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Fine-tuning of spark-discharge aerosol CVD reactor for single-walled carbon nanotube growth: the role of *ex situ* nucleation

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ABSTRACT

We report a development of recently designed apparatus equipped with a spark discharge generator of catalytic nanoparticles for robust aerosol CVD synthesis of single-walled carbon nanotubes. We achieve a profound control over the diameter distribution and the defectiveness of carbon nanotubes produced. By providing a justified comparison of the apparatus with the most abundant aerosol CVD reactor utilizing ferrocene as a catalyst precursor, we reveal the role of the activation procedure: while spark-discharge generator provides aerosol of nanoparticles (*ex situ* route), the ferrocene vapor decomposes in the nanotube growth zone providing an *in situ* formation of the catalyst. With other parameters being equal, we reveal the differences in the nanotube growth (diameter and length distribution, yield, defectiveness) employing a comprehensive set of methods (the analysis of differential mobility of the aerosol particles, optical spectroscopy, scanning and transmission electron microscopy, Raman spectroscopy, and atomic force microscopy). We show the *ex situ* activation in the spark discharge reactor to provide a lower utilization degree of the nanoparticles due to over-coagulation. However, the same method provides an independence of the key performance parameters of the nanotubes opening a room for scaling the apparatus.

KEYWORDS

aerosol CVD synthesis; floating catalyst; spark-discharge generator; single-walled carbon nanotubes; catalyst activation; differential mobility analyzer.

HIGHLIGHTS

- A justified comparison of nanotube growth in spark and ferrocene reactors performed;
- *In situ* activation of the catalyst provides high degree of Fe utilization;
- The ferrocene residuals are proposed to play a significant role in nanotube growth;
- Spark discharge reactor provides high scalability opportunities.

GRAPHICAL ABSTRACT

1. Introduction

Carbon nanotubes and their functionalized derivatives form a class of materials with a wide range of properties: the thinnest single nanotube is 0.3 nm in diameter [1], while the upper boundary between thick multi-walled carbon nanotubes and carbon nanofibers is still uncertain [2,3]; the nanotube conductivity [4] can be easily varied in range of 10^7 by a fluorination [5]; the Young's modulus varies in a several orders of magnitude [6]. However, the unique set of mechanical, electrical, optical, and structural characteristics have been luring the scientific community for more than 25 years promising next technological step in different fields: from medicine to energetics, from nanoelectronics to space elevators, from sports to portable sensors [7–10]. Nevertheless, the efforts resulted in commercial applications of carbon nanotubes mostly represented by composites [11] whereas the nanotube-based electronics is still challenging. This is mostly due to severe requirements for the control of the single-walled carbon nanotube (SWCNT) properties (chirality, aspect ratio, alignment, and agglomeration morphology) [12,13]. Interestingly, while a certain progress has been recently shown even towards such a complex topic as a SWCNT synthesis with a single chirality [14–18], the non-damaging disentanglement of carbon nanotube agglomerates is still challenging for long nanotubes [19,20] as π -stacking energy of micron-length tubes is several times higher than a single covalent C-C bond [21,22]. Thus, the techniques providing an extremely diluted nanotube mesh – the substrate CVD [23,24] and more recent and facile aerosol CVD [25,26] – are of interest for transparent electrodes [27–29], integrated circuits [30,31], transistors [32,33], and other electronic devices [34].

