PREPARATION AND CHARACTERIZATION OF MULTIWALL CARBON NANOTUBE FILMS

Ph.D. thesis

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1. Introduction

Carbon nanotubes (CNTs) have been in the focus of nanotechnology research ever since their discovery because of their unique physical properties and wide range of potential applications. More and more materials science laboratories became involved in studying the properties of this special material. Several interesting nanotube applications have been described in the literature already, e.g. as radiofrequency filters, artificial muscles, chemical and mechanical sensors.

Although carbon nanotube films are synthesized since the second half of the 1990's, for a long time they were only regarded as a practical way to handle carbon nanotubes. It is only recently that interest in the properties of carbon nanotube films as standalone materials appeared. CNT films are characterized by a macroporous structure, ease of chemical functionalization, low density, good electrical conductivity and mechanical stability.

Various methods have been described in the literature for the preparation of CNT films; however, dead-end filtration is by far the most widespread of all. Filtration is popular because it is cheap, easy to upscale and allows the versatile combination of carbon nanotubes with modifiers. The thickness of CNT films prepared by filtration can be continuously varied between "real" film thickness (a few μm) and "paper" thickness (~250 μm).

Since carbon nanotube films were originally developed to facilitate the handling of single-wall carbon nanotubes in e.g. spectroscopic and electrochemical measurements, information about the structure and properties of multi-wall carbon nanotubes films is especially scarce in the literature. My goal in this Ph.D. thesis was to contribute to the understanding of these materials, in particular by doing research in the following areas:

1. Morphological characterization of multi-wall carbon nanotube films
2. Gas permeability measurements on multi-wall carbon nanotube films
3. Spectroscopic studies on carbon nanotube – inorganic nanostructure composite films
4. Thermosensibilization of multi-wall carbon nanotube films
5. Studying the changes in the electrical resistance of multi-wall carbon nanotube films upon dropping a small amount of organic solvent on them.

2. Experimental

Multi-wall carbon nanotube films were prepared by filtration. Carbon nanotubes synthesized by catalytic chemical vapour deposition were sonicated for 30 min in N,N-dimethyl-formamide or acetil-acetone, then the homogeneous suspension was filtered through a 0.45 mm pore diameter nylon membrane filter. The filtrate was dried to yield the final product, the flexible, self-supporting CNT film.

The morphology of the CNT films was primarily characterized by scanning electron microscopy (SEM). Moreover, filtration curves recorded by our own purpose-built instrument proved to be rather useful for CNT film characterization, since they allowed the calculation of the specific filtrate resistance α and the specific filter resistance R_m. We have studied the effect of the basic filtration parameters (amount of CNT, solvent used) on the structure of the film. In addition, N_2 adsorption isotherms of the CNT films were recorded at -196 ^oC. The gas permeability of the CNT films was characterized in our own purpose-built system, in which the studied gas is allowed to expand from 1 atm into dynamic vacuum through the carbon nanotube film.

Three different methods were utilized for the modification of CNT films: (i) porous Teflon coatings were deposited on their surface using Pulsed Laser Deposition, (ii) suspensions of pyroelectric crystals were dropped onto their surface, and (iii) tin-oxide and vanadium-oxide modifiers were incorporated into the films.

Basic morphological characterization was done on all modified films. In addition, the oxide-modified films were studied by IR, XPS and Raman spectropscopy. The electrical resistance vs. temperature characteristics of the pyroelectrically modified films were recorded in the 25-70 °C range using a purpose-built instrument. The same instrument was also capable of recording the resistance vs. time profiles of unmodified CNT films subjected to drops of various organic solvents. We refer to these profiles as “evaporation profiles”. We have studied the effect of measurement conditions on the shape of the evaporation profile and were able to show that it is possible to identify several solvents on the basis of their evaporation profile alone.

3. New scientific results

1. Results about the structure of unmodified multi-wall carbon nanotube films

1.1 We developed a measurement technique enabling us to quantitatively monitor the filtration behaviour of multi-wall carbon nanotube suspensions. We applied this technique to determine the dependence of the filtration parameters calculated from the Carman equation (α and R_m) from the type of solvent used and the concentration of the filtered suspension. We offered a qualitative explanation to explain the characteristic differences observed in the specific filtrate resistance of thin and thick nanotube films.

1.2 By performing image analysis on scanning electron microscopic images of CNT films we were able to calculate certain morphological descriptors of the films. For the first time in the literature we demonstrated that the morphology of multi-wall carbon nanotube films prepared by filtration is largely independent of the operational parameters of the filtration itself.

