INFLUENCE OF SYNTHESIS PARAMETERS ON CCVD GROWTH OF VERTICALLY ALIGNED CARBON NANOTUBES STRUCTURE

Doctoral (Ph.D.) Theses

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2021

1. Introduction and objectives

Over the last 30 years, research of carbon nanotubes with outstanding physical and chemical properties has become an important role of materials science. They are characterized by good thermal conductivity, high tensile strength, and specific electrical properties, and can be used in a wide range of applications, such as various electrochemical applications and in the production of composite materials. Vertically Aligned Carbon Nanotubes (VACNTs), often referred to in the literature as carbon nanotube forests, are one field of carbon nanotube research, a structure first successfully produced by a Beijing group in 1996. These carbon nanotube forests, which are also produced on conductive substrates, have outstanding electrical properties, making them suitable for use in a variety of electronic equipment.

In my doctoral thesis, I aimed to study the growth of carbon nanotube forests on different conducting substrates (aluminum, titanium). To this end, I wanted to investigate the effect of the concentration and the ratio of the catalyst ink on the two different substrates. I also wanted to study the effect of the layer building on the growth of carbon nanotube forests, using a simple layer building technique (dip-coating) and a more complex technique (PLD (Pulsed Laser Deposition)). I also aimed to investigate the influence of the parameters used in the CCVD (Catalytic Chemical Vapor Deposition) synthesis (reaction time, water vapor, different carbon sources) on the height and orientation of the carbon nanotube forests. In addition, I aim to prepare carbon nanotube forests in the presence of nitrogen-containing compounds and to investigate the incorporation of nitrogen into the structure of carbon nanotubes and to obtain information on the changes in the structure of carbon nanotube forests. For this purpose, I wanted to use two different methods (bubbling and injection techniques), and to study the effect of hydrogen, different nitrogen containing compounds and layer building on the incorporation of nitrogen into carbon

nanotubes. Finally, I wanted to gain information on the possibility of forming a composite between metal oxides and carbon nanotube forests, and therefore I wanted to investigate TiO_2 and ZnO, which I wanted to composite with carbon nanotube forests using the ALD (Atomic Layer Deposition) method.

2. Experimental methods and procedures

In my experiments, carbon nanotube forests were prepared by CCVD. Two methods were used to build the catalyst layers on the substrates, the first one was dip-coating, where the catalyst solution contained iron(III)-nitrate and cobalt(II) nitrate. While for PLD, the pastilles were made of Fe- and Co-oxides. The synthesis was carried out after catalyst layer formation, where the synthesis temperature was 640°C for aluminum substrate and 700°C for titanium substrate. The reaction time differed when using the two substrates, 15 min for the aluminum substrate and 30 min for the titanium substrate. In the cases where I doped the carbon nanotube forests with nitrogen containing compounds, I used different nitrogen containing compounds, which were: NH_3, acetonitrile (ACN), and tripropylamine (TPA). The different carbon sources were acetone, ethanol, brandy, cyclohexane, diethyl-ether and ethyl-acetate.

The scanning electron microscope (SEM: Hitachi S-4700 Type II FE-SEM) was used to determine the height and structure of the carbon nanotube forests.

The transmission electron microscopy (TEM: FEI Tecnai17G2 20 X-TWIN) was used to determine the diameter of the carbon nanotubes and the number of walls of the carbon nanotubes.

The composites and nitrogen incorporation were analyzed by energy dispersive spectroscopy (EDX: HITACHI S-4700 Röntec QX2).

A Raman spectroscope (Thermo Scientific DXR) was used to determine the graphiticity of the carbon nanotube forests and the ordered of the carbon structure.

The electrical contact between the carbon nanotube forests and the substrate was determined using cyclic voltammetry.

Photoelectron spectroscopy (XPS: Specs Phoibos 150 MCD) was used to investigate the nitrogen incorporated in the carbon nanotubes.

3. Summary of new scientific results

T1. The concentration of the catalyst ink and the metal ratio used in the layer construction affect the height and structure of the carbon nanotube forests during the syntheses on aluminum and titanium substrates.

T1.1. The different catalyst concentrations and ratios were used to form the catalyst film, demonstrating that the most suitable catalyst concentration for aluminum and titanium substrates is 0.11 M, while the most ideal catalyst ratio is Fe:Co = 2:3, which is different from the Fe:Co = 1:1 ratio most commonly used in the literature. Using these parameters, the highest carbon nanotube forests can be achieved on aluminum and titanium substrates.

