Preparation and characterization of large networks of one dimensional nanostructures with controlled morphology

OTKA NNF 78920 project final research report

Dr. Ákos Kukovecz

11 April, 2011

Publications and dissemination:

The anticipated publication output of the project was 4-7 research papers and 3 conference presentations. These indicators were met. We published a total of 18 research papers related to the project, 15 of which were published in journals with an impact factor (IF) and 3 more appeared in international, peer-reviewed English journals that do not have an IF yet. The cumulated IF of the papers is 44.270. The project was realized from 1.80 FTE researcher time and 15528 thousand HUF support, thus the following indicators can be derived:

IF/FTE = 24,594 IF/support = 2,851 1/million HUF Publications/support = 1,352 1/million HUF

Members of the group presented 13 conference lectures and posters related to the project results. These were: (i) the PI was invited speaker at the E-MRS 2009 Symposium N, students (ii) Mária Darányi, (iii) András Sápi and (iv) Gábor Kozma gave talks at the 2009 annual meeting of the Hungarian Microscopist Society, the PI was invited speaker at the (v) COST 539 „ELENA" final workshop, 2009. October 28-30, Averio, Portugal, the (vi) 1st FP7 RP „DEMATEN" workshop on 2009. December 4, Novi Sad, Serbia and the (vii) annual meeting of the OTKA NNF projects in Budapest, 15 April, 2010. Furthermore, (viii) Mária Darányi and (ix) Melinda Mohl gave talks at the 2010 annual meeting of the Hungarian Microscopist Society, (x) János Halász at the 16th IZC Conference (July 2010, Sorrento), (xi) Henrik Haspel at the BDS2010 conference (September 2010. Madrid) and (xii) Zoltán Győri at the „Nanoparticles: Production pathways and appealing applications" conference (2011. January 31, Dunaújváros). Finally, (xiii) the PI presented a poster at the 25th International Winterschool on Electronic Properties of Novel Materials (IWEPNM) conference (2011. February 26 – March 5, Kirchberg in Tirol).

I attempted to raise general public awareness towards the project through the following actions: (i) a "poplar nanotechnology" talk presented to chemistry-oriented students of the Miklós Radnóti High School, Szeged on 4th November, 2009, (ii) I was interviewed as "Researcher of the Month" in January 2010 on the OTKA homepage and (iii) in the Journal of the Hungarian Chemist Association. I was invited to write the foreword (iv) for the April 2010 issue of the Journal of the Hungarian Chemist Association. Furthermore, the commencement of our FP7 STREP "THEMA-CNT" project (related to OTKA NNF 78920) has received considerable attention in the Hungarian media, see e.g. Figyelő 2010/20 issue.

EU projects and international relations:

The original plan was to submit one FP7 project related to OTKA NNF 78920. Actually, we managed to win two FP7 projects. The FP7 STREP „THEMA-CNT" project (where the present PI acts as Szeged node head) is focused on the application of carbon nanotube networks for the cooling of switching elements in power electronics. The goal of the FP7 INCO "NAPEP" project (Szeged node head: Dr. Zoltán Kónya, Szeged operative manager: the present PI) is to create a nanotechnology optics and photonics platform in cooperation with colleagues from Finland and Azerbaijan.

The broad international cooperative character of our work in OTKA NNF 78920 is demonstrated well by the large number of foreign co-authors in our papers. I consider this a major asset in the rapidly evolving and resource-intensive field of nanotechnology research. I hope that we will be able to maintain the developed international collaborative network operational even when the present project is finished.

Personnel:

The original plan was to form a research group based on graduate and undergraduate students. This goal was achieved: 10 students worked on the project in the past two years. Group efforts were co-ordinated by grad students Melinda Mohl and Maria Darányi. Although no senior researchers other than the PI were originally involved in the project, in the third phase it became necessary for Janos Halasz to join the project. He is a well-known expert in zeolite chemistry and the chairman of the Hungarian Zeolite Association. His zeolite expertise was needed in the development of nanotube-zeolite interfaces of future catalytic importance, specifically for tasks 3.2 (catalytic carbon nanotube synthesis) and 4.3 (water purification application research). A total of 1.80 FTE senior researcher effort was devoted to the project: 1.40 FTE for the PI and 0.40 FTE for Janos Halasz. Since I am not aware of a model suitable for calculating FTE values for undergraduate students, their work was not taken into account in the FTE calculation for sake of clarity. If requested, I am ready to make corrections to the FTE value provided that unambiguous guidance for undergraduate students is available.