1.3 We prepared CNT films from MWCNTs cut into smaller pieces with a known length distribution. We have shown that there exists a saturation-type relationship between the length of the nanotubes and the apparent pore diameter of the CNT film prepared from them. The most probable pore diameter can be fine tuned in the 13.5-43 nm range by controlling the length of the nanotubes, however, the pore diameter distribution function is always lognormal regardless of the nanotubes used.

1.4 We developed a system suitable for measuring the gas permeability of carbon nanotube films. We applied this system to measure the permeability of MWCNT films to six different gases (He, H_2, CO_2, CH_4, N_2, and O_2) and calculated the effective gas diffusivities (D_{eff}) through various carbon nanotube films. We demonstrated that D_{eff} is related to the kinetic diameter of the gas molecules and is independent of the synthesis conditions of the CNT film.

2. Results on modified MWCNT films

2.1 We were the first to use the PLD method to deposit a Teflon layer on the surface of multi-wall carbon nanotube films prepared by filtration. The resulting structures were

characterized by SEM and AFM imaging as well as N_2 permeability measurements. We were able to prove that the permeability of CNT-Teflon composite films is solely determined by the porosity of the CNT layer.

2.2 We surface-doped MWCNT films by pyroelectric crystals $CsNO_3$ and $LiNbO_3$ and recorded the electrical resistance vs. temperature function of the resulting films in the 25-70 ^oC range. We demonstrated that the temperature response can increase by one order of magnitude as a result of the pyroelectric modification, and that the surface-doped films can be used for temperature measurement in the mentioned range with ~3 °C accuracy and ~10 °C precision.

2.3 We incorporated vanadium-oxide nanowires and tin-oxide nanoparticles into multi-wall carbon nanotube films prepared by filtration. On the basis of IR, XPS and Raman spectroscopic measurements we were able to suggest the existence of a surface interface layer between the carbon nanotubes and the *in situ* synthesized nanopartices. Such interface layer could not be found in simple physical mixtures of carbon nanotubes and nanoparticles.

3. Results related to evaporation profiles measured on MWCNT films

3.1 We developed a method for measuring evaporaton profiles on multi-wall carbon nanotube films prepared by filtration. We demonstrated that the shape of the evaporation profile is unaffected by gravity and the frequency of the measuring signal (in the studied 4 Hz-400 kHz range). On the other hand, the shape of the evaporation profile strongly depends on the temperature of the CNT film and the type of solvent dropped onto the film.

3.2 We measured the evaporation profile of 17 different organic solvents and demonstrated that the evaporation profile is reproducible for each solvent. We used cluster analysis to prove that the solvents can be identified on the basis of their evaporation profiles, that is, the evaporation profile measurement is solvent specific.

3.3 We conducted successful preliminary experiments to uncover the relationship between the composition of a binary solvent mixture and the shape of its evaporation profile. Our results have confirmed the existence of such a relationship and can serve as a basis for the development of evaporation profile measurement into a quantitative analytical method.

4. Practical applicability of the results

In their present form our results should be considered as fundamental research. However, we were able to identify three areas where the results of my Ph.D. thesis could potentially be developed towards the practical application of multi-wall carbon nanotube films. These are:

- Films with controlled pore structure, prepared from adequately functionalized carbon nanotubes could be utilized in environmental (most likely, in water treatment) technologies.
- Carbon nanotube films surface-doped with pyroelectric crystals could be utilized as temperature sensors in special technologies which are incompatible with conventional, metal-based temperature measurement methods (e.g. thermocouples, Pt-wire etc.) Since the other properties of the CNT films (pore structure, gas permeability, mechanical properties) are unaffected by the surface doping, the thermosensibilized CNT films could be utilized in the same applications where unmodified CNT films can be used. In this case the added value of the pyroelectric doping will be the extra information (temperature) that can be collected about the system.
- Evaporation profile measurement enables us to identify several solvents from sample amounts comparable with those typical in gas chromatography (0.5-1.5 μl). Since evaporation profiles can be measured at a low cost and they offer much better selectivity than conventional sensors, it seems possible that evaporation profile measurement could be developed into a useful supplementary method of routine chemical analysis.

5. Papers related to the present thesis

1. **Contact sensor behavior of multi-wall carbon nanotube films**

   R. Smajda, Á. Kukovecz, Z. Kónya

   Proceedings of the sixth students' meeting – SM-2005 School of Ceramics, December 1-2, 2005, Novi Sad, Serbia and Montenegro, Editors: V.V. Srdic, J. Ranogajec, ISBN 86-80995-52-5

   IF: -, independent citations: 0

2. **Structure and gas permeability of multi-wall carbon nanotube buckypapers**

   R. Smajda; Á. Kukovecz; Z. Kónya; I. Kiricsi

   Carbon **45** (2007) 1176-1184

   IF: 3.884, independent citations: 2

3. **Spectroscopic studies on self-supporting multi-wall carbon nanotube based composite films for sensor applications**

