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Production of carbon nanotubes: the light approach

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Abstract

In this article we present an overview about the current state of the art using highly concentrated light in the production process of carbon nanotubes. Firstly, the most common approaches using laser light or solar radiation are described and their production possibilities are compared. Secondly, important growth parameters and their complex interactions are discussed. It is shown that a key issue in the production of nanotubes is the creation of the proper temperature conditions. This concerns the temperature of both the target surface and the gas-phase. While the first controls the number and kinetics of evaporated species, the second affects the assembling of nanotubes in the gas-phase. Thirdly, the problem of obtaining high-quality nanotube materials in an up-scaled production process is addressed. Here, a solution may be related to the finding of advantageous light–target interactions. © 2002 Published by Elsevier Science Ltd.

Keywords: A. Carbon nanotubes; B. Laser irradiation

1. Introduction

The basic principle for the synthesis of carbon nanotubes is very easy: a carbonaceous feedstock has to be brought into the gas-phase where subsequently the evaporated species can self-assemble into the tubular structures. This process usually requires high temperatures, especially if a solid carbonaceous feedstock like graphite is used. In this case, the evaporation usually is realized by either resistive heating using an electric arc-discharge system [1–4] or by employing concentrated light using as source lasers [5–7] or even the sun [8]. However simple the basics are, today, the controlled production of high-quality nanotubes with well-defined properties in large quantities and in an economically attractive way still remains a major challenge to solve.

Historically, the electric arc-discharge was the first technique for the production of both multi-wall carbon nanotubes (MWNTs) [1] and single-wall carbon nanotubes (SWNTs) [2,3]. Using suitable catalysts and buffer-gases, this technique was improved towards the growth of bundles of SWNTs in large amounts [4]. Here, within relatively short experimental times (typically less than 5 min) roughly 500 mg of SWNT-containing soot material can be obtained. However, in this process the environment favorable for the growth of nanotubes is largely determined by the highly fluctuating behavior of the created plasma. Consequently, it is very difficult to gain greater control of the experimental parameters as well as to model and understand the formation process of carbon nanotubes. This, on the other hand, would be essential for the production of nanotubes in well-defined yields, accompanied by negligible amounts of undesired by-product such as amorphous carbon and catalytic nanoparticles, and with determined diameters and chiralities.

The use of concentrated light for the production of nanotubes offers a promising alternative. Its great advantage is the control of space and time of the various interaction processes taking place during the evaporation experiments, especially in the case of light originating from laser sources. Therefore, these techniques offer a wide range of possibilities in studying and modeling the influence of various parameters independently of each other. Even in-situ spectroscopic measurements can easily be applied. All this not only gives a better understanding of the formation process of carbon nanotubes but also facilitates tackling the problem of producing nanotubes with tailored properties. Additionally, large-scale production can be envisaged by automatizing the technique leading to long-term unattended and continuous production.

In the following we will present an overview about the current state of the art using concentrated light in the

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production of carbon nanotubes. Here, we will describe firstly the typical experimental systems and their production possibilities, focusing on production rates, yields and structural characteristics of the grown nanotube materials. Then we will discuss various parametric studies done by several groups and extract from their observations the common factors, which seem to be important towards a controlled production of carbon nanotubes. Last but not least we will address the limitations of these approaches: the compatibility between an up-scaled production and the quality of the grown nanotube materials as well as the question of an economic production. A short outlook on future perspectives will conclude this review.

2. Experimental systems and production results

Depending on the nature of the light used—its wavelength and its wave-mode—the interaction with the target material as well as the evaporation environment can greatly differ and influences the outcome of the production process. Therefore, essentially three different kinds of experimental approaches are employed today. These systems and their current state of the art in the production of carbon nanotubes will be described in this section.

The use of light for the growth of carbon nanotubes was first reported by Guo et al. [9]. They developed an experimental set-up, which today still is the base for almost all experiments with the pulsed Nd:YAG-laser (Fig. 1). It is a horizontal configuration, which consists in a quartz-tube mounted in a temperature-controlled furnace. A target rod is placed axially in the middle of the high temperature zone. After sealing and evacuating the tube, a buffer gas is flowed through it. Subsequently, a pulsed Nd:YAG laser is focused onto the target rod. The carrier gas-flow sweeps most of the carbon species produced by the laser evaporation out of the furnace zone depositing it as soot on a water-cooled copper rod. The favorable standard conditions of this as well as of the other systems are summarized in Table 1. The first experiments were performed with a target rod consisting of pure graphite, which was evaporated by the second harmonic (532 nm) of the pulsed Nd:YAG laser. During the operation, the focused laser beam was scanning across the target surface to maintain a smooth evaporation. Furnace temperatures of 1200, 900 and 200 °C were employed. Examination of the deposited soot materials by transmission electron microscopy (TEM) revealed the existence of MWNTs with 4 to 24 layers and lengths up to 300 nm. Also found were fullerene structures as well as graphite-like nanoparticles (slightly elongated structures that closed before substantially lengthening). Yield and quality of MWNTs strongly depends on the furnace temperature. While at 1200 °C all MWNTs were free of defects and closed-ended, at 900 °C the number of defect structures increased and at 200 °C no MWNTs were detected anymore. No SWNTs have been found in these experiments. Using a target rod composed of graphite and a small percentage of certain kinds of metals Guo et al. [10] could prove the operational functionality of this system for the synthesis of SWNTs. Enhanced yields of SWNTs were found at furnace temperatures close to 1200 °C. At this temperature, of the single metals studied, nickel produced the greatest yields. This could be increased by a factor of 10–100 by the use of bi-metals like cobalt/nickel and nickel/platinum. Here, a rubbery sheet of soot material has been deposited at the cold copper collector. The SWNT yield amounts to 50 vol.% of the carbonaceous material in the obtained soot material. Additionally, it was estimated that about 15 wt.% of all carbon evaporated has transformed into SWNTs.[1]

