

RELEVANT CHARACTERISTICS OF THE PLASMA FOR SIGNIFICANTLY INCREASING THE SELECTIVITY AND PURITY OF SWNT SYNTHESIS USING THE ELECTRIC ARC PROCESS

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Abstract

This work aims to optimise the synthesis of single walled carbon nanotubes (SWNTs) by the electric arc technique while using regular “heterogeneous” graphite anodes (i.e., whose emptied core is filled with Ni and Y catalysts along with graphite powder) under standard pressure, current, and voltage conditions. Parameters were (1) the type of hybridisation (either sp^2 (graphite) or sp^3 (diamond)) of the co-filling carbon powder; (2) the grain size (100 or 1 μm) of the latter; (3) the inner volume of the reactor. The physical properties (temperature fields, CI and NiI concentrations) of the plasma generated were determined by in situ emission spectroscopy. On the other hand, with respect to standard conditions (large-grain graphite powder), a dramatic improvement of SWNT selectivity (resulting in higher yield) and purity (resulting in easier subsequent purification) is achieved when either small-grain graphite or diamond powder is used. The results are explained via the effect of the varied thermal conductivity of the anode onto the specific erosion modes of the heterogeneous anode. Maintaining a steady plasma composition and a CI/NiI concentration ratio higher than 10^8 are identified as two conditions required for optimising SWCNT synthesis. The study provides clues for the explanation of results from literature, and is likely to help electric arc technique to remain an economically competitive process.

Introduction

In spite of the large development and interesting versatility of the catalyst-assisted chemical vapour deposition method (CCVD), the electric arc method is still widely used for the synthesis of nanotubes including for commercial production, because of its low cost and simplicity and in spite of some drawbacks (e.g., discontinuous synthesis). However, key problems remain to understand the influence of the main and numerous physical parameters (typically: arc current, pressure, anode composition and mobility, type of catalysts...). One of them is to achieve the controlled, selective synthesis of the desired carbon nanotube (CNT) type (i.e., not only SWNTs, but also DWNTs and MWNTs) while minimising the occurrence of by-products. Indeed, when produced via the electric arc process (as well as via the laser or solar process), SWNTs always come along with large proportions of amorphous carbon, polyaromatic carbon shells, fullerenoids, catalyst remnants, etc. Because most of the impurities are partly or totally built from sp^2 carbon just as CNTs are, purification and separation steps are inefficient or problematic for the least. We have therefore attempted to study other parameters that are less trivial, including replacing graphite by diamond as the carbon powder filler of heterogeneous anodes. Preliminary studies have shown that this resulted in a dramatic influence on the type, variety, abundance, and purity of the carbon nanophases formed. Specifically, though reasons were not clear, a remarkable gain in SWNT yield and purity was obtained when using diamond powder instead of graphite powder as the filler for heterogeneous anodes (Pacheco 2002, 2003; Razafinimanana, 2003). Understanding the reasons for such a result had therefore become a major issue to achieve the full control of the synthesis of CNTs by the electric arc process, meanwhile hopefully providing the clue to find a suitable and economically viable alternative to the use of diamond, whose intrinsic cost makes it difficult to consider as a possible feedstock for commercial, large-scale production. Such an understanding was achieved in the work presented in this proceeding, as well as in a more detailed paper (Mansour, in press).

Experimental

The arc chamber device is sketched in Figure 1. Inter-electrode gap was maintained at 1 mm at a constant z position. Experiments were run for few minutes. Starting pressure in-jar was 60 kPa. Current intensity was 80 A, inducing a voltage variation from 32 to 45 V depending on the anode type and the arc fluctuations. Both electrodes were made of poly-granular graphite.

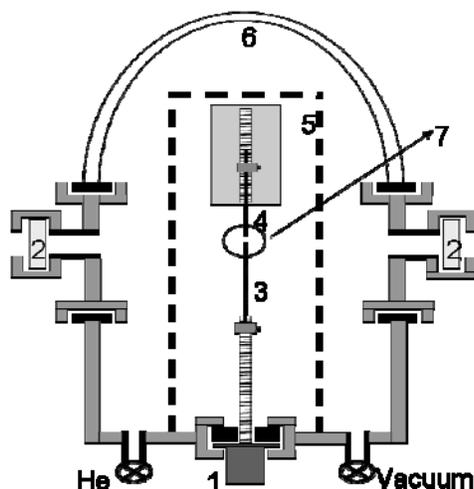


Figure 1. Sketch of the electric arc device. 1: motor for anode position control to maintain a constant inter-electrode distance. The cathode displacement is similarly controlled independently; 2: quartz windows (for emission spectroscopy); 3: anode; 4: cathode; 5: electrode holding frame; 6: vacuum bell jar. 7: location of the plasma.