T1.2. On the aluminum substrate, cyclic voltammetry measurements were performed on samples prepared at different concentrations, demonstrating that there is an electrical connection between the substrate and the carbon nanotubes, and that the highest charge capacity was observed at a concentration of 0.11 M, thus proving that the highest electrochemical surface area is achieved at this concentration.

T1.3. By comparing the parameters (catalyst concentrations and ratios) investigated for carbon nanotube forests produced on two different substrates, it is demonstrated that higher carbon nanotube forests can be achieved using the aluminum substrate than the titanium substrate, thus allowing the cost-effective production of carbon nanotube forests using a cheaper substrate.

T2. The methods used in layer building (dip-coating, PLD) influence the growth of carbon nanotube forests during syntheses.

2.1. I have demonstrated that the dip-coating method of layer formation does not require the thermal treatment of the substrate, which can lead to the formation of a support-oxide layer on the substrate surface, thus allowing for the simplification of the synthesis and the direct production of carbon nanotube forests on the substrate, which can be advantageous in electrochemical applications, as the absence of an insulating oxide layer facilitates the direct contact of carbon nanotubes with the substrate.

2.2. I have found that the presence of alumina-oxide on the substrate is not necessary for the formation of carbon nanotube forests when using the PLD layer building method, contrary to the fact that this support layer is often used in the literature, which may negatively affect the formation of electrical contacts between the carbon nanotubes and the substrate.

T3. The parameters used during CCVD synthesis (reaction time, water vapor flow rate, different carbon sources) influence the growth of carbon nanotube forests during their production.

3.1. I found that the most ideal water vapor saturated nitrogen flow rate on aluminum substrate is 30 cm^3/min, at which the highest carbon nanotube forest can be observed from SEM images, and on titanium substrate the presence of water vapor is not required in the system during the formation of carbon nanotube forest structure, thus simplifying the synthesis.

3.2. During the syntheses, the production of carbon nanotube forests was investigated in the interval of 5-20 min for the aluminum substrate and in the range of 10-50 min for the titanium substrate. From which I have demonstrated that the ideal reaction time is 15 min for the aluminum substrate and 30 min for the titanium substrate, and that higher carbon nanotube forests are formed on the substrate surface in the former case, and that it is possible to reduce the height of the carbon nanotube forests by reducing the reaction time (6.7 μm for aluminum and 3.0 μm for titanium, which is significantly lower than the literature data).

3.3. I found that at 700˚C, without water vapor and using a reaction time of 30 min in the absence of ethylene carbon source, using the other carbon sources (acetone, ethanol, brandy, cyclohexane, diethyl ether and ethyl acetate), carbon nanotube forests were observed on the titanium substrate only in the presence of cyclohexane, while for the other carbon sources only disordered carbon nanotubes were formed on the substrate.

T4. The parameters used in the study of nitrogen incorporation (different nitrogen containing compounds, the use of layer building methods, the effect of hydrogen, the method of nitrogen loading) influence the growth of carbon nanotube forests during the syntheses and the incorporation of nitrogen into carbon nanotubes.

4.1. I found that when acetone solutions of different nitrogen compounds (NH_3, ACN, TPA) are used, only in the presence of TPA-acetone the carbon nanotube forest structure is formed on the substrate surface, while for the other nitrogen compounds only carbon nanotubes are observed in SEM images.

4.2. I have demonstrated that the catalyst building method influences the nitrogen incorporation into carbon nanotubes: using the PLD method, EDX measurements show that nitrogen incorporation into carbon nanotubes is assumed, which is likely due to the presence of an alumina-oxide support layer on the substrate surface.

4.3. I have shown that the presence of hydrogen is sufficient only in the reduction phase, in which case the highest carbon nanotube forests are observed in the SEM images. In addition, this short hydrogen presence is assumed to the most ideal for nitrogen incorporation into the carbon nanotubes, the highest nitrogen incorporation being observed in the EDX measurements.

4.4. I found that among the methods used to introduce nitrogen-containing compounds (bubbling, injection), the injection method is more effective for incorporating nitrogen into carbon nanotubes. EDX and XPS measurements were used to verify the incorporation of nitrogen into carbon nanotubes, and TEM images were used to demonstrate the bamboo structure, which is a typical structure for nitrogen doped carbon nanotubes. Furthermore, we have demonstrated that, under the above parameters, the formation of extremely low carbon nanotube forests with a height of only 1.6 μm is possible.

