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## Activation of Catalyst Particles for Single-walled Carbon Nanotube Synthesis

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#### **Graphical abstract**



#### Abstract

In this work, we evaluate the effect of ferrocene delivery in the reactor on the growth of single-walled carbon nanotubes (SWCNTs) in an aerosol CVD utilizing carbon monoxide as a feedstock. For this purpose, we assess the reactor output parameters varying a gas flow rate through a ferrocene vapor injector in the hot zone with other conditions (temperature, total flow rate, and reactant concentration) being fixed. Our experimental results reveal the adjustment of the ferrocene injection strategy (injector flow rate) to cause a 9-fold improvement in the synthesis yield while preserving the SWCNT properties. We show the catalyst injection optimization to enhance catalyst activation degree as a result of a streamline catalyst delivery, preventing particle over-growth; the experimental data are supported by the computational fluid dynamics. We believe our work to highlight the importance of appropriate aerosol CVD reactor engineering and to

towards SWCNT-based technology.

**Keywords:** Aerosol CVD synthesis; Floating catalyst; In situ activation; Catalyst activation; Single-walled carbon nanotubes; Equivalent sheet resistance.

#### **1. Introduction**

Single-walled carbon nanotube (SWCNT) synthesis is an advanced direction of nanomaterial technology receiving tremendous effort of the scientific community and high-tech industry due to a great application promise [1]. Nanotube production technology has come a long way from physical methods (e.g. arc-discharge, laser ablation [2]) to a chemical vapor deposition (CVD) approach, which nowadays is considered to be the most convenient technique for many applications [3]. Among various strategies, an aerosol (floating catalyst) CVD method [4] is one of the most promising because of significant technological advantages, namely scalability, continuous operation mode, robust material handling involving both SWCNT thin-film dry transfer as well as the direct nanotube deposition onto any desired substrate, eliminating additional time and resource-consuming procedures. Moreover, the floating catalyst approach provides SWCNTs of a superior quality and purity, the fundamental aspects uncovering the unique nanotube properties [5]. Despite all the advantages of the process, there are still challenges to overcome: along with the general goal of the chirality control [6], productivity enhancement is a critical unsolved objective for the SWCNT mass production, preventing widespread nanotube implementation [7]. One of the main drawbacks of the current synthesis state is a low catalyst activation degree (fraction of catalyst nanoparticles that facilitated nanotube nucleation and contributed in SWCNT growth). Indeed, usually a significant part of the catalyst nanoparticles are not active, which hampers the nanotube growth and deteriorates the final properties of the produced material [8]. For this reason, a catalyst activation study and optimization of the catalyst

Journal Pre-proofs unization (catalyst productivity) are fundamental changes of the aerosof CVD nanotube production from the perspective of technology cost-effectiveness and material performance.

Even though a number of studies related to the SWCNT synthesis by the aerosol CVD method have been carried out (various catalyst formation techniques [9,10], carbon feed-stocks [11–14], and catalyst activation promoters/etching agents [15,16]), there is still a lack of reports providing insights in the gas-phase nanotube nucleation and catalyst activation. This can be due to both extreme dilution of an unsupported catalyst and continuous changes along the reactor resulting in a lack of direct methods for the activation assessment. Being a fundamental step of the SWCNT growth, catalyst activation defines not only synthesis productivity but also the characteristics of the produced nanotubes. Indeed, nanotube chirality is usually determined by a cap formation on a catalyst surface [17] and is unlikely to change during the growth [18]. Previously-reported correlation between catalyst and nanotube diameters [19], supported by a geometric increment in growth rate with a particle size increase [20], highlights the importance and need to control the catalyst nanoparticle growth until the nanotube nucleation starts. Recently, a comparative analysis of two catalyst formation approaches, namely ferrocene thermal decomposition (so-called in situ route) and spark discharge generator (ex situ route), revealed a more efficient catalyst utilization in terms of the joint catalyst particle formation and nucleation in contrary to ex situ nanoparticle formation [21]. Since ferrocene (one of the most widely used precursors for SWCNT growth catalysts [22]) decomposes at temperatures above 400°C [23], it is usually introduced directly into hot zone through a thin water cooled injector probe [24]. This technique helped both to "delay" ferrocene decomposition (and, as follows, to prevent an excessive increase in the catalyst nanoparticle size until the nanotube nucleation point is reached) and to preserve longer growth (residence) time. A recent study revealed the significance of the appropriate mixing of the catalyst precursor with other injected reactants in the reactor and how it affects the crystallinity of the produced material [25]. At the same time, it was demonstrated that varying the position of the water-cooled injector probe in the reactor, nanotube diameter, length,

and detectiveness could be effectively tuned as a result of the change is residence time and temperature profile adjustment [26]. However, the efficiency of the catalyst delivery through the injector probe and, in particular, its effect on the synthesis efficiency – which could uncover the features of gas-phase catalyst activation - have not been properly evaluated yet, while being an important aspect of the process design.

Here, we close this gap by examining how the catalyst delivery speed influences the synthesis output and activation conditions on the basis of the aerosol CVD approach using carbon monoxide as a carbon feedstock and ferrocene as a catalyst precursor. We replaced the traditional water-cooled part by a tube-injector, which simplifies the system and does not require additional attention to carry out the experiments. Employing a comprehensive study of the SWCNT characteristics (diameter distribution, defectiveness, conductivity, yield) and applying reactants (carbon dioxide) known to affect the SWCNT nucleation, we assess the nucleation pattern and provide an insight on the optimal strategy for the catalyst activation in order to optimize the synthesis productivity.

