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Published in:

Chemical Engineering Journal

DOI:

[10.1016/j.cej.2019.04.173](https://doi.org/10.1016/j.cej.2019.04.173)

Published: 15/09/2019

Document Version

Peer reviewed version

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Please cite the original version:

Krasnikov, D. V., Zabelich, B. Y., Iakovlev, V. Y., Tsapenko, A. P., Romanov, S. A., Alekseeva, A. A., Grebenko, A. K., & Nasibulin, A. G. (2019). A spark discharge generator for scalable aerosol CVD synthesis of single-walled carbon nanotubes with tailored characteristics. *Chemical Engineering Journal*, 372, 462-470. <https://doi.org/10.1016/j.cej.2019.04.173>

A spark discharge generator for scalable aerosol CVD synthesis of single-walled carbon nanotubes with tailored characteristics

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ABSTRACT

We have designed and built an exhaust-free spark discharge generator for robust aerosol CVD synthesis of single-walled carbon nanotubes. The systematic study has shown the generator to provide a facile and repeatable route to precisely control the size of the catalyst particle and, therefore, carbon nanotube growth. Using 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 have revealed the relation between the defectiveness, length, diameter distribution of carbon nanotubes and specific features of a generator such as electrode characteristics (breakdown voltage, composition, and current) as well as the nature of the surrounding media (carrier gas nature, flow rate). The design used has resulted in separation of the nanoparticle formation and carbon nanotube nucleation processes. This provides a mutual independence of the growth parameters and the diameter distribution of the single-walled carbon nanotubes enhancing the scalability of the process. For instance, the breakdown voltage has been shown to have nearly zero effect on diameter and length distribution of carbon nanotubes produced while strictly governing the yield. We focus here on producing specifically short carbon nanotubes ($l < 500\text{nm}$) of pronounced defectiveness for drug delivery and transistor applications.

KEYWORDS

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

HIGHLIGHTS

- A spark-discharge generator was implemented for aerosol CVD growth of carbon nanotubes;
- The current and the breakdown voltage affect the yield of single-walled carbon nanotubes;
- The current and the breakdown voltage have zero effect on the diameter;
- Separation of the nanoparticle formation and nanotube nucleation provides a mutual independence of key variables enhancing the scalability;
- The aerosol of single-walled carbon nanotube of mean $l < 500$ nm was obtained.

GRAPHICAL ABSTRACT

1. Introduction

Synthesis of single-walled carbon nanotubes (SWCNT) for targeted applications has attracted a serious attention of the scientific community for the last 25 years by promising new generation of numerous devices, materials, and technological approaches due to an exceptional set of characteristics [1–4]. The efforts devoted to the research ($> 70\,000$ papers since landmark publication in 1991 [5]) resulted in a few techniques for the SWCNT production that shown not only considerable fundamental development [6–8] but also went commercial [9]: catalytic chemical vapor deposition (CVD) in fluidized beds [10–12], floating bed of catalyst [13,14], high pressure CO (HiPCO) decomposition of ferrocene [15]. While large-scale synthesis [16] of carbon nanotubes mostly relies on fluidized beds and floating catalysts covering the composite and functional material applications, the fabrication of “a next generation” sensors, electronics, and transparent conductors is strictly bound with individual carbon nanotubes of controlled chirality, diameter, length, alignment, and agglomeration degree [17]. The last parameter is the key barrier for the advanced applications demanding either or both precise control of the band structure and as high aspect ratio of the nanotube/bundle as possible. Indeed, the disentanglement of carbon nanotube agglomerates produced by large-scale synthesis techniques to individual tubes implies a challenging task as Van der Waals interaction – usually considered as a weak one, glues two coaxially bundled carbon nanotubes with an energy of $950\text{ eV}/\mu\text{m}$ [18] providing enough energy even for ion excitations from carbon nanotubes [19]. The techniques for dispersion of carbon nanotubes developed so far, namely mechanical dispersion, ultrasonication, calendaring process, and ball milling lead either to low degree of disentanglement or to high damage of carbon nanotubes (length reduction, defect concentration increase) [20]. This, in turn, draws a certain need for low-yield but scalable production of high-quality single-walled carbon nanotubes. Aerosol CVD [21] – the specific case of the reactor type with floating bed of extremely diluted catalyst – is considered to be the most suitable technique for production of SWCNT for advanced applications [17,22,23].

