Controlled Synthesis of Carbon Nanotube Forests:

Characterization, Modification and Potential Applications

Duration (3.5 years) of current project provided a great opportunity to answer many questions arose during writing proposal. According the original plan, experimental work was done at different laboratories: researchers at the Department of Applied and Environmental Chemistry were responsible for the growth of vertically aligned carbon nanotubes (CNT forest) *via* catalytic chemical vapor deposition (CCVD). Colleagues at the Department of Optics and Quantum Electronics provided thin layers with catalytic materials *via* pulsed laser deposition (PLD) technique. Participants from the Department of Oral Biology and Experimental Dental Research performed cell culture experiments for potential modification of dental implants. In spite of the fact that finally we had no contractual obligation for international collaboration, from our side it was considered as a bilateral project. Consequently, we also obtained joint results with the Swiss group (EPFL).

For the proposed biomedical applications, carbon nanotubes (CNTs) with appropriate mechanical properties and morphology had to be synthetized. The fine tuning of these properties necessitates the precise control of the production steps. In our approach, most of the chemical vapor deposition procedure of the CNT synthesis were done applying catalytic layers produced by pulsed laser deposition (PLD). Therefore, we had to assembly and test the PLD setup and characterize the properties of different support and catalytic layers.

For the PLD setup, a Nd:YAG laser was purchased and installed, while for the characterization of the catalytic layers/layer systems, spectroscopic ellipsometry was applied. This contactless optical measurement tool enabled the precise determination of layer thicknesses, and based on these data, the deposition rates for the different target materials were calculated (Al2O3, Fe-Co 1:1, Fe-Co 2:1, CaCO3, ZnO, NiO composites in the form of pressed powder tablets). Optical properties of the layers can also be deduced from ellipsometric measurements providing information e. g. on the porosity of the layers deposited in different background pressures of the PLD chamber.

The calculated deposition rates and the information concerning the effects of the background pressure on the layer porosity of the layers were necessary to investigate the influence of catalytic layers' thickness and structure on the CNTs' properties. Since the first part of the CVD synthesis is the annealing of the catalytic layers, - promoting the formation of droplet like catalytic centers, - we wanted to tune this drop formation by introducing defects into the layers trough the production of the porous structure. In the case of Fe-Co 1:1, layers with different thicknesses and porosity were deposited. An important result of this study is that maximum CNT height (larger than 1 mm determined by scanning electron microscope – Fig. 1) was reached at 4 nm Fe-Co layer thickness considering dense layer structure. Similarly, other parameters can be optimized for different purposes. These results are summarized in our manuscript entitled "*Height and diameter dependence of carbon nanotube forests on the porosity and thickness of catalytic layers*" (Z. Pápa, et al. Applied Surface Science (2018)).

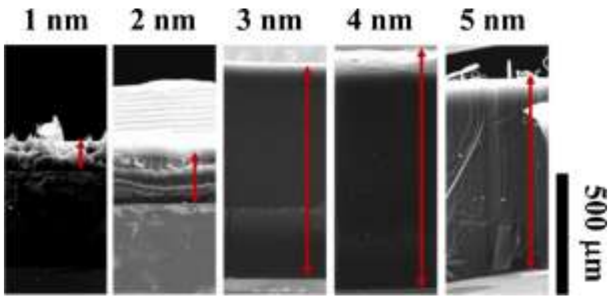


Fig. 1. Scanning electron microscope (SEM) images of the CNT forests grown on the samples with different Fe-Co layer thickness. Note that SEM images were taken by tilting the samples at 45◦. Therefore, the apparent height is smaller than the actual height of the forests.