Being a specific case of the reactor type with floating bed of extremely diluted catalyst, aerosol CVD methods resulted in various techniques for a catalyst formation [18]. An introduction of volatile catalyst precursors (ferrocene, iron pentacarbonyl, *etc.*) is followed by an *in situ* nucleation of catalyst nanoparticles and growth of nanotubes in the same reactor position [35–37]. The other approach is based on the introduction of pre-formed catalyst nanoparticles produced *ex situ* from metal vapor by the hot-wire [38] or a spark discharge generator [39,40]. Moreover, the nature of a catalyst (chemical composition, method for particle formation, impurities) has been proven to play a decisive role for the SWCNT performance [41–44]. The recent developments in the aerosol CVD method equipped with a spark discharge generator have proven this technique to provide a route for controlled scaling: the reactor provides an independent behavior of the defectiveness, the yield, and the diameter distribution of SWCNTs [45]. Such a behavior not only positively differs the spark discharge equipped aerosol CVD from the most abundant ferrocene-based aerosol CVD technology [46–49], but also unusual for carbon nanotube growth [50,51] and aerosol science [52] in general. However, a valid assessment of the comparative performance a spark-discharge generator equipped apparatus and ferrocene-based reactor is still challenging. This is not only due to unclear kinetic model of the carbon nanotube synthesis [53–56] affected by an entanglement of different mechanisms but also by the general inconsistency between the reactor parameters, materials, *etc.* [42,57,58].

In this work, we report the fine-tuning of spark-discharge equipped aerosol CVD reactor enhancing the control over the SWCNT performance with a special focus here on short carbon nanotubes ($l < 500\text{nm}$) of pronounced defectiveness for drug delivery [59,60]. We assess the perspectives of the reactor by a justified comparison with the similar ferrocene-based reactor (the partial pressures of the N_2 , CO , CO_2 , the temperature profile, the contact time, the amount of Fe catalyst). The carbon nanotubes obtained were examined by a set of the various methods (differential mobility analyzer of the aerosol particles, UV-vis-NIR and Raman spectroscopy,

scanning and transmission electron microscopy, and atomic force microscopy) in order to provide a comprehensive insight into the relation between the growth conditions and SWCNT properties.

2. Material and methods

A spark discharge generator for nanoparticle production follows the classical design [61] and was equipped with two cylindrical Fe (99.99%) electrodes with the diameter of 4 mm and the interspace distance of 6 mm (top in Figure 1). The discharge was provided by a high voltage generator Heinzinger PNC 20000-10 (Germany) combined with a 45 nF capacitor. The partial evaporation of the electrodes due to the discharge (0.8 mA current and 2kV breakdown voltage) was followed by the condensation of the electrode material within a N₂ stream (99.999%; time from the spark generator to the reactor hot zone is *c.a.* 0.12 s).

A ferrocene cartridge (bottom in Figure 1) was filled with the mixture of ferrocene powder (Fe(C₅H₅)₂, Sigma Aldrich, 98%) and SiO₂ spheres (diameter *c.a.* 0.7 mm) to facilitate the flow. The volatile ferrocene ($P_{eq} = 0.6$ Pa at 20 °C [62]) was then transferred by the nitrogen stream to the heated zone within a warm gas line (~70 °C) for further decomposition (at T>400 °C [63]). It should be mentioned that the SiO₂ spheres are located exclusively within the ferrocene cartridge as the vapor pressure of SiO₂ or other corresponding forms is negligible (<10⁻³ Pa) [64,65].

Figure 1: A schematic representation of spark discharge (top) and ferrocene (bottom) reactors.

Both Fe nanoparticles from the spark discharge generator in the nitrogen flow and the Fe(C₅H₅)₂/N₂ mixture were introduced in exactly the same manner. The catalyst-containing flow was fed through the quartz tube injector ($d_{\text{inner}} = 4$ mm) near the hot zone of the reactor (at T~500 °C) and mixed with the carbon source (CO; 99.999%) and CO₂ (99.995%) as an etching agent of the Boudouard reaction ($2\text{CO} = \text{C} + \text{CO}_2$). The residence (contact) time (6 s), the partial pressures of N₂, CO, CO₂ (28 % vol., 72-70 % vol., 0-2 % vol., respectively), the total pressure in the reactor (~ 1 atm), hot zones of the (680 – 1080 °C) were fixed for both: a reactor equipped with the spark