Financial:

The full support was used for realizing the project. The planned instrument was purchased and personnel payments were made. The largest part of the OTKA-NNF support was spent on conference attendances, consumables (chemicals, lab parts, books) and other costs and services (e.g. fees of access to instruments, instrument maintenance costs, scientific networking etc.) necessary for project completion. The largest difference between the planned and the actual budget is that less money was spent on student employment to compensate for overspending in daily allowances. As indicated already back in my 3rd period project report, this minor change effects only the ratio of rows 1.5 and 1.7 and did not cause any overspending in total personnel costs. I trust that the OTKA-NNF committee will take into account that our group made 13 conference appearances instead of the originally planned 3 occasions and consequently, it will accept the overspending of conference-related daily allowances.

New scientific results

1) Large quantities of multi-wall carbon nanotubes were produced by CCVD. These were converted into random networks to study two phenomena: (i) a comprehensive study on the adsorption of C6 hydrocarbon rings on as-synthesized nanotubes, cut nanotubes, mesoporous amorphous carbon and SBA-15 yielded information on the tunability of the properties of carbon nanotube networks by the adsorption of small organic molecules, and (ii) the applicability of carbon nanotube network thin films as selective gas sensors using Fluctuation Enhanced Sensing (FES). Sensor response was not influenced by the gate voltage. On the other hand, a major increase in selectivity could be achieved by choosing the optimal sampling frequency and noise spectrum frequency range. Our results suggest that carbon nanotube network sensors operated as FES units are capable of providing both qualitative and quantitative information about their gaseous environment. Qualitative identification properties can be improved by the functionalization of carbon nanotubes, in particular, by decorating the tubes with amine groups.
2) In order to control carbon nanotube network morphology we converted aligned multiwall carbon nanotube forests into epoxy composites. The anisotropy of the ac and dc electrical conductivity was studied and results were interpreted in the framework of the percolation theory using an equivalent circuit model.
3) It is common knowledge that ZnO nanostructures of controlled morphologies can be prepared from suitable precursor shapes, e.g. Zn-oxalates. We succeeded in demonstrating that the reverse reaction route is also feasible, that is, ZnO nanorods can be converted into Zn-glycerolate (ZnGly) by reacting them with glycerole in a way that preserves the one-dimensional morphology of the starting ZnO material in the product ZnGly. The resulting ZnGly complex microstructures are hugely different from both carbon nanotubes and metal-oxide nanowires and therefore, they created a good possibility for broadening the range of potential network-forming nanomaterials. Further broadenings of scope were realized by the synthesis of semiconducting TiOx, VOx and WOx nanorods as well as metallic Au, Ni and Cu nanowires.
4) We developed a new cost-effective method for the synthesis of noble metal nanowires from Ni nanowires. The method was used for the synthesis of Pt and Pd nanowires. Furthermore, our work resulted in a novel hydrothermal synthesis route that yields ultralong copper nanowires in a system where glucose is responsible for crystal seed growth control, nanowires are stabilized by hexadecile amine and the product nanostructures consist of pure elemental copper. We were the firsts to report the applicability of the galvanic exchange reaction to the synthesis of bimetallic Cu-Pd and Cu-Pt nanowires.
5) We prepared a complex membrane architecture by the controlled growth of carbon nanotube networks on Si. The resulting membrane is capable of filtering submicron particles from air with efficiency above 99 %. Depositing Pd nanoparticles on the membrane nanotubes resulted in a hydrogenation/dehydrogenation membrane catalyst that was tested in the model reaction of catalytic propene hydrogenation.
6) We studied the broadband dielectric properties of titanate nanotubes and performed an in-depth study on the applicability of numerical differentiation methods in general, and the Savitzky-Golay method in particular for the processing of the discrete permittivity function. On the basis of these results we measured the dielectric spectra of titanate nanotubes in the 200-350 K temperature and 6 – 84 RH% relative humidity ranges and found a pronounced dependence of dielectric

properties on sample humidity. VFT type processes dominate low temperature behavior and Arrhenius type processes can be identified at higher temperatures.

