A SIMPLE METHOD TO BUILD CATALYST LAYERS FOR THE SYNTHESIS OF VERTICALLY ALIGNED CARBON NANOTUBES

Lilla Nánai[1,2], Anna Szabó[2], Tamás Gyulavári[2], Zsejke Réka Tóth[2,3], Klára Hernádi[1]

[1]Institute of Physical Metallurgy, Metal forming and Nanotechnology, University of Miskolc, H-3515 Miskolc, Hungary
[2]Department of Applied and Environmental Chemistry, University of Szeged, H-6720 Szeged, Rerrich Béla tér 1, Hungary
[3]Nanostructured Materials and Bio-Nano-Interfaces Center, Interdisciplinary Research Institute on Bio-Nano-Sciences, Babes-Bolyai University, T. Laurian 42, 400271 Cluj-Napoca, Romania
e-mail: nanai.lilla@student.uni-miskolc.hu

Abstract
Nowadays, environmental protection and sustainability are getting more and more attention. Thus, our aim was to develop a cost and energy efficient catalyst layer building method for the synthesis of carbon nanotube forests. A simple spray coating method was used to develop a catalyst layer on the surface of the titanium substrates. Then vertically aligned carbon nanotubes (VACNTs) were synthesized directly on the substrate *via* catalytic chemical vapor deposition (CCVD) method. During our research, the effect of catalyst layer deposition parameters on the structure of CNTs was investigated and characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy.

Introduction
Vertically aligned carbon nanotubes (VACNTs) have been in the focus of intense research over the years due to their remarkable mechanical and chemical properties such as exceptional electrical and thermal conductivities. VACNTs and their composites are also getting more attention in environmental engineering applications based on their features, for example, sorption capacity, component separation and catalytic activity as well [1,2]. Catalytic chemical vapor deposition (CCVD) is a favored method for the mass production of CNTs it is cost-efficient and simple to use, moreover, it is the only suitable process to synthesize VACNTs [3]. Comparing the possibilities for the production of VACNTs, there are several methods for the formation of thin catalyst layers (i.e., atomic layer deposition (ALD), physical vapor deposition (PVD), pulsed laser deposition (PLD), magnetron sputtering (MS), dip-coating etc. [4,5]) which are able to control layer thickness and morphology, however, they require rather expensive instruments. Among these methods, dip-coating might be an exception, because it requires less complicated instruments, thus, it is widely used for catalyst layer deposition. Spray coating might be an even cheaper method than dip-coating to build thin layers and it also has more variations (thermal, plasma, manual etc. [6,7]). In this research our aim was to study the efficiency of manual spray coating for building bimetallic catalyst layers containing iron and cobalt. Then, their applicability for VACNTs synthesis *via* CCVD was investigated, which was carried out on the surface of titanium substrates. To gain knowledge about the efficiency of manual spray coating in this specific application, the parameters of the layer formation (substrate pretreatment, coating temperature and number of spraying cycles) were investigated.

Experimental

During the synthesis, a titanium substrate was used to build up the catalyst layers with a spray gun, also used for car painting or art drawing. The concentration of catalyst ink was 0.11 M and the ratio of Fe:Co was 2:3. The latter was prepared from $Fe(NO_3)_3 \times 9H_2O$ and $Co(NO_3)_2 \times 6H_2O$ precursors that were dissolved in absolute ethanol. The Ti substrate was heat treated for 1 h at 400 °C before and after the deposition of the catalyst. This was carried out in a static oven to form a native TiO_2 layer on the surface and oxidize the catalytic particles. The TiO_2 layer might block the diffusion of catalyst particles into the substrate. In some cases, heat treatment process was changed. To prepare thin layers, the pretreated Ti substrate was placed on a heated plate (120-200 °C), then the catalyst ink was sprayed onto the substrate surface. For this purpose, compressed air and a spray gun was used that was operated at constant speed and distance. In one spraying cycle the ink was sputtered 10 times from both directions. The whole process was repeated 5 times (5×10) applying a 30 second-pause to evaporate the solvent from the surface. For the growth of VACNTs, CCVD was used during which the gas feed contained ethylene (70 cm^3/min) as carbon source, nitrogen (50 cm^3/min) as carrier gas, hydrogen (50 cm^3/min) for reductive environment and water vapor (30 cm^3/min) for prolonging the activity of catalyst particles. The synthesis time was 35 min and the temperature was 700 °C. The scheme of the production of VACNTs is presented in Fig. 1.