Aerosol CVD technique have been usually applied for transparent electrodes [24,25], integrated circuits [26,27], thin film transistors [28,29], bolometers [30], or fiber lasers [31] requiring long individual carbon nanotubes. However, some applications such as drug delivery, composites, or transistors on individual carbon nanotubes demand short nanotubes and controlled defectiveness [17,32,33]. During the last 15 years, aerosol CVD setups have been equipped with a number of catalyst producing setups: decomposition of catalyst precursors (ferrocene, iron pentacarbonyl, *etc.*) followed by sintering and *in situ* nucleation of nanotubes [34,35], hot-wire generator producing vapor of active metals [36], a spark discharge generator producing also vapor of active metals [28,37]. The last apparatus developed by Mustonen *et al.* [28] has shown the smallest among the others length of carbon nanotubes ($\sim 4\text{ }\mu\text{m}$), though only a small fraction of the metal particles produced was employed for SWCNT growth (0.4-3%) [37] while the most of the catalyst was subjected to exhaust. The only technique for production of short SWCNTs by the aerosol method have been demonstrated by Tian *et al.* [38] using a ferrocene reactor with precise temperature control where short nanotubes were collected via thermophoresis on a cold finger inside the hot zone of the reactor reducing both the scalability of the technique and the range of the substrates available.

In this work, we developed an exhaust-free spark discharge generator for scalable synthesis of ultrashort single-walled carbon nanotubes with controlled diameter distribution and defect concentration with a secondary goal to get rid of wasting the most of a catalyst to exhaust. The

nanoparticles generated by the spark discharge electrodes as well as SWCNTs were examined by the set of the methods (the analysis of differential mobility of the aerosol particles, optical and Raman spectroscopy, scanning and transmission electron microscopy, and atomic force microscopy) in order to provide scalable synthesis of short carbon nanotubes (1<500 nm) of pronounced defectiveness for drug delivery and transistor applications.

2. Material and methods

A spark discharge generator was equipped with two Fe electrodes (99.99%; 40-mm long cylinders with d of 4 mm) with the variable distance between of 0.1-5 mm controlled by a micrometric manipulator, a nozzle for effective mass transfer, and flow channel for transporting the iron nanoparticles produced to the aerosol CCVD reactor for SWCNT growth. We used a high voltage generator Heinzinger PNC 20000-10 ump (Germany) combined with 45 nF (C) capacitor for collecting a charge until discharge occurs with frequency f (eq. 1):

$$f = \frac{I}{CV} , \quad (1)$$

where V is a recharge voltage (0.1-3 kV in this work), I is the current (0.05-1 mA). The energy (E) of a single charge can, thereby, be presented as:

$$E = \frac{CV^2}{2} . \quad (2)$$

The discharge leads to a plasma formation followed by a fractional evaporation of the electrode material. The electrodes were subjected to the flow of a carrier gas (0.5-5 LPM; Ar (99.999%), H₂ (99.999%), or N₂ (99.999%)) that carried the Fe vapor to the reactor (Figure 1) for the forthcoming SWCNT synthesis (time from the spark to the reactor hot zone is of 0.05-0.5 s).

Figure 1: the general scheme of the spark discharge generator integrated with tubular growth zone to provide the aerosol reactor of SWCNT synthesis.

The nanoparticles obtained were then subjected to the tubular quartz reactor (isothermic zone ~800 mm, d=50 mm) and mixed with the carbon source – CO (99.999%; 1-5 LPM). The Boudouard reaction on the catalyst surface taking place within the hot zone results (the contact time is of 6 s; the total pressure in the reactor ~ 1 atm) in SWCNT growth. The SWCNTs obtained were filtered with HAWP filter (Merck Millipore, USA) with typical collection time of 15 min for further dry transfer to glass substrate suitable for Raman and UV-vis-nIR studies [39] or to provide free-standing film (Figure 2). It should be stressed that unlike the most spark-discharge processes [28,37] the reactor developed is exhaust free – all the nanoparticles are delivered to the reactor.

Figure 2: a photo of a free-standing thin film (left) and thin film on a filter of SWCNTs (thickness of the film is of 60 nm in both cases) produced by the spark discharge aerosol CVD method.

