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Ahmad, Saeed; Zhang, Qiang; Ding, Er Xiong; Jiang, Hua; Kauppinen, Esko I.

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Multi-nucleation of single-walled carbon nanotubes in floating catalyst chemical vapor deposition

Saeed Ahmad^{a,b,*}, Qiang Zhang^a, Er-Xiong Ding^a, Hua Jiang^a, Esko I. Kauppinen^{a,*}

^a Department of Applied Physics, Aalto University School of Science, 15100, FI-00076 Aalto, Finland

^b Department of Physics, Government Postgraduate College Mansehra, 21300, Pakistan

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ABSTRACT

Floating-catalyst CVD (FCCVD) is a highly promising technique for the scalable synthesis of single-walled carbon nanotubes (SWCNTs). The number concentration (NC) of catalyst particles is one of the process parameters which mainly influences yield of as-produced SWCNTs. In the conventional FCCVD methods, catalyst particles are usually synthesized by thermal decomposition of organometallic compounds inside the FCCVD reactor. Being in-situ catalyst formation in conventional FCCVD, it is an open question that how many SWCNTs a single catalyst particle can grow? Herein, we employed our novel spark discharged based FCCVD technique which decouples the formation of catalyst particles and SWCNTs synthesis into two subsequent process to investigate effects of catalyst NC on SWCNTs synthesis. The NC of both catalyst particles and SWCNTs in gas-phase were quantitatively compared using differential mobility analyzer (DMA). The DMA measurements corroborated with atomic force microscopy and X-rays photoelectron spectroscopy revealed that under carefully chosen reaction conditions in FCCVD, a single catalyst particle can grow more than one SWCNTs. We propose that after the growth of 1st SWCNT, the catalyst particle detach itself to start nucleating 2nd SWCNT and this process continues as long as the catalyst remains in the growth region of the FCCVD reactor.

1. Introduction

Single-walled carbon nanotube (SWCNT) is one-dimensional synthetic allotrope of carbon. Since their discovery in 1990's [1], they have been a subject of great interest due to their widespread potential applications in the fields of energy storage [2], mechanics [3], optoelectronics and photonics [4]. The synthesis of SWCNTs through chemical vapor deposition (CVD) technique [5–7] requires catalyst particle as a seed for their growth. The catalyst particle is one of the key growth parameter which significantly tune morphology and chirality of the resulting SWCNT [8–10]. For the substrate based CVD methods (where catalyst is supported on some solid material [5,6]), the *in-situ* electron microscopy growth mechanism study [11] has revealed that a single catalyst particle can grow more than one SWCNTs. The morphology of successive SWCNTs from a single catalyst has been observed entirely different due to possible changes in the catalyst-nanotube interface after growing first nanotube. These experimental results indicate that the role of catalyst in the substrate CVD method to control morphology and especially chirality of SWCNTs is very complicated and needs further investigations. Moreover, the *in-situ* formation mechanism explained in

the earlier study [11] might be only applicable under high-vacuum conditions inside the microscope and may produce different results when it comes to *ex-situ* real CVD growth processes. The situation becomes more complicated when the catalyst is suspended in the gaseous environment, so called floating catalyst CVD (FCCVD) technique [7,12,13]. In conventional FCCVD method normally catalyst particles are obtained by thermal decomposition of volatile organometallic compounds such as ferrocene and nickelocene inside the hot furnace [7,14]. Unfortunately, at such an elevated temperature (700–1200 °C) together with very short residence time (usually < 10 s) it is practically not possible to measure the size and gas-phase number concentration (NC) of catalyst particles before they start growing SWCNTs. Hence, this technique gives limited information about the effect of catalyst NC on SWCNT growth.

In the present work we have for the first time reported that in real FCCVD synthesis reactors, even with very small residence time of ~ 10 s, a single suspended catalyst particle can grow more than one SWCNT. For this purpose, we systematically investigated the effect of catalyst NC on yield and NC of SWCNTs in the gas-phase. The SWCNTs were synthesized by our well-established spark discharged based FCCVD technique

* Corresponding authors at: Department of Applied Physics, Aalto University School of Science, 15100, FI-00076 Aalto, Finland (S. Ahmad).

E-mail addresses: saeedgcuahmad87@gmail.com (S. Ahmad), esko.kauppinen@aalto.fi (E.I. Kauppinen).

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[12,13,15] enabling independently the measurement of number size distributions (NSDs) of both catalyst particles (before feeding into the reactor) and SWCNTs (at the outlet of the reactor) in gas-phase by external means. Here we employed a differential mobility analyzer (DMA)—a widely adopted method in aerosol research—to categorize the size (and NC) of gas-suspended particles [16–18]. Our DMA results corroborated with atomic force microscopy (AFM) and X-rays photoelectron spectroscopy (XPS) revealed that in FCCVD technique a single catalyst particle can grow more than one SWCNTs if the reaction conditions are favorable. We propose that the catalyst particle at the growing edge of the nanotube due to de-wetting [19] is detached from the 1st SWCNT and then it starts growing 2nd SWCNT. This process continues as long as the catalyst floats in the growth region (>700 °C) of the FCCVD reactor. Our result provides first direct evidence of multi-nucleation process in the FCCVD synthesis of SWCNTs and opens new ways towards the single-step and dry manufacturing of ultra-clean SWCNTs with as low as 0.18 wt% of metal impurities.

