Fluid identification and filtration using morphologically controlled large networks of one dimensional nanostructures

OTKA NNF2 85899 project final research report

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Publications and dissemination:

The anticipated publication output of the project was 3 research papers and 1 conference presentations. These indicators were met. Since this project was very short (only 12 months) it was not possible to make the measurements, interpret the data, write all papers AND get them accepted during the lifetime of the project. Therefore, there is one additional result directly related to this project which is currently in the status of "submitted for publication" and two more papers summarizing the evaporation profile related results are being written now. Since these last two manuscripts are continuously evolving, they are available from the PI upon direct request.

The project was realized from 0.7 FTE researcher time and 6149 thousand HUF support, thus the following indicators can be derived from the published 4 research papers. Please note that these indicators are likely to improve in 2012 as the currently submitted and prepared manuscripts get accepted.

	Publications	Impact factor	IF/FTE	IF/million HUF support	Publications/million HUF support
Papers	4	10,132	14,47	1,65	0,65

Related projects and international relations:

Our research group was able to win a third FP7 project under the support of OTKA NFF2 85899. The new FP7 STREP "SusFoFlex" consortium (www.susfoflex.com) started its operation on 1 January 2012 and will be active in the development of new packaging materials. The present PI serves as the Szeged node head and project level dissemination manager of the SusFoFlex network. We consider our involvement in this consortium a direct recognition of the expertise developed in the OTKA NNF 78920 and NNF2 85899 projects because our SusFoFlex responsibilities include the development of nanoparticle composite sensor networks and the environmental monitoring of nanoparticle release.

Another major improvement in our international relations during the NNF2 85899 lifetime was the successful application for the Hungarian-Serbian cross-border collaboration program. Our IPA project 1002/214/188 "MATCROSS" commenced in November 2011 will develop nanoparticle related groundwater and sediment remediation technologies.

Personnel:

The support provided by the OTKA NNF2 85899 project allowed me to continue running my small research group. Both grad students originally associated with this group (Melinda Mohl and Mária Darányi) have successfully defended their PhD thesis' in 2011 during the lifetime of the NNF2 85899 project. Current team members include graduate students Henrik Haspel, Gábor Kozma and Zoltán Győri, plus undergraduate students Timea Simon, Zita Papp and Dorina Dobó.

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-NNF2 support was spent on 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.

New scientific results

1) We have analyzed the charge transport mechanism in humid titanate nanowires networks (TiONW) at room temperature by extracting the variation of dc conductivity, mobility, diffusion coefficient, and charge carrier concentration with the relative humidity of the environment in the 6 - 100 RH% range. Transient current measurements (ITIC) in combination with dielectric spectroscopy (DRS) are excellent tools to obtain both qualitative and quantitative information about charge transport processes. We have found good correlation in dc conductivity extracted from both techniques, while its constituent parameters provided deeper insight into the underlying mechanism. It seems that changes in charge carrier concentration govern mostly the dc conductivity, while ionic mobility has less pronounced effect. In order to unravel which type of water is involved in the humidity related dielectric processes of TiONW, the variation of the interlamellar distances with RH i.e. the variation of the structural water content was determined from XRD analysis. It has been pointed out that only adsorbed water contributes to the RH induced variation of dielectric properties. From the moisture adsorption isotherm and calorimetric measurements both the amount and the thermodynamic state of the adsorbed water were determined, and changes in ionic mobility in the investigated humidity range were successfully assigned to changes in the structure and thermodynamic state of adsorbed water

molecules. Nevertheless the origin of the exponentially increasing carrier concentration sill remains an open question.

2) A galvanic replacement reaction has been successfully applied to prepare CuPd and CuPt bimetallic nanotubes. The nanotubes were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) techniques. Ultralong, single crystalline copper nanowires (NWs) with a diameter of ~64 nm and a length of several micrometers were used as template material. By controlling the amount of noble metal salt added, nanotubes with different compositions were obtained. After the replacement of Cu with Pt, nanotubes composed of a PtCu alloy were formed. EDS analysis revealed that the Pt content increased until about 66%. No further increase in the molar ratio resulted in any additional Pt incorporation into the alloy. As for the replacement of Cu with Pd the thickening of the nanotubes was observed indicating that nanotubes composed of Pd nanoparticles were formed. Backscattered electron imaging and SEM-EDS revealed CuPd nanotubes with approximately 2.3% Cu content. These remarks indicate different evolution mechanism for the nanotubes in the two systems.

3) The influence of Co and Ni compounds on the carbonization behaviour of PAN membranes was studied by Raman and ATR FT-IR spectroscopy, thermogravimetry, electrical conductivity measurement and scanning electron microscopy. In the presence of metal ions the evolved heat and the cyclization temperature decrease significantly. Cobalt and nickel ions both interact directly with the C≡N triple bond to promote cyclization and dehydrogenation reactions and also play a role in preventing the premature loss of hydrogen as ammonia or HCN. The overall structure of the product carbon membrane appears to be that of nanocrystalline graphite. The crystallite structure and consequently, the electrical conductivity of the membrane can be fine tuned by controlling the carbonization temperature and the amount of the metal catalyst. Cobalt appears to be more suitable for tuning the properties of PAN-derived carbon membranes than nickel because it offers control on a broader scale.