discharge generator (hereinafter “spark discharge reactor”) and an apparatus with the ferrocene cartridge (hereinafter “ferrocene reactor”). It goes without saying that the fluid dynamics results in a certain residence time distribution [46,66], here we employ the residence time parameter (a quotient of the reactor volume divided by flowrate) as a batch parameter describing the reactor design. The amount of the catalyst introduced to the reactor was comparable: for the ferrocene cartridge the vapor pressure described above provides the concentration of iron atoms of $4 \cdot 10^{13}$ #/cm³; an estimation for the spark discharge generator of the electrode erosion is a complex task: a widely employed for the spark discharge apparatus [67–70] theoretical estimation according to Jones equation (1) [71] gives $3 \cdot 10^{13}$ #/cm³ (more at S1), while the aerosol measurements by differential mobility analyzer at the end of the generator line followed by the integration provide Fe atom concentration of $0.9 \cdot 10^{13}$ #/cm³ [45]:

$$C_{Fe} = \frac{N_A \nu}{u M_{Fe}} \frac{E_{sp} - E_{rad} - E_{dis}}{E_h + E_{melt} + E_{boil}} \quad (1)$$

where N_A is the Avogadro number; ν is the frequency of a sparks; u is the flowrate; M_{Fe} is iron molar weight; E_{sp} is a single spark energy; E_{rad} is an energy lost due to the radiation from a single spark; E_{dis} is an energy that dissipates by heat conductivity (through a gas and the electrode material) during the heat transfer from a single spark to electrode material; E_h , E_{melt} , and E_{boil} are specific energies needed to heat, melt, and evaporate the electrode material, respectively.

The discrepancy between the atomic concentration provided by the Jones equation (1) and DMA measurements can be attributed to various effects (or their superposition): (i) the diffusion of Fe nanoparticles to the walls of the gas line, (ii) the accuracy of the model for the spark discharge apparatus [67–70], size effect of density [72]. Nevertheless, the comparison is still justified as the diameter distribution and the defectiveness were found not to be affected by the yield of nanoparticles [45] (can be easily normalized over the amount of Fe).

Nitrocellulose filters (HAWP, Merck Millipore, USA) were used for collection of the SWCNT aerosol (with the typical collection time of 15 min) for further dry transfer to glass substrate suitable for Raman and UV-vis-NIR studies. Differential mobility analyzer (DMA) equipped with condensed particle counter (Scanning Mobility Particle Sizer Spectrometer (SMPS) 3938, TSI, USA) was employed to study the SWCNT aerosol, namely the number size distribution in the range of the effective diameters from 6 up to 230 nm. The effective diameter corresponds to the size of the spherical particle with the mobility coefficient equal to the value measured by the DMA. This results in the effective SWCNT diameter to be measured in the range of 40-100 nm depending on the length distribution of individual nanotubes and the morphology of their agglomerates within the aerosol [73]. Nevertheless, the technique allows one to distinguish the conditions of the nanotube synthesis from the inactive catalyst particles (effective mobility diameter in the typical range of 6-20 nm) [38].

The yield and the diameter distribution of nanotubes [74] were assessed by means of UV-vis-NIR spectroscopy (Perkin Elmer Lambda 1050; wavelength 300 – 2600 nm with 1 nm resolution). The diameter was reliably calculated from the Van Hove singularities of the S_{11} transition observed by UV-vis-NIR spectra [75]; the detailed procedure was described elsewhere [76]. The defective structure of SWCNTs was examined with Raman spectroscopy (Horiba LabRAM HR Evolution system; green laser (532 nm; 2.33 eV) with power of 0.1 mW). The SWCNT structure and the

morphology of the thin films were studied by transmission (FEI Tecnai G2 F20 TEM; TEM lacey Cu-300 grid) and scanning (FEI Helios Nanolab 660) electron microscopies as well as atomic force microscopy (AFM; Multimode V8 Atomic Force Microscope operating in PeakForce tapping mode equipped with Bruker ScanAsist-Air cantilevers ($k = 0.4 \text{ N/m}$); image processing was done by opensource Gwyddion software). The samples for AFM and TEM studies were collected in a similar manner. A substrate (small SiO_2 wafer or TEM lacey Cu-300 grid) was placed on the filter within the flow of SWCNTs for several tens of seconds to obtain the desired density (individual SWCNTs near percolation threshold were usually preferred).