2. Experimental set-up and characterizations

Various catalyst particles including Fe, Co and Co-Ni were synthesized using spark discharge generation technique [20] in the presence of nitrogen (N_2) as a carrier gas. Aerosol catalyst particle from the spark discharge generator (SDG) suspended in N_2 atmosphere were characterized in gas-phase, using DMA (scanning mobility particle sizer equipped with Faraday's cup electrometer, the GRIMM Aerosol Technic GmbH, Germany) before feeding into the vertical FCCVD reactor. SWCNTs were synthesized in the FCCVD reactor using either ethylene (C_2H_4) as a carbon source (200 ppm) in the presence of hydrogen (~ 20 vol%) and hydrogen sulfide ($ca. 3$ ppm) with ~ 80 vol% N_2 carrying catalyst from SDG. In addition, we studied carbon monoxide as the carbon source ($CO \sim 50$ vol%) in the presence of hydrogen (~ 05 vol%) and ~ 45 vol% N_2 from SDG carrying catalyst. In both cases, the total flow rate of all the gases in FCCVD reactor was kept constant at 0.5 lpm [20]. The temperature of the furnace was set at 880 °C for CO and 1050 °C for C_2H_4 as carbon source, respectively. The synthesis conditions (for both CO and C_2H_4) were optimized to get maximum yield of high purity SWCNT in the sample. The average residence time in the growth region of SWCNTs (>700 °C) is roughly 10 s. The more exhaustive details of the reactor design and complete experimental set up can be found in our earlier works [12,13,20].

As-synthesized SWCNTs were either directly characterized in gas-phase at the outlet of the reactor using DMA or were collected on membrane filter in the form of thin film and were transferred on transparent quartz slides (HQS300, Heraeus) by dry press-transfer technique [21] or were deposited on mica substrate (V-4 grade electron microscopy sciences, U.S.A.) using thermophoresis technique [22] for further investigations. The optical absorption spectra (OAS) of the SWCNT thin film was obtained using Agilent Carry 5000 UV-vis-NIR spectrometer (Agilent Technologies, Inc.) and Raman spectra was acquired by Horiba Labram-HR 800 (Horiba Jobin-Yvon) Raman spectrometer using 633 nm laser. For the measurement of bundle diameter distribution of SWCNTs, samples were directly deposited on transmission electron microscope (TEM) copper grid and were characterized using double aberration-corrected high-resolution TEM (HR-TEM) (JEOL-2200FS, JEOL Ltd., Japan). AFM images were acquired using AFM dimension icon (Scan asyst mode: Bruker nano surfaces U.S.A.). Elemental analysis of sulfur-assisted SWCNTs films was carried out by using a Kratos Axis Ultra spectrometer with monochromated $Al_{K\alpha}$ -radiation, a pass energy of 40 eV, X-ray power of 225 W and an analysis area of approximately $700 \mu m \times 300 \mu m$. The sample of CNTs film was dry transferred on gold substrate for X-ray photoelectron spectroscopy (XPS) analysis. The high-resolution scanning transmission electron microscopy images were obtained using an aberration-corrected Nion UltraSTEM 100 operated with a 60 keV primary beam energy with a pressure of 5×10^{-10} mbar at the sample.

3. Results and discussions

We observed that in FCCVD method a single catalyst particle can grow more than one SWCNTs, if it has long enough time in the SWCNTs growth region of the reactor for detaching from 1st SWCNT and to nucleate 2nd SWCNT. For this purpose, we measured real time NC of catalyst particles and SWCNT-bundles (Fig. 1a and b) in the gas-phase using DMA. SWCNTs while floating in gas-phase collide with each other and tend to form their bundles [23]. Bundle size depends on the gas-phase NC/yield of the SWCNTs. The DMA measurement counts number of SWCNT-bundles in the gas-phase rather than their individual NC. From here on while analyzing DMA data, we will mainly cite the SWCNT-bundles with occasional reference to individual SWCNT.

The first experiment was purposefully devised for high NC/yield of SWCNTs by utilizing C_2H_4 as a carbon source [12,13]. The NSDs of catalyst particles (Fe, Co and Co-Ni) were measured before feeding into the FCCVD reactor, whereas NSDs of SWCNT-bundles were obtained directly in gas-phase by connecting DMA at the outlet of the FCCVD reactor. NSDs from DMA (Fig. 1a and b) clearly indicated that the NC of the catalyst particles is roughly half of the NC of SWCNT-bundles. It's worth mentioning here that the diffusion losses for the aerosol particles is proportional to the distance they travel and their gas-phase NC [24,25]. The total length of the stainless-steel tube connecting SDG to DMA is ~ 105 cm, whereas from SDG to SWCNTs growth region in the FCCVD reactor is approximately 63 cm (see Fig.S1). Being longer in length, the diffusion losses in the stainless-steel tube from SDG to DMA are higher than from SDG to SWCNT growth region in the FCCVD reactor. Therefore, before calculating the average number of SWCNTs per catalyst particle we experimentally measured diffusion losses in the stainless-steel tubes. For this purpose, the NC of catalyst particles from SDG to DMA were measured with varying lengths of the stainless-steel tubes in the range 100–200 cm having same composition and diameter. We found that particles with an electrical mobility diameter (D_M) of ~ 3.5 nm having total NC of $\sim 2.5 \times 10^6$ cm^{-3} have an approximate loss of 2.5×10^4 cm^{-3} particles in one cm length of the stainless steel tube. On the basis of these experimental observations, we estimated the real total NC of the catalyst particles (see Table S1) inside the FCCVD reactor at a point (i.e.700 °C temperature), where SWCNTs may start nucleating on the catalyst particles.