Further optimization of this process has been reported by Thess et al. [5]. The initial laser pulse (532 nm, 250 mJ, 10 Hz, 5 mm diameter spot) was followed 50 ns later by a second pulse (1064 nm, 300 mJ, 10 Hz, in a 7 mm diameter spot coaxial with the first laser spot). This provided a more uniform evaporation of the used graphite/

[1]Comment of the authors regarding the values indicating the SWNT yield in vol.%: it is important to keep in mind that these values, in most of the cases, are estimations from extensive electron microscopy analyses. These give a first idea about the quality of the sample. However, more meaningful values referring to weight percentages are difficult to obtain and rarely given in the literature.

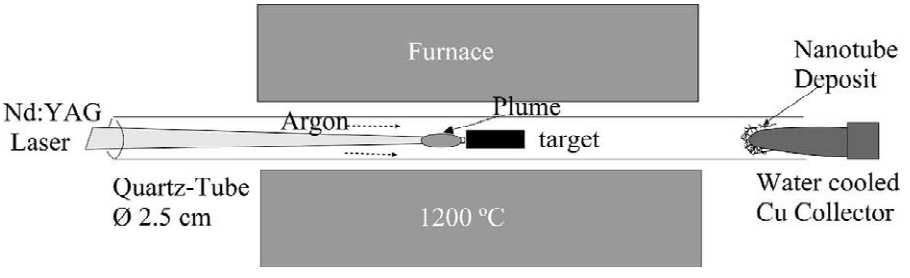

Fig. 1. Experimental set-up for the basic Nd:YAG-laser evaporation system [9]. Instead of using only a single laser pulse with a frequency of 532 nm, a second time-delayed laser pulse with a frequency of 1064 nm can be employed leading to increased SWNT yields [10].

Table 1
Some favorable standard conditions for synthesis of nanotubes using the basic light production systems

Source	Source conditions	Reaction system	Target	Temperature	Gas	Results
Single pulsed Nd:YAG [9,10]	λ: 532 nm L_{pulse}: 10 ns E_{pulse}: 250–300 mJ Rep-rate: 10 Hz $\varnothing$ Spot: 3.6 mm	Horizontal set-up: 2.5-cm $\varnothing$ quartz-tube inside furnace	Graphite G 100 at.% G/Ni/Co 98/0.6/0.6 at.%	Furnace at 1200 °C	Argon 50 kPa 0.06 l/min	MWNTs SWNTs 50 vol.%
Double pulsed Nd:YAG [5,11]	λ_1: 532 nm E_{pulse1}: 250–490 mJ Rep-rate: 10–30 Hz $\varnothing_1$ Spot: 5–6 mm t_{delay}: 42–50 ns λ_2: 1064 nm E_{pulse2}: 300–550 mJ $\varnothing_2$ Spot: 6–7 mm	Horizontal set-up: 2.5-cm $\varnothing$ quartz-tube inside furnace Double quartz-tube system: 5-cm $\varnothing$ quartz-tube inside furnace 2.5-cm $\varnothing$ quartz-tube coaxially inside first tube	G/Ni/Co 98/0.6/0.6 at.%	Furnace at 1200 °C	Argon 50 kPa 0.1 l/min	SWNTs 70–90 vol.% 80 mg/day SWNTs 60–90 vol.% 1 g/day
cw-CO_2 [7]	λ: 10.6 μm P_{cw}: 12 kW/cm^2 $\varnothing$ Spot: 1 mm	Vertical evaporation chamber	G/Ni/Y 95/4/1 at.% G/Ni/Co 96/2/2 at.%	No furnace	Argon 27–53 kPa 0–1 l/min	SWNTs 80 vol.% 130 mg/h
Solar light [8]	λ: sun-light 2 kW set-up $Flux_{Solar}$: 1000 W/m^2 $Power_{focus}$: 1300 W $\varnothing$ Spot: 1.5 cm	Vertical evaporation chamber	G/Ni/Co 96/2/2 at.% G/Ni/Y 95/4/1 at.%	No furnace	Argon 25 kPa 3 l/min 40–60 kPa 3 l/min	MWNTs and few SWNTs SWNTs

Definitions of parameters used: λ, wavelength; L_{pulse}, pulse length; E_{pulse}, energy per pulse; Rep-rate, repetition rate; $\varnothing$ Spot, diameter of laser spot on target surface; t_{delay}, time of delay between two laser pulses; P_{cw}, power density of laser operating under continuous wave-mode conditions (cw); MWNT, multi-wall carbon nanotubes; SWNT, single-wall carbon nanotubes. The given vol.% for the SWNT yield refer to values obtained from SEM/TEM observations.

cobalt/nickel target resulting in increased SWNT yields of 70 to 90 vol.% of the carbonaceous material in the obtained samples. The SWNTs are remarkably uniform in diameter and self-organized into bundles via van-der Waals forces. Consisting of 100 to 500 SWNTs, their diameters range from 10 to 20 nm and their lengths can reach values between 10 and 100 μm. TEM and X-ray diffraction studies show that these bundles form a two-dimensional triangular lattice with a lattice constant of 1.7 nm. The mean individual tube diameter is calculated to 1.38 nm, corresponding to the metallic (10,10) armchair tube which was thought to be the dominant component. The bundles are randomly oriented and pass through zones of amorphous carbon in which nickel–cobalt nanoparticles are embedded. The ends of the tubes seem to be perfectly closed with hemispherical end caps with no evidence of any associated metal catalyst particle. MWNTs have not formed in this process.