4) Low-temperature thermal chemical vapor deposition (thermal CVD) synthesis of multi-walled carbon nanotubes (MWCNTs) was studied using a large variety of different precursor compounds. Cyclopentene oxide, tetrahydrofuran, methanol, and xylene:methanol mixture as oxygen containing heteroa- tomic precursors, while xylene and acetylene as conventional hydrocarbon feedstocks were applied in the experiments. The catalytic activity of Co, Fe, Ni, and their bi- as well as tri-metallic combinations were tested for the reactions. Low-temperature CNT growth occurred at 400 8C when using bi-metallic Co-Fe and tri-metallic Ni-Co-Fe catalyst (on alumina) and methanol or acetylene as precursors. In the case of monometallic catalyst nanoparticles, only Co (both on alumina and on silica) was found to be active in the low temperature growth (below 500 8C) from oxygenates such as cyclopentene oxide and methanol. The structure and composition of the achieved MWCNTs products were studied by scanning and

transmission electron microscopy (SEM and TEM) as well as by Raman and X-ray photoelectron spectroscopy (XPS) and by X-ray diffraction (XRD). The successful MWCNT growth below 500 8C is promising from the point of view of integrating MWCNT materials into existing IC fabrication technologies.

5) A number of different carbon allotropes were used as supports for palladium nanoparticles to prepare catalysts and investigate the effects of different support structures. Oxidative functionalization was found to prevent the aggregation of primary palladium nanoparticles into larger clusters. There is a correlation between acid site concentration on supports and catalyst deactivation, however, structural differences can overcome such negative effects as demonstrated by the case of functionalized carbon nanotubes. Despite the ~4 times lower specific surface area of CNTs as compared to activated carbon they exhibited similar catalytic activity which can be attributed to the special metal-support interactions and surface diffusion properties of the gaseous reactant partners. The observed decline in catalytic activity can be attributed to the rapid coke formation on acidic active sites of the support surface. The formed coke can choke the pores of the support, and thus block reactant access to the Pd nanoparticles. The apparent contradiction between the highest acidity and best deactivation tolerance of functionalized multi-walled carbon nanotubes could be explained on a morphological basis. The large diameter intertube pore channels of carbon nanotube samples are more difficult to choke than the in-block pores in e.g. activated carbon. Combined with the beneficial effect of oxidative functionalization on hindering Pd particle aggregation, this makes functionalized MWCNT supported palladium catalysts promising candidates for hydrogenation reactions.

6) A passive air sampler device and the corresponding operating protocol were developed for collecting carbon nanotubes from ambient lab air and thus assessing the nanotube exposure. The passive air sampler unit in consists of a 0.22 μm soluble cellulose nitrate membrane filter placed on a stamp pad wetted by silicone oil. This is necessary so that re-entry of dust particles into the air can be prevented by the wet filter. Silicone oil will be used because it is inert, non-toxic, odorless and has such a low vapor pressure that it can keep stamp pads wet for a long time. Moreover, silicone oil is also our chosen dispersion medium for the quantitative CNT analysis experiments where the CNT concentration is calculated from the dielectric spectroscopic response of the dissolved filter.

7) We identified seventeen different organic solvents on the basis of their evaporation profiles measured on multi-wall carbon nanotube networks in the form of approx. 150 μm thick films (buckypaper). The shape of the evaporation profile was analyzed by Kohonen-type self-organizing maps and three layer feed-forward artificial neural networks. Moreover, the performance of the evaporation profile based analysis was also assessed by principal component analysis (PCA) as depicted in Figure 1 and discriminant analysis presented in Figure 2.