3. Results and discussion

3.1 The role of CO_2 and temperature in SWCNT growth in the spark discharge reactor

The SWCNT growth in the ferrocene reactor has been widely studied over the last 15 years [25,26,46,77–83]. When CO is applied as a carbon source, the temperature-dependence of SWCNT growth usually shows a narrow optimum at $\sim 880 \text{ }^\circ\text{C}$ [80]. At the same time the addition of CO_2 [82] increases SWCNT mean diameter, lowers defectiveness, and shows a volcano-like (or a bell-shaped) temperature dependence for the yield (with a single maximum). However, the corresponding parameters for a spark discharge reactor have not been studied yet. In this section, to provide a justified comparison, we consider the influence of the CO_2 and the temperature on SWCNT growth in the spark discharge reactor.

As a rule addition of carbon dioxide enhances the catalytic activity of Fe nanoparticles for the ferrocene reactor [47,48,83]. However, in case of the spark-discharge reactor, we observe an opposite behavior: increase of CO_2 concentration inhibits SWCNT growth (Figure 2). A decrease of the observed effective size of aerosol particles (Figure 2a) can be attributed to either reduced catalytic activity of Fe species (leading to a shorter nanotubes) or to suppressed activation of the catalyst (leading to a lower amount of produced SWCNTs). The latter effect corresponds to the fact that the diameter value provided by the DMA is a function of the mobility coefficient which, in turn a complex function not only of SWCNT length but also a function of agglomerate morphology (shape, density, etc.). However, the SWCNT length distribution based on the statistical analysis of AFM topography data clearly rejects the former hypothesis (Figure 2b, c). Thus, low amounts of CO_2 do not affect the rate of steady-state SWCNT growth and decrease the ratio of active Fe nanoparticles. The lower concentration of active catalyst leads to lower SWCNT concentration which, in turn, inevitably affects the agglomerate morphology resulting for example in less dense bundles or bundles of different shape. This finding will be also supported by the CO_2 effect on the yield discussed in the next section (Figure 6a).

Figure 2: Influence of CO₂ on the SWCNT growth in the spark discharge reactor: a) DMA number size distributions of SWCNTs produced under different concentration of CO₂; the length distribution of SWCNTs based on AFM statistics for the sample produced b) without CO₂ and c) with 0.5 vol. % of CO₂ (d_{GM} – geometric mean diameter, GSD – geometric standard deviation, d_M – mobility diameter). Consistently to previous findings [45] SWCNTs obtained are of short length favorable for their dispersibility.

The effect of CO₂ on SWCNT nucleation is not limited to the fraction of active Fe nanoparticles. The mean diameter of SWCNTs (provided by UV-vis-NIR spectra) – a parameter defined during the nanotube nucleation – tends to increase with addition of carbon dioxide to the spark discharge reactor (Figure 3a) similarly to the effect observed for the ferrocene reactor [48,82]. This can be explained as follows. The addition of CO₂ shifts the size-dependent

equilibrium of the Boudouard reaction on the catalyst surface leading to the etching of small-diameter nanotube caps during nucleation stage. The hypothesis of partial etching of the most unstable or defective species in the ensemble is supported (Figure 3b) by the increase of the ratio for intensities of G and D modes (I_G/I_D) in Raman spectra (corresponds to a reverse defect concentration [84]). Moreover, apart from etching of defective species, the I_G/I_D growth can also be affected by the shift in SWCNT diameter distribution (thicker nanotubes correspond to higher I_G/I_D [85,86]).

Figure 3 Influence of CO₂ concentration on the SWCNT thin films produced in the spark discharge reactor: UV-vis-NIR spectra (a; diameter distribution) and Raman spectra (b; defectiveness, the inset shows enlarged zone of radial breathing modes). S₁₁ transition position corresponding to the distance between the Van Hove singularities of the SWCNTs corresponds to the diameter distribution.