#### 2. Material and Methods

### 2.1 Reactor set-up and aerosol particle number-size distribution measurements

SWCNTs were produced using an aerosol (floating catalyst) CVD set up depicted in Figure 1 and described in detail elsewhere [24]. Briefly, the reactor operates at ambient pressure and consists of a three-zone tubular glass furnace (1.5 m length, inner and outer diameters of 72 and 78 mm, 1 m long hot zone) heated to 880°C and a gas supply system consisting of Bronkhorst mass-flow controllers. Ferrocene vapor was used as a catalyst precursor and carried by CO (Linde gas, 99.99%) flow of 0.5 lpm passing through a thermally insulated cartridge (at 24°C) containing ferrocene (Sigma-Aldrich, 98%) mixed with silica particles as a carrier. The gas flow with the precursor was then mixed with an additional flow of CO and introduced directly into the reactor hot zone through a thin (4 mm inner diameter) injector probe tube. An injector outlet position was

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optimized to introduce the now directly to the reactor not zone and from the other side to prevent the tube from clogging (caused by ferrocene decomposition on walls). As a result, the injector end position was fixed at a position, corresponding to a temperature of *c.a.* 400°C. Hereinafter the total flow through the injector tube is called an injector flow. An additional flow of a CO/CO<sub>2</sub> mixture was introduced into the reactor keeping the total flow rate introduced into the reactor constant at 5.0 lpm. The CO<sub>2</sub> concentration was varied in the range from 0.15 to 1.78 vol. % [27]. SWCNTs were collected at the outlet of the reactor using nitrocellulose membrane filter (MF-Millipore, 0.45  $\mu$ m pore size) and then dry-transferred on a glass slide for further characterization; samples for a TEM observation were directly deposited on Lacey carbon grids (PELCO Carbon 400 Mesh Cu, 42  $\mu$ m hole-size TED PELLA Inc.) at the downstream of the reactor.

A differential mobility analyzer (DMA) equipped with a condensation particle counter (Scanning Mobility Particle Sizer Spectrometer 3938, TSI, USA) was used to investigate aerosol number-size SWCNT/catalyst nanoparticle distribution at the output of the reactor.



Figure 1. Scheme of the inlet part of the an aerosol CVD reactor based on ferrocene thermal decomposition.

<sup>2.2</sup> Sample characterization

The optical absorption spectroscopy was performed in the wavelength range from 200 to 2600 nm using Perkin Elmer UV-vis-NIR spectrophotometer Lambda 1050. The optical density of the film at 550 nm was used to estimate the yield of produced SWCNT films. The yield was calculated as a collection rate of 90% transmittance (T) film according to the following formula:

$$Y\left[min^{-1}\right] = \frac{\log_{0.9}(T)}{t}$$

Here, we consider the total flow rate through an 11 mm-diameter filter used to be fixed at the value of 3.6 lpm (excess gas flow went to an exhaust line), while collection time (t) was adjusted to obtain a film reasonably (around 20 nm) thick for characterization. It should be noted that the wavelength of 550 nm was chosen as it is mostly affected by the  $\pi$ -plasmon contribution (typical for graphitic materials [28]) and the optical absorption coefficient of SWCNT films in this region was shown to match that one of graphite [29]; though this approach may lead to a certain inaccuracy it overmatches other methods to directly determine SWCNT amount in a thin film: the weight of microgram-scale limits common weighing, while the methods describing thickness (e.g. AFM, cross-section SEM, etc.) are sensitive to the film bulk density which can be varied due to, for example, capillary forces of solvents.

Raman measurements of the films were performed at 532 nm excitation wavelength by Thermoscientific DXRxi Raman Imaging microscope with the lowest available excitation power of 0.1 mW and 0.16 s exposure time. The signal was automatically averaged more than 100 times.

SWCNT film sheet resistance was measured by a Jandel RM3000 four-probe tool. The measurements were repeated at least three times in different directions and the obtained values were averaged.

TEM images were obtained using FEI Tecnai G2 F20 transmission electron microscope.

#### 2.3 CFD calculations

In order to evaluate the temperature and velocity profiles inside the reactor, computational fluid dynamics (CFD) calculations were carried out using COMSOL Multiphysics software. The 2D axisymmetric nonisothermal flow model taking into account vorticity associated with buoyancy forces was developed. Both laminar flow and turbulent flow (k- $\varepsilon$  model) approximations were tested and demonstrated similar results. Indeed, considering 4-mm diameter of injector probe and linear velocity varying from 1 to 10 m/s (corresponding to injector flow variation in range of 0.5-4.5 lpm), as well as carbon monoxide dynamic viscosity and density at 400°C (corresponding to injector end position; discussed further) of 3.2 Pa·s and 0.5 kg/m<sup>3</sup> correspondingly [30] we can expect Reynolds numbers to be in the range of 100-1000 and associated with laminar flow regime.