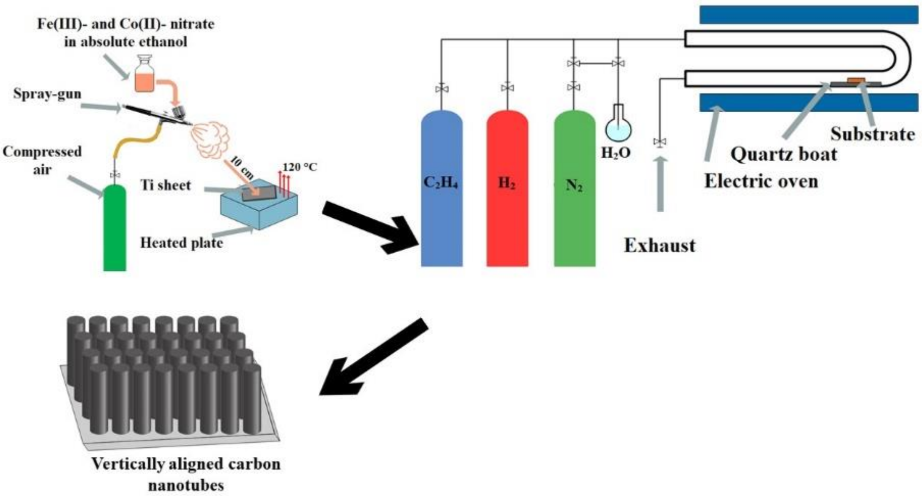

Figure 1. The scheme of manual spray coating layer deposition and production of VACNTs *via* CCVD

Results and discussion

Since the parameters of the catalyst layer significantly affect the growth VACNTs during CCVD synthesis, they were examined during this work. The effects of heat treatment of Ti substrate, spraying temperature on the properties of VACNTs growth, and number of sputtering cycles were investigated in detail.

In the first sample series, the effect of heat treatment of Ti substrate was investigated during the fabrication of catalyst layer. For this purpose, four different samples were prepared: heat treatment a) before and after – as a reference –, b) only before, c) only after spray coating, and d) without any treatment (Fig.2). VACNTs were grown successfully in the first three cases, while in the fourth case only amorphous carbon was deposited onto the surface of Ti substrate. Heat treatment before spray coating forms a native titania layer that might allow the better adhesion of catalyst ink to the surface. At the same time, heat treatment after spray coating stabilizes the catalyst layer by converting metal nitrate layer into metal oxid layer. The Raman spectroscopy results indicated that heat treating the substrate was benefictial for the graphitic

properties of VACNTs. For the verification of carbon deposit, samples were investigated by SEM (Fig. 2).
The thickness of the catalyst layer can be controlled by the number of spraying cycles, which also influences the formation of separated catalyst particles. Therefore, the number of spraying cycles were varied between 1, 2, 3, 4, 5 and 10 cycles. SEM measurements showed that 1×10 spraying could not provide enough catalyst particles on the surface for the growth of VACNTs. However, applying 10×10 spraying cycles yielded too many catalyst particles that merged together resulting in thick carbon fibers grown on the surface. Applying 2×10 or 5×10 spraying cycles resulted in VACNTs with 8.1 µm or 12.2 µm of height, respectively.

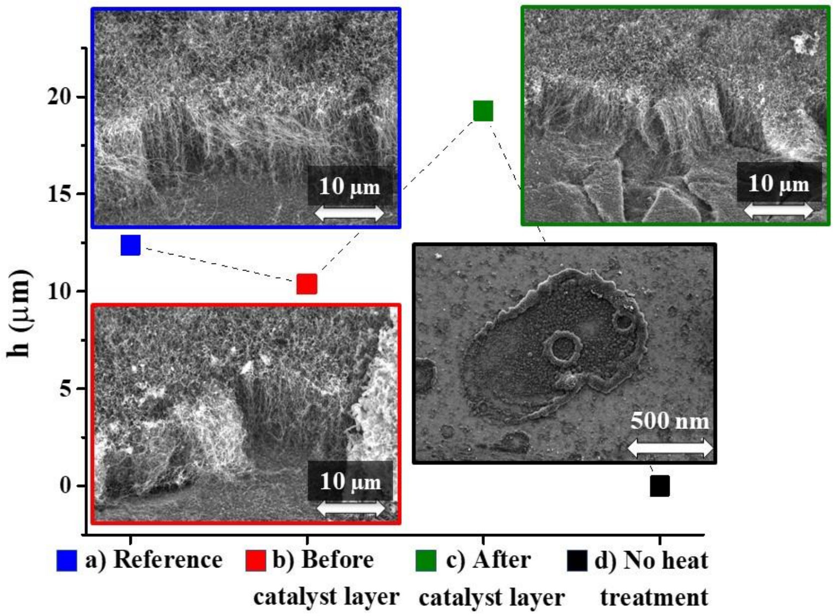

Figure 2. SEM images of VACNTs grown on different heat treated Ti substrates and their corresponding heights