Since the production rate of this SWNT material was only 80 mg/day, as a next step, Rinzler et al. [11] attempted to scale up this kind of laser-oven evaporation method. Since the limiting factor in the original 2.5-cm-diameter flow-tube system was plugging off the tube around the target by the web-like SWNT deposit, firstly, the dimension of the flow-tube was increased and a 5-cm-diameter horizontal flow tube was used. After optimizing parameters (laser powers, spot sizes, timing, gas flow rate, and pressure) it was found that the generation of material containing more than 50 vol.% SWNTs required a modification which mimicked, in part, the geometry of the original 2.5-cm-diameter flow-tube apparatus. This involved adding a 2.5-cm-diameter quartz tube coaxial with the 5-cm-tube extending from the front flange to within 4 mm of the target face (Fig. 2). With this new configuration the evaporation plume now lifted off the target face to extend well into this inner tube such that the nucleation and much of the SWNT growth took place within the confines of this tube. Following this modification the SWNT yield ranged from 60 to 90 vol.% of the carbonaceous soot material and about 1 g/day could be synthesized. In order to further increase the production, the target-pitting problem—drop down of evaporation due to the growth of faceted peaks with increasing exposure time—had to be tackled. A solution was achieved by using a 10-cm-flow tube system accommodating a 5-cm-long (2.5-cm-diameter) vertical rotating target rod which was repetitively scanned up and down the cylindrical surface. However, due to the moving plume this set-up was

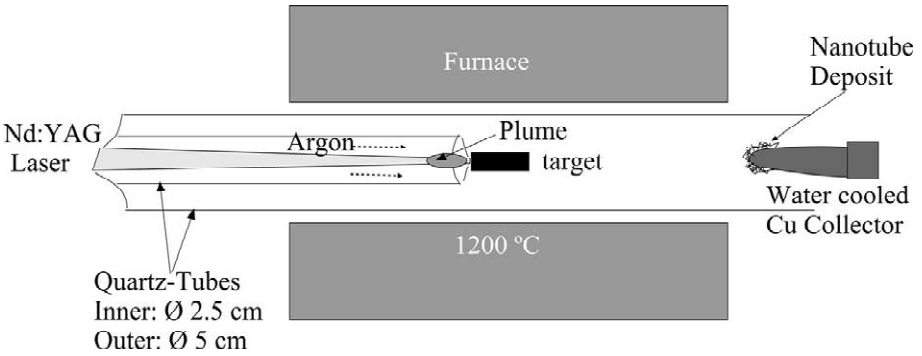

Fig. 2. Sketch of the up-scaled Nd:YAG laser evaporation experiment [11]. Although the dimensions of the outer quartz-tube are larger, a smaller inner quartz-tube had to be added mimicking the system shown in Fig. 1. This leads to confinement of species in the vapor plume, which seems to be crucial for improving the quality of nanotubes [11,37].

incompatible with a plume confinement tube and due to the increased dimensions of the flow tube the optimal operating temperature of 1200 °C could not be reached. This led to reduced yields of SWNTs. Using dual laser pulses which both are operating at a wavelength of 1064 nm resulted in the production of 20 g of 40 to 50 vol.% of SWNT material in 48 h of continuous operation. Therefore, with this system a relatively fair compromise between long-term unattended production and sample quality was found.

Maser et al. [7] followed a different approach for the production of carbon nanotubes. Using a CO_2 laser with a wavelength of 10.6 μm operating in continuous wave-mode (cw) and taking advantage of the different light–target interaction they developed a simple vertical experimental set-up (Fig. 3). It consists of an evaporation chamber in whose center is placed a target rod. No additional external furnace is used. After evacuating the chamber, a buffer gas is flowed vertically from the bottom to the top of the chamber. Then, the cw-CO_2 laser is focused on the lateral side of the target rod, which is continuously rotated as well as up-and-downward translated in order to maintain a uniform evaporation. The carrier gas-flow sweeps most of the carbon species produced by the laser evaporation out of the hot growth zone inside a quartz-tube vertically placed above the target rod. Here, the soot deposits on an entangled copper wire. Like with the Nd:YAG laser, bi-metals like nickel/yttrium or nickel/cobalt result in the formation of rubbery web-like soot. Analysis of this soot material reveals similar results than those obtained with the Nd:YAG system: the soot contains large amounts of clean bundles of SWNTs with diameters of around 20 nm. Their lengths may exceed 1 μm. The average tube diameter is about 1.4 nm and the diameter distribution ranges from 1.1 to 1.7 nm. The bundles of SWNTs are passing through areas of amorphous carbon, which contain metal nanoparticles with diameters between 5 and 25 nm. No obvious link between the particles and the SWNTs has been observed. The evaporation rate can be as high as 200 mg/h (four times 15 min of experimental time). Here, about 80 mg/h have transformed into web-like soot with an SWNT yield of about 80 vol.%, while 50 mg/h resulted in rubber-like soot with a slightly lower yield. Typical TEM images of SWNT-containing soot are shown in Fig. 4.