Fluid dynamics module was coupled with following heat transfer equation:

$$\rho c_p \boldsymbol{u} \nabla T + \nabla \mathbf{q} = \mathbf{Q} + Q_p + Q_{vd},$$

where  $\rho$ ,  $c_p$ , T and u – gas density, heat capacity, temperature and velocity vector, correspondingly;  $\mathbf{q}$  – heat flux, Q,  $Q_p$  and  $Q_{vd}$  – constant heat source, work done by pressure changes and viscous dissipation, correspondingly.

The boundary conditions were as follows. Inside the oven, the experimental wall temperatures were used, while the wall temperature outside the oven (on the top) was calculated employing the convective cooling conditions. Two set CO mass flow rates at the input of the reactor tube (main flow) and injector probe (injector flow), making up the total flow of 5.0 lpm, as well as the open boundary at the tube end (outflow), represented flow dynamics boundary conditions. The injector flow also contained an extremely diluted ferrocene vapor concentration, which was recalculated for every value of injector flow rate in order to keep the ferrocene feed rate constant, as it was realized in our experiments. Thermal decomposition of ferrocene vapor inside the hot zone of the reactor was modeled as a single-step process using the following rate constant:

$$k[s^{-1}] = 10^{14} \cdot \exp(-E_a/RT),$$

Journal Pre-proofs where  $E_a$  is the activation energy of  $207 \frac{R}{mol}$ , R is the universal gas constant, T is absolute temperature [31]. The heat release during the ferrocene decomposition was not taken into account in the reactor heat transfer because of negligibly small partial pressure of ferrocene vapor (around 0.1 Pa [32]).

#### 3. Results and discussion

### 3.1 Rate-limiting step for SWCNT activation

In case of aerosol CVD, the catalyst injection rate might affect the nanotube growth from the very first step – SWCNT nucleation. The nanotube nucleation is a complex and temperaturedependent process taking place at the point when catalyst nanoparticle is enriched with carbon enough to form a nanotube cap (yarmulke mechanism) with a diameter defined by the size of the active catalyst particle [19].

The size of nanoparticles in the reactor constantly increases as a result of particle collision (coagulation), which is a time- and temperature-dependent process. Thus, one of the expected outcomes of the injector/main flow rate variation is a shift in the mean SWCNT diameter as a result of the change in coagulation conditions, associated with the velocity field and temperature profile modification. Surprisingly, the results obtained with both UV-vis-NIR spectroscopy and TEM statistics (Figure 2) reveal no effect on the SWCNT mean diameter even under a dramatic change in the injection rate (from 0.5 to 4.5 lpm). Indeed, absorption spectra of SWCNTs collected for injector flow rates of 0.5, 1.5, and 4.5 lpm consist of the similar peaks associated with Van Hove singularities for 1.3-1.7 nm nanotubes (S<sub>11</sub> transition energy of 0.75-0.6 eV, correspondingly; [33]); the same pattern is observed for radial breathing modes of the Raman spectra (see Supporting information, Figure S1). Though peak positions remain constant, variation in peak intensity is observed. One can attribute this effect to changes in chirality composition associated with the complex kinetic process of nanotube nucleation, preserving diameter distribution.

agreement as well, taking into account the dispersion in the experimental data (Figure 2 b,d,e).



Figure 2. Optical absorption spectra and nanotube diameter distribution (based on TEM statistics) for SWCNT samples produced at  $0.59 \text{ vol. } \% \text{ CO}_2$  concentration and catalyst precursor feed rate of (a, b) 4.5 lpm, (c, d) 1.5 lpm, and (e, f) 0.5 lpm.

It should be noted that carbon dioxide concentration is widely known to tune SWCNT diameter in aerosol CVD based on the Boudouard reaction [34]. The effect is usually attributed to carbon etching from catalyst surface resulting in a nucleation delay and diameter shift [27,35]. Having observed a similar trend, we, however, prove the catalyst injection not to affect the diameter distribution within the range studied (Figure S2 a,b). Moreover, the mean diameter is shown to change insignificantly with growth temperature (Figure S2 c). Thus, considering a small fluctuation in the diameter distribution in terms of injector flow rate variation, we can conclude the nanotube nucleation to be limited not by the catalyst agglomeration but rather by the carbon source supply (affected by  $CO_2$  concentration and temperature). Thus, we can expect that

competing rates of particle confision and carbon enrichment (including the processes of leed-stock dissociation and carbon diffusion) result in only a certain part (diameter range) of catalyst nanoparticles to be activated and sustain the nanotube growth.

## 3.2 Catalyst delivery and SWCNT yield

Synthesis yield as a function of the injector flow rate at different CO<sub>2</sub> concentrations is presented in Figure 3. The obtained results reveal a bell-shaped flow rate dependence (as well as on CO<sub>2</sub> concentration; Figure S2 d) with a pronounced maximum slightly shifted from 2 lpm at high CO<sub>2</sub> concentration (>1.33 vol. %) to 1.5 lpm at lower ones. The highest yield of  $Y = 0.31 \text{ min}^{-1}$ is achieved at 0.59 vol. % of CO<sub>2</sub> and 2 lpm injector flow rate. The demonstrated up to a 9-fold increase in the yield as a result of the flow adjustment (from  $Y = 0.03 \text{ min}^{-1}$  at 4.5 lpm to Y = 0.28min<sup>-1</sup> at 1.5 lpm; 1.33 vol. % CO<sub>2</sub> concentration) indicates a significant improvement in catalyst utilization. Indeed, given that the catalyst concentration (amount of catalyst introduced per unit of time) is fixed in our experiments, the increase in productivity (catalyst utilization) might be interpreted as either a rise in the number of growth centers (activation degree) and/or enhanced growth efficiency (higher catalyst productivity).