Anodes were so-called *heterogeneous* anodes (Figure 2), i.e. they consisted in a pure graphite rod of 6 mm in diameter (5 cm long), in which a coaxial cavity of 3.5 mm in diameter was drilled, then filled with nickel/yttrium/graphite (0.6/0.6/23 at.% respectively) or nickel/yttrium/diamond powders (0.6/0.6/31 at.% respectively), in which “100 %” accounts for the total amount of atoms from both the filling materials (i.e., catalysts and diamond or graphite powders) and the tubular, pure graphite part of the anode. Grain sizes for the graphite powder was either $\sim 100\ \mu\text{m}$, which is a regular grain-size, and $\sim 1\ \mu\text{m}$. Grain size for the diamond powder was $\sim 1\ \mu\text{m}$. All grain sizes were checked by scanning electron microscopy. Apparent density of the resulting anode with fine grain powders (1.51 and 1.56 g/cm^3 for graphite and powder respectively) was significantly higher than when using large grain graphite (1.25 g/cm^3), meaning that a better compaction was achieved.

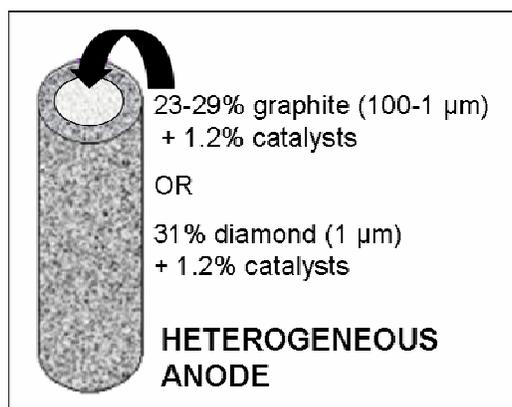


Figure 2: Principle for making so-called “heterogeneous anodes”.

For each experimental run, emission spectra were recorded for 500 ms exposure time, allowing temperature profiles (at $\pm 5\%$) and species concentration profiles to be obtained. Only CI (neutral carbon) and NiI (neutral nickel) will be reported here because they were the most abundant in the temperature range 3000-7000 K. In addition, we have already shown that C_2 species were shown to be prevalent in building MWNTs at the cathode, but to be subordinate regarding SWNT growth (Pacheco, 2002). The experimental setup for the spectroscopic diagnostic of the plasma will be fully described elsewhere along with the procedure and measurement methods (Mansour, submitted).

All the materials formed during our experiments were investigated by high resolution transmission electron microscopy (HRTEM) using a Philips CM12 TEM (Lab6 electron source) operated at 120 kV and equipped with a Super-Twin stage allowing a point resolution of 0.3 nm. The preparation of the specimen for TEM investigation includes gentle grinding and short time sonication in ethanol, before depositing a drop of the suspension onto holey-carbon-coated copper grids. HRTEM identified the various carbon and non-carbon nanophases (including impurities) present in the material gathered at the various

locations in the reactor (i.e., cathode deposit, collaret, and soot), here listed according to the nomenclature proposed in (Mansour, in press): amorphous carbon (AC), single-wall carbon nanocapsules (SWNCs, which include single-wall nanohorns (Iijima, 1999)), single wall carbon nanotubes (SWCNTs), fullerenoids, poorly organized polyaromatic carbon (POPAC), multi-wall carbon shells (MWS), catalyst particles (which are remnants of the catalysts which the heterogeneous anodes were filled with).

SWNT Yields were estimated (by $\pm \sim 15\%$) by considering: (i) the total weight of collaret formed per gram of eroded anode; (ii) the proportion of SWCNTs relative to the other phases (carbon by-products, catalysts, ...) in the collaret as estimated from HRTEM. The various experiments will be referred to the experiment for which so-called ‘standard’ conditions were used, i.e., typically the experiment carried-out with a heterogeneous anode whose cavity was filled with 0.6 Ni, 0.6 Y, and graphite powder with 100 μm average grain size. The latter conditions are believed to be similar or close to that reported in literature for ‘large-scale’ synthesis (Journet, 1997, 1998).