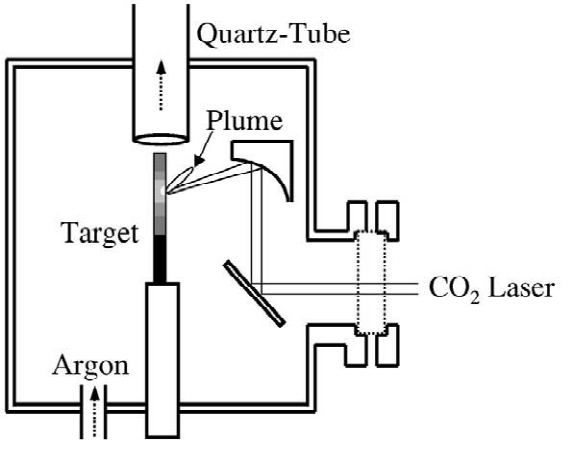

Fig. 3. Drawing of the cw-CO_2 laser evaporation system [7]. In contrast to the pulsed Nd:YAG laser approaches no external furnace is required. The target rod is heated by the laser itself (indicated by different gray tones) and therefore creates favorable growth conditions.

Concerning yields and structural characteristics of the produced nanotubes no big differences exist in the use of Nd:YAG and CO_2 laser. Nevertheless, the production rates for high yield SWNT material synthesized by the simple cw-CO_2 laser process exceed easily by a factor of two to three the ones obtained by the improved Nd:YAG system. However, further attempts in up scaling or automatizing the cw-CO_2 laser process have not been reported yet.

The use of concentrated solar light for the production of nanotubes was described by Laplaze et al. [8]. The reaction chamber (Fig. 5a) consists of a Pyrex balloon flask located

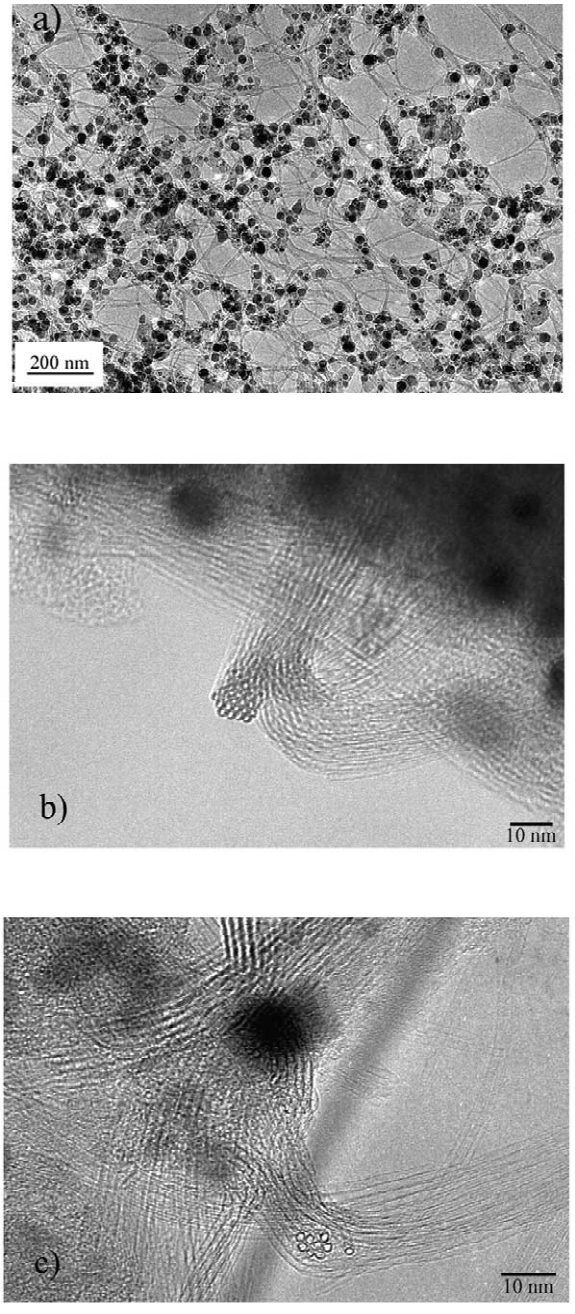

Fig. 4. Transmission electron micrographs (TEM) of SWNT-containing soot typically obtained from samples produced by the laser evaporation technique. (a) Overview of an entangled fibril network composed of bundles of SWNTs passing through zones of amorphous carbon and metal nanoparticles. (b) Cross-section of a rope of SWNTs showing the packing of individual SWNTs into a bundle. (c) Bundles of SWNTs close to a catalyst metal nanoparticle. This type of image could suggest that individual nanotubes or bundles are connected to the metal nanoparticles and therefore could grow out of these. However, today, the growth discussion still remains an open question.

on top of a water-cooled brass support. In its center vertically is placed a graphite crucible containing graphite/metal powders as target material. The crucible is surrounded by a graphite pipe which is connected to a filter inside the water-cooled brass cylinder. The chamber is purged and a constant flow of buffer gas (argon) is established passing through the graphite pipe on its way out. A parabolic mirror above the chamber focuses the collected sunlight on top of the target material. Under clear sky conditions temperatures of around 3000 K can be reached at the 2 kW set-up of the solar station in Odeillo (France) and the evaporation process can start. The evaporated material is drawn immediately through the graphite pipe, which acts as a thermal screen by reducing radiative losses (Fig. 5b). On its walls the produced soot material in the form of rubbery sheets can be collected. Especially nickel/cobalt and nickel/yttrium in the graphite–target mixtures result in the formation of soot containing carbon nanotubes. Depending on the pressure and flow conditions, either bamboo-like MWNTs, or MWNTs and SWNTs together or only SWNTs in the form of long bundles can be found. Additionally, the nanotubes are accompanied by amorphous carbon and metal nanoparticles. The diameter distribution of the SWNTs lies in the range of 1.2 to 1.5 nm and the sample purity can be as good as the one of the materials produced by the laser methods. The solar process can lead to production rates of 100 mg per each run (per hour) if the weather conditions allow to keep the temperature during the experiment at 3000 K. Improvement in the production rate can be envisaged by adapting the experimental set-up to the more powerful 1 MW facility at the Odeillo station.