The SWCNT yield is a function of two main parameters: catalyst activation degree and nanotube length (defined by the growth rate and growth time). Considering only a small-scale shift in a temperature profile with injector flow rate variation (will be further discussed) at fixed total flow rate, we can assume the residence time as well as the growth rate (at fixed CO<sub>2</sub> concentration) to be almost constant in our experiments. This fact may indicate insignificant changes in the nanotube length and provide evidence for the variation of a catalyst activation degree. To explore the nanotube length evolution with the injector flow rate we evaluated the equivalent sheet resistance ( $R_{90}$ , sheet resistance of the SWCNT film with a 90% transmittance in the middle of the visible range) data for the randomly oriented pristine SWCNTs produced in our experiments. The equivalent sheet resistance is known to be a function of a nanotube length [36], defectiveness,

anameter distribution [57], and electronic type (in case of metallic/semiconducting nanotube enriched samples [38], not relevant for classical CO-based system [39]), and bundle diameter [40]. As far as the injector flow rate variation is demonstrated not to affect mean nanotube diameter significantly (Figure 2), we additionally examined only nanotube defectiveness employing D-band to G-band Raman intensity ratio ( $I_D/I_G$ ) [41].







**Figure 4.** Equivalent sheet resistance  $(R_{90})$  and Raman intensity ratio  $(I_D/I_G)$  as a function of the catalyst precursor feed rate for different CO<sub>2</sub> concentrations.

Figure 4 represents the equivalent sheet resistance and  $I_G/I_D$  plot *versus* the injector flow rate at three different CO<sub>2</sub> concentrations. Overall, no explicit trend could be found at various CO<sub>2</sub> concentrations; moderate changes (less than 3-fold) in the equivalent sheet resistance and Raman peak intensity ratio, which are comparable with deviation from average, are observed. The data confirms the prevalent effect of CO<sub>2</sub> on the equivalent sheet resistance, discussed previously [27]. Besides, the  $I_D/I_G$  relation demonstrates a plot pattern similar to  $R_{90}$  that highlights the interconnection between nanotube defectiveness and film conductive properties.

The increase in yield might also lead to an increase in bundle diameter (since nanotubes have higher collision probability); but, considering both small changes in R90 and its correlation

with defectiveness, we can conclude the results of equivalent sheet resistance to marcate the changes of nanotube length and bundling degree either to be insignificant or, less likely, mutually suppressing (e.g. a decrease in nanotube length and reduced bundle size). The first option (constant length) is also supported by aerosol number-size distribution measurements revealing no noticeable change in a mean particle diameter (Figure S4 a; corresponding to nanotube effective size (length) [42]) and total concentration dependence on injector flow rate similar to that one of yield (Figure S4 b). Thereby, the principal cause of the yield enhancement is attributed to the increase in the catalyst activation degree.

#### 3.3 Optimal activation

Exploring the impact of reactor engineering on characteristics of produced material, we also addressed the underlying processes responsible for the observed effects. For this purpose, we conducted a computational fluid dynamics (CFD) study of our system intending to find out more about flow dynamics inside the reactor and provide a proper explanation of the experimental trends presented. The CFD results (Figure 5) demonstrate the reactor flow evolution at different ratios of the injector and main flow rates.

Despite the total flow rate is kept constant, the injector flow rate affects the velocity field distribution significantly and shifts the temperature profile. This fact is especially noticeable in the vicinity of the reactor inlet (set as a reference point z = 0) and at the beginning of the hot zone – both are significantly affected by vortexes associated with buoyancy forces. Two recirculation zones are observed at simulated conditions: the first one takes place directly after the reactor inlet (z = 0-0.2 m), while the second one corresponds to the mixing region located right after the injector probe end (z = 0.28-0.5 m). Higher injector flow rate, as expected, corresponds to a more vivid recirculation effect, displayed by streamlines of the velocity field (Figure 5c). In contrast, at lower

injector now rates the gas stream transforms to a fully developed now earlier and exhibits a lower

(a) (b) (c) r (mm) r (mm) r (mm) 30 15 0 15 30 30 15 0 15 30 30 15 0 15 30 ļg U (m/s) 0.0 0.5 lpm 100 1.5 lpm 100 4.5 lpm 200 8.00 4.00 200 200 300 2.00 0.2 400 300 300 500 1.00 400-400 500 0.50 z (m) 600 600 0.4 600 0.25 700 0.13 700 700 800 0.06 ROO 800 0.6 850 0.03 850 0.02 T (°C) T (°C) T (°C) 0.01 Reaction rate (mmol/m³s) 0.4 Injectior flow rate (Ipm): 0.5 0.3 njector end 1.0 1.5 0.2 3.0 4.5 0.1 0.0 0.3 0.4 0.5 0.6 0.2 z (m)

radial temperature gradient Figure 5a).



Nevertheless, a low injector flow rate results in a less effective ferrocene delivery in the reactor hot zone that is displayed in the calculated decomposition rate at the reactor axis depicted in Figure 5d. At the injection rate of 0.5 lpm ferrocene vapor decomposes earlier and it takes more time to get to the high temperature zone (>800°C), where SWCNT nucleation takes place [43].