Results

Products Synthesised

In contrast with regular electric arc experiments dedicated to large-scale synthesis of SWNTs (Journet, 1997, 1998; Dai, 2001; Pacheco, 2003), the web is systematically absent in our experiments. This statement sounds surprising since our set of conditions is similar to what is commonly reported in literature regarding the type and proportion of catalysts (0.6 Ni + 0.6 Y), the type of graphite anode (heterogeneous, prepared from standard commercial grade graphite anode), range of current (~ 80 A), atmosphere (He), and starting pressure (60 kPa). Assuming that the web actually grows from nanosized catalyst particles/droplets recurrently re-injected into the nanotube-growing zone upon the effect of the convection flows that settle within the reactor, the reason for this lack of web may be the short duration of the experiments, which did not allow sufficient catalyst internal recycling.

Therefore, we mostly investigated the collaret material, for containing a highly dense array of SWNTs (and the soot material, for possibly containing SWNTs along with other phases). Results are gathered in Table 1.

Table 1. Data related to the erosion of each of the three types of anode: Ni/Y/graphite ($\Phi = 100 \mu\text{m}$), Ni/Y/graphite ($\Phi = \sim 1 \mu\text{m}$) and Ni/Y/diamond ($\Phi = 1 \mu\text{m}$). Erosion rates are given at $\pm 15\%$ for the Ni/Y/Graphite (100 μm) anode type and at $\pm 5\%$ for the two other anode type.

Anode type Parameter	Ni/Y/graphite $\Phi_{\text{graphite}} = 100 \mu\text{m}$	Ni/Y/graphite $\Phi_{\text{graphite}} = \sim 1 \mu\text{m}$	Ni/Y/diamond $\Phi_{\text{diamond}} = 1 \mu\text{m}$
Erosion rate (mg/s)	33	30	28
Carbon nanostructures present in collaret	SWCNTs (“not clean”), AC, catalysts, POPAC, SWNCs, fullerenoids, MWS	“clean” SWCNTs (bundled, isolated), AC, catalysts	“clean” SWCNTs (thick bundles, few isolated), AC, catalysts
SWNT proportion (volume)	20	70	60
Weight balance of material deposited (g/g of eroded anode)	Collaret: 0.16 Cathode deposit: 0.30 Soot: 0.54	Collaret: 0.20 Cathode deposit: 0.25 Soot: 0.55	Collaret: 0.18 Cathode deposit: 0.22 Soot: 0.60

Table 1 shows that using regular conditions (i.e., large-grain graphite powder) yields to a large variety of carbon nanophases in the collaret, in addition to SWNTs, as usually described in literature (Journet, 1997, 1998; Dai, 2001; Pacheco, 2003). The SWNT yield expressed as the ratio of [SWNTs] to [whole material] is low, about 20% (volume), due to both the large variety and amount of impurities in the material. Hence, isolating the SWNTs by means of a purification procedure would appear to be problematic and likely to come with significant damages – or even partial destruction – brought to the

SWNTs, due to the fact that most of the impurities are graphene-based materials, i.e. with a chemical reactivity close to that of SWNTs. The need for severe (i.e., highly oxidizing) chemical purification treatments and subsequent SWNT damaging or destruction are actually a current observation for mass production of SWNTs via electric arc or other processes.

In contrast, Table 1 shows that collarets obtained with fine-grain size ($\Phi = \sim 1 \mu\text{m}$) for both graphite and diamond powders resulted in a significant augmentation in SWNT yield, with a [SWNTs] to [whole material] ratio estimated at 60-70 % (volume). In addition, SWNTs appeared in the form of much cleaner bundles (i.e., SWNT surface is no longer coated with carbon impurities). This suggests that the subsequent purification procedure could be simpler, due to the limited variety of by-products, and milder, due to the difference in structure of the impurities to be removed (amorphous carbon and catalyst particles) and the phase to recover (SWNTs). As a consequence, (i) the SWNT structure would be much less damaged than with current standard purification procedures, and (ii) yield after purification would be further increased, since no or little amount of SWNTs would be eliminated by the purification treatment.