Although the production rates are lower than the ones of the laser experiments, the use of solar radiation is comparable to the one of the CO_2 laser approach. In both cases light in continuous wave-mode has been used and a very simple vertical set-up without the need for an external furnace has been employed. Therefore, both systems allow the performance of complementary parametric studies under very similar conditions.

For the three systems described here the various groups have found their own ‘optimal’ conditions for the production of nanotubes. These depend on a lot of factors and interaction processes, which we will try to elucidate in the next section.

3. Understanding the production process

3.1. The target

Already in the first experiments it became obvious that the composition of the target material is a crucial factor in the production of carbon nanotubes. Here, graphite usually provides the carbonaceous feedstock. It is commonly observed that by evaporating pure graphite the only tubular

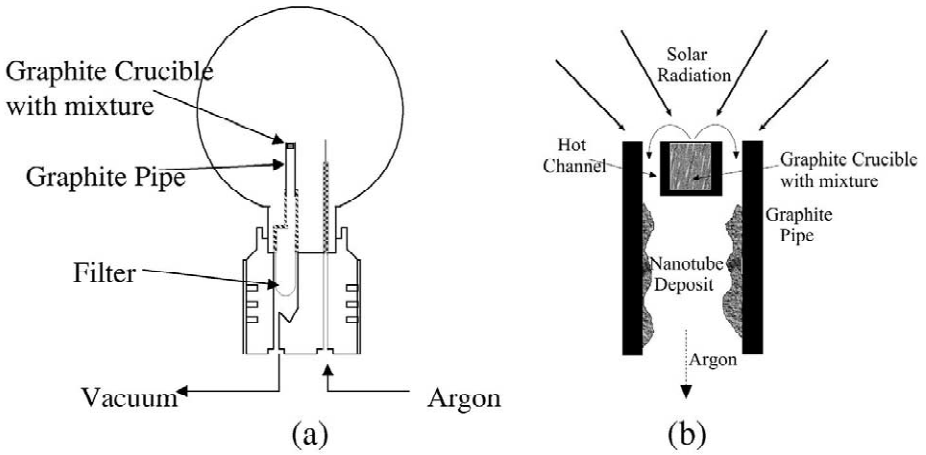

Fig. 5. Experimental set-up of the solar evaporation system [8]. (a) Overview, (b) detail of evaporation zone in the solar system. Target and pipe are heated by the solar radiation. The hot channel between both acts as local furnace. Therefore, no external furnace has to be used.

structures being formed are MWNTs [9]. However, using a target which consists of graphite mixed with a small amount of certain kinds of metals leads to the growth of SWNTs [5,7,8,10]. The type of metal and its content in the target influences the production rate of SWNT-containing material and its SWNT yield. Transition metals like nickel, cobalt, iron, and platinum lead to the formation of soot containing only few and isolated SWNTs often covered with amorphous carbon [7,10]. The SWNT yields are about a few percent and decrease in the following order Ni>Co≫Fe, Pt. Employing bi-metal combinations, rubbery or web-like soot is produced. Here, SWNTs are arranged in thick and relatively clean bundles. Their amount is 10 to 100 times higher compared to the one obtained with single metals and results in yields between 50 and 90 vol.%. The order of yield (from highest to lowest) corresponds to the following sequences: Ni/Co≈Co/Pt>Ni/Pt≫Co/Cu as observed in Nd:YAG experiments [10], and Ni/Co≈Ni/Y≫Ni/Fe≈Ni/La≈Co/Y as found both in CO_2 laser production [12] and in solar processes [13]. The advantage of using bi-metal mixtures additionally was confirmed by Yudasaka et al. [14] who also identified the commonly accepted order: Ni/Co≫Ni>Co. Furthermore, Kataura et al. [15] reported on the use of RhPt and RhPd leading to yields comparable to Ni/Co mixtures. Here, it is also shown that by using different mixtures the diameters of SWNTs could be selectively influenced. Small tubes were obtained with Rh/Pd (0.86–1.24 nm), medium tubes with Ni/Co (1.24–1.4 nm) and large tubes with RhPt (1.4–1.46 nm). In the cw-CO_2 experiments the diameter distribution of SWNTs in case of bi-metals generally ranges from 1.1 to 1.6 nm [12]. However, it was observed that in case of yttrium-containing mixtures the fractional yield of tubes having diameters of 1.6 nm increases while in case of Ni/La the one of tubes having small diameters of 1.1 nm was more pronounced. Alvarez et al. [13] also noticed that by adding sulfur to the graphite/metal mixtures very small SWNTs with diameters between 0.8 and 0.9 nm can be found. From all these results it becomes clear that bi-metal mixtures lead to enhanced yields of SWNTs and favor their growth in the form of bundles. Furthermore, the type of metal seems to control the diameter or diameter distribution of SWNTs. However, the deeper reason for the synergetic effect as well as the diameter influence still remains unknown.