7) Complex film membranes were assembled from multiwall carbon nanotubes and poly-acrylonitrile (PAN) so that they could be pyrolized into carbonaceous coatings. Sample conductivity was improved considerably by the presence of carbon nanotubes even below the percolation threshold. This observation was interpreted by the favorable effect of carbon nanotubes on PAN graphitization.
8) We created three-dimensionally ordered film patterns ("sandwich" samples) from anatase nanowires (obtained by the heat treatment of titanate nanowires) and multi-wall carbon nanotubes. The photocatalytic activity of the sandwiches was compared to that of the reference P25 TiO_2 material. Carbon nanotubes caused a major improvement in the photocatalytic activity. Nanostructured TiO_2 was also prepared from $TiCl_4$ using the sol-gel method. Once the photocatalytic activity of these samples was demonstrated in phenol degradation, we attempted preparing crack-free, homogeneous coatings on carbon nanotube surfaces. We realized that the interaction between nanotubes and solvent molecules may hinder the formation of good coatings and that $TiBr_4$ is a better precursor than $TiCl_4$.
9) We conducted a series of preliminary experiments to study the interaction between metallic nanoparticles and potential network matrices. Pd, Fe and Ni nanoparticles were formed in PDMS membranes by utilizing the low degradation temperature of the precursor metal acetylacetonates. The resulting membranes were catalytically active in the ethylene hydrogenation model reaction. Au, Rh and Au-Rh nanoparticles were deposited onto titanate nanotubes and nanowires. Studies on the structure of the nanoparticles revealed that while in untreated systems gold covers the rhodium particles almost completely, in the presence of CO the surface undergoes surface reconstruction. We demonstrated that self-supporting network films of titanate nanowires decorated by Pd and Pt nanoparticles exhibit a photocatalytic activity commeasurable with the water decomposition activity of their non-self-supporting bulk powder counterparts. These experiments indicate that combining titanate nanowires with the mono- or bimetallic nanowires developed in the project could lead to complex networks with beneficial properties.

<u>Verifiable results:</u>

A total of 8 verifiable result milestones were defined in the original workplan, two for each 6-month period. These were achieved as follows:

E1.1 The literature survey and the experiment plan were completed to serve as a basis for future research efforts. Components of the literature survey were incorporated into the peer-reviewed publications related to the project.
E1.2 Multiwall carbon nanotubes, TiO_x nanowires, VO_x nanowires, WO_x nanowires were synthesized as planned.
E2.1 Filtration experiments were conducted and documented.
E2.2 Using the partial least squares method to find out the global optimum of the system we devised a model to estimate the filter cake resistance on dead-end filtration membranes. This model is continuously developed and expanded to take other 1D nanostructures into account as well.

E3.1 More than 20 different CNT patterns were grown by CVD. Our current research interests are related to scaling up of low temperature synthesis.
E3.2 We created several complex three dimensional patterns from one dimensional nanostructures. The combinations MWCNT- acrylonitrile and MWCNT-photocatalytically active titanate nanotubes (nanowires) resulted in particularly interesting properties (see e.g. scientific results above).
E4.1 We developed a new evaporation profile analysis instrument for measuring evaporation profiles simultaneously as electrical resistance increase or as weight decrease.
E4.2 Sandwich structures composed of titanate nanotubes and nanowires are available for photocatalytic activity measurements.

<u>Summary:</u>

The financial support provided by the OTKA NNF 78920 project between April 2009 and March 2011 has allowed me to start a research group based on students. Our group studied the synthesis, modification and networking properties of selected one dimensional nanostructures. The field has proven to be even more fruitful than originally anticipated and is sure to provide some interesting new findings in the future yet. I am thankful to the OTKA and the Norwegian Fund for their support and appreciate the fact that they will continue funding our research for one additional year through the OTKA NNF2 #85899 project. I trust that by Spring 2012 we will be able to assemble the intelligent self-cleaning nanocomposite membrane device whose building blocks were developed in the present project.