This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Iakovlev, Vsevolod Ya; Krasnikov, Dmitry V.; Khabushev, Eldar M.; Kolodiaznaia, Julia V.; Nasibulin, Albert G.

Artificial neural network for predictive synthesis of single-walled carbon nanotubes by aerosol CVD method

Published in:
Carbon

DOI:
[10.1016/j.carbon.2019.07.013](https://doi.org/10.1016/j.carbon.2019.07.013)

Published: 01/11/2019

Document Version
Peer reviewed version

Published under the following license:
CC BY-NC-ND

Please cite the original version:
Iakovlev, V. Y., Krasnikov, D. V., Khabushev, E. M., Kolodiaznaia, J. V., & Nasibulin, A. G. (2019). Artificial neural network for predictive synthesis of single-walled carbon nanotubes by aerosol CVD method. *Carbon*, 153, 100-103. <https://doi.org/10.1016/j.carbon.2019.07.013>

Artificial neural network for predictive synthesis of single-walled carbon nanotubes by aerosol CVD method

Vsevolod Ya. Iakovlev¹, Dmitry V. Krasnikov^{1, °}, Eldar M. Khabushev¹, Julia V. Kolodiazhaia¹,
Albert G. Nasibulin^{1,2,*}

¹ Skolkovo Institute of Science and Technology, Nobel Str. 3, Moscow, 121205, Russia

² Aalto University, Espoo, 00076, Finland

Corresponding author: * A.Nasibulin@skoltech.ru ° D.Krasnikov@skoltech.ru

Abstract:

We propose to use artificial neural networks to process the experimental data and to predict the performance of the aerosol CVD synthesis of single-walled carbon nanotubes based on Boudouard reaction. We employ five key input parameters of the growth (pressures of CO, CO₂ and ferrocene as well as residence time and temperature) to control the performance of produced nanotube films (yield, mean and standard deviation of diameter distribution, and defectiveness). The prediction errors were found to be comparable with the corresponding experimental errors. We believe the proposed approach is of great interest for the synthesis of nanocarbons with tailored characteristics.

Graphical abstract:

A schematic representation of the hierarchical architecture of the experimental setup and artificial neural network connection for controlled and predictive SWCNT synthesis.

Synthesis of carbon nanotubes with tailored characteristics has been one of the most important goals of nanotechnology for the last two decades promising a generation of novel functional nanomaterials, nanoelectronic devices, nanomedical tools, *etc.* [1,2] However, the complexity of mechanisms for the nanotube nucleation, growth, and termination inhibited the progress towards the control of the product with defined parameters. The lack of the general model (a quantitative correlation between the synthesis process and SWCNT parameters) and systematic datasets are still the key barriers for the controlled synthesis and therefore for a wide range of applications [3–5]. Here, for the first time we employ an artificial neural network (ANN) methodology that proved itself for complex multi-parameter tasks [6,7] for processing of the experimental data to enhance the control over single-walled carbon nanotube synthesis conditions and to predict the experimental results.

We employ the aerosol CVD synthesis (Figure S1) of single-walled carbon nanotubes (SWCNTs) based on Boudouard reaction ($2\text{CO}=\text{C}+\text{CO}_2$) [8]. This relatively simple method allows us to minimize the number of input parameters avoiding the influence of a substrate, catalyst activation procedure and to decrease a variety of the possible chemical reactions during the synthesis. Ferrocene was used as a catalyst precursor [9], and small amounts of CO_2 were utilized to enhance the SWCNT synthesis (increase of the yield, diameter, quality) [10]. The setup is a vertical hot wall tubular reactor with a supply of $\text{CO}/\text{CO}_2/\text{N}_2$ mixtures (purity >99.995%) as shown in Figure S1. The grown aerosol SWCNTs were collected on a filter (HAWP, Merck Millipore) for the following characterization: UV-vis-NIR spectroscopy (Perkin Elmer Lambda 1050), Raman spectroscopy (Horiba LabRAM HR Evolution system), scanning electron microcopy (FEI Helios Nanolab 660).