Beside the target composition, its structure or its structural changes can drastically affect the evaporation conditions and therefore the characteristics of the produced soot material. Here, the ‘pitting’-problem [11,12,16] (see also Section 2) is one example where due to the increase in roughness of the target surface the free expansion of the evaporated materials, i.e. the delivery of feedstock species into the gas-phase cannot be maintained. Dillon et al. [17] also pointed out that the porosity and thermal conductivity of the target strongly influences the dissipation of the arriving laser energy, which can lead to quite different surface temperatures of the target. This shows that there is a clear interplay between target and energy delivery parameters changing the evaporation and growth conditions for SWNTs. This further was underlined by Maser et al. [18]. Using pitch as carbonaceous feedstock, they observed that the major part of the laser energy is consumed during the liberation of gases and in subsequent melting processes therefore not leaving enough energy for the evaporation of carbonaceous species. On the other hand, working with coke, they saw that evaporation takes place, but due to the structure of coke no proper heating of the target surface occurs and thus not leading to the proper temperature conditions. Therefore, these authors argue that a balanced equilibrium for the laser energy distribution into heat and evaporation has to be established.

As one can see, it is not only the composition and structure of the target but actually the laser–target interaction, which influences the evaporation of the precursor species into the gas-phase and thus the conditions for the assembling of nanotubes and other nanostructures. Here, an optimal growth environment depends on a favorable gas-phase feedstock, consisting of an optimal concentration of metal and carbon species with advantageous kinetic and thermal energies, which has to be provided and maintained. Therefore, different target structures and compositions may result in changed gas-phase characteristics. Consequently, for each type of metal or metal mixture there may exist an optimal concentration in the target material, which also depends on other experimental parameters, like type of ambient gas, pressure and flow, laser mode and intensity, temperature etc. This further explains why the 'optimal' target conditions may vary from group to group. Today, the mixtures most frequently used are the ones of nickel/cobalt (1/1 and 0.6/0.6 at.%) in Nd:YAG, CO_2, and solar systems, as well as nickel/yttrium (4/1 and 2/0.5 at.%) in CO_2 and solar experiments. However, the general objective, from an economic point of view and for reasons of sample purity, is to produce high yield SWNT material by keeping the metal concentration as low as possible.

3.2. The temperature

Already in their first Nd:YAG laser experiments, Guo et al. [9,10] noted that nanotube yield and quality were highest when working at 1200 °C. Lowering the temperature to 900 °C, defects became increasingly prevalent and at 200 °C no tubes were observed anymore. Bandow et al. [19] as well as Yudasaka et al. [20] reported on a low threshold for the furnace temperature of 850 °C and 900 °C, respectively. Below these values the amount of SWNTs is drastically reduced, and predominantly amorphous carbon structures are formed. Therefore, all groups using the Nd:YAG laser technique preferentially work at furnace temperatures of 1200 °C. Bandow et al. [19] further observed a shift of the diameters of SWNTs from 0.81 nm to 1.51 nm by increasing the temperature from 850 to 1050 °C. The effect of higher surrounding background temperatures on the diameter distribution also was confirmed by Rinzler et al. [11].

The important role of the proper temperature environment for the formation of carbon nanotubes also has been observed in cw-CO_2 laser experiments where no external furnace was used [7]. Due to favorable laser–target interactions part of the incoming laser energy continuously dissipates as heat into the target. Its surface temperature amounts to 3000 °C in the focal spot and gradually decreases along its length having still a value of about 1200 °C at a distance of 1 cm as indicated in Fig. 3. Emitting this heat as black-body radiation the target itself acts as a local furnace and heats the surrounding of the evaporation zone. Once in the gas-phase, the evaporated species then directly experience an environment of sufficient thermal energy suitable for the assembling of SWNTs. Their yield is strongly related to the maintenance of this favorable temperature environment i.e. to low temperature gradients. This clearly can be deduced from experiments performed under pulse-mode conditions. Here, no heating of the target rod has been observed and the SWNT yield is drastically reduced [21].

Using a pulsed CO_2 laser in the Nd:YAG configuration, Kokai et al. [22] found that low yield SWNT material was obtained keeping the furnace at room temperature. Higher yields were achieved by increasing the temperature up to 1200 °C. Additionally, like in the case of the Nd:YAG, the trend towards larger SWNT diameters was observed.

The importance of maintaining the proper temperature conditions also was confirmed by the solar experiments [13]. Here, the channel between graphite pipe and target crucible (Fig. 5b) acts as furnace and thus creates the favorable temperature environment close to the evaporation region. However, changed gas flow rates or flow directions let the evaporated species experience a different temperature gradient while passing through the pipe. This results in the reduction of the nanotube yield. The temperature gradient also may be responsible for the observation of the diameter distribution.

All these experiments clearly demonstrate that the local temperature conditions experienced by the evaporated species close to the target play a key role in the formation process of SWNTs. Therefore, in order to favor the growth of SWNTs a sufficient high temperature environment with a small temperature gradient has to be established and maintained during the evaporation experiments.