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I ne calculated time from the location of maximum terrocene decomposition (marked by colored circles in Figure 5d) to the high temperature zone is 1.03 s at 0.5 lpm versus 0.75 s at 1.5 lpm. Nevertheless, a further increase in the injector flow rate (above 1.5 lpm) does not lead to significant improvement in the delivery speed with the transfer time reaching 0.71 s at 4.5 lpm. The rapid ferrocene decomposition results in an overlap of the decomposition region with buoyancy vortexes, especially evident at the injector rate of 4.5 lpm. The swirl flow and associated high radial temperature gradient could be one of the main reasons for the lack of noticeable improvement in ferrocene delivery speed in reactor hot zone and could lead to intensive catalyst nanoparticle loss due to deposition on the reactor walls and uncontrollable increase in the particle size (over-coagulation) in the recirculation region. The discussed trade-off between catalyst delivery speed and flow laminarity, supports the experimental data (Figure 3) of the synthesis efficiency, highlighting injector flow rate of 1.5-2.0 lpm to provide the most productive conditions, which corresponds to the highest ferrocene introduction depth (decomposition point marked by colored circles in Figure 5d; the obtained result is relevant even in terms of different kinetic constants (Figure S5) avoiding significant recirculation effects. At the same time, experimentally observed a dramatic decrease in the synthesis yield at higher injector flow rates could be attributed to the discussed recirculations (especially pronounced in the case of the fast catalyst precursor injection). Assuming that the delivery time is determined by the linear velocity after the injector probe, we can also expect that the injector probe with a smaller diameter can help to avoid issues associated with vorticity, maintaining high delivery speed.

Unfortunately, the direct investigation of the particle size distribution at the nanotube nucleation step is a challenging task in terms of the aerosol CVD process, since the evolution takes place directly in the gas phase. Taking into account the correlation between the particle size distribution during the nucleation and its further coagulation, we conducted TEM statistics of non-activated nanoparticles, collected downstream of the reactor (Figure 6; Figure S4), in striving to

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get insignts into the nucleation. According to the statistics, the geometric mean diameter ( $\mu_G$ ) of non-activated Fe nanoparticles is 2–4 nm at all injector flow rates that is consistent with the typical diameter range suitable for the nanotube nucleation [20]. Thus, most of the particles were capable of nucleating SWCNTs from the geometrical point of view.





Surprisingly, the number size distribution of non-active particles obtained at the optimal conditions (the injector flow rate of 1.5 lpm; Figure 6 b) possesses both higher geometric mean and standard deviation with a significant part of particles in larger diameter (>5 nm) region. The volume size distribution, depicted on the same graph, emphasizes the largest fraction of non-activated particles to be found with the size of 10 nm at 1.5 lpm injector flow rate (that is not observed at low yield conditions Figure 6a, c).

This seemingly unusual result fits well with the previously-discussed paradigm. Since the catalyst nanoparticles tend to coagulate and increase their size, we can expect small diameter non-

Journal Pre-proofs activated particles (lound in TENT) to be associated with the carbon encapsulation process (i.e.failed the SWCNT nucleation) [42]. The encapsulation results in a carbon shell formation, which prevents further particle growth and nanotube nucleation. This can be described in terms of classical nucleation theory: nanotube nucleation requires a considerable oversaturation of the catalyst with carbon. From that perspective, a bigger fraction of small non-activated particles with the diameter suitable for nanotube growth, found at 0.5 lpm injector flow rate, indicates less favorable nucleation conditions. High particle mean diameter, observed downstream of the reactor at optimal injection conditions (Figure 6b), corresponds to the high-diameter tail of a log-normal distribution of particles (Figure 6d) and reflects higher catalyst activation degree, with an insignificant fraction of particles below 5 nm (which may support the SWCNT growth). In case of fast catalyst injection (injector flow rate of 4.5 lpm), we observe an intermediate bimodal distribution, which is presumably associated with partially efficient catalyst delivery accompanied by uncontrolled growth of particles (and as follows poor activation) due to previously-discussed flow dynamics. Thus, the TEM results support our claims on the catalyst activation degree variation and very likely to indicate the carbon encapsulation to be one of the main factors inhibiting the catalyst activation. Summarizing, the CFD study and the TEM measurements support the effect of injector flow rate on catalyst activation and highlight the importance of catalyst delivery speed in reactor hot zone as well as flow laminarity.

#### 4. Conclusions

In conclusion, we thoroughly investigated how the ferrocene injection affects the aerosol CVD synthesis in the geometry of the CO-based reactor system. For this purpose, we examined the synthesis output varying the injector flow rate together with ferrocene vapor at several  $CO_2$ concentrations and assessed obtained SWCNT properties. Our experimental results revealed that the injector flow rate adjustment could lead to a 9-fold increase in the synthesis productivity while preserving most of the SWCNT characteristics such as diameter, defectiveness, and film Journal Pre-proof

conductivity. Based on that we concluded the injector now rate to affect the catalyst activation degree that was highlighted by TEM statistics of non-activated catalyst nanoparticles. Moreover, we consider carbon source supply to be rate-limiting step during the SWCNT nucleation as the diameter distribution is insensitive to catalyst precursor delivery. Numerical modeling of flow dynamics pointed out the injector flow rate to govern catalyst delivery speed in the hot zone reactor. The optimum experimental conditions (in terms of SWCNT yield) are consistent with numerical results revealing the lowest delivery time and moderate flow laminarity. Our research highlights the importance of appropriate catalyst injection and its effect on the catalyst activation process. We believe our work to be interesting from the perspective of chemical engineering of the aerosol CVD process, providing a simple and elegant route to enhancement of synthesis productivity.