The temperature dependence of the yield shows a volcano-like shape (Figure 4a) with an optimal point *c.a.* 880-980 °C similar to the ferrocene reactor. I_G/I_D constantly increases with temperature (Figure 4b) that corresponds to the decrease of the defects in nanotubes due to either higher probability of defective carbon to be restructured [85,87] or increase of SWCNT diameter [85,86].

Interestingly, a small shift in the SWCNT diameter (which is proportional to the size of a catalytic nanoparticle [88]) with an increase of the growth temperature (Figure 4c) shows an apparent activation energy of 9 kJ/mol (Figure 4c inset). In general, During the nucleation, SWCNTs is generally considered to be a competition between the size of the catalyst and concentration of carbon intermediates [51,89]. Thus, there are two processes which can control SWCNT diameter – agglomeration of catalyst particles or decomposition of carbon source. For aerosol CVD the agglomeration of catalyst particles is a simple coagulation (no activation energy but depends on the temperature). This results in apparent activation energy to be of RT (~ 8 - 10 kJ/mol at $T \sim 1000$ K; R is the gas constant [90]). In case of spark discharge reactor, the competing processes are divided implying the coagulation to take the major part. Nevertheless, the findings shown can be used as an additional for the coagulation of aerosol nanoparticles be the rate-limiting step during the SWCNT nucleation on the catalyst surface.

Figure 4: Effect of the temperature on the SWCNT growth in the spark discharge reactor: a) DMA number size distributions of SWCNTs produced; b) Raman spectra of SWCNT thin films obtained, the inset shows enlarged zone of radial breathing modes; c) UV-vis-NIR spectra of SWCNT thin films, the inset corresponds to the Arrhenius plot of the SWCNT mean diameter.

Thus, despite a minor loss in the yield, the addition of CO₂ provides a way for tuning the SWCNT mean diameter and defectiveness within a wide range, while the decrease of the yield can be countered with increase in concentration of the catalyst nanoparticles [45].

3.2 Comparison of the spark discharge and the ferrocene reactors

Difference in architecture of the ferrocene and the spark discharge reactors affects the

catalyst activation pattern (Figure 5) leading to *in situ* (the ferrocene reactor) and *ex situ* (the spark discharge reactor) pathways for the formation of Fe nanoparticles. This results in a separation of the two steps preceding the SWCNT nucleation, which, in turn, defines such nanotube characteristics as diameter distribution, ratio of active Fe nanoparticles, *etc.* [42,91,92]. It is without any doubt that the particle distributions are different as it is key distinguishing point between the reactors. While the influence of the growth temperature was shown to be similar for both ferrocene and spark discharge reactors the difference in the role of carbon dioxide is more distinctive.

Figure 5: Schematic representation of the differences in catalyst formation and forthcoming SWCNT nucleation in the ferrocene (left) and the spark discharge (right) reactors.

Unlike the ferrocene reactor, CO₂ addition does not result in an increase of SWCNT yield followed by the inhibition for the spark discharge reactor (Figure 6). However, trends corresponding to a decrease in the catalyst productivity are similar: the apparent reaction order with respect to carbon dioxide is ~ -0.5 (see supporting information for details). Fractional nature of the value corresponds to the complex mechanism of the Boudouard reaction on catalyst surface. While the particular rate-limiting step is unclear we can neglect the influence of the mass-transfer (due to low size of the particles and high pressure of the process (1 atm)) [93,94] presuming the influence of equilibrium and/or adsorption to play a key role [95]. This allows us to consider the mechanism for inhibiting catalytic activity in SWCNT growth by CO₂ to be similar for both spark discharge and ferrocene reactors. As discussed in the previous section for the spark discharge reactor, the addition of CO₂ decreases the fraction of active catalytic nanoparticles.

