and an arc is struck by advancing the consumable rod at 10 mm/min. The advance rate of the consumable rod is maintained throughout the run. The current is typically around 70 to 90 A and may fluctuate 10 A during a run. A run typically lasts 30 to 40 min and is limited by the length of the consumable rod. After the completion of each run, the system is allowed to cool. The quartz tube is removed from the apparatus, once cool, and the material is collected. The tube is turned vertically and gently tapped to collect loose material. Separately, stainless steel scraping rods are used to remove and collect material that remains affixed to the tube walls.

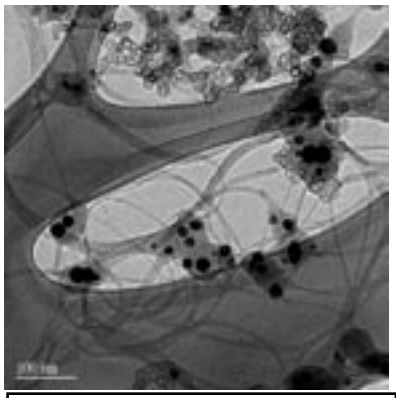

Figure 3. High quality lower magnification TEM image from 100 sccm run.

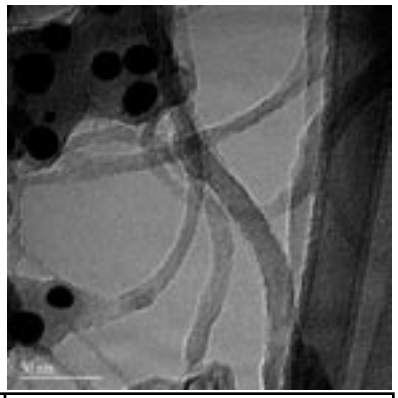

Figure 4. High quality higher magnification TEM image from 100 sccm run.

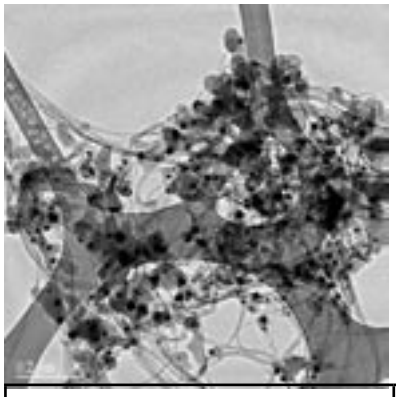

Figure 5. High quality lower magnification TEM image from 500 sccm run.

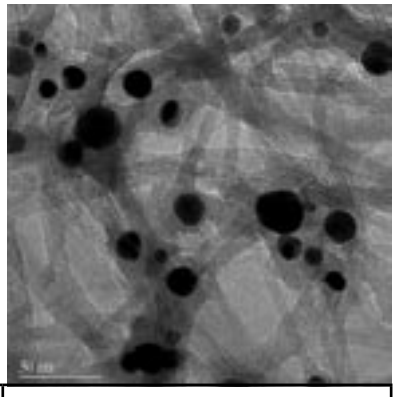

Figure 6. High quality higher magnification TEM image from 500 sccm run.

Arc discharge runs were completed at flow rates ranging from 100 to 500 sccm. Transmission electron microscopy (TEM) and Raman spectroscopy were used to analyze the samples.

RESULTS

A black deposit immediately began to collect on the walls of the quartz tube at the start of each run, and the deposit area depended on the He flow rate. After runs with a 100 sccm flow rate, the black deposit extended 5.7 cm on the upstream side of the arc and 12.7 cm on the downstream side of the arc. Runs conducted at 500 sccm exhibited a black deposit 5.1 cm on the upstream side of the arc and 18 cm on the downstream side of the arc. A brown deposit extended another 14 cm beyond the black deposit for runs at 500 sccm. The black soot deposited on the tube walls was light and feathery, similar to results obtained for traditional arc discharge apparatus [3,9].

TEM images confirm production of SWNTs in some samples of collected soot. Figures 3 and 4 are TEM images of high quality soot synthesized at 100 sccm flow rate. Figures 5 and 6 TEM images of high quality SWNT soot synthesized at 500 sccm.

Raman spectroscopy also confirms the presence of SWNTs in some samples. Figure 7 shows Raman spectra of high quality samples taken with a 488 nm Ar-ion laser. G-band to D-band ratios, a measure of SWNT concentration [13], indicate that high quality material was synthesized, with a top G/D value of 156. Figure 8 compares a Raman spectrum of high quality SWNT soot produced in our modified arc discharge system to Raman spectra of typical laser vaporization material and typical Carbolex AP material, a commercially available source of high quality arc discharge-synthesized SWNTs.

The brown soot produced in 500 sccm runs was also analyzed using Raman spectroscopy; a typical spectrum is shown in Figure 9. A weak G-band was observed, indicating a small quantity of SWNTs, along with a peak at 1465 cm^{-1}, which was not present in Raman spectra of black soot. The 1465 cm^{-1} peak indicates the presence of C_{60}.

Reproducibility issues do exist with the current configuration of the system. Data displayed in the figures is admittedly the best that the system has produced; several runs with similar parameters produced no SWNT material. While reproducibility obviously needs to be improved, data displayed illustrates the quality of material the system is capable of producing.