We define five key input parameters, namely, the partial pressure of CO , CO_2 and ferrocene as well as the residence time and temperature, for a comprehensive description of the process within the experimental architecture used. These parameters are not the only affecting the SWCNT growth, however, the other variables are kept constant (*e.g.*, catalyst composition, way of catalyst production, reactor type). The complex effect of each input parameter on the SWCNT characteristics [11] (*e.g.*,

both CO₂ concentration as well as temperature affect the diameter distribution, defectiveness and the yield [8–10,12]; even the partial pressure of CO affects both nucleation and growth providing a non-trivial dependences [5]) inhibit a simple processing becoming, thereby, the main drivers leading us to the ANN employment.

Using such a set of input parameters, we acquired a dataset of 98 points (Table S1) with four key performance SWCNT parameters: the diameter distribution (mean diameter and standard deviation, respectively, d_{CNT} and σ_d), the yield, the ratio of intensities of G and D modes of a Raman spectrum (I_G/I_D). Figure 1 shows a typical range of the key performance parameters within the dataset: Raman spectroscopy provides the I_G/I_D ratio, UV-vis-NIR spectroscopy allows us to estimate the thickness of the film, which is proportional to the absorbance (according to the Lambert–Beer law), and the diameter distribution that can be reliably calculated from the Van Hove singularities of the S_{11} transition [13,14]. The thickness of the film provided by UV-vis-NIR spectroscopy corresponds to the yield (section S2) and allows a more precise validation than gravimetric studies owing to a small weight of the collected SWCNT films.

Figure 1: Typical data describing SWCNTs: a) Raman spectra with a typical SEM microphotograph (the inset); b) UV-vis-NIR spectra with the photograph inset of the SWCNT films of different thicknesses.

Self-geometry of the ANN is based on a sequential model (Figure 2) developed in Python programming language using the Keras open-source neural-network library. We vary

hyperparameters of the ANN (the number of hidden layers, number of nodes, activation function, optimizer, batch size, number of training epochs as shown in Table S2) to define the optimal ANN architecture and conditions providing minimal errors. For simplification of the training process we use four independent ANNs with the same five key input parameters and four single outputs: either the mean diameter, the deviation, the yield or the I_G/I_D (Table S3). We use the mean absolute error (standard deviation) as a loss and mean absolute percentage error (relative standard deviation) as statistical criteria for the accuracy of the ANN prediction.

Figure 2: A scheme for the data preparation and processing in the ANN.

The input data are handled in the following way (Figure 2). First, we transform the experimental data (temperature distribution, gas flowrates and reactor geometry) into five key input parameters (partial pressures of gaseous components, the residence time and reactor temperature). Then, we shuffle the samples and randomly split the data into training (80%) and validation (20%) datasets. We obtain the input as an array of n -dimensional vectors $[[X_{11} \dots X_{1n}] \dots [X_{i1} \dots X_{in}]]$, where $n = 5$ is the number of key input parameters, i is the index number in the dataset from 1 to 98. Third, we employ a common data augmentation [15] that provides a dataset of a size acceptable for the ANN training and, thereby, significantly improves the prediction performance (Section S5). Each

experimental vector can be transformed in a family of vectors (20 in our case) by a normal randomization of each coordinate with a dispersion, which is equal to the standard deviation of the corresponding key input parameter. As the key input parameters have four orders of magnitude deviation, in prior to feeding the input neurons, the data were normalized as $X=(X-X_{\text{mean}})/\sigma$, where σ is the dispersion of a parameter.

The ANN training (Figure 3; Table S3) can be represented as a simple iteration algorithm consisted of a set of epochs: a forward propagation of input vectors through the ANN is followed by a back propagation of errors (error distribution for the nodes to correct the weights).