Plasma Characteristics

A detailed analysis of the plasma characteristics obtained from emission spectroscopy will be provided elsewhere (Mansour, submitted), including examples of reproducibility, concentration profiles for CI, C_2 , NiI, etc. Each of the temperature and CI/NiI concentration profiles shown in this section (Figures 3 and 4 respectively) were obtained from an average trend of five runs. Only experiments involving fine-grain graphite or diamond are reproducible. In contrast, experiments involving large-grain graphite show stochastic and non reproducible profiles with large variations within a single run. Such variations are still observable in Figure 3 in spite of the effect of averaging. Such a feature is likely to originate from an unsteady erosion of the anode.

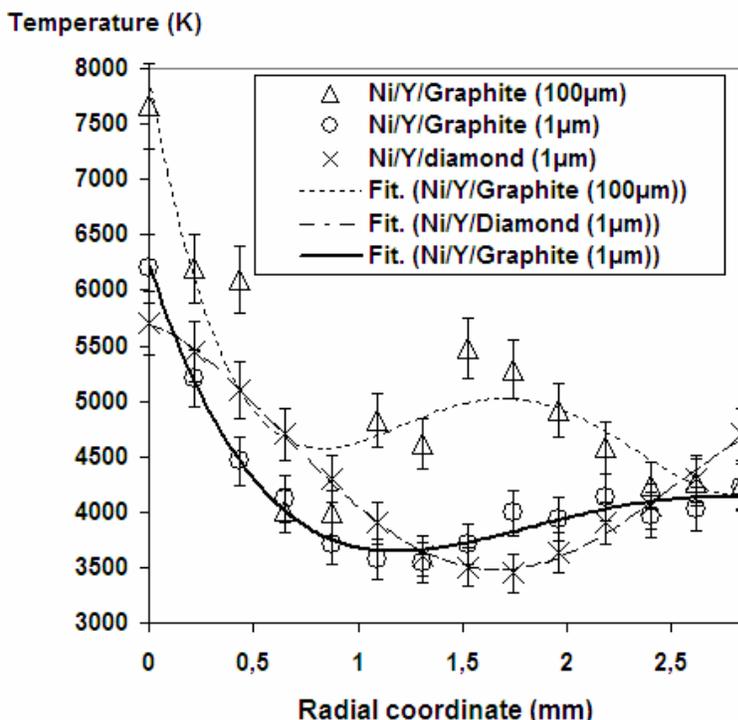


Figure 3. Radial temperature profiles for Ni/Y/graphite ($\Phi = 100\mu\text{m}$), Ni/Y/graphite ($\Phi \sim 1 \mu\text{m}$) and Ni/Y/diamond containing anodes respectively. The least square method was used to fit each of the temperature curves.

In contrast, the overall plasma temperature profiles obtained using either the Ni/Y/graphite ($\Phi \sim 1 \mu\text{m}$) anode or the Ni/Y/diamond anode are much smoother, meanwhile exhibiting less extreme temperatures ($\sim 6200 \text{ K}$ for the highest, as opposed to $\sim 8000 \text{ K}$ for the standard anode) and lower temperature gradients. This should somehow relate to a steadier erosion event. In this regard, it might be significant that the smoothest temperature profile over the longest radial distance is obtained for the Ni/Y/graphite ($\Phi \sim 1 \mu\text{m}$) anode, which has resulted in the highest SWNT yield (Table 1).

The CI/NiI concentration ratio profile for the Ni/Y/graphite ($\Phi = 100 \mu\text{m}$) heterogeneous anode also shows fluctuations (Figure 4) and meanwhile exhibits the lowest average concentration ratio ($\sim 5 \cdot 10^5$) due to a relatively low carbon concentration. Because carbon species are very emissive in the range 4500-6000 K, radiative losses are less significant when plasmas are depleted in carbon species, which correlates well with the related temperature profile in Figure 3 which exhibits the highest average plasma temperature.