Interestingly, NSDs measurement of the as-produced SWCNT-bundles revealed that the NC/yield of SWCNTs strongly depends on the nature of metal catalyst particles. The reason might be the dependence of carbon solubility and its precipitation on the composition of metal catalyst particles as has been reported in earlier studies [12,13,26]. The average bundle size of Fe-SWCNT obtained from carefully analyzing 180 HR-TEM micrographs of SWCNT-bundles (Fig. 1e: an HR-TEM image of a typical SWCNT-bundle) is ~ 3.7 nm and their corresponding bundle diameter distribution is provided in Fig. 1f. OAS and Raman spectra of the SWCNT thin films were employed to estimate average diameter of SWCNTs present in the sample. In the OAS (Fig. 1g), the first inter-band transition in semiconducting (S_{11}) nanotubes occurs at ~ 1456 nm wavelength which analyzed based on Kataura plots [27,28] gives *ca.* mean diameter 1.2 nm of the nanotubes. Similarly, radial breathing mode (RBM) of Raman spectra (Fig. 1h) with 633 nm laser was also analyzed to get mean diameter of as-synthesized SWCNTs [29]. Consistent with the OAS, the maximum intensity peak in RBM also indicated a mean diameter of the nanotubes around 1.2 nm. Hence, on average an individual SWCNT-bundle of ~ 3.7 nm size contains 4 to 5 individual SWCNTs having diameter 1.2 nm.

It is worth mentioning that D_{ME} of our SWCNT-bundle lies in the range 20–80 nm, i.e. ~ 6 –15 times that of D_{ME} of catalyst particles. The D_{ME} of SWCNT-bundle not only depends on the bundle size but is also proportional to the bundle-length of the nanotubes [30]. Due to larger D_{ME} , the diffusion losses for the SWCNT-bundle from the outlet of the FCCVD reactor to DMA are nominal ($<10\%$) and can be omitted here for simplification (see SI). Based on these experimental observations we

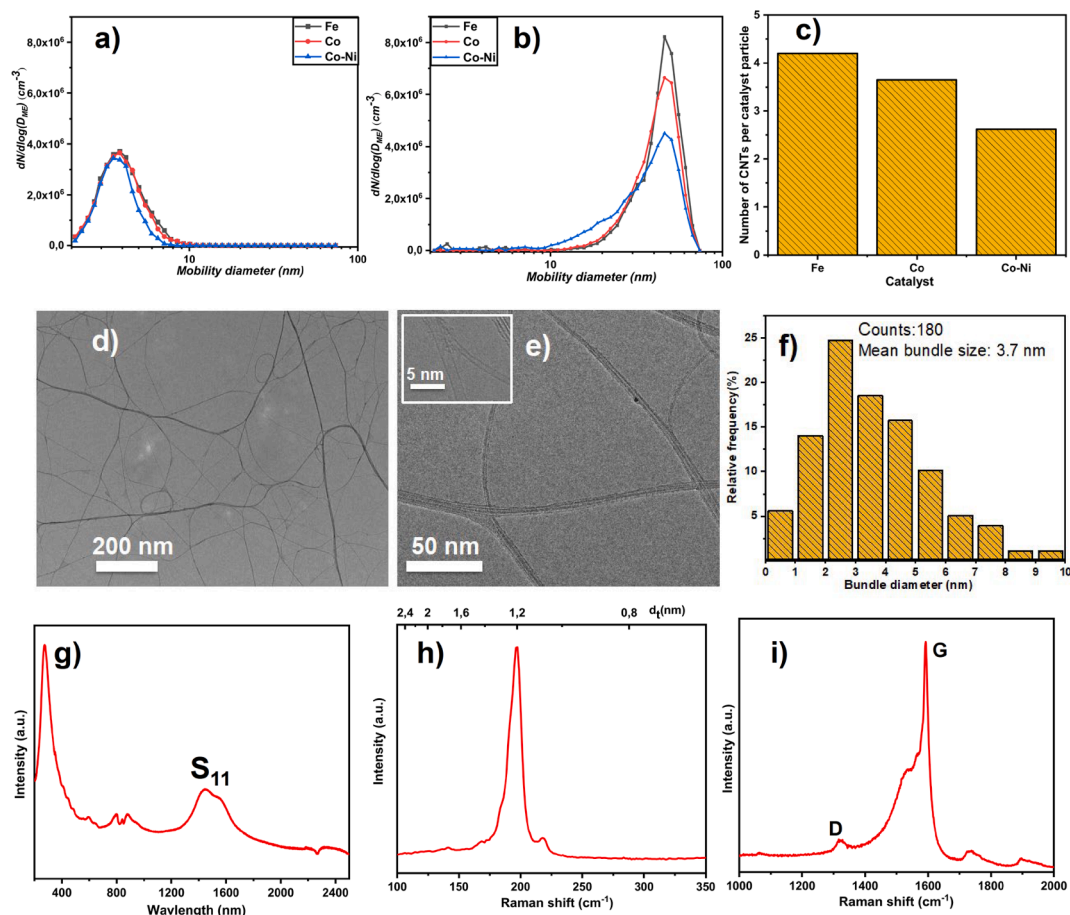


Fig. 1. Multi-nucleation of SWCNTs in ethylene based floating catalyst CVD (FCCVD) method. Gas-phase number size distributions (NSDs) of **a)** catalyst particles (Fe, Co and Co-Ni) and **b)** corresponding SWCNT-bundles measured from differential mobility analyzer (DMA) (total sample flow i.e. 1 lpm to DMA was obtained by 50 vol% addition of pure N_2). **c)** Average number of SWCNTs per catalyst particle. **d)** An overview of SWCNTs network having very high content of SWCNTs and low content of catalyst particles. **e)** Typical high-resolution transmission electron microscope (HR-TEM) image of SWCNT-bundles of various sizes. The inset in (e) shows a Y-junction bundle of SWCNT composed up of two SWCNTs. **f)** Bundle diameter distributions of SWCNTs synthesized with Fe catalysts as measured from HR-TEM micrographs. **g)** Optical absorption spectra and **h)** radial breathing mode (a characteristic of SWCNTs) of Raman spectra of as-synthesized SWCNT film, revealed average mean diameter 1.2 nm of Fe-SWCNTs. **i)** The intensity ratio of graphitic (G) to defective (D) mode of Raman spectra for our sample is ~ 20 , which indicates the presence of high-quality SWCNTs in the sample.