The TEM images also verified that VACNTs grown on the surface of Fe:Co = 2:3 and 5×10 spraying cycles catalyst layer show good graphitic properties with only few defect sites in their walls, which is in good agreement with Raman spectroscopy results.
Finally, the effect of temperature during spray coating on the formation of VACNTs was also investigated. During spraying, the Ti plate was heated between 120-200 °C to evaporate absolute ethanol rapidly from the surface, on which the catalyst particles were uniformly deposited. VACNTs only formed at 120 °C and 140 °C; the corresponding SEM images and height distributions of these samples are shown in Fig. 3.

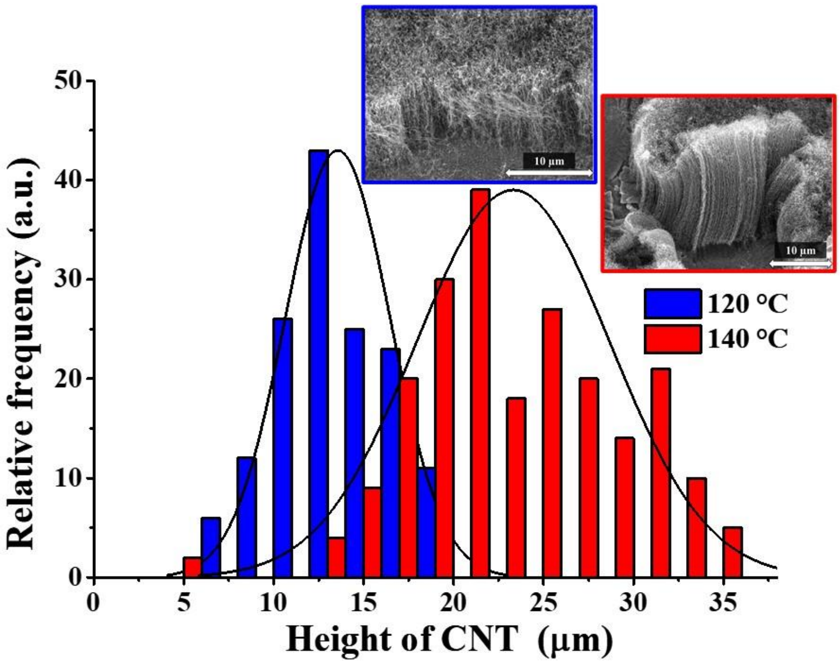

Figure 3. Height distribution and SEM images of VACNTs synthesized at different spraying temperatures

The evaporation rate above 140 °C was too high, thus no homogenous catalyst layer was formed on the Ti substrate.

Conclusions

In summary, spray coating process was proved to be a suitable method for the formation of thin catalyst layers during the production of VACNTs. Heat treatment of Ti substrate, especially after catalyst layer deposition, is needed to sustain stable catalyst layer and synthesize VACNTs with satisfactory orientation. The optimal number of spraying cycles to obtain VACNTs on the surface of Ti substrate was 5 cycles. Increasing the temperature to 140 °C during spray coating can result in higher VACNTs with better quality.

Acknowledgements

The author appreciates the financial support of NKFIH 2019-2.1.11-TÉT-2020-00134.

References

[1] W. Shi, D.L. Plata, Green Chem., 2018, 20, 5245-5260
[2] M. Bodzek, K. Konieczny, A. Kwiecińska-Mydlak, Archives of Environmental Protection, 2021, 43, 3-27
[3] G. D. Nessim, Nanoscale, 2010, 2, 1306–1323
[4] D. Fejes, Z. Pápa, E. Kecsenovity, B. Réti, Z. Toth, and K. Hernadi, Appl. Phys. A Mater. Sci. Process., 2015, 118, 855–861
[5] Y. Guo, G. Zhai, Y. Ru, C. Wu, X. Jia, Y. Sun, J. Yu, Z. Kang, B. Sun, AIP Advances, 2018, 8, 035111-12
[6] M. K. Singla, H. Singh, V. Chawla, JMMCE, 2011, 10, 717-726
[7] R. Xiang, H. Zeng, Y. Su, X. Gui, T. Wu, E. Einarsson, S. Maruyama, Z. Tang, Carbon, 2013, 64, 537-540