Figure 3. The evolution of losses of the key performance parameters of the SWCNT synthesis during the training of the ANN. The values for corresponding experimental and prediction errors are 8% and 23% (I_G/I_D), 5% and 14% (Yield), 0.7% and 4.0% (d_{CNT}), 4 and 22% (σ_d), respectively.

We achieve the modelling error comparable with the experimental error (based on the parameter dispersion throughout repetitive experiments; Figure S2) proving the methodology proposed (Figure

3; Table S3). After a certain number of epochs (iterations) we naturally observed the common overfitting by the ANN that can be attributed to the description of the training data too closely that it fails to process additional dataset (testing data) accurately [16]. It is worth noting that the ANN show an acceptable prediction of the experimental output parameters when compared to real values: experimental and prediction errors are 8% and 23% (I_G/I_D), 5% and 14% (Yield), 0.7% and 4.0% (d_{CNT}), 4 and 22% (σ_d), respectively. Though some parameters are in a good agreement (*e.g.*, the mean absolute percentage error for the diameter is 0.7% corresponds to the ANN accuracy of the prediction <0.1 nm), the model accuracy can be enhanced by an enlarged dataset, an extended set of input parameters or by a decreased scattering of the experimental data. Moreover, there is a room for improvement for the methodology proposed by, for example, reducing the effect of the black-box via identification of the relations underlying between the input and output parameters or improved data representation [17]. Nevertheless, the approach employed can be extrapolated to the other performance parameters of the collected SWCNT thin films: sheet resistance, length distribution, chirality distribution, *etc.* Thus, we believe this methodology is to provide a facile and a resource-efficient route for processing and collecting the comprehensive data with a capability of revealing hidden dependencies in case of multiple input parameters. However, such results are a subject of our future studies.

In conclusion, for the first time we employ the artificial neural network (ANN) methodology for the predictive synthesis of single-walled carbon nanotubes (SWCNTs). We achieve an acceptable agreement between the key input parameters of the nanotube growth (partial pressures of CO, CO₂, the catalyst precursor as well as the residence time and the reaction temperature) and the prediction of the key performance characteristics of the SWCNT synthesis (the yield, mean and standard deviation of nanotube diameter distribution, I_G/I_D intensity ratio of Raman spectra): from 4.0% for the diameter up to 23 % for I_G/I_D . Though the ANN developed is limited by a small dataset for training (98 points),

number of input parameters (5), and the experimental data error (up to 8%), the results obtained justify further studies.

Acknowledgements: Authors thank Ms. Daria Satco and Mr. Stepan Romanov for fruitful discussions. This work was supported by the Russian Science Foundation (No. 17-19-01787).

References

- [1] M.F.L. De Volder, S.H. Tawfick, R.H. Baughman, A.J. Hart, Carbon Nanotubes: Present and Future Commercial Applications, *Science* (80-.). 339 (2013) 535–539.
doi:10.1126/science.1222453.
- [2] J. Zhang, M. Terrones, C.R. Park, R. Mukherjee, M. Monthieux, N. Koratkar, Y.S. Kim, R. Hurt, E. Frackowiak, T. Enoki, Y. Chen, Y. Chen, A. Bianco, Carbon science in 2016: Status, challenges and perspectives, *Carbon N. Y.* 98 (2016) 708–732.
doi:10.1016/j.carbon.2015.11.060.
- [3] V. Jourdain, C. Bichara, Current understanding of the growth of carbon nanotubes in catalytic chemical vapour deposition, *Carbon N. Y.* 58 (2013) 2–39. doi:10.1016/j.carbon.2013.02.046.
- [4] O. Rabinovich, A. Tsytseuka, V. Kuznetsov, S. Moseenkov, D. Krasnikov, A. Tsytseuka (Blinova), V. Kuznetsov, S. Moseenkov, D. Krasnikov, A model for catalytic synthesis of carbon nanotubes in a fluidized-bed reactor: Effect of reaction heat, *Chem. Eng. J.* 329 (2017) 305–311. doi:10.1016/j.cej.2017.06.001.
- [5] K.J. MacKenzie, O.M. Dunens, A.T. Harris, An Updated Review of Synthesis Parameters and Growth Mechanisms for Carbon Nanotubes in Fluidized Beds, *Ind. Eng. Chem. Res.* 49 (2010) 5323–5338. doi:10.1021/ie9019787.
- [6] Z. Zhang, Y. Hong, B. Hou, Z. Zhang, M. Negahban, J. Zhang, Accelerated discoveries of mechanical properties of graphene using machine learning and high-throughput computation, *Carbon N. Y.* 148 (2019) 115–123. doi:10.1016/J.CARBON.2019.03.046.
- [7] Z. Yang, W.-M. Qiao, X.-Y. Liang, Modelling and optimization of the pore structure of