Characterization of the CNT carpets generally means the determination of the height and the properties of the individual nanotubes. Due to the small sizes involved, these individual nanotubes are investigated by transmission electron microscopy (TEM). Although the data is valid and the process is technically sound, TEM investigations are time consuming and require invasive sample preparation. Ellipsometry can be an appropriate tool to investigate the properties of CNT carpets, since it is a fast, contact free-method. We therefore investigated the applicability of ellipsometry as a potential characterization technique of CNT carpets. Despite the low reflectivity of CNT samples, we could carry out ellipsometric measurements on the side of the CNT carpet. We found that ellipsometric evaluation of the measured spectra can provide information about the density and the optical properties of the nanotubes; however, the properties of the individual nanotubes (diameter, wall number) can not be taken into account during conventional ellipsometric modeling, although the ellipsometric response of samples with different CNT properties are slightly different. To better understand the ellipsometric behavior of this kind of structure the measurement results were compared to Finite Difference Time Domain (FDTD) simulations. Performing simulations with different sample parameters enabled also us to test how sensitively ellipsometry can follow the changes in different sample properties (Fig. 2) and opens a way to precisely evaluate the ellipsometric spectra.

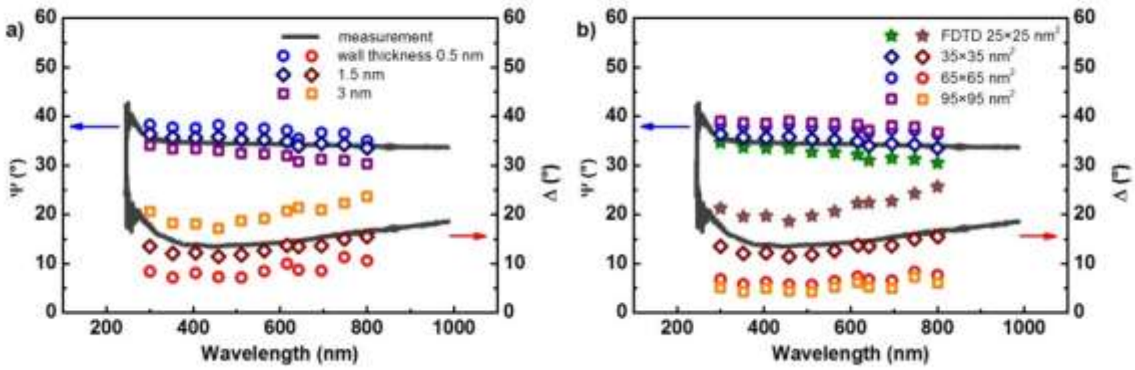


Fig. 2. Ψ and Δ curves belonging to different CNT parameters (AOI=75°). a) Effect of the wall thickness on the determined spectra is shown; b) spectra calculated with different FDTD volume determining the spacing between the CNTs are plotted.

These results were presented on two international conferences of the ellipsometric community (poster presentations on 7th International Conference on Spectroscopic Ellipsometry (2016) and 10th Workhop Ellipsometry (2018)) and can be found in more detail in a research article entitled „Ellipsometric Analysis of Aligned Carbon Nanotubes for Designing Catalytic Support Systems" (Z. Pápa, et al. Journal of Nanoscience and Nanotechnology (2018)). We believe that our investigations can contribute to the fast and non-invasive characterization of CNT carpets.

To study the ability of other techniques to build thin catalyst layers both dip coating and spray coating was tested. A cheap and easy method was presented for the production of VACNTs onto conductive substrate. It was shown that CNT forest height grown onto an Al plate during CCVD synthesis can be controlled by numerous parameters. When varying catalyst ink concentration during the formation of catalyst layer *via* dip coating, the highest forest was obtained at Fe:Co = 1:3 ratio. Increasing the catalyst ink concentration, it was found that approximately above 0.11 M the height of the forest did not change significantly. The components of gas feed during CCVD also affected the parameters of forming CNT forests, however, water vapor has the most determinate role on their height. It was established that no considerable alignment occurs when CNTs are shorter than 10 µm. Above this value the orderliness of CNT forests becomes conspicuous more or less independently of either reaction time or catalyst ink concentration. From the analysis of CNT diameter, it was concluded that the catalyst ink concentration does not affect the diameter of catalyst particles significantly. It is presumed that both the quality of the ink and CCVD conditions control the diameter of CNT (A. Szabó, et al., Scientific Reports (2017)). The effectiveness of manual spray coating method was also investigated for building Fe-Co layers on titanium substrate. During layer formation heat treatment was found to be a crucial parameter for the stabilization of catalyst layer, especially after spray coating. Examinations with catalyst inks of varying Fe:Co ratio highlighted again, that optimum ink composition might alter depending on many parameters such as the quality of substrate, the method of layer deposition, etc. Obvious correlation was found between the morphology of catalyst layer and the quality of carbon nanotubes composing the aligned structure. It was concluded, that after proper optimization manual spray coating proved to be a very cheap and promising technique for layer deposition (L. Nánai, et al., Thin Solid Films (2019)). For better electrical contacts of potential devices, growth of vertically aligned carbon nanotubes (CNT forests) directly onto conductive substrates is an emerging challenge. Applying titanium plates as a substrate it was found that the presence of an alumina layer on the surface significantly modifies the morphology of the catalyst layer (before reaction), thus influencing the CNT forest growth. Nevertheless, it was attested that the insulating layer plays a significant role in CNT forest formation: both the height and the quality of CNT forest depended on the initial structure of the catalyst layer (A. Szabó, et al., Frontiers in Chemistry (2018)).