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#### References

- R. Rao, C.L. Pint, A.E. Islam, R.S. Weatherup, S. Hofmann, E.R. Meshot, F. Wu, C. Zhou, N. Dee, P.B. Amama, J. Carpena-Nuñez, W. Shi, D.L. Plata, E.S. Penev, B.I. Yakobson, P.B. Balbuena, C. Bichara, D.N. Futaba, S. Noda, H. Shin, K.S. Kim, B. Simard, F. Mirri, M. Pasquali, F. Fornasiero, E.I. Kauppinen, M. Arnold, B.A. Cola, P. Nikolaev, S. Arepalli, H.M. Cheng, D.N. Zakharov, E.A. Stach, J. Zhang, F. Wei, M. Terrones, D.B. Geohegan, B. Maruyama, S. Maruyama, Y. Li, W.W. Adams, A.J. Hart, Carbon Nanotubes and Related Nanomaterials: Critical Advances and Challenges for Synthesis toward Mainstream Commercial Applications, ACS Nano. 12 (2018) 11756–11784. doi:10.1021/acsnano.8b06511.
- [2] N. Arora, N.N. Sharma, Arc discharge synthesis of carbon nanotubes: Comprehensive

- C. Journet, M. Picher, V. Jourdain, Carbon nanotube synthesis: From large-scale production to atom-by-atom growth, Nanotechnology. 23 (2012). doi:10.1088/0957-4484/23/14/142001.
- [4] A. Kaskela, A.G. Nasibulin, M.Y. Timmermans, B. Aitchison, A. Papadimitratos, Y. Tian,
  Z. Zhu, H. Jiang, D.P. Brown, A. Zakhidov, E.I. Kauppinen, Aerosol-synthesized
  SWCNT networks with tunable conductivity and transparency by a dry transfer technique,
  Nano Lett. 10 (2010) 4349–4355. doi:10.1021/nl101680s.
- [5] K. Mustonen, P. Laiho, A. Kaskela, T. Susi, A.G. Nasibulin, E.I. Kauppinen, Uncovering the ultimate performance of single-walled carbon nanotube films as transparent conductors, Appl. Phys. Lett. 107 (2015) 1–6. doi:10.1063/1.4932942.
- [6] F. Yang, M. Wang, D. Zhang, J. Yang, M. Zheng, Y. Li, Chirality Pure Carbon Nanotubes : Growth, Sorting, and Characterization, (n.d.). doi:10.1021/acs.chemrev.9b00835.
- [7] C. Liu, H. Cheng, Carbon nanotubes: controlled growth and application, Mater. Today. 16
  (2013) 19–28. doi:10.1016/j.mattod.2013.01.019.
- [8] S.A. Romanov, A.A. Alekseeva, E.M. Khabushev, D. V Krasnikov, A.G. Nasibulin,
  Rapid, efficient, and non-destructive purification of single-walled carbon nanotube films from metallic impurities by Joule heating, Carbon N. Y. (2020).
  doi:10.1016/j.carbon.2020.06.068.
- K. Mustonen, P. Laiho, A. Kaskela, Z. Zhu, O. Reynaud, N. Houbenov, Y. Tian, T. Susi,
  H. Jiang, A.G. Nasibulin, E.I. Kauppinen, Gas phase synthesis of non-bundled, small
  diameter single-walled carbon nanotubes with near-armchair chiralities, Appl. Phys. Lett.
  107 (2015) 10–15. doi:10.1063/1.4926415.

- Journal Pre-proois D. v. Krasnikov, B. I. Zabelich, v. I. lakovlev, A.P. Isapenko, S.A. Komanov, A.A. 1101 Alekseeva, A.K. Grebenko, A.G. Nasibulin, A spark discharge generator for scalable aerosol CVD synthesis of single-walled carbon nanotubes with tailored characteristics, Chem. Eng. J. 372 (2019) 462–470. doi:10.1016/j.cej.2019.04.173.
- [11] T. Saito, S. Ohshima, T. Okazaki, S. Ohmori, M. Yumura, S. Iijima, Selective Diameter Control of Single-Walled Carbon Nanotubes in the Gas-Phase Synthesis, 8 (2008) 6153– 6157. doi:10.1166/jnn.2008.SW23.
- E.X. Ding, A. Hussain, S. Ahmad, Q. Zhang, Y. Liao, H. Jiang, E.I. Kauppinen, High-[12] performance transparent conducting films of long single-walled carbon nanotubes synthesized from toluene alone, Nano Res. 12 (2019). doi:10.1007/s12274-019-2581-7.
- [13] A. Hussain, Y. Liao, Q. Zhang, E. Ding, P. Laiho, S. Ahmad, N. Wei, Y. Tian, H. Jiang, E.I. Kauppinen, Floating catalyst CVD synthesis of single walled carbon nanotubes from ethylene for high performance transparent electrodes, Nanoscale. 10 (2018) 9752–9759. doi:10.1039/C8NR00716K.
- L.F. Su, J.N. Wang, F. Yu, Z.M. Sheng, H. Chang, C. Pak, Continuous production of [14] single-wall carbon nanotubes by spray pyrolysis of alcohol with dissolved ferrocene, Chem. Phys. Lett. 420 (2006) 421-425. doi:10.1016/j.cplett.2005.12.046.
- [15] B. Yu, C. Liu, P.-X. Hou, Y. Tian, S. Li, B. Liu, F. Li, E.I. Kauppinen, H. Cheng, Bulk Synthesis of Large Diameter Semiconducting Single-Walled Carbon Nanotubes by Oxygen-Assisted Floating Catalyst Chemical Vapor Deposition, J. Am. Chem. Soc. 133 (2011) 5232–5235. doi:10.1021/ja2008278.
- Z. Zhu, H. Jiang, T. Susi, A. Nasibulin, E. Kauppinen, The Use of NH<sub>3</sub> to Promote the [16] Production of Large-Diameter Single-Walled Carbon Nanotubes with a Narrow (<italic>n,m</italic>) Distribution, J. Am. Chem. Soc. 133 (n.d.) 1224–1227.