found that a single catalyst particle can grow more than one SWCNTs (in our case: 2 to 4) depending on the nature of catalyst as has been depicted in Fig. 1c. The more detailed calculations can be found in Table.S1. These results showed that although typical residence time in the growth region of the reactor in FCCVD methods is very short (~ 10 s) compared to substrate-based CVD growth process [11,31], but still a single catalyst can grow more than one SWCNT. To the best of our knowledge, this is the first report on multi-nucleation of SWCNTs in FCCVD system. It is worth mentioning that the multinucleation of SWCNTs reported in earlier work for substrate CVD has been realized in *in-situ* TEM experiments [11] under the high-vacuum conditions, which may limit the applicability of those results to real CVD systems. On the other hand, our experiment was performed utilizing lab-scale FCCVD reactor, operating at atmospheric pressure, under typical growth parameters for the synthesis of SWCNTs [12,13], which makes our results more realistic and applicable for the real CVD systems.

It has been observed that the presence of high metal-impurities can significantly tune the properties of as-received SWCNT samples [32] and hence the performance of the resulting devices [33]. For such applications, removing the unwanted metal catalyst impurity (unintentionally coming from SWCNT growth process) is a time consuming and tedious work. Various post-synthesis, wet-chemical and chromatographic purification methods [34,35] have been developed to remove metal catalyst particles. However, these rigorous, multi-step and complicated

purification procedures on one hand might damage the structure and intrinsic properties of SWCNTs and on the other side practically fails to fully remove the metal impurities [36]. Alternatively, we believe that if a single catalyst can grow more than one SWCNT, then through multi-nucleation process, under certain optimized conditions this process has potential to produce highly pure SWCNTs with low metal content, which could be beneficial for SWCNT as transparent conductive films [33] or for biocompatible applications of SWCNTs, especially in biomedicine field [36,37]. The metal content in our SWCNT film was determined using X-ray photoelectron spectroscopy (XPS) analysis. SWCNT film was directly collected at the outlet of the FCCVD reactor by gas-phase filtration technique [21]. An overall composition of the film obtained from XPS analysis is provided in Fig. 2a, where we observed carbon (C_{1s}), iron (Fe_{2p}), sulfur (S_{2p}) and oxygen (O_{1s}) peaks in the sample. The O_{1s} peak (Fig. S4) in the spectra can be assigned to adsorbed oxygen impurities [38] and S_{2p} peak is the result of the sulfur used in the synthesis process of SWCNTs. The detail of the synthesis process and more comprehensive details about the XPS analysis are omitted here and can be found in our earlier work [13]. The two most important spectrum to discuss at the moment are C_{1s} spectrum found at 284.5 eV (Fig. 2b) attributed to C-C bonding in SWCNTs and Fe_{2p} spectrum (Fig. 2c) consisting of two peaks observed around 707 eV ($2p_{3/2}$) and 720 eV ($2p_{1/2}$), representing metallic iron catalyst particles [13]. The content of Fe catalyst particles was found ~ 0.18 wt% (0.04 at.%) and that of

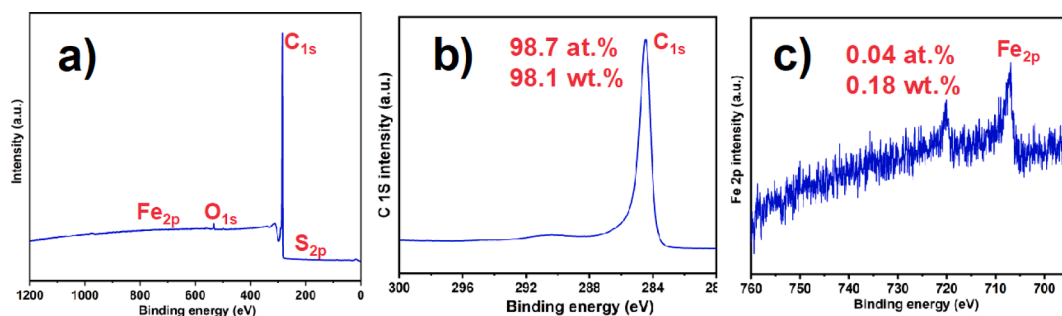


Fig. 2. X-ray photoelectron spectroscopy (XPS) analysis of sulfur-assisted Fe-SWCNT films (~ 20 nm in thickness) revealed very low metal content (~ 0.18 wt%) in our sample mainly consisting of pure carbon (~ 98.1 wt%). **a)** Overall view of the typical XPS spectra showing very high C_{1s} peak compared to Fe_{2p} peak. **b)** C_{1s} spectrum representing C-C bonding (at 284.5 eV) of SWCNT. **c)** The hardly detectable (noisy) Fe_{2p} spectrum due to very low metal content in the SWCNT film. The oxygen and sulfur spectrum are provided in Fig.S4.

carbon ~ 98.1 wt% (98.7 at.%) in the sample. The high intensity ratio of graphitic ($G \sim 1590$ cm^{-1}) to disorder-induced ($D \sim 1345$ cm^{-1}) mode in the Raman spectra (Fig. 1i) indicates the presence of high-quality graphitic structure (i.e. SWCNTs) in the film with very low defects/amorphous carbon. The carbon detected in the XPS is mainly from SWCNTs in the film. However, small fraction of carbon in XPS may also be contributed by possible defects/ amorphous carbon in the film.