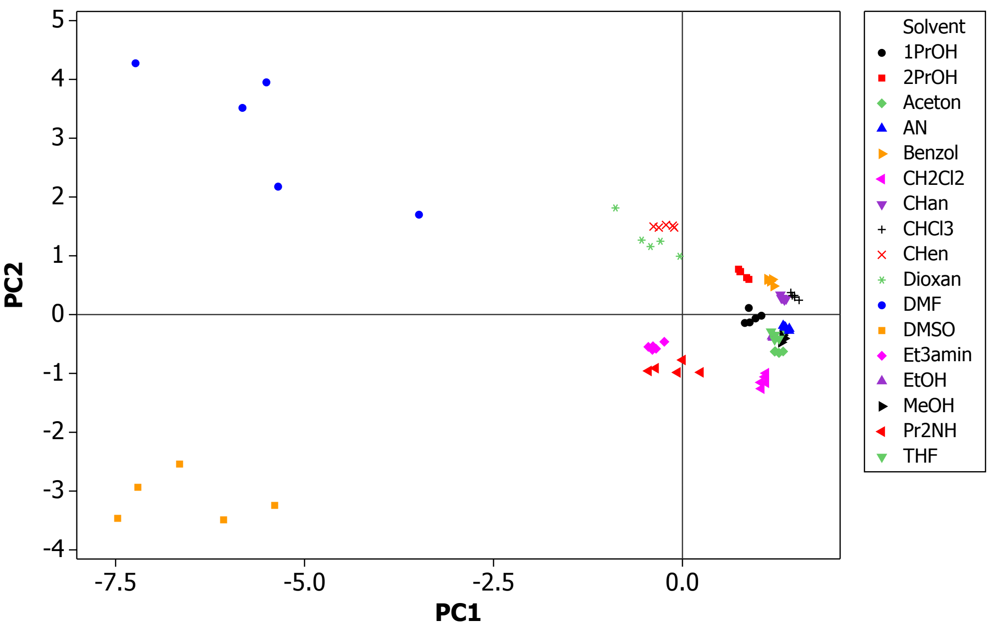

Figure 1. Principal component analysis mapping of the evaporation profiles of 17 different solvents.

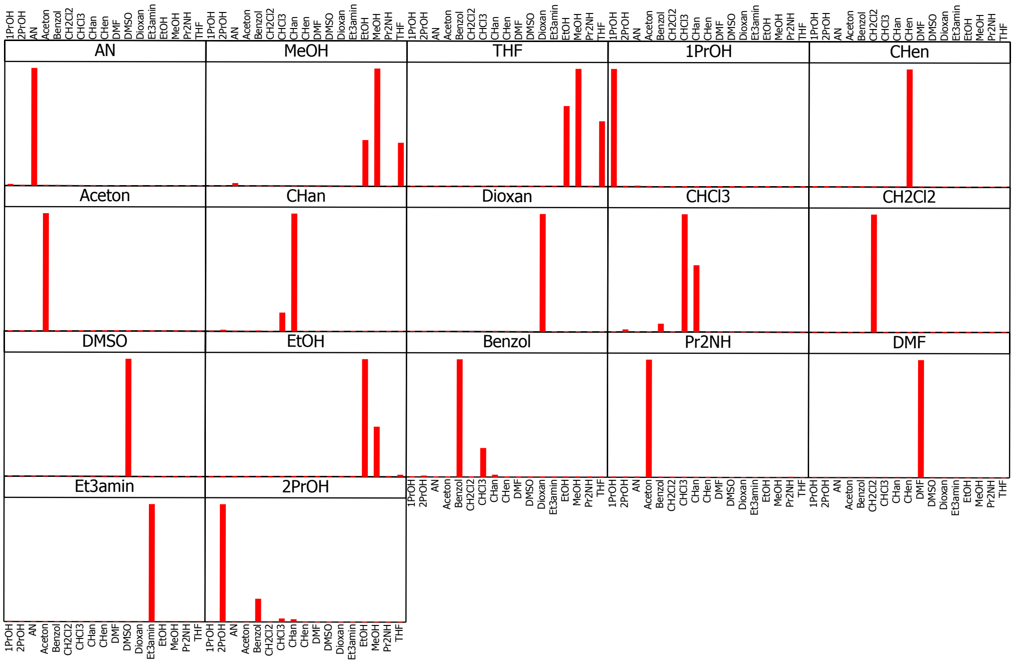

Figure 2. Discriminant analysis of the evaporation profiles collected during this project.

Verifiable milestones:

A total of 5 verifiable result milestones were defined in the original workplan. These were achieved as follows:

E1.1 The evaporation profiles of 10 different organic solvents were measured on the new carbon nanotube patterns consisting of multi-wall carbon nanotubes synthesized at very low temperatures.

E1.2 We synthesized 1.5 g Cu nanowires, 1.0 g Cu-Pd nanowires and over 10 g of functionalized titanate nanowires to achieve this milestone.

E1.3 A measurement protocol for the quantitative assessment of CNT concentration in lab air has been established and tested. See scientific result 6 above.

E2.1 The evaporation profile descriptors of 17 organic solvents were arranged into a database. This database was used to train the artificial neural network pattern recognition algorithm.

E2.2 We combined the TiO_2 nanowire – carbon nanotube sandwich photocatalyst device developed in our predecessor OTKA NNF project (Darányi et al., Nanotechnology 2011) with the evaporation profile based solvent identification technique realized here. Test results on the performance of this composite filter can be expected from the second half of 2012.

Summary:

The financial support provided by the OTKA NNF2 85899 project between April 2011 and March 2012 has allowed me to continue running my research group formed with the support of the predecessor OTKA NNF project. Our group studied the synthesis, modification and networking properties of selected one dimensional nanostructures. Objectives defined in the original proposal were achieved, publication goals were met. The results obtained have formed a major part of the background of my OTKA NF and HAS “Lendület” project applications submitted in Spring 2012. I am thankful to the OTKA and the Norwegian Fund for their support.