T5. The ALD method used in the composite design of carbon nanotube forests with metal oxides allows the carbon nanotubes that build the carbon nanotube forests to be decorated with the metal oxides.

5.1. I have demonstrated that it is possible to decorate carbon nanotube forests with ZnO and TiO_2 by ALD method. The SEM and TEM images and Raman spectroscopy measurements, it was demonstrated that the composite formation does not only take place on the outer surface of the carbon nanotube forests, but also metal oxides appear on the (inner) carbon nanotubes that build up the carbon nanotube forests.

4. Publications and conference participations

Hungarian Scientific Bibliography (MTMT) identifier: 10064918

Publications related to the scientific topic of the dissertation:

[1] **A. Szabo**, E. Kecsenovity, Z. Papa, T. Gyulavari, K. Nemeth, E. Horvath, K. Hernadi: *Influence of synthesis parameters on CCVD growth of vertically aligned carbon nanotubes over aluminum substrate*
Scientific Reports, 7 (2017) 9557.
IF = 4.122 **Citations: 27 (21)**

[2] **A. Szabó**, P. Andricevic, Z. Pápa, T. Gyulavári, K. Németh, E. Horváth, L. Forró, K. Hernadi: *Growth of CNT Forests on Titanium Based Layers, Detailed Study of Catalysts*
Frontiers in Chemistry, 6 (2018) 593.
IF = 3.782 **Citations: 4 (0)**

[3] **A. Szabó**, L.P. Bakos, D. Karajz, T. Gyulavári, Z.R. Tóth, Z. Pap, I.M. Szilágyi, T. Igricz, B. Parditka, Z. Erdélyi, K. Hernadi: *Decoration of Vertically Aligned Carbon Nanotubes with Semiconductor Nanoparticles Using Atomic Layer Deposition*
Materials, 12 (2019) 1095.
IF = 3.057 **Citations: 5 (2)**

[4] **A. Szabó**, T. Gyulavári, Zs.-R. Tóth, Zs. Pápa, J. Budai, K. Hernadi: *The effect of various substrates and catalyst layer deposition on the incorporation of nitrogen into carbon nanotube forest structures,*
Thin Solid Films, 709 (2020) 138194.
IF=2.183 **Citations: 5 (5)**

[5] **A. Szabó**, L. Nánai, Zs. R. Tóth, K. Hernadi: *Simplification of the CCVD method used in the growth of carbon nanotube forests on titanium substrate*,
Solid State Sciences, 117 (2021) 106648.
IF=3.059 **Citations: 1 (1)**

[6] **A. Szabó**, P. G. Szekeres, T. Gyulavári, Zs. R. Tóth, Zs. Pápa, Á. Szamosvölgyi, A. Sápi, Z. Kónya, K. Hernadi: *Systematic investigation of experimental parameters on nitrogen incorporation into carbon nanotube forests*
major revision, Materials Research Bulletin
IF = 4.641

∑IF = 16,203

Σ Citations 42 = (Independent: 29)

Other publications:

[7] T. Szabó, R. Janovics, M. Túri, I. Futó, I. Papp, M. Braun, L. Rinyu, K. Németh, G. P. Szekeres, A. Kinka, **A. Szabó**, K. Hernádi, K. Hajdu, L. Nagy: *Isotope analytical characterization of carbon based nanocomposites*,
Radiocarbon, 60(4) (2018) 1101-1114
IF: 1.531 **Citations: 2 (2)**

[8] N. Justh, B. Berke, K. László, L.P. Bakos, **A. Szabó**, K. Hernádi, and I.M. Szilágyi: *Preparation of Graphene Oxide/Semiconductor Oxide Composites by Using Atomic Layer Deposition*,
Applied Surface Science, 453 (2018) 245-251
IF: 5.155 **Citations: 19 (15)**

[9] Zs. Pápa, E. Kecsenovity, J. Csontos, **A. Szabó**, Zs. Toth, J. Budai: *Ellipsometric Analysis of Aligned Carbon Nanotubes for Designing Catalytic Support Systems,*
Journal of Nanoscience and Nanotechnology, 19 (2019) 395-399
IF: 1.354 **Citations: 1 (1)**

[10] T. Nagyné-Kovács, G. Shahnazarova, I. E. Lukács, **A. Szabó**, K. Hernádi, T. Igricz, K. László, I. M. Szilágyi, Gy. Pokol: *Effect of pH in the hydrothermal preparation of Bi2WO6 nanostructures*,
Materials 12 (2019) 1728
IF: 3.057 **Citations: 8 (8)**