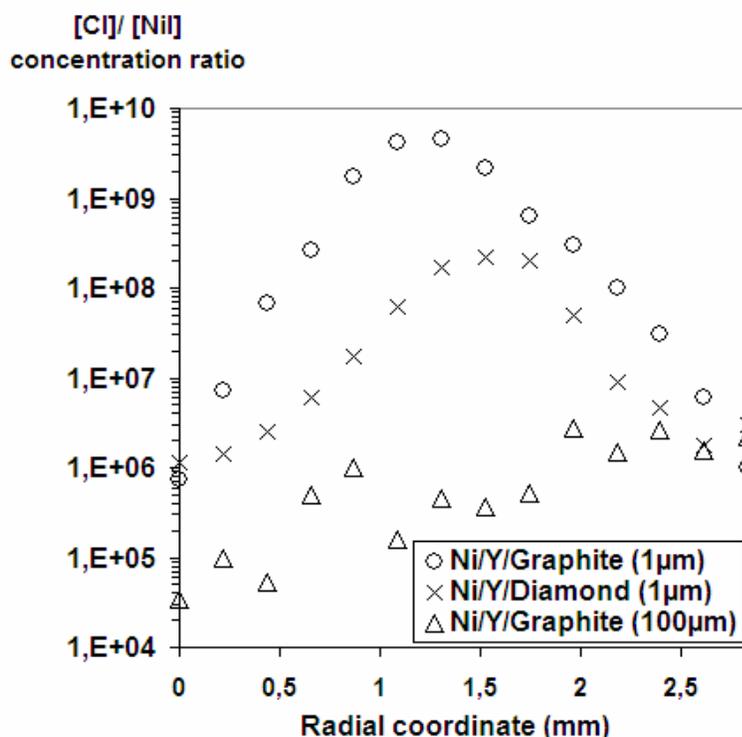


Figure 4. Radial [C]/[Ni] concentration ratio for Ni/Y/graphite ($\Phi = 100 \mu\text{m}$), Ni/Y/graphite ($\Phi \sim 1 \mu\text{m}$), and Ni/Y/diamond -containing anodes respectively. The nickel concentration distribution (not shown here) is similar for the three types of anode, so the discrepancies between the different C/Ni profiles are mainly due to the variation in carbon concentration.

In contrast, the C/Ni concentration ratio profiles related to either the Ni/Y/graphite ($\Phi \sim 1 \mu\text{m}$) anode or the Ni/Y/diamond anode exhibit a fluctuation-free regime all along the radial coordinates of the plasma cross-section, with a unique maximum at $\sim 1.3\text{-}1.5 \text{ mm}$ from the plasma axis. Such a feature is again consistent with a steady erosion. It is also worth noting that areas where C/Ni ratio is maximum relate to areas where temperature values are minimum in Figure 3. In addition, the C/Ni concentration ratio is up to about 3-5 orders of magnitude higher for the fine-grain graphite-containing anode and the diamond-containing anode than for the large-grain graphite-containing anode. Moreover, the C/Ni concentration ratio is even higher of ~ 1.5 order of magnitude for the fine-grain graphite-containing anode than for the diamond-containing anode. All the latter features correlate pretty well with the SWNT yield values for each anode (see Table 1).

Discussion

We do believe that these results are highly dependent on the variation of anode thermal conductivity. One supporting experiment was to prepare model anodes in which each of the filling elements were used alone: anode filled with yttrium (0.6%Y, 99.4%graphite), anode filled with nickel (0.6% Ni, 99.4% graphite), and anode filled with graphite powder (large grains). The highest erosion rate (40 mg/s) was found to correspond to the anode filled with the element having the lowest TC (yttrium, which exhibits a TC of 0.172 W/cm.K at 298 K, as opposed to 0.907, 1.29, and $2.3 \text{ W.cm}^{-1}.\text{K}^{-1}$, for nickel, graphite, and diamond respectively). The likely reason is, if the thermal conduction across the anode is low, energy accumulates on the upper surface of the anode, which leads locally to a strong increase in temperature hence to a rapid erosion of the anode material. On the opposite (anode with high TC), the energy supplied to the anode flows across it resulting in heating the whole anode, therefore decreasing the erosion rate of it. In fact, the thermal conductivity of a poly-granular material increases when the apparent density of the powder increases (Tavman, 1996; Gonzo, 2002) because decreasing the grain size results in decreasing the inter-grain empty volume (i.e., interstices) (Gonzo, 2002) which is poorly thermally conductive (TC of air is 0.262 W/cm.K at 298 K).