Furthermore, various studies with the Nd:YAG laser [6,14,17,20], the CO_2 laser [18,21] and the solar experiment [23,24] show in great agreement that the favorable temperature conditions are determined largely by the light–target interaction and therefore is influenced strongly by the energy delivery parameters of the employed system (intensity, wave-mode, pulse width, pulse frequency, peak pulse power etc.). Among these parameters it is especially the average power density (intensity, solar flux) which contributes to the heat accumulation in the target and therefore to an increased temperature of the target surface. This influences both the evaporation process determining the concentration and the kinetics of the evaporated species and the temperature environment close to the target leading to favorable SWNT assembling conditions. The use of an external furnace in pulsed laser experiments is comparable to an evaporation process employing higher average laser powers. It leads to an increased temperature of the target surface facilitating the evaporation process and helps to maintain the favorable growth environment in the gas-phase. All in all, the key for the production of SWNTs lies in establishing the 'optimal' temperature conditions controlling the process of evaporation and, equally important,

the processes in the gas-phase where the assembling of the released species into SWNTs is taking place. However, the solution to this problem is connected to many other parameters in a quite complex way which is illustrated in Fig. 6.

3.3. The gas-phase

Since the formation of carbon nanotubes takes place in the gas-phase, parameters of further importance are the nature of the buffer gas, its pressure and its flow rate. In the case of the Nd:YAG systems operating with argon as buffer gas at a furnace temperature of 1200 °C, Yudasaka et al. [25] found that below a pressure of 100 Torr (13 kPa) only amorphous carbon gets formed. From 200 Torr (27 kPa) on, SWNTs can be found and enhanced yields can be obtained by increasing the pressure up to 600 Torr (80 kPa). This pressure resulted in the formation of thick SWNT bundles and small amounts of amorphous carbon. The use of nitrogen leads to similar results [26]. On the other hand, it was remarked that depending on the metal concentration in the target and on the laser ablation time, the low-pressure threshold could approach a value of 100 Torr (13 kPa) [25]. The same authors also observed that at a furnace temperature of 900 °C the threshold value for SWNT formation rises up to 600 Torr (80 kPa) [27]. Therefore, this result may point to a close relationship between pressure and temperature conditions. Furthermore, a close link between temperature and flow-rate has been observed by Sen et al. [28]. They showed that the flow rate generally determines the time the evaporated species can stay within the temperature zone favorable for the growth of SWNTs. This proves that proper flow rates can help to balance too large temperature gradients and therefore can be used to control the relative yields and diameters of SWNTs.

The pressure–yield behavior for the cw-CO_2 laser system is quite similar to the Nd:YAG one [12,29]. Below an argon pressure of 200 Torr (27 kPa), the soot is dominated by amorphous carbon. Maximum SWNT yields are obtained between 200 Torr (27 kPa) and 400 Torr (53 kPa) while further increase of the pressure leads to reduced yields. A similar pressure dependence, but slightly lower yields has been observed using nitrogen as buffer gas. Helium does not lead to the formation of nanotubes in the investigated pressure range of 50 Torr (7 kPa) to 500 Torr (67 kPa). Working with flow rates between 0 and 1 l/min, no changes in the yield or structural characteristics of the SWNTs were observed in all these experiments. However, Loiseau [30] observed the formation of SWNTs using helium at a pressure of 500 Torr (67 kPa) and a flow rate of 3 l/min, which again shows that flow rates have an influence on the formation process.

A clear dependence on pressure and flow also was reported for the solar experiments [8,13]. At low pressures (12 kPa) no nanotubes are found. At 25 kPa the majority of the collected soot material consists of MWNTs with bamboo-like shapes and only a few small bundles of

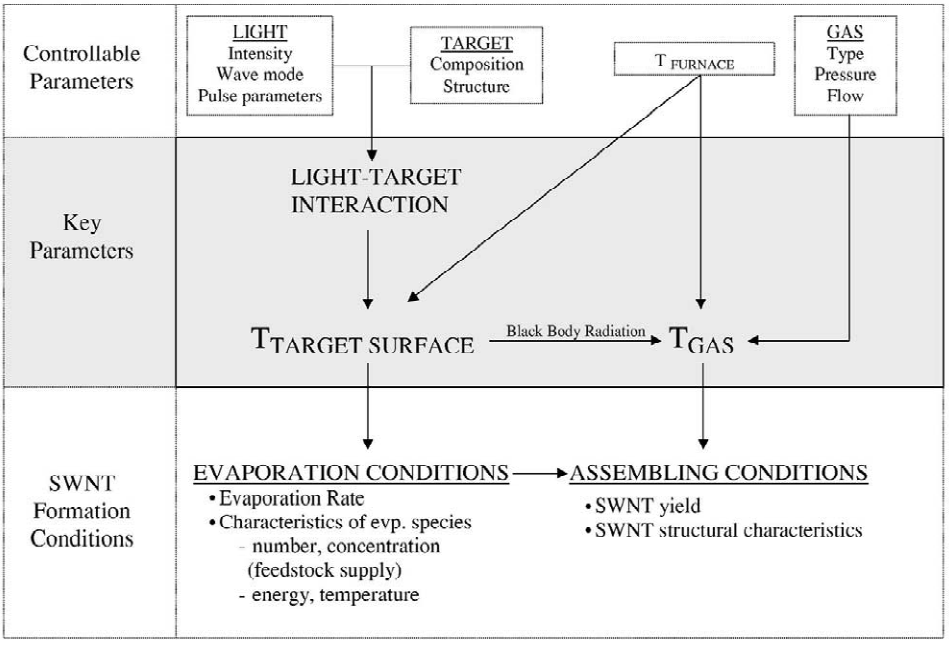

Fig. 6. Parameters important for the growth of SWNTs and their complex interactions. The key issue to solve lies in establishing temperatures, which facilitate the supply of an 'optimal' feedstock of evaporated species as well as in creating favorable assembling conditions in the gas-phase.