The possibility that hydrocarbon carbon source (in this case C_2H_4)

would self-decompose on such a high temperature (1050 $^{\circ}C$) and grow SWCNTs without catalyst particle cannot be immediately excluded. One can further postulate that hydrocarbon sources are always required for the multi-nucleation of SWCNTs in FCCVD technique. To find the answer, we turned our attention to explore what kind of carbon source is required to observe multi-nucleation phenomenon in the FCCVD reactors? In the subsequent experiments, we intentionally selected CO as a carbon source which can decompose only on the surface of the catalyst

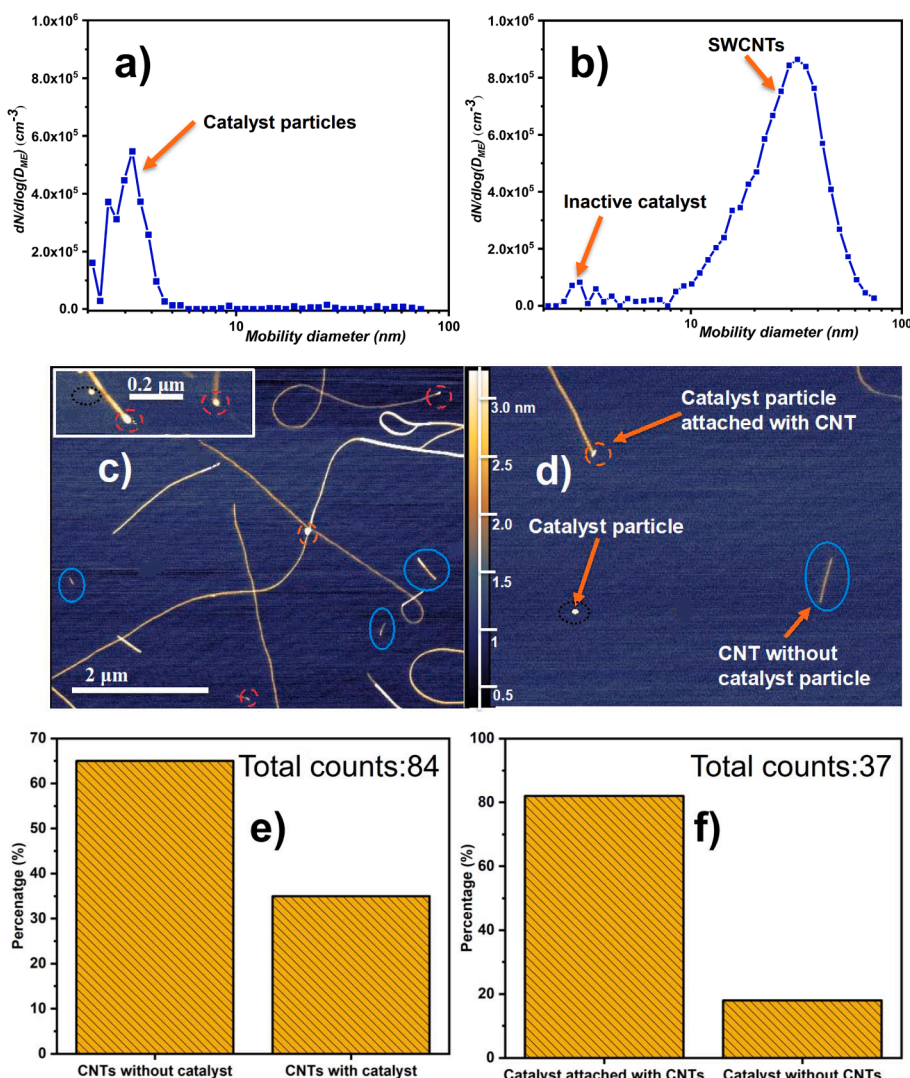


Fig. 3. Multi-nucleation of SWCNT observed in FCCVD technique for highly individual (60–70%) SWCNTs made using CO as a carbon source in the presence of Fe catalyst particles. Gas-phase NSDs of **a)** Fe-catalyst particles and **b)** SWCNTs from DMA having small fraction of inactive/detached catalyst roughly 3 nm in size. **c-d)** Typical atomic force microscope (AFM) images of individual/small bundled SWCNTs on mica substrate (collected via thermophoresis method [22]), where catalyst particles attached with CNTs are encircled with red color, inactive/detached catalyst with black circles, and shorter SWCNTs in cyan circles, apparently without catalyst particles at their end. The inset in subpanel c) depicts high-resolution AFM image of catalyst particle at the end of SWCNT. Histograms based on AFM images presenting **e)** higher fraction of SWCNTs without catalyst and **f)** a statistical comparison of active and inactive/detached catalyst particles in the sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

particle [39]. The low conversion rate and slow kinetics of CO disproportionation reaction limits the yield of SWCNTs and hence CO based reaction, produces very low yield of SWCNTs as compared to highly reactive C_2H_4 as carbon source [39,40]. This benefits in the synthesis of highly individual SWCNTs (60–70%) as has been reported in our earlier work [15]. More importantly, it simplifies the calculations and makes the NC comparison of catalyst particles and SWCNTs more straightforward.

A typical NSD of Fe catalyst particles used for the growth of SWCNTs by CO (50 vol%) as a carbon source is provided in Fig. 3a. Total NC of catalyst particles was reduced to $\sim 2.13 \times 10^5 \text{ cm}^{-3}$ (roughly 10% of as used for C_2H_4 case) to get highly individual SWCNTs and to minimize bundle formation. Interestingly, from DMA of SWCNTs (Fig. 3b) the total NC of SWCNTs ($\sim 4.12 \times 10^5 \text{ cm}^{-3}$) was found approximately double as that of catalyst particles. The DMA measurements clearly indicated that although with CO as a carbon source, the number of SWCNTs per catalyst particle reduced compared to that of C_2H_4 as carbon source. But still a single catalyst particle through multi-nucleation process is growing more than one SWCNTs. It is worth mentioning that number of SWCNTs per catalyst strongly rely on the experimental conditions. For example, under similar NSDs of catalyst particles, when we tuned synthesis temperature in the range 700–880 °C, the NC of SWCNTs significantly increased with the increase in the temperature as has been shown in Fig. S2. Furthermore, increasing amount of CO in the synthesis reactor from 10 to 50 vol% (keeping catalyst NSDs and temperature constant) drastically increased (~ 100 times) NC of SWCNTs (see Fig. S3).