The increased Fe activity in the case of the ferrocene reactor can be attributed to the following processes. Similar to the role of the water vapor in the super-growth process [96], the CO₂ is considered to etch the amorphous carbon species on the catalyst surface (which can form amorphous carbon species on the free catalyst surface deactivating it during the steady-state growth of SWCNTs) [47,48,83]. Due to thermodynamic peculiarities [97], CO pyrolysis is inhibited at high temperature making it one of the most stable carbon species along with methane. The only difference between the reactors considered in terms of carbon source is ferrocene residuals. Taking into account that ferrocene residuals were shown to integrate within SWCNT

structure [98], we presume that it is the ferrocene hydrocarbon residuals who tunes the catalytic activity within the process. Due to peculiarities of aerosol CVD design the hypothesis proposed cannot be directly proved by *in situ* or *operando* methods. Thus, we supposedly observe an interesting balance in case of the ferrocene reactor between the enhance of the SWCNT steady-state growth and decrease in the ratio of the active Fe nanoparticles during the SWCNT nucleation.

Figure 6: Comparison of the SWCNT growth under different CO₂ concentration in the spark discharge and ferrocene reactors in terms of a) the yield; b) DMA number size distributions of SWCNT aerosols.

The ferrocene reactor provides a higher SWCNT yield (Figure 6): ~260 nm SWCNT films from ferrocene, while only ~35 nm thick films in case of spark discharge reactor. This can be attributed to the peculiarities of the Fe catalyst formation procedure: *ex situ* formation in the case of the spark discharge reactor (Figure 5) leads to a lognormal particle size distribution at the beginning of the growth zone [45,88]. This results in the higher fraction of large inactive Fe nanoparticles when compared to the *in situ* activation (ferrocene reactor) reducing the cumulative yield of the SWCNT growth process (as nanoparticles with only certain diameter range can produce nanotubes [88,99]). However, a simple and independent relations between key SWCNT

performance parameters (yield, diameter, defectiveness) [45] provide a much facile route for scaling rather than complex relations of the ferrocene reactor.

The increase of the SWCNT mean diameter and I_G/I_D is similar for both reactors implying that the role of CO_2 during the nucleation step is roughly the same (Figure 7). Indeed, as we discussed above, the catalyst coagulation is supposed to be the rate-limiting step of the nanotube nucleation. Small additions of carbon dioxide are implied to have zero effect on the coagulation rate. The role of CO_2 as etching agent removing the defective part of SWCNTs is also similar for both nucleation strategies proving the similarities of both reactors [47,48,83]. The values of I_G/I_D obtained for both reactors are substantially lower than those considered for SWCNTs of low defectiveness [100]. High defectiveness of carbon nanotubes will improve the dispersibility and affinity for functionalization promoting the material for drug delivery [59,60]. The ratio of intensities is a complex function of reaction conditions, catalyst nature, and reactor design [76].

Thus, the difference in the architecture of the aerosol CVD reactors affects the nucleation patterns of the SWCNT growth providing both *ex situ* (spark discharge reactor) and *in situ* (ferrocene reactor) formation of the Fe catalytic nanoparticles. On the one hand, the *ex situ* formation of aerosol Fe particles in the spark discharge generator leads to a lognormal particles size distribution (shown for example in [45]) inhibiting the yield by decreased utilization degree due to the fraction of large Fe nanoparticles. On the other, the SWCNT growth in the spark discharge reactor shows a simple relation between the CO_2 content and the diameter distribution while the yield can be independently tuned in a wide range by the parameters of the spark discharge [45]. The temperature shows a minor effect on the diameter with the apparent activation energy $\sim \text{RT}$.

Figure 7: Comparison of the SWCNT growth under different CO_2 content in the spark discharge and ferrocene reactors: a) the mean diameter, b) the defectiveness.