Since CNT composites with inorganic layer of metal oxides are expected to deliver improved performance in solar cells, and various nano-electronic devices, nanocomposite formation was implemented with both unarrayed and aligned carbon nanotubes. Homogeneous and stable inorganic coating of SnO_2, SiO_2, Al_2O_3 and TiO_2 was obtained on the surface of multiwall carbon nanotubes (MWNTs) by mechanically mixing them with precursor compounds in a planetary ball mill and by subsequent hydrolysis (K. Nemeth, et al. + J. Major, et al., JNN (2019)). A carefully designed, multiple-step electrodeposition protocol was also developed that ensured homogeneous coating of CNTs with Cu_2O nanocrystals (E. Kecsenovity, et al., J. Mater. Chem. A (2016)). In order to produce tungsten oxide-VACNT based (nano)structures, the influence of solvent and precursor was investigated. The results shown that the precursor, the solvent and the synthesis pathway had strong influence on the composition and structure of the resulted composites. Using $WOCl_4$ and different organic solvents, mixed Al-based hydroxide or non-stochiometric tungsten oxide was obtained in composite with VACNT. On the other hand, using WCl_6 as precursor and impregnation/precipitation method, WO_3/VACNT composites with specific semiconductor structure were obtained (A. Szabó, et al., JNN (2019)). Surveying the relevant literature, it became obvious that the deposition of different materials into the interior region of CNT forests is a real challenge. Probably due to wettability problems, conventional impregnation techniques are generally unavailable for this purpose. Therefore, we applied atomic layer deposition for the fabrication semiconductor/CNT forest nanocomposites using either Ti or Zn precursor. Characterization results revealed that the decoration of CNT forest with both Ti_2O and ZnO was successful in the whole bulk of VACNTs (A. Szabó, et al., Materials (2019)).

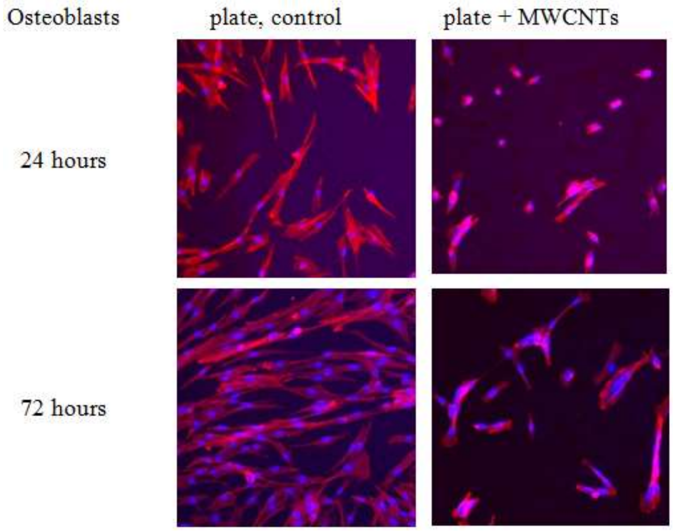
In collaboration with EPFL, we reported the growth of $MAPbBr_3$ single crystals interpenetrating VACNT forests, engulfing individual nanotubes as protogenetic inclusions. This approach resulted in the formation of a three-dimensionally enlarged photosensitive interface. Millimeter-sized photodetector devices were obtained, capable of detecting low light intensities (20−200 nW) from the UV range to 550 nm. Importantly, photocurrent was measured at zero external bias voltage, which points to the formation of a p−n junction during the single crystal inclusion into the vertically aligned carbon nanotube forest. Therefore, pristine or functionalized VACNTs are potential candidates for fabrication of metallic or selective semiconducting, p- or n-type, electrodes, thus leading toward future operationally stable perovskite-based optoelectronic devices (P. Andričević, et al., J. Phys. Chem. C (2017)).