The AFM images of SWCNTs (Fig. 3c-d) synthesized at standard conditions (i.e. 50 vol% CO and 880 °C) provided more direct evidences of SWCNTs multi-nucleation. The catalyst particles attached with the ends of SWCNTs (typical high-resolution AFM images can be seen in inset Fig. 3c) have been highlighted with the red circles. A small fraction of SWCNTs (35%) were found having catalyst particles at one of their ends. Most of the SWCNTs (65%), especially short nanotubes (in cyan circles) were apparently observed without any catalyst particles. Out of total counted catalysts particles in the sample, 17% were found isolated (in black circles), representing inactive/detached catalyst particles. It is necessary to acknowledge that the statistics obtained from AFM analysis and DMA measurements are on entirely different sample scales. Sample size for DMA measurements is approximately 5 order of magnitudes greater than that of used in AFM analysis and hence they cannot be

straightforward correlated. However, both the characterization techniques revealed that under optimal conditions in FCCVD method a single catalyst grows more than one SWCNTs.

Based on the above-mentioned experimental facts we propose a new mechanism of SWCNTs synthesis starting from nucleation on catalysts particles. During the growth process, if at some point the SWCNT is detached from catalysts through de-wetting process [41] then the SWCNTs becomes free of catalyst particles. The existence of such kind of nanotubes (especially shorter in length) have been directly evidenced from our AFM observations. The detached catalyst acts as a seed for the growth of another SWCNT, if it has long enough residence time in the growth region of reactor. On the other hand, if the rim of CNTs is strongly bounded with the catalyst, in that case a single catalyst possibly grows only one SWCNT as has been explained in the Fig. 4a-b. This attachment-detachment process depends on nanoparticle facets and the competition between van der Waals forces and de-wetting of SWCNT rim with the catalysts [41]. Another possible mechanism explaining multi-nucleation process is evaporation of catalyst at high temperature zone inside the FCCVD reactor. The catalyst while evaporation detach itself from CNT and at lower temperature (either along radial or longitudinal direction inside the FCCVD reactor) may re-nucleate itself and starts growing another CNT. The temperature difference between the center and reactor wall is one of the important parameters for controlling multi-nucleation of SWCNTs. By optimizing the synthesis conditions (e.g. nature of catalyst, synthesis temperature and amount of carbon source) for both hydrocarbon and non-hydrocarbon sources a single catalyst particle has potential to grow more than one SWCNTs in the FCCVD technique.

4. Conclusion

In summary, we have for the first time reported multi-nucleation of both individual and bundled SWCNTs in FCCVD technique using a variety of spark produced pre-made catalyst particles (Fe, Co, Co-Ni). The number concentration of catalyst particles in gas-phase was measured before feeding into the FCCVD, whereas that of SWCNTs at the outlet the FCCVD reactor using DMA. We observed that number of as-synthesized SWCNTs per catalyst particle depends on the reaction conditions including nature of carbon source, synthesis temperature, and composition of catalyst particles. Our XPS measurements of SWCNTs thin films

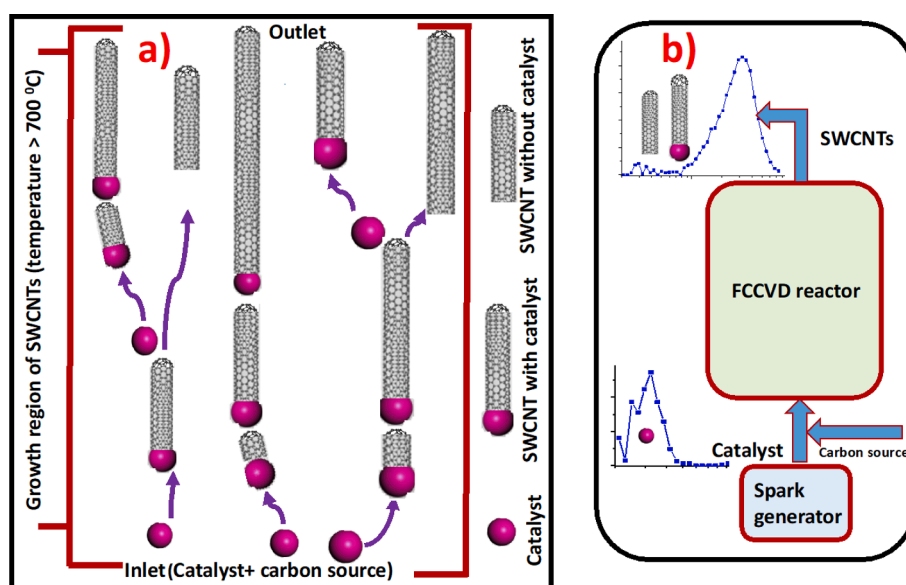


Fig. 4. Proposed mechanism for multi-nucleation of SWCNTs in FCCVD technique. a) Catalyst detachment from 1st SWCNT and growth of 2nd SWCNT from the same catalyst, resulting higher NC of SWCNTs compared to catalyst particles. b) Schematic of our especially designed pre-made catalyst based FCCVD system enabling the measurement of catalyst NSDs in gas-phase before feeding into FCCVD reactor and that of SWCNT at the outlet of the FCCVD reactor.

indicated highly pure SWCNTs (98.10 wt%) with very low content of metal impurities (0.18 wt%). The more direct evidence of multi-nucleation of SWCNTs was found using AFM, where quantitatively 65% of the total nanotubes were found without catalyst particles. Our method opens up new avenues towards the ultra-fast, single-step manufacturing of high-purity SWCNTs in gas-phase and provides scientific community new insights into the synthesis mechanism of SWCNTs via FCCVD.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2022.140185>.