SWCNT growth is a multi-parametric process with a complex relation of the synthesis conditions, catalyst nature, and the reactor design with nucleation, steady-growth, and termination of nanotube synthesis [51,58,101,102]. This fact inhibits the scalability of SWCNT growth. The reactor scaling is usually divided by certain levels starting from the investigation of the chemical kinetics on a single catalytic center followed by optimization of the catalytic bed and heat- and mass-transfer processes [95,103,104]. In this light, the scalability is extremely vulnerable to in general can be improved by developing of the synthesis strategies with simple dependencies (without any extrema). Thus, the spark discharge reactor developed provides a route for

independent tuning of the yield (via breakdown voltage, the current [45]), diameter distribution (CO₂ content), defectiveness (gas composition) opening an avenue for scalable aerosol CVD growth of SWCNTs with tailored properties.

4. Conclusions

We have performed a comparative study of the single-walled carbon nanotube (SWCNT) growth in the aerosol CVD reactors equipped with a ferrocene cartridge and spark discharge generator of Fe nanoparticles while other key input parameters of the process (temperature, gas composition, catalyst composition, *etc.*) were kept similar. The difference in the architecture of the reactors studied affects the nucleation patterns of the SWCNT growth providing both *ex situ* (spark discharge reactor) and *in situ* (ferrocene reactor) formation of the Fe catalyst. On the one hand, the *ex situ* activation in case of the spark discharge reactor leads to lognormal particles size distribution inhibiting the yield by decreased utilization degree due to the presence of high fraction of large Fe nanoparticles (as nanoparticles with only certain diameter range can produce nanotubes [99]); on the other, the SWCNT growth in the spark discharge reactor shows a simple (no extrema) dependence on the carbon dioxide content controlling the diameter while the yield can be independently tuned in a wide range (shown in [45]), whereas the temperature variation shows a minor effect on the diameter with the apparent activation energy $\sim RT$. We attribute the CO₂-induced increase of the yield in case of the ferrocene reactor (*in situ* formation of Fe) to the etching of amorphous carbon intermediates. We show the same mechanism for the growth inhibition via the decrease of the ratio for active catalyst nanoparticles. The mutual independence of the yield, diameter distribution, defectiveness provides a route for fine-tuning of the active particles (composition, size distribution) and forthcoming SWCNTs opening a route for scalable SWCNT growth in the spark discharge equipped aerosol CVD reactors.

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Fine-tuning of spark-discharge aerosol CVD reactor for single-walled carbon nanotube growth: the role of *ex situ* nucleation

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S1: Erosion of the electrode of the spark discharge generator

Jones model [71] provides a description of the amount of the electrode material evaporated due to the discharge (current 0.8 mA and average discharge voltage of 2000 V)

$$C_{Fe} = \frac{N_A v}{u M_{Fe}} \frac{E_{sp} - E_{rad} - E_{dis}}{E_h + E_{melt} + E_{boil}} = \frac{N_A v}{u M_{Fe}} \frac{\alpha 0.5 c_e V^2 - 2\pi r^2 \sigma \tau (T_{boil}^4 - T^4) - 2\pi r \tau (\kappa_{el} + \kappa_{am})(T_b - T)}{c_s (T_{melt} - T) + \Delta H_m + c_l (T_{boil} - T_{melt}) + \Delta H_v}$$

where N_A is the Avogadro number, v is the frequency of sparks, u is the flowrate, M_{Fe} Fe molecular weight, α is the energy efficiency factor, $\alpha 0.5 c_e V^2$ is the energy stored in capacitor, r is the “hot spot” radius, σ is the Stefan-Boltzman constant, τ is the discharge time, T_{boil} is the boiling temperature, T is the ambient temperature, T_{melt} is the melting point of Fe, c_s , c_l are the thermal capacities of solid and liquid electrode material, respectively, H_m , H_e are the enthalpy of melting and evaporation, κ_{el} , κ_{am} are the thermal conductivity of the electrode material and carrier gas, respectively. The values employed for the parameters are presented in Table S1.