Ideally, plain and dense anodes should be subjected to a steady erosion rate which results in a given plasma composition with a [carbon species] to [catalysts] concentration ratio that remains constant or evolves monotonously. This would enable

the selective formation of a limited variety of carbon morphologies. However, due to the intrinsic heterogeneous nature of the anodes, erosion mechanisms are assumed to vary with time as erosion proceeds, according to three different but successive modes:

- (i) First, the filling material (graphite powder + nickel and yttrium catalyst powder) is preferably evaporated into the arc-plasma, as the part of the anode with the lowest TC. In most experiments, the remaining part of the anodes was actually found bevelled and having their cavity empty once the experiment is stopped. The resulting plasma is enriched in nickel and yttrium compared to what is expected from the overall starting composition. The preferred formation of short nanotubes and polyaromatic carbon shells around the catalysts are likely to be favoured in such conditions due to the lack of sufficient carbon feedstock to allow regular SWNTs to grow.
- (ii) Then the remaining anode body, made of pure poly-granular graphite, is mainly evaporated, thereby generating a plasma containing few or no catalysts. The preferred formation of carbon products such as fullerenoids, amorphous carbon, soot and SWNCs, whose growth does not require any catalyst, is therefore assumed (Table 1) (Wang, 2004).
- (iii) Finally, there might be a situation for which the respective levels of the outer graphite surface and the inner [catalysts + graphite or diamond powders] filling make that they both evaporate for a while, thereby generating a plasma supplied with carbon and catalysts with a concentration ratio which is that expected from the overall starting anode composition, thereby promoting the preferred growth of SWNTs with high yield.

The three steps just described occur successively within few milliseconds, while the recording time is 500 ms, meaning that they cannot be discriminated, although each of them leads to different deposit morphologies.

Considering both the relative thermal conductivity of powders with different grain sizes and the three-step erosion mechanisms above is able to explain all our observations. Typically, it explains why large-grain-graphite-containing anode exhibits the highest erosion rate and large fluctuations of the plasma characteristics, and results in the largest variety of carbon nanophases formed, as opposed to small-grain graphite or diamond powder-containing anodes. This also explain the results from previous experiments involving homogeneous anodes (i.e., anodes in which catalysts are homogeneously dispersed all over the whole anodes (Pacheco, 2001, 2002, 2003; Razafinimanana, 2003), which were shown to favour a much higher nanotube yield, that we now understand as the result from the steady erosion event, originating from the anode homogeneity.

It could be wonder, since using diamond resulted in the lowest anode erosion rate among the three anode-types investigated, why both the SWCNT yield and selectivity were not further enhanced with respect to using small grain graphite instead of merely being of the same range. This could originate from an intrinsic limitation of diamond, whose low electrical conductivity (with respect to graphite) might somehow hinder the benefits expected from its high thermal conductivity. Further investigation of this aspect is in progress. Likewise, considering that the temperature values involved within the first 3 mm away from the discharge axis are above 3000 K, i.e., far above the actual temperature of SWCNT formation (1000-1500 K, referring to temperatures currently used with CCVD), it might be wondered how the plasma characteristics relate to the SWCNT growth. Answering this question is not easy, because emission spectroscopy is inefficient within the area of SWCNT growth. Experiments are in progress to tentatively overcome this inefficiency, e.g., by disposing thermocouples away from the plasma zone. Whatever, it already sounds reasonable that carbon moieties present in the plasma zone are building blocks controlling the formation of more complex carbon species that build beyond this zone, while the type of such complex species (e.g., C_n with $n > 4$, coranulene, etc.) is determinant for controlling SWCNT growth efficiency.

Conclusion

One key parameter for controlling and enhancing the SWNT yield when using the electric arc process is to use conditions where C/NI concentration ratio in the plasma reaches a threshold value of 10^8 (or higher) at least within the first 2-3 mm away from the plasma centre. Lower C/NI concentration ratio values are likely to correspond to insufficient carbon feedstock, resulting in low yield of SWNTs. The second key parameter is to stabilise the plasma characteristics (species concentration profiles, specifically) over a radial distance as extended as possible with respect to the discharge axis. Such a condition promotes a better selectivity of the carbon nanophases formed, by favouring the preferred transformation of the carbon species into SWNTs instead of balancing between their transformation into SWNTs, fullerenoids, amorphous carbon, etc., within the same run. The way to insure such a stability is to provide the anode with a high and homogeneous thermal conductivity. In this regard, using small-size graphite grains, and/or packing as well as possible any powder compound to minimise interstices (heterogeneous anodes), and/or making the catalysts homogeneously dispersed all over the anode (homogeneous anodes), and/or adding high thermal conductivity additive, are examples of the various ways to suitably modify anodes so that to obtain slow and steady erosion rates of the anode, subsequently resulting in optimising the SWNT yield. Beyond the electric arc process, the results are likely to apply to any SWNT-synthesis process using high temperature plasma and graphite-based targets (e.g., laser vapourisation, or focused solar light).

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