References

- [1] S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, *Nature*. 363 (1993) 603–605, <https://doi.org/10.1038/363603a0>.
- [2] S. Arepalli, H. Fireman, C. Huffman, P. Moloney, P. Nikolaev, L. Yowell, K. Kim, P. A. Kohl, C.D. Higgins, S.P. Turano, W.J. Ready, Carbon-nanotube-based electrochemical double-layer capacitor technologies for spaceflight applications, *JOM*. 57 (12) (2005) 26–31.
- [3] M. Lan, H. Waisman, Mechanics of SWCNT Aggregates Studied by Incremental Constrained Minimization, *J. Nanomechanics Micromechanics*. 2 (2) (2012) 15–22.
- [4] 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, W.W. ACS Nano 12 (12) (2018) 11756–11784.
- [5] K. Hata, D.N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes, *Science* (80-.). 306 (2004) 1362–1364, <https://doi.org/10.1126/science.1104962>.
- [6] M. He, A.I. Chernov, E.D. Obratzsova, J. Sainio, E. Rikkinen, H. Jiang, Z. Zhu, A. Kaskela, A.G. Nasibulin, E.I. Kauppinen, M. Niemelä, O. Krause, Low Temperature Growth of SWNTs on a Nickel Catalyst by Thermal Chemical Vapor Deposition, *Nano Res.* 4 (2011) 334–342, <https://doi.org/10.1007/s12274-010-0088-3>.
- [7] A.G. Nasibulin, A. Moisala, D.P. Brown, H. Jiang, E.I. Kauppinen, A novel aerosol method for single walled carbon nanotube synthesis, *Chem. Phys. Lett.* 402 (2005) 227–232, <https://doi.org/10.1016/j.cplett.2004.12.040>.
- [8] F. Yang, X. Wang, D. Zhang, J. Yang, D.a. Luo, Z. Xu, J. Wei, J.-Q. Wang, Z. Xu, F. Peng, X. Li, R. Li, Y. Li, M. Li, X. Bai, F. Ding, Y. Li, Chirality-specific growth of single-walled carbon nanotubes on solid alloy catalysts, *Nature*. 510 (7506) (2014) 522–524.
- [9] S. Zhang, L. Kang, X. Wang, L. Tong, L. Yang, Z. Wang, K. Qi, S. Deng, Q. Li, X. Bai, F. Ding, J. Zhang, Arrays of horizontal carbon nanotubes of controlled chirality grown using designed catalysts, *Nature*. 543 (7644) (2017) 234–238.
- [10] W.-H. Chiang, R. Mohan Sankaran, Linking catalyst composition to chirality distributions of as-grown single-walled carbon nanotubes by tuning Ni x Fe 1x nanoparticles, *Nat. Mater.* 8 (11) (2009) 882–886.
- [11] L. Zhang, M. He, T.W. Hansen, J. Kling, H. Jiang, E.I. Kauppinen, A. Loiseau, J. B. Wagner, Growth Termination and Multiple Nucleation of Single-Wall Carbon Nanotubes Evidenced by in Situ Transmission Electron Microscopy, *ACS Nano*. 11 (5) (2017) 4483–4493.
- [12] S. Ahmad, Y. Liao, A. Hussain, Q. Zhang, E.-X. Ding, H. Jiang, E.I. Kauppinen, Systematic investigation of the catalyst composition effects on single-walled carbon nanotubes synthesis in floating-catalyst CVD, *Carbon N. Y.* 149 (2019) 318–327.
- [13] S. Ahmad, E.-X. Ding, Q. Zhang, H. Jiang, J. Sainio, M. Tavakkoli, A. Hussain, Y. Liao, E.I. Kauppinen, Roles of sulfur in floating-catalyst CVD growth of single-walled carbon nanotubes for transparent conductive film applications, *Chem. Eng. J.* 378 (2019), 122010, <https://doi.org/10.1016/j.cej.2019.122010>.
- [14] W.H. Chiang, R.M. Sankaran, Linking catalyst composition to chirality distributions of as-grown single-walled carbon nanotubes by tuning Ni x Fe 1x nanoparticles, *Nat. Mater.* 8 (2009) 882–886, <https://doi.org/10.1038/nmat2531>.
- [15] 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 (1) (2015) 013106.
- [16] D.-R. Chen, D.Y.H. Pui, D. Hummes, H. Fissan, F.R. Quant, G.J. Sem, Design and evaluation of a nanometer aerosol differential mobility analyzer (Nano-DMA), *J. Aerosol Sci.* 29 (5-6) (1998) 497–509.
- [17] Y. Kousaka, K. Okuyama, M. Adachi, Determination of particle size distribution of ultra-fine aerosols using a differential mobility analyzer, *Aerosol Sci. Technol.* 4 (2) (1985) 209–225.
- [18] Y. Tian, N. Wei, P. Laiho, S. Ahmad, Y. Magnin, Y. Liao, C. Bichara, H. Jiang, E. I. Kauppinen, Cutting floating single-walled carbon nanotubes with a ‘CO2 blade’, *Carbon N. Y.* 143 (2019) 481–486, <https://doi.org/10.1016/j.carbon.2018.11.035>.
- [19] M. Diarra, A. Zappelli, H. Amara, F. Ducastelle, C. Bichara, Importance of carbon solubility and wetting properties of nickel nanoparticles for single wall nanotube growth, *Phys. Rev. Lett.* 109 (18) (2012), <https://doi.org/10.1103/PhysRevLett.109.185501>.
- [20] S. Ahmad, P. Laiho, Q. Zhang, H. Jiang, A. Hussain, Y. Liao, E.X. Ding, N. Wei, E. I. Kauppinen, Gas phase synthesis of metallic and bimetallic catalyst nanoparticles by rod-to-tube type spark discharge generator, *J. Aerosol Sci.* 123 (2018) 208–218, <https://doi.org/10.1016/j.jaerosci.2018.05.011>.
- [21] 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 (11) (2010) 4349–4355.
- [22] P. Laiho, K. Mustonen, Y. Ohno, S. Maruyama, E.I. Kauppinen, Dry and Direct Deposition of Aerosol-Synthesized Single-Walled Carbon Nanotubes by Thermophoresis, *ACS Appl. Mater. Interfaces*. 9 (2017) 20738–20747, <https://doi.org/10.1021/acsami.7b03151>.
- [23] 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 (14) (2015) 143113.
- [24] P. Kumar, P. Fennell, J. Symonds, R. Britter, Treatment of losses of ultrafine aerosol particles in long sampling tubes during ambient measurements, *Atmos. Environ.* 42 (38) (2008) 8819–8826.
- [25] D.A. Knopf, U. Pöschl, M. Shiraiwa, Radial Diffusion and Penetration of Gas Molecules and Aerosol Particles through Laminar Flow Reactors, Denuders, and Sampling Tubes, *Anal. Chem.* 87 (7) (2015) 3746–3754.
- [26] W. Zhou, L. Ding, J. Liu, Role of catalysts in the surface synthesis of single-walled carbon nanotubes, *Nano Res.* 2 (2009) 593–598, <https://doi.org/10.1007/s12274-009-9068-x>.
- [27] H. Kuzmany, W. Plank, M. Hulman, C.h. Kramberger, A. Grüneis, T.h. Pichler, H. Peterlik, H. Kataura, Y. Achiba, Determination of SWCNT diameters from the Raman response of the radial breathing mode, *Eur. Phys. J. B.* 22 (3) (2001) 307–320.
- [28] Y. Tian, H. Jiang, J.v. Pfaler, Z. Zhu, A.G. Nasibulin, T. Nikitin, B. Aitchison, L. Khriachtchev, D.P. Brown, E.I. Kauppinen, Analysis of the size distribution of single-walled carbon nanotubes using optical absorption spectroscopy, *J. Phys. Chem. Lett.* 1 (7) (2010) 1143–1148.
- [29] M.S. Dresselhaus, G. Dresselhaus, A. Jorio, A.G. Souza Filho, R. Saito, Raman spectroscopy on isolated single wall carbon nanotubes, *Carbon* 40 (12) (2002) 2043–2061.
- [30] 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 (10) (2005) 2066–2074.
- [31] I. Ibrahim, J. Kalbacova, V. Engemaier, J. Pang, R.D. Rodriguez, D. Grimm, T. Gemming, D.R.T. Zahn, O.G. Schmidt, J. Eckert, M.H. Rummeli, Confirming the Dual Role of Etchants during the Enrichment of Semiconducting Single Wall Carbon Nanotubes by Chemical Vapor Deposition, *Chem. Mater.* 27 (17) (2015) 5964–5973.
- [32] H. Hu, B. Zhao, M.E. Itkis, R.C. Haddon, Nitric Acid Purification of Single-Walled Carbon Nanotubes, *J. Phys. Chem. B.* 107 (50) (2003) 13838–13842.
- [33] E.-X. Ding, A. Hussain, S. Ahmad, Q. Zhang, Y. Liao, H. Jiang, E.I. Kauppinen, High-performance transparent conducting films of long single-walled carbon nanotubes synthesized from toluene alone, *Nano Res.* 13 (1) (2020) 112–120.