DISCUSSION AND CONCLUSIONS

Although arc discharge SWNT synthesis systems have typically produced raw soot of much lower yields than soot produced by laser vaporization, we present evidence that yields can be significantly increased in arc discharge systems through changes in system design. G-band to D-band ratios from Raman spectral analysis suggest that our system is capable of producing soot with SWNT concentrations higher than that produced by traditional arc discharge methods and comparable

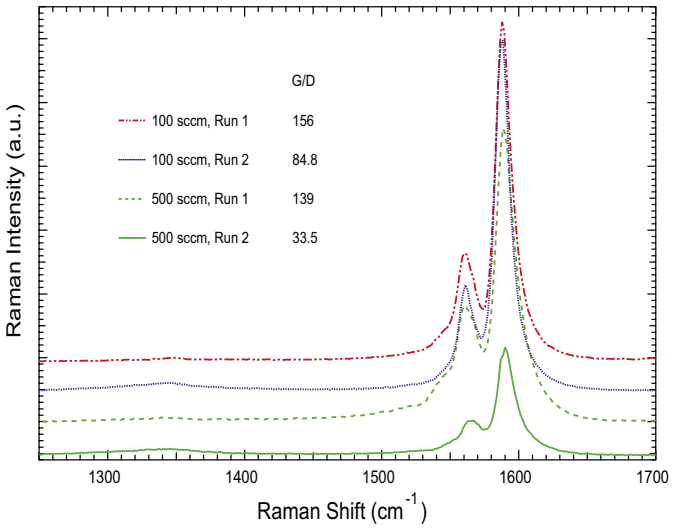

Figure 7. SWNT tangential mode Raman spectra at 488 nm of four high quality arc discharge runs in this experiment.

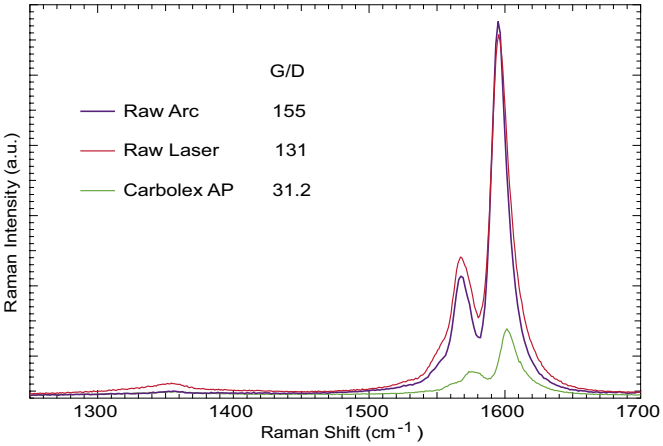

Figure 8. SWNT tangential mode Raman spectra at 488 nm comparing typical material made by laser vaporization and commercially available Carbolex AP

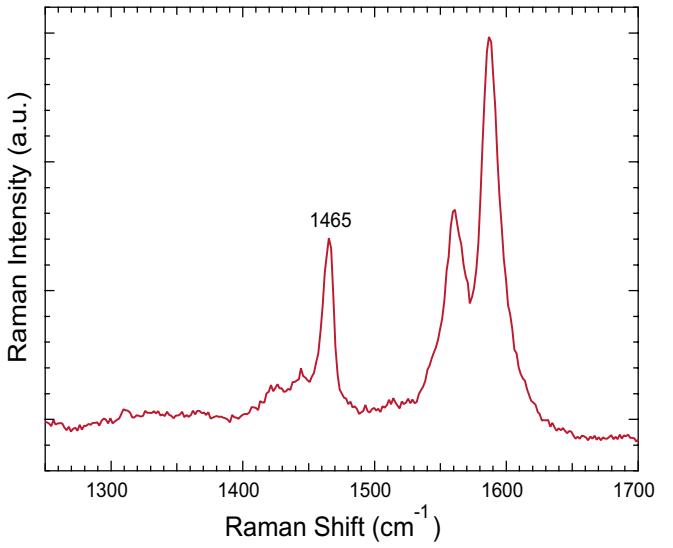

Figure 9. Raman spectrum of brown soot from 500 sccm runs taken at 488 nm. The 1465 cm-1 indicates the presence of C60.

to soot produced by laser vaporization. However, TEM images show certain undesirable carbon impurities, even in soot with high SWNT concentration. Further analysis is required to determine exact mass percents of SWNTs in the produced raw soot.

Regardless of questions that remain, we have made some improvements upon traditional arc discharge design. The design implemented here has been used in two other studies [14,15]. However, the arc in these two studies was pulsed and did not run continuously. Reported results were not similar to those we achieved. We speculate that the pulsed arc systems never reached a steady-state environment conducive to nanotube growth, which our continuous arc discharge system did achieve.

Earlier we noted two distinct differences between traditional arc discharge systems and laser vaporization systems: geometry and thermal gradient. C.D. Scott et al. have reported that the confined geometry of laser vaporization systems may have a significant impact on SWNT synthesis [2]. Part of the success of our arc discharge system may be attributable to the confinement that the geometry allows, but the mean free path for vaporized carbon molecular fragments is on the order of 1 μm, four orders of magnitude less than the diameter of the quartz tube. Changing the geometry, however, did significantly change the thermal gradient of the arc discharge system. The quartz tube acts as a temperature barrier between the heat of the arc and the ambient room temperature. We ultimately attribute the apparent purity of the SWNT soot to the change in the thermal profile facilitated by the change in geometry from traditional arc discharge systems.

Further study, both in the number of arc-discharge samples analyzed and the analysis methods employed, is necessary to draw final conclusion. Beyond the methods of this experiment, further modification to the arc-discharge system may prove beneficial. In the future, we plan to study temperature effects on steady-state arc-discharge SWNT synthesis through the addition of external heating to our system.

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