Dental implantation is a widely applied method for permanent replacement of missing teeth. Especially in the case of the older population, dental implantation is often not successful due to osteoporosis. It is a challenge to reinforce the bone by a formation of a nanocomposite from MWCNT and hydroxy-apatite, formed by human osteoblast cells. Therefore, in our research the interaction of primary human osteoblast cells with MWCNTs was studied. Recent results on the compatibility of CNTs with osseointegration processes is overviewed by a literature search.

The protocol for cell culture of primary human osteoblast cells was developed. Bone fragments were collected from healthy adult donors (age 18-46) undergoing a dento-alveolar surgery at the Dept. of Oral Surgery of University of Szeged. (Ethical license number: 188/2013.) In 2 weeks osteoblast cells could be isolated from the bone by enzymatic digestion. The size of osteoblast cells (20-30 m) was determined from the first cell culture experiments. For successful migration and adherence of the osteoblast cells, the optimal density of MWCNTs was determined (30 to 50 m). The cells were identified by their expression of characteristic genes of the osteoblast lineage, such as osteocalcin and alkaline phosphatase, which was observed by RT-PCR. LDH cytotoxicity measurement was performed to detect the LDH enzymatic activity in the cell culture media. The ideal cell number for the different dishes was determined.

Due to the compactness of the MWCNT forests, the MWCNTs were separated and homogenized in 96% ethanol by ultrasonic treatment. After the fixation of the MWCNTs to the special cell growing dish (48 and 24 well plates) the CNT-ethanol solution was placed into the wells, then in a laminar flow chamber the ethanol was evaporated in sterile condition. 1 hour UV-C radiation was used to sterilize these samples. MWCNTs on the bottom of the dishes had sufficient adherence when cell culture media was taken to the well. After 1 week, the MWCNTs were still fixed the bottom of the wells, and the media could be changed without removing the MWCNTs.

In our systematic *in-vitro* experiments the toxicity of MWCNTs on primary osteoblast cells, that isolated from the maxilla of different dental patients was investigated. Bottoms of 6-well plates were coated with MWCNTs using a spray coating technique. Three independent origin cell lines were tested with the control plate and three different MWCNT densities. 100.000 and 200.000 osteoblast cells were plated in the 48 well plate in the 24 well plates, respectively. After 48 hours the cells were attached to the bottom and the culture was confluent. The low density MWCNT samples had a free place for the cells to migrate. On the medium density sample the free areas were matched to cell sizes, and on the high density sample forced interaction of osteoblast cells with MWCNTs could be studied. Attachment in early (24h) and late proliferation (72h) was investigated: Thiazolyl Blue Tetrazolium Bromide (MTT) and Lactate Dehydrogenase (LDH) colorimetric assays were used to test the viability of the cells and the toxicity of the MWCNTs. The possible changes of cell morphology were observed with fluorescent staining. In the Figure below fluorescent images from these experiments can be seen.



After 24 and 72 hours incubation times the control experiments and low density MWCNT samples showed normal adherence and proliferation. However, the increase of MWCNT density reduced the proliferation rate and led to altered cell morphology. The results of the first experiments were presented in poster at IADR conference in London 25-28 July 2018. The results of MWCNT cell interaction survey and the cell culture experiments were published in the Journal of Nanoscience and Nanotechnology (K. Ungvári, et al., JNN (2019)).