- S. Reich, L. Li, J. Robertson, Structure and formation energy of carbon nanotube caps, Phys. Rev. B - Condens. Matter Mater. Phys. 72 (2005) 1–8. doi:10.1103/PhysRevB.72.165423.
- [18] S. Hofmann, R. Sharma, C. Ducati, G. Du, C. Mattevi, C. Cepek, M. Cantoro, S. Pisana, A. Parvez, F. Cervantes-Sodi, A.C. Ferrari, R. Dunin-Borkowski, S. Lizzit, L. Petaccia, A. Goldoni, J. Robertson, In situ Observations of Catalyst Dynamics during Surface-Bound Carbon Nanotube Nucleation, Nano Lett. 7 (2007) 602–608. doi:10.1021/nl0624824.
- [19] A.G. Nasibulin, P. V. Pikhitsa, H. Jiang, E.I. Kauppinen, Correlation between catalyst particle and single-walled carbon nanotube diameters, Carbon N. Y. 43 (2005) 2251–2257. doi:10.1016/j.carbon.2005.03.048.
- [20] C. Cheng, S.T.S. Bukkapatnam, L.M. Raff, M. Hagan, R. Komanduri, Monte Carlo simulation of carbon nanotube nucleation and growth using nonlinear dynamic predictions, Chem. Phys. Lett. 530 (2012) 81–85. doi:10.1016/j.cplett.2012.01.067.
- [21] V.Y. Iakovlev, D. V. Krasnikov, E.M. Khabushev, A.A. Alekseeva, A.K. Grebenko, A.P. Tsapenko, B.Y. Zabelich, J. V. Kolodiazhnaia, A.G. Nasibulin, Fine-tuning of spark-discharge aerosol CVD reactor for single-walled carbon nanotube growth: The role of ex situ nucleation, Chem. Eng. J. (2019) 123073. doi:10.1016/j.cej.2019.123073.
- [22] H.M. Cheng, F. Li, G. Su, H.Y. Pan, L.L. He, X. Sun, M.S. Dresselhaus, Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbons, Appl. Phys. Lett. 72 (1998) 3282–3284. doi:10.1063/1.121624.
- [23] L.M. Dyagileva, V.P. Mar'in, E.I. Tsyganova, G.A. Razuvaev, Reactivity of the first transition row metallocenes in thermal decomposition reaction, J. Organomet. Chem. 175 (1979) 63–72. doi:10.1016/S0022-328X(00)82299-8.

- A. Moisaia, A.G. Nasiouin, D.P. Brown, H. Jiang, L. Knriachichev, E.I. Kauppinen, [24] Single-walled carbon nanotube synthesis using ferrocene and iron pentacarbonyl in a laminar flow reactor, Chem. Eng. Sci. 61 (2006) 4393-4402. doi:10.1016/j.ces.2006.02.020.
- J.H. Park, J. Park, S.H. Lee, S.M. Kim, Continuous synthesis of high-crystalline carbon [25] nanotubes by controlling the configuration of the injection part in the floating catalyst chemical vapor deposition process, Carbon Lett. (2020). doi:10.1007/s42823-020-00131-3.
- [26] Y. Tian, M.Y. Timmermans, M. Partanen, A.G. Nasibulin, H. Jiang, Z. Zhu, E.I. Kauppinen, Growth of single-walled carbon nanotubes with controlled diameters and lengths by an aerosol method, Carbon N. Y. 49 (2011) 4636–4643. doi:10.1016/j.carbon.2011.06.036.
- E.M. Khabushev, D. V. Krasnikov, O.T. Zaremba, A.P. Tsapenko, A.E. Goldt, A.G. [27] Nasibulin, Machine Learning for Tailoring Optoelectronic Properties of Single-Walled Carbon Nanotube Films, J. Phys. Chem. Lett. 10 (2019) 6962–6966. doi:10.1021/acs.jpclett.9b02777.
- L. Calliari, S. Fanchenko, M. Filippi, Plasmon features in electron energy loss spectra [28] from carbon materials, Carbon N. Y. 45 (2007) 1410-1418. doi:https://doi.org/10.1016/j.carbon.2007.03.034.
- [29] F. De Nicola, C. Pintossi, F. Nanni, I. Cacciotti, M. Scarselli, G. Drera, S. Pagliara, L. Sangaletti, M. De Crescenzi, P. Castrucci, Controlling the thickness of carbon nanotube random network films by the estimation of the absorption coefficient, Carbon N. Y. 95 (2015) 28-33. doi:10.1016/j.carbon.2015.07.096.
- H.W. Hilsenrath, Joseph; Beckett, Charles W.; Benedict, William S.; Fano, Lilla; Hoge, [30]