[11] L. Nánai, **A. Szabó**, T. Gyulavári, J. Budai, K. Hernadi: *Manual spray coating: A cheap and effective method to build catalyst layers for carbon nanotube forest growth*
Thin Solid Films, (2019) 137491.
IF = 2.03 **Citations: 2 (0)**

[12] T. Nagyné-Kovács, I. Endre Lukács, **A. Szabó**, K. Hernadi, T. Igricz, K. László, I. M. Szilágyi, Gy. Pokol: *Effect of pH in the hydrothermal preparation of monoclinic tungsten oxide,*
Journal of Solid State Chemistry, 281 (2020), 121044
IF = 2.726 **Citations: 7 (7)**

[13] L. P. Bakos, L. Sárvári, K. László, J. Mizsei, Z. Kónya, Gy. Halasi, K. Hernádi, **A. Szabó**, D. Berkesi, I. Bakos, I. M. Szilágyi: *Electric and photocatalytic properties of graphene oxide depending on the degree of its reduction*,
Nanomaterials 10 (11), (2020), 2313.
IF: 5.076 **Citations: 1 (1)**

[14] K. Ungvári, S. Mészáros, **A. Szabó**, K. Hernádi, Zs. Tóth: *In vitro biocompatibility test of multiwall carbon nanotubes with human osteoblast cells: potential application for bone implant interface reinforcement*,
Journal of Nanoscience and Nanotechnology, 21 (2019) 2394-2403
IF: 1.354 **Citations: 0 (0)**

[15] **A. Szabó** & G. Kovács, A. Kovács, K. Hernadi: *Different pathways for synthesis of WO_3 and vertically aligned carbon nanotube-based nanostructures,*
Journal of Nanoscience and Nanotechnology, 21 (2019) 2388-2393
IF: 1.354 **Citations: 0 (0)**

[16] T. Gyulavári, K. Kovács, K. Magyari, K. Baán, **A. Szabó**, G. Veréb, Zs, Pap, K. Hernadi: *Unexpected Link between the Template Purification Solvent and the Structure of Titanium Dioxide Hollow Spheres,*
Catalysts 11 (2021) 112
IF: 4.146 **Citations: 0 (0)**

[17] O. Kéri, E. Kocsis, D. A. Karajz, Zs. K. Nagy, B. Parditka, Z. Erdélyi, **A. Szabó**, K. Hernádi, I. M. Szilágyi: *Photocatalytic Crystalline and Amorphous TiO2 Nanotubes Prepared by Electrospinning and Atomic Layer Deposition*,
Molecules 26, (2021), 5917.
IF: 4.411 **Hivatkozások: 0 (0)**

∑IF = 32,194

∑∑összIF = 48,397

∑ Citations = 82 (Independent 63)

Conference publication

(1) **Anna Szabó**, Zsuzsanna Pápa, Tamás Gyulavári, Krisztián Németh, Diána Nagy, Klára Hernádi: *Growth of CNT Forests on Titanium Substrates: Effect of Catalyst Ration and Hydrogen on the Incorporation of Nitrogen into Carbon Nanotube Structure,*
25th International Symposium on Analytical and Environmental Problems, ISBN 978-963-306-702-4 (403 – 407)

(2) **Anna Szabó**, Lilla Nánai, Zsejke-Réka Tóth, Klára Hernádi: *Production of CNT forests by a simple layer building method on a conductive substrate,*
26th International Symposium on Analytical and Environmental Problems, ISBN 978-963-306-771-0 (333 – 334)

National and international conference participations

(1) **Szabó Anna**: Szén nanocső erdők CVD növesztése alumínium szubsztráton
SZTE-TTIK Tudományos Diákköri Konferencia
Szeged, Hungary (2016) – oral presentation (2st place)

(2) **Szabó Anna**: Szén nanocső erdők CVD növesztése alumínium szubsztráton
XXXIII. OTDK Országos Tudományos Diákköri Konferencia, Kémiai és Vegyipari Szekció
Miskolc, Hungary (2017) – oral presentation

(3) **Szabó Anna**: Szén nanocső erdők CVD növesztése alumínium szubsztráton
XVIII. Műszaki Tudományos Diákköri Konferencia
Timisoara, Romania (2017) – oral presentation

(4) **Szabó Anna**, Kovács Anita, Gyulavári Tamás, Kovács Gábor, Pap Zsolt, Hernádi Klára: *Synthesis and characterization of vertically aligned carbon nanotubes and CNT-WO3-based composites*
5th European Conference on Environmental Applications of Advanced Oxidation Processes
Prague, Czech Republic (2017) – poster presentation