The number size distributions of both Fe nanoparticle and SWCNT aerosols were studied using differential mobility analyzers (DMA) capable to measure the particles of effective diameter from 0.7 nm up to 60 nm (1nm Scanning Mobility Particle Sizer Spectrometer, TSI, USA) and from 6 nm to 230 nm (Scanning Mobility Particle Sizer Spectrometer 3938, TSI, USA). It should be mentioned that the separation based on the mobility followed by the data processing based on the implication of the spherical shape of the aerosol particles studies (standard software of Scanning Mobility Particle Sizer Spectrometer). This results in the effective diameter of SWCNT to be observed by this technique in the range of 40-100 nm. Moreover, the possible formation of the agglomerates of non-cylindrical shape will also affect the distribution and cannot be distinguished from an individual SWCNT. Though such values of effective diameter correspond mostly to the projected area diameter [40], it allows us to distinguish the nanotubes from metal nanoparticles (effective diameter of 1-20 nm). In case of nanoparticles produced by a spark discharge generator, the direct correlation between the TEM statistics and DMA measurements was reported elsewhere [41,42].

The UV-vis-nIR spectra were collected using Perkin Elmer Lambda 1050 within the range of 300 – 2600 nm with the resolution of 1 nm. The Raman spectra were recorded at the wavelength of 532 nm (2.33 eV) with laser power of 0.1 mW (Horiba LabRAM HR Evolution system). FEI Tecnai G2 F20 TEM microscope was used to the morphology and diameter distribution of SWCNTs. The samples were collected as follows. The TEM lacey Cu-300 grid was placed on the filter within the flow of SWCNTs for 20-200 s to obtain the desired density. The length distributions of SWCNTs produced were obtained using Bruker Multimode V8 Atomic Force

Microscope (AFM) in Peak-Force™ mode equipped with Bruker ScanAsist-Air cantilevers.

3. Results and discussion

3.1 An effect of spark discharge parameters

The frequency of the spark discharge within the generator is proportional to the current between the electrodes according to eq. (1). In terms of materials produced, this gives us an opportunity to increase the yield of both iron nanoparticles and SWCNTs produced while the number size distributions might be monitored using the DMA (Figure 3 A,B). Indeed, we observed the linear dependence of the yield of carbon nanotubes (Figure 3 B,C), while the average diameter was proven to be constant and of 1.0 nm (based on the energy of S_{11} transition) [43]. Such increase in the yield without any harm to the diameter and the length distribution is not typical for both aerosol science and carbon nanotube growth in general: usually the particles of higher concentration tend to agglomerate faster providing more or less the same concentration [44], while the carbon nanotube synthesis mechanism is still challenging [45–47] due the entanglement of different kinetic steps (*e.g.*, complex relation between the reaction parameters, diameter, and the yield). This allow us to consider the most part of the active catalyst particle agglomeration to be performed in plasma or nearby hot zone (~ 1 mm from the spark [48]) while the following transport to the SWCNT synthesis zone of the reactor has minor effect (Figure 1).

Figure 3: Influence of the current between electrodes on nanoparticle generation and SWCNT growth: A – DMA number size distributions of iron nanoparticles at the end of the spark apparatus (distance between the electrodes of 6 mm; $U \sim 1.3 \text{ kV}$); B - DMA number size distributions of carbon nanotubes produced in the reactor under complementary spark generator parameters (880°C ; 2 LPM N_2 ; 4 LPM CO);

*C – UV-vis-nIR spectra of SWCNT thin films, the inset shows the current dependence of the film thickness;
D – Raman spectra (2.33 eV) of SWCNT thin films obtained at different current parameters of spark discharge generator, the inset shows enlarged zone of radial breathing modes.*

Interesting feature of the spark generator developed is enhancement in the quality of SWCNTs with higher yield. This can be accounted for etching role of the second product of the Boudouard reaction (1st – carbon) – CO₂: higher yield results in higher conversion of the carbon monoxide providing the more effective etching of amorphous or defective carbon impurities of nanotubes [49].

Oppositely to the current, the breakdown voltage shows almost negligible effect of the defect concentration within the SWCNTs (Figure 4D). This may be due to the parabolic enhance of the yield producing too much CO₂ that capable also to etch the SWCNT structure [50]. The diameter distribution of SWCNTs is not affected by both the current and breakdown voltage (Figure 4B,C) implying the most of particle formation takes place within the plasma zone nearby the spark discharge. Nevertheless, the influence of the breakdown voltage on SWCNT yield can be described well with parabolic function (Figure 4 C; inset) analogous to the equation (2), taking into account direct correlation between the amount of nanoparticles formed and SWCNT concentration (Figure 4 A,B). It should be mentioned that we did not observe any additional chiral indexes in the pool while varying the breakdown voltage. Thus, the breakdown voltage and current allow us to manipulate precisely the yield of single-walled carbon nanotubes and their defective structure preserving the diameter distribution. This may be due to unusual situation for carbon nanotube growth – the relatively inhibited sintering of the active particles in the zone of the reactor preceding the nucleation – formation of carbon nanotube cap [10,51,52]. Thus, we can consider the two fundamental steps of the carbon nanotube nucleation, namely, the sintering of the active particles and their saturation with carbon intermediate species [53–55], to be separated in space and time providing a direct route to the scalable robust technology of SWCNT growth.