   R. Smajda, Z. Győri, A**.** Sápi, M. Veres, A. Oszkó, J. Kis-Csitári, Á. Kukovecz, Z. Kónya, I. Kiricsi

   J. Mol. Struct. **834-836** (2007) 471-476

   IF: 1.495, independent citations: 2

4. **Morphology and N_2 permeability of multi-wall carbon nanotube–Teflon membranes**

   R.Smajda, Á. Kukovecz, B Hopp, M. Mohl, Z. Kónya, I. Kiricsi

   J. Nanosci. Nanotech. **7** (2007) 1604-1610

   IF: 2.194, independent citations: 0

5. **Temperature response of carbon nanotube films modified with pyroelectric materials**

   R. Smajda, Á. Kukovecz, M. Őze, H. Haspel, Z. Kónya, I. Kiricsi

   Proceedings of the seventh students' meeting – SM-2007 School of Ceramics, December 6-8, 2007, Novi Sad, Serbia and Montenegro, Editors: V.V. Srdic, J. Ranogajec, ISBN 978-86-80995-62-5

   IF: -, independent citations: 0

6. **Controlling the pore diameter distribution of multi-wall carbon nanotube buckypapers**

   Á. Kukovecz, R. Smajda, Z. Kónya, I. Kiricsi

   Carbon **45** (2007) 1696-1716

   IF: 3.884, independent citations: 1

7. **Pyroelectric temperature sensitization of multi-wall carbon nanotube papers**

   Á. Kukovecz, R. Smajda, M. Őze, H. Haspel, Z. Kónya, I. Kiricsi

   Carbon (2008) in press

   IF:3.884, independent citations: 0

6. Talks and posters related to the present thesis

1. **Contact sensor behavior of multi-wall carbon nanotube films**

   R. Smajda, Á. Kukovecz, Z. Kónya

   SM-2005 School of Ceramics

   Novi Sad, Serbia and Montenegro, December 1-2, 2005, (oral)

2. **Permeability studied on multi-wall carbon nanotube films**

   R. Smajda, Á. Kukovecz, Z. Kónya, I. Kiricsi

   Materials Science committee of the Hungarian Academy of Sciences

   Debrecen, 2006 spring meeting (oral)

3. **Buckypaper gas chromatograph: evaporation profile based identification of liquid analytes using multi-wall carbon nanotube films**

   R. Smajda, Á. Kukovecz, H. Haspel, Z. Kónya, I. Kiricsi

   IWEPNM 2007

   Kirchberg in Tirol, Austria, 2007. 03. 10 – 2007. 03. 17 (poster)

4. **Morphology and gas permeability of multi-wall carbon nanotube based membranes**

   R. Smajda, Á. Kukovecz, Z. Kónya, I. Kiricsi

   CESEP, Carbon for Energy Storage and Environmental Protection

   Krakow, Polad, September 2-6 2007, (poster)

5. Temperature response of carbon nanotube films modified with pyroelectric materials

R. Smajda, Á. Kukovecz, M. Őze, H. Haspel, Z. Kónya, I. Kiricsi

SM-2007 School of Ceramics

Novi Sad, Serbia and Montenegro, December 6-8, 2007 (oral)

6. Low impedance multi-wall carbon nanotube films made suitable for temperature and pressure measurement by localized charge injection

Á. Kukovecz, R. Smajda, M. Őze, B. Schaeffer, H. Haspel Z. Kónya, I. Kiricsi

IWEPNM 2008

Kirchberg in Tirol, Austria, 2008. 03.01 - 2008. 03.08. (poster)

7. Other publications

1. Wastewater treatment in the animal protein industry (ATEV Rt. Hódmezővásárhely)

R. Smajda, G. Szabó, J. Halász

8th International Symposium on Interdisciplinary Regional Research,

Hungary-Romania-Serbia and Montenegro, Szeged, 19-21 of April 2005 (poster)

2. Synthesis and applications of inorganic nanotubes

R. Smajda, Z. Kónya, Á. Kukovecz, I. Kiricsi

7th Scientific student Conference on technical Sciences

Timisoara, 22-24 of April 2005 (oral)

3. Tubular inorganic nanostructures

I. Kiricsi, Á. Fudala, D. Méhn, Á. Kukovecz, Z. Kónya, M. Hodos, E. Horváth, M. Urbán, T. Kanyó, É. Molnár, R. Smajda

Current Applied Physics 6 (2006) 212-215

IF: 1.116, independent citations: 2

Peer-reviewed papers total: 8, out of this, related to the topic of thesis: 7

Cumulative impact factor: 16.457, out of this, related to the topic of thesis: 15.341

Independent cites total: 7, out of this, related to the topic of thesis: 5