- [34] X.H. Chen, C.S. Chen, Q. Chen, F.Q. Cheng, G. Zhang, Z.Z. Chen, Non-destructive purification of multi-walled carbon nanotubes produced by catalyzed CVD, *Mater. Lett.* 57 (3) (2002) 734–738.
- [35] P.X. Hou, S. Bai, Q.H. Yang, C. Liu, H.M. Cheng, Multi-step purification of carbon nanotubes, *Carbon N. Y.* 40 (1) (2002) 81–85.
- [36] C. Ge, Y. Li, J.J. Yin, Y. Liu, L. Wang, Y. Zhao, C. Chen, The contributions of metal impurities and tube structure to the toxicity of carbon nanotube materials, *NPG Asia Mater.* (2012). <https://doi.org/10.1038/am.2012.60>.
- [37] A.K. Jain, N. Kumar Mehra, N. Lodhi, V. Dubey, D.K. Mishra, P.K. Jain, N.K. Jain, Carbon nanotubes and their toxicity, *Nanotoxicology*. 1 (3) (2007) 167–197.
- [38] T.I.T. Okpalugo, P. Papakonstantinou, H. Murphy, J. McLaughlin, N.M.D. Brown, High resolution XPS characterization of chemical functionalised MWCNTs and SWCNTs, *Carbon N. Y.* 43 (1) (2005) 153–161.
- [39] A. Moiala, A.G. Nasibulin, D.P. Brown, H. Jiang, L. Khriachtchev, E.I. Kauppinen, Single-walled carbon nanotube synthesis using ferrocene and iron pentacarbonyl in a laminar flow reactor, *Chem. Eng. Sci.* 61 (13) (2006) 4393–4402.
- [40] A. Hussain, Y. Liao, Q. Zhang, E.-X. 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 (20) (2018) 9752–9759.
- [41] M.-F. C. Fiawoo, A.-M. Bonnot, H. Amara, C. Bichara, J. Thibault-Pénisson, A. Loiseau, Evidence of correlation between catalyst particles and the single-wall carbon nanotube diameter: A first step towards chirality control, *Phys. Rev. Lett.* 108 (19) (2012), <https://doi.org/10.1103/PhysRevLett.108.195503>.