SWNT. Between 40 kPa and 60 kPa thick bundles of SWNTs are formed. Although the yield–pressure dependence is comparable to the one of the laser systems the presence of both types of nanotubes at pressures of 25 kPa is curious since their simultaneous existence normally is not observed in the laser experiments. This probably may reflect the fact that the evaporation conditions in the solar system are not as homogeneous as in the laser experiments. Furthermore, reducing the flow rate from 6 to 3 l/min at 50 kPa resulted in highest yields. Here, like in the experiments of Sen et al. [28] the flow rate was used to control the temperature gradient.

Muñoz et al. [12,16] suppose a close relation between the gas parameters and the temperature conditions in the gas-phase. The pressure, i.e. gas density, affects the density of the evaporated species (evaporation rate is inversely proportional to the density of gas) and influences the temperature through the number of gas particles to be heated. Therefore, there exists an optimal pressure range—apparently between 200 and 400 Torr (27 and 53 kPa)—where the expansion of the vapor plume is restricted and excessive cooling of the evaporated species is avoided. The optimal confinement provides the most suitable temperature and concentration conditions for the evaporated species leading to high SWNT yields. At higher pressures, the collision rate of the evaporated species with the surrounding gas-molecules increases and leads to enhanced cooling rates. This results in larger temperature gradients and therefore the efficiency for the growth of SWNTs gets reduced. On the other hand, at too low pressures, a too rapid expansion of the vapor plume takes place resulting in a too rapid cooling of the evaporated species and, additionally, the optimal carbon–metal concentration cannot be maintained. The favorable temperature conditions cannot be created anymore. Kokai et al. [31–33] also pointed out the importance of collisions, i.e. the dissipation of kinetic energy of the evaporated species. Growth velocities (expansion of vapor plume) and the yield of SWNTs (or other carbonaceous structures in general) depend on features of the laser plume. These are determined by the vaporized species (quantities, kinetic energy, and temperature) which on the other hand are strongly influenced by the ambient gas and its pressure (diffusion process, cooling rate, evaporation rate, and confinement).

Currently, many groups are analyzing the processes taking place in the gas-phase, especially in what concerns the vapor plume, by spatial and time resolved in-situ video imaging techniques as well as emission spectroscopy. All the groups applying these methods observed that the species evaporated from the heated target consist of atomic or/and molecular structures like C, C_2, C_3, atomic nickel, cobalt and possibly small clusters of catalyst [31–37]. Their amount in the gas-phase is strongly dependent on the surface temperature of the target [17–21,37]. These species form a hot vapor plume, which expands into the surrounding gas and cools rapidly. During this cooling process, small carbon molecules and atoms quickly condense to form larger clusters. The catalysts also begin to condense, but more slowly (by a factor of 10) than low weight molecular carbon structures. This points to a sequential condensation of C and Co clusters [35]. Since the spectroscopic methods cannot distinguish the type of carbonaceous clusters being formed, the difficulty in the interpretation of the condensation process lies in the determination of the time-scale on which nanotube growth occurs. This directly leads to the question if the metal influences the nanotube growth by either acting as atom or as very small cluster at very early times on a microsecond-scale, as suggested by Scott et al. [37], or as larger metal or carbon/metal cluster formed somewhat later on a time-scale larger than a millisecond, as proposed by Puretzky et al. [35]. However, both approaches do not exclude each other and both kinds of scenarios could be taken into account in the highly dynamic process of the formation of carbon nanotubes. The discrimination of nanotubes in the plethora of carbonaceous clusters in the vapor plume would be an important step forward in the understanding of the formation process.

4. Perspectives

In recent years great efforts have been undertaken by many groups in elaborating a process for the controlled production of carbon nanotubes and in understanding the complex process. From an experimental point of view, the key issue in the production remains to keep the favorable conditions in the vicinity of the evaporation zone. This concerns especially the temperature—responsible for greater ablation, slower cooling of particles and a higher vapor pressure of small carbon and catalyst clusters—as well as the concentration of evaporated species. Confinement of ablation products to the neighborhood of the laser beam as shown in the experimental set-up of Rinzler [11] and Scott [37] enhances the conversion of evaporated carbon species into nanotubes. Unfortunately this approach towards high yield production is incompatible with a large-scale production. For any progress towards this objective, it therefore would be crucial not only to maintain the conditions close to the evaporation zone, but even more, to spatially extend the favorable formation environment or/and to decrease the expansion velocities. Here, to a certain extent the use of a CO_2 laser is a first approach. Its use not only results in the evaporation of larger amounts of carbon and metal species—the vaporization quantities are 60 to 300 times larger compared to the Nd:YAG laser—but also in reduced plume expansion velocities—1000 times smaller than in Nd:YAG systems—which therefore indirectly results in a reduced temperature gradient [33]. As one can see, one solution towards the production of high-quality material in larger amounts may be to take advantage of changed light–target interactions by employing different

kinds of light sources. There is still a large unexplored potential in using different lasers or combinations of lasers, which may lead to drastically improved evaporation conditions in a controllable way and therefore influencing positively the quality and quantity of carbon nanotube materials. Avoiding covering of windows and mirrors, as well as plugging-off flow tubes by created soot material, and automatizing the system could further increase the production rates. Long-unattended continuous production, cheaper feedstock materials and a more efficient process for the preparation of the target materials would be desirable for a low cost production.

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