Journal Pre-proofs Harold J.; masa, Joseph F.; Nuttan, Kaiph L.; Touloukian, Yeram S.; wooney, Tables of thermal properties of gases comprising tables of thermodynamic and transport properties of air, argon, carbon dioxide, carbon monoxide hydrogen, nitrogen, oxygen, and steam, 1960.

- K. Kuwana, K. Saito, Modeling CVD synthesis of carbon nanotubes: Nanoparticle [31] formation from ferrocene, Carbon N. Y. 43 (2005) 2088–2095. doi:10.1016/j.carbon.2005.03.016.
- M. Fulem, K. Růžička, C. Červinka, M.A.A. Rocha, L.M.N.B.F. Santos, R.F. Berg, [32] Recommended vapor pressure and thermophysical data for ferrocene, J. Chem. Thermodyn. 57 (2013) 530–540. doi:10.1016/j.jct.2012.07.023.
- [33] H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, Y. Achiba, Optical properties of single-wall carbon nanotubes, Synth. Met. 103 (1999) 2555-2558. doi:10.1016/S0379-6779(98)00278-1.
- Y. Liao, A. Hussain, P. Laiho, Q. Zhang, Y. Tian, N. Wei, E.X. Ding, S.A. Khan, N.N. [34] Nguyen, S. Ahmad, E.I. Kauppinen, Tuning Geometry of SWCNTs by CO2 in Floating Catalyst CVD for High-Performance Transparent Conductive Films, Adv. Mater. Interfaces. 5 (2018) 1–10. doi:10.1002/admi.201801209.
- [35] Y. Tian, M.Y. Timmermans, S. Kivistö, A.G. Nasibulin, Z. Zhu, H. Jiang, O.G. Okhotnikov, E.I. Kauppinen, Tailoring the diameter of single-walled carbon nanotubes for optical applications, Nano Res. 4 (2011) 807-815. doi:10.1007/s12274-011-0137-6.
- [36] D. Hecht, L. Hu, G. Grüner, Conductivity scaling with bundle length and diameter in single walled carbon nanotube networks, Appl. Phys. Lett. 89 (2006) 1-4. doi:10.1063/1.2356999.
- E.M. Khabushev, D. V. Krasnikov, J. V. Kolodiazhnaia, A. V. Bubis, A.G. Nasibulin, [37]

doi:10.1016/j.carbon.2020.01.068.

- [38] G. Gruner, M.A. Topinka, D. Goldhaber-Gordon, D.S. Hecht, M.D. McGehee, M.W.
  Rowell, Charge Transport in Interpenetrating Networks of Semiconducting and Metallic
  Carbon Nanotubes, Nano Lett. 9 (2009) 1866–1871. doi:10.1021/nl803849e.
- [39] Y. Liao, H. Jiang, N. Wei, P. Laiho, Q. Zhang, S.A. Khan, E.I. Kauppinen, Direct Synthesis of Colorful Single-Walled Carbon Nanotube Thin Films, J. Am. Chem. Soc. 140 (2018) 9797–9800. doi:10.1021/jacs.8b05151.
- [40] Y. Liao, A. Hussain, P. Laiho, Q. Zhang, Y. Tian, N. Wei, E. Ding, S.A. Khan, N.N.
  Nguyen, S. Ahmad, Tuning Geometry of SWCNTs by CO 2 in Floating Catalyst CVD for
  High-Performance Transparent Conductive Films, Adv. Mater. Interfaces. 1801209
  (2018) 1–10. doi:10.1002/admi.201801209.
- [41] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Raman spectroscopy of carbon nanotubes, Phys. Rep. 409 (2005) 47–99. doi:10.1016/j.physrep.2004.10.006.
- [42] A. Moisala, A.G. Nasibulin, S.D. Shandakov, H. Jiang, E.I. Kauppinen, On-line detection of single-walled carbon nanotube formation during aerosol synthesis methods, Carbon N. Y. 43 (2005) 2066–2074. doi:10.1016/j.carbon.2005.03.012.
- [43] A.S. Anisimov, A.G. Nasibulin, H. Jiang, P. Launois, J. Cambedouzou, S.D. Shandakov,
  E.I. Kauppinen, Mechanistic investigations of single-walled carbon nanotube synthesis by
  ferrocene vapor decomposition in carbon monoxide, Carbon N. Y. 48 (2009) 380–388.
  doi:10.1016/j.carbon.2009.09.040.

#### Journal Pre-proofs

#### HIGHLIGHIS

- Proper activation of the catalyst gives a 9-fold increase in the yield;
- Carbon nanotube length and defectiveness can be preserved when activation tuned;
- Optimal activation comprises efficient delivery and flow dynamics;
- Carbon nanotube diameter distribution is not affected by the injection flowrate;
- Supply of carbon intermediates is rate-limiting step for nanotube nucleation.

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