Figure 4: Influence of the breakdown voltage between the electrodes on nanoparticle generation and SWCNT growth: A – DMA number size distributions of iron nanoparticles at the end of the spark apparatus ($I=0.5$ mA; $U\sim 1.3$ kV); B - DMA number size distributions of carbon nanotubes produced in the reactor under complementary spark generator parameters (880°C ; 2 LPM N_2 ; 4 LPM CO); C – UV-vis-nIR spectra of SWCNT thin films, the dependence of the film thickness on the breakdown voltage is in inset; D – Raman spectra (2.33 eV) of SWCNT thin films obtained at different breakdown voltage parameters of spark discharge generator, the inset shows enlarged zone of radial breathing modes.

3.2 An influence of the media nature within the spark discharge generator

The increase of the carrier gas flow rate results in significant decrease of iron particle diameter (Figure 5 A, B), while the influence on the SWCNT growth is more complicated: the higher flow rate of nitrogen dilutes the carbon monoxide decreasing the rate of CNT growth due to lower partial pressure of the carbon source. This results in volcano-like dependence of the effective aerosol size of the nanotubes (Figure 5C) and of the yield (Figure 5D) while the changes in the diameter distribution according to the TEM statistics are rather minor (Figure 6). The iron nanoparticles observed at Figure 6 correspond to non-activated catalyst particles. Indeed, the DMA measurements of the Fe nanoparticles show a small fraction of metal species to be larger than 5 nm. As under CVD conditions the particle size and SWCNT diameter usually are almost the same [8,10] and due to the feature of Boudouard reaction based nanotube synthesis (no formation of multi-walled carbon nanotubes [21,36]), the particles larger than 5 nm would not provide a SWCNT nucleation. As CO decomposition is still possible on the surface of such nanoparticles, a certain carbon concentration is reached under the growth conditions providing a graphitic core at the room temperature due to dramatic decrease of the carbon solubility.

Figure 5: Influence of the carrier gas flow rate on nanoparticle generation and SWCNT growth: (A) a few patterns of DMA number size distributions of iron nanoparticles at the end of the spark apparatus ($I=0.5$ mA; $U\sim 1.3$ kV); B -DMA number size distributions of carbon nanotubes produced in the reactor under complementary spark generator parameters (880°C ; total flow of 6 LPM, N_2/CO); C– UV-vis-nIR spectra of SWCNT films, the dependence of the film thickness on the breakdown voltage is in inset; D – Raman spectra (2.33 eV) of SWCNT films obtained at different carrier gas flow rate within the spark discharge generator, the inset shows enlarged zone of radial breathing modes.

The crucial role of the carbon monoxide feeding was confirmed by controlling the amount of carbon monoxide while the contact time varied (Figure 7): this resulted in the same parameter dependence as the abovementioned breakdown voltage and the current SWCNT growth – the diameter distribution and the observed defectiveness (Figure 7 A,C) are almost the same. However, the particle size distribution obtained by DMA shows an interesting dependence, while the total concentration of the particles constantly grows, the mean observed diameter shows an extremum value at the flow rate of 1.7 LPM.

Figure 6: TEM microphotographs of SWCNTs produced under different nitrogen flow rate through the spark discharge generator: A – 0.5 LPM N_2 , B – 2 LPM N_2 (880 °C; total flow of $N_2/CO=6$ LPM); the insets show the diameter distributions based on TEM statistics.