(5) Tibor Szabó, Róbert Janovics, Marianna Túri, István Futó, László Rinyu, Krisztián Németh, Gergő Péter Szekeres, Anikó Kinka, **Anna Szabó**, Klára Hernádi, Kata Hajdu, László Nagy: Isotope analytical characterization of carbon based nanocomposites,
2nd International Radiocarbon in the Environment Conference,
Debrecen, Hungary (2017) – poster presentation

(6) Kovács Gábor, **Szabó Anna**, Kovács Anita, Gyulavári Tamás, Pap Zsolt, Hernádi Klára: *Függőlegesen rendezett szerkezetű szén nanocsövek és CNT-WO3-alapú kompozitjainak előállítása és jellemzése*
23rd International Conference on Chemistry
Deva, Romania (2017) – poster presentation

(7) Klára Hernádi, **Anna Szabó**, Zsuzsanna Pápa, Tamás Gyulavári, Krisztián Németh, Judit Budai: *CCVD growth of vertically aligned carbon nanotubes over various substrates*
III. International Symposium on Nanoparticles/Nanomaterials and Applications
Lisbon, Portugal (2018) – oral presentation

(8) **Szabó Anna**, Pápa Zsuzsanna, Kecsenovity Egon, Csontos János, Toth Zsolt, Budai Judit: *Ellipsometric Analysis of Aligned Carbon Nanotubes,*
10th Workshop Ellipsometry (WSE 10)
Chemnitz, Germany (2018) – poster presentation

(9) Klára Hernádi, **Anna Szabó**, Zsuzsanna Pápa, Tamás Gyulavári, Krisztián Németh, Zsolt Tóth, Judit Budai: *Challenges in The Growth of Vertically Aligned Carbon Nanotubes: Substrate, Catalyst Layer, CVD Conditions and Much More*
Nanoworld Conference: Useful Science and Technology for a Just World
San Francisco, USA (2018) – oral presentation

(10) Krisztina Ungvari, Sandor Meszaros, Egon Kecsenovity, **Anna Szabó**, Zsolt Tóth, Kinga Turzo, Klára Hernádi: *Viability of Human Primary Osteoblast on Multi-walled Carbon Nanotubes*
96th General Session & Exhibition of the IADR IADR Pan European Regional Congress, London, United Kingdom (2018) – poster presentation

(11) **Anna Szabó,** Egon Kecsenovity, Zsuzsanna Pápa, Tamás Gyulavári, Krisztián Németh, Horvath Endre, Klára Hernádi: *CVD growth of Carbon Nanotube forests on aluminum substrate*
12th International Conference on Physics of Advanced Materials (ICPAM-12),
Crete, Croatia (2018) – poster presentation

(12) Lilla Nánai, **Anna Szabó**, Tamás Gyulavári, Klára Hernádi: *Catalyst layers built by spray-coating for carbon nanotube forests growth on titanium substrate*
XVIth International Conference Students for Students
Cluj-Napoca, Romania (2019) – oral presentation

(13) Lilla Nánai, **Anna Szabó**, Tamás Gyulavári, Judit Budai, Klára Hernádi: *Katalizátorréteg kialakítása kézi spray-coating módszerrel titán hordozón szén nanocső erdők szintéziséhez*
25th International Conference on Chemistry
Cluj-Napoca, Romania (2019) – poster presentation

(14) **Anna Szabó**, Zsuzsanna Pápa, Tamás Gyulavári, Krisztián Németh, Diána Nagy, Klára Hernádi: *Growth of CNT Forests on Titanium Substrates: Effect of Catalyst Ration and Hydrogen on the Incorporation of Nitrogen into Carbon Nanotube Structure,*
25th International Symposium on Analytical and Environmental Problems
Szeged, Hungary (2019) – poster presentation

(15) **Anna Szabó**, Lilla Nánai, Zsejke-Réka Tóth, Klára Hernádi: *Production of CNT forests by a simple layer building method on a conductive substrate,*
26th International Symposium on Analytical and Environmental Problems
online (2020) – poster presentation

(16) Zsejke-Réka Tóth, János Kiss, Alexandra Feraru, **Anna Szabó**, Klára Hernádi, Emilia Licarete, Lucian Baia, Klára Magyari: *How can have a bioactive glass antibacterial and cell viability character simultaneously?*
31th Conference of the European Society for Biomaterials
online (2021) – poszter presentation