In general, the spark discharge generator provides stable (at low frequencies <100 Hz) method for nanoparticles with a narrow distribution. It does not depend on any external factors and consumes only a little amount of energy (in order of units of watts). It can be supposed that effective decomposition of a carbon source gas for carbon nanotube synthesis might demand regulation of releasing energy and spark repetition rate for the efficiency of utilization of catalyst material. Also, precise control of spark discharge parameters and *ex situ* formation of nanoparticles can be useful for the creation of the material with the different presence of catalytic particles.

Table S1. Constants used in the calculations and material properties [53,68]

N_A, mol^{-1}	6.02×10^{23}	ν, min^{-1}	3500
$u, \text{cm}^3/\text{min}$	1700	$M_{\text{Fe}}, \text{g/mol}$	56
α	0.0018	$T_{\text{boil}}, \text{K}$	3150
$0.5CV_d^2, \text{J}$	1.3×10^{-5}	T, K	300
r, m	1.5×10^{-6}	$T_{\text{melt}}, \text{K}$	1800
τ, s	1.2×10^{-6}	$c_s, \text{J K}^{-1} \text{g}^{-1}$	0.62
$\sigma, \text{kg s}^{-3} \text{K}^{-4}$	5.7×10^{-8}	$c_l, \text{J K}^{-1} \text{g}^{-1}$	0.82
$\kappa_{el}, \text{W m}^{-1} \text{K}^{-1}$	43.3	$\Delta H_m, \text{J g}^{-1}$	277
$\kappa_{am}, \text{W m}^{-1} \text{K}^{-1}$	2.6×10^{-3}	$\Delta H_v, \text{J g}^{-1}$	6120

S2: AFM and TEM images of SWCNTs

Figure S1: AFM images of SWCNTs produced under different concentration of CO_2 : left – without CO_2 , right – with 0.5 vol. % of CO_2

Figure S2: TEM microphotographs of SWCNT films obtained in the spark discharge (left) and ferrocene reactor (right); 880 °C, 1% of CO₂.

S3: Sheet resistance of short SWCNT films

The equivalent sheet resistance (R_{90} , resistance of the SWCNT film with a 90 % transmittance at 550 nm[47]) data is presented in the Table S2.

Table S2. The equivalent sheet resistance of short SWCNT films

Ferrocene reactor		Spark discharge reactor	
CO ₂ content, vol. %	R_{90} , k $\Omega/\square$	CO ₂ content, vol. %	R_{90} , k $\Omega/\square$
0	15	0	106
0.2	16	0.2	145
0.3	16	0.3	48
0.5	17	0.5	66
0.7	20	0.7	880
0.8	11	0.8	NaN
1.0	10	1.0	NaN
1.2	6		
1.3	8		
1.5	11		
1.6	17		
1.8	26		
2.0	49		

S4: SWCNT growth apparent order with respect to carbon dioxide

With other parameters being equal (collection time, size of the filter, the partial pressures of the N₂, CO, CO₂, the temperature profile, the contact time, the amount of Fe catalyst), the

SWCNT film thickness can be considered as an integral measure of the SWCNT growth rate. Moreover, as aerosol CVD deals with extreme dilutions, we can employ a simple Van't Hoff method of excessive reagents. This allows us to employ a formal kinetic relation for the apparent order with respect to carbon dioxide (n) implying the following relation:

$$\text{Film thickness} = kP_{\text{CO}_2}^n.$$

Figure S2 shows the graphical representation of the SWCNT growth apparent order with respect to carbon dioxide within the region of CO₂-induced inhibition of SWCNT growth (Figure 6). The apparent reaction order with respect to carbon dioxide is found to be of ~ -0.5 for both the spark discharge and the ferrocene reactor. Negative value of the reaction order proves the inhibition of the SWCNT growth by the addition of CO₂. Fractional nature of the value corresponds to the complex mechanism of the Boudouard reaction on catalyst surface. This allows us to consider the mechanism for inhibiting catalytic activity in SWCNT growth by CO₂ to be similar for both reactors.

Figure S2: Comparison of the SWCNT growth under different CO₂ content in the ferrocene-based and spark discharge reactors.