Figure 7: Influence of the nitrogen flow rate on Fe particle generation and SWCNT growth under constant CO flow: A – UV-vis-nIR spectra of SWCNT films ($I=0.8$ mA; $U\sim 2$ kV); B – DMA number size distributions of SWCNTs; C – Raman spectra (2.33 eV) of SWCNT thin films obtained at different nitrogen flow rate within the spark discharge generator, the inset shows enlarged zone of radial breathing modes. The colors of the samples at figures A-C are the same: black line – 0.7 LPM of N_2 through the spark discharge generator, 4.3 LPM of CO through the side flow after the generator; red – 1.7 LPM N_2 , 4.3 LPM CO; blue – 2.7 LPM N_2 , 4.3 LPM CO; magenta – 3.7 LPM N_2 , 4.3 LPM CO; olive – 4.7 LPM N_2 , 4.3 LPM CO.

Using this interesting feature we have optimized the length of SWCNTs to be lower than 500 nm (eight times lower than in [28]) according to AFM statistics (Figure 8) providing a route for scalable production of the individual nanotubes for drug delivery and transistors. Once again the volcano-like (single-extremum) dependence might be implied on the basis of the AFM data (Figure 8).

Figure 8: A, B – the typical AFM images of SWCNTs on SiO₂ substrate; the length distributions based on AFM statistics for different contact time within the reactor – 7 s (C; 2 LPM N₂, 2.5 LPM CO), 5 s (D; 2 LPM N₂, 4 LPM CO), 2.5 s (E; 4 LPM N₂, 9 LPM CO).

From the first principles the carrier gas nature should affect the breakdown voltage providing a smooth control of the nanoparticles produced. We have employed nitrogen, argon, and hydrogen as model gases for the SWCNT growth. Moreover, the hydrogen is considered to be a promotor in the SWCNT growth process via aerosol CVD approach [14]. We have found the carrier gas nature to have a crucial impact of SWCNT growth when using the spark discharge generator as a catalyst source (Figure 9). Number size distributions of both Fe nanoparticles and SWCNTs produced show a significant decrease of the material produced coinciding with phenomenological Pachsens' law for discharge [56]. Moreover, the introduction of hydrogen stopped the production of SWCNTs providing more than 1000 ppm of water in the exhaust. This may be due to hydrogen ionization in spark generator hot zone. Nevertheless, the Ar/N₂ mixtures can be considered as a route for smooth tuning of the defective structure of SWCNT.

Figure 9: Influence of the carrier gas nature within the spark discharge generator on the production of Fe nanoparticles and SWCNT growth: A – DMA number size distributions of iron nanoparticles at the end of the spark apparatus ($I=0.5$ mA; $U\sim 1.3$ kV); B - DMA number size distributions of carbon nanotubes produced in the reactor under complementary spark generator parameters (880 °C; 2 LPM of a carrier gas ; 4 LPM CO); C – UV-vis-nIR spectra of SWCNT thin films, the dependence of the film thickness on carrier gas nature is in inset; D – Raman spectra (2.33 eV) of SWCNT thin films within different carrier gas nature spark discharge generator, the left inset shows enlarged zone of radial breathing modes.

Unfortunately, we are not able to provide valid quantitative comparison of different aerosol CVD reactors as different research groups using different reactor chambers, materials, and *etc.* This results in fractional or sometimes controversial data and conclusions [10]. Thus, only a systematic study with controlled comparison of the parameters may provide the quantitative data. Nevertheless, the independence of the diameter and the yield opens a promising window for scaling the technology for aerosol CVD production of SWCNTs.

4. Conclusions

We have developed an exhaust-free spark discharge generator of metallic nanoparticles for the robust growth of single-walled carbon nanotubes with the length less than of 500 nm, controlled diameter distribution and defectiveness. We have observed a rare (in terms of SWCNT growth) case of independent product characteristics – the changes in the current between the Fe electrodes affects the yield, but not the diameter distribution, while the breakdown voltage has neglectable influence on the defect concentration of SWCNTs providing parabolic boost in the

yield. We have shown the ability for tuning the defectiveness though changes in the nature of a media within the generator: the substitution of nitrogen on argon as a carrier gas drops the quality of nanotubes. This is may be due to the separation of the nanoparticle formation and carbon nanotube nucleation processes – the most part of agglomeration to take place in plasma or nearby hot zone of the generator while the effect of the following transport to the SWCNT synthesis zone of the reactor is rather minor. This feature, unusual for SWCNT growth reactors, grants us an extra degree of freedom in terms of fine tuning of the materials produced. The presence of the hydrogen within the discharge zone inhibits the growth of SWCNTs opposite to its promoting role when introduced into the SWCNT growth zone of the reactor.

Acknowledgement

This work was supported by the Skoltech Biomedical Initiative, project Assignment No 2017-7/SBI.

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