- carbon aerogels using an artificial neural network, *NEW CARBON Mater.* 32 (2017).
doi:10.1016/S1872-5805(17)60108-2.
- [8] A.G. Nasibulin, A. Kaskela, K. Mustonen, A.S. Anisimov, V. Ruiz, S. Kivistö, S. Rackauskas, M.Y. Timmermans, M. Pudas, B. Aitchison, M. Kauppinen, D.P. Brown, O.G. Okhotnikov, E.I. Kauppinen, S. Kivistö, S. Rackauskas, M.Y. Timmermans, M. Pudas, B. Aitchison, M. Kauppinen, D.P. Brown, O.G. Okhotnikov, E.I. Kauppinen, Multifunctional free-standing single-walled carbon nanotube films, *ACS Nano*. 5 (2011) 3214–3221.
doi:10.1021/nn200338r.
- [9] D.P. Brown, A.G. Nasibulin, E.I. Kauppinen, CFD-aerosol modeling of the effects of wall composition and inlet conditions on carbon nanotube catalyst particle activity, *J. Nanosci. Nanotechnol.* 8 (2008) 3803–3819. doi:10.1166/jnn.2008.453.
- [10] A.G. Nasibulin, D.P. Brown, P. Queipo, D. Gonzalez, H. Jiang, E.I. Kauppinen, An essential role of CO₂ and H₂O during single-walled CNT synthesis from carbon monoxide, *Chem. Phys. Lett.* 417 (2006) 179–184. doi:10.1016/j.cplett.2005.10.022.
- [11] Q. Zhang, N. Wei, P. Laiho, E.I. Kauppinen, Recent Developments in Single-Walled Carbon Nanotube Thin Films Fabricated by Dry Floating Catalyst Chemical Vapor Deposition, *Top. Curr. Chem.* 375 (2017) 1–30. doi:10.1007/s41061-017-0178-8.
- [12] 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 CO₂ in Floating Catalyst CVD for High-Performance Transparent Conductive Films, *Adv. Mater. Interfaces*. 1801209 (2018) 1–10.
doi:10.1002/admi.201801209.
- [13] 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 (2010) 1143–1148. doi:10.1021/jz100161p.

- [14] D. V. Krasnikov, B. Yu. Zabelich, V. Ya. Iakovlev, A.P. Tsapenko, S.A. Romanov, A.A. 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.* (2019). doi:10.1016/j.cej.2019.04.173.
- [15] L. Taylor, G. Nitschke, Improving Deep Learning using Generic Data Augmentation, (2017). <http://arxiv.org/abs/1708.06020> (accessed June 6, 2019).
- [16] D.M. Hawkins, The Problem of Overfitting, *J. Chem. Inf. Comput. Sci.* 44 (2004) 1–12. doi:10.1021/ci0342472.
- [17] Z. Li, S. Wang, H. Xin, Toward artificial intelligence in catalysis, *Nat. Catal.* 1 (2018) 641–642. doi:10.1038/s41929-018-0150-1.