PREPARATION AND CHARACTERIZATION OF CARBON NANOTUBE NANOCOMPOSITES BASED ON INORGANIC METAL OXIDES

Ph.D. theses

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1. Introduction

During the history of humanity, its desire for innovation was the incentive of technological advancement. It was observable not only at several fields of science (e.g. chemistry and material science) but at many other fields of life as well. The bronze and iron ages began and ended as parts of this process and the new natural and synthetic materials (e.g. different kinds of polymers) – which are the basis of our further technological progress – had been promoted as a result of these events.

The different types of composite materials had important part of people's life for centuries (e.g. adobe houses) and they became even more significant from the 20th and 21th centuries due to conscious planning. Reinforced concrete is a good example – without this material it couldn't be possible to build the skyscrapers of huge metropolises – or we can think about the innovations of modern material sciences like sports and protective equipment reinforced with carbon fibers. The goal of preparing such kinds of materials is to improve the properties of components or to fabricate a product which has entirely different properties compared to raw materials. This effort can also be observed at the distinct part of nanotechnology which goal is to prepare and investigate various nanocomposites.

Similarly to the development of composite materials, in the 20th century carbon chemistry also improved significantly. While the multi-walled carbon nanotubes (MWCNT) – which are the focus of my Ph.D. theses – were investigated thoroughly only from the end of the century, nowadays they are very prevalent at numerous fields of sciences (e.g. material, electronical and sensory studies). The main reason for it is these nanometric sized materials have very different chemical and physical properties like the other previously known forms of carbon (e.g. graphite, diamond). It is evident, that in the future carbon nanotubes will have important role at the fields of nanotechnology and technology development.

My doctoral research was carried out in the Applied Nanotube Technology (ANT) group led by Prof. Dr. Klara Hernadi at the Department of Applied and Environmental Chemistry of University of Szeged. This group in collaboration with both foreign and domestic colleagues is focusing on the synthesis of different type of carbon nanotubes and fibers and on the preparation, investigation and application (e.g. photocatalysis, gas sensors, medical implants) of carbon nanotube composite materials based on different types of metal oxides for more than 20 years. It can be concluded based on the previous results that the preparation processes of carbon nanotube nanocomposites based on inorganic metal oxides could bear a lot of resemblances but inherently different because of the different chemistry of metal oxides. The different synthesis parameters have different effects on the structure of the prepared composites depending on the applied metal oxides. In my work, I have attempted to reveal and present these such important synthesis parameters.

2. Objectives

One of my goals was the preparation of TiO_2/MWCNT nanocomposites and the investigation of the correlation between the speed of hydrolysis and the size of alkoxy groups of organic precursor compounds and its effect on the photocatalytic activity of the produced nanocomposites.

The fabrication of WO_3/MWCNT composite materials with different kinds of impregnation methods and solvents was also in focus of my work. The effect of minor changes in the temperature of heat treatment on the structure of prepared nanocomposites was also examined.

During my doctoral work, it was imperative to investigate how indium containing nanocomposites with various crystal structures can be prepared using different calcination times and temperatures. The possible existence of a chemical connection between multi-walled carbon nanotubes and inorganic covering layers formed during the synthesis was also studied.

Lastly, I wanted to invent the most feasible synthesis method to prepare ZrO_2/MWCNT nanocomposites suitable to be used as reinforcement material in dental implants.

3. Experimental methods and procedures

The multi-walled carbon nanotubes used as raw material in case of all composite preparation were produced by our colleagues at École Polytechnique Fédérale de Lausanne (EPFL). The following impregnation and solvothermal synthesis methods were used for the preparation of nanocomposites:

- TiO_2/MWCNT: impregnation combined with slow hydrolysis
- WO_3/MWCNT: simple impregnation method and impregnation combined with precipitation
- In_2O_3/MWCNT: simple impregnation method
- ZrO_2/MWCNT: impregnation combined with fast hydrolysis (drop by drop and mixing methods), impregnation combined with slow hydrolysis and solvothermal synthesis

The composite products were investigated with many different methods and equipment such as:

- Transmission electron microscope (TEM) [Philips CM 10, and FEI Tecnai G^2 20 X-TWIN]
- Scanning electron microscope (SEM) [Hitachi S-4700 Type II FE-SEM, and Zeiss SUPRA 35VP]
- Energy-dispersive X-ray spectroscopy (EDX) [Hitachi S-4700 Type II FE-SEM combined with Röntec XFlash Detector 3001 SDD]
- X-ray diffractometer (XRD) [Rigaku Miniflex-II Diffractometer]
- Raman microscopy [Thermo Scientific DXR]
- Thermogravimetric analysis (TG) [NETZSCH STA 409 PC]
- Infrared spectroscopy (FT-IR) [Bio-Rad Digilab FTS65A/896 FT-IR]
- BET analysis [Micromeritics Gemini BET, valamint BELCAT-A]

4. Summary of new scientific results

T1. The effect of precursor on the preparation of TiO_2/MWCNT nanocomposites

T1.1. It was verified that in case of TiO_2/MWCNT nanocomposites prepared *via* impregnation combined with slow hydrolysis the surface of carbon nanotubes has drastically changed *viz.* an inorganic covering layer can be observed on them. It was revealed that this amorphous titania layer was transformed into crystalline, pure anatase phase after the heat treatment performed at 400°C in case of all three precursors and the existence of a chemical connection between MWCNTs and TiO_2 layers was also proved. Based on these results it can be stated that impregnation combined with slow hydrolysis is an appropriate method to form TiO_2/MWCNT nanocomposite materials.

T1.2. It was proved by BET analysis that in case of using organic precursors having different alkoxy groups composite prepared with $Ti(OEt)_4$ had the highest and the composite prepared with $Ti(OBu)_4$ had the lowest specific surface area so it can be concluded that the surface have decreased with the increase of the size of organic group in the precursor compound. It is probably because of the bigger alkyl chain cause slower hydrolysis and during this time bigger nanoparticles can form which have lower specific surface area.

T1.3. As-prepared TiO_2/MWCNT nanocomposite samples were tested in photocatalytic decomposition. It was observed that with increasing length of alkyl group of the Ti-containing precursor the photocatalytic activity was decreasing. Despite of that all synthesized samples have shown good photocatalytic efficiency. Among the composites the one produced from $Ti(OEt)_4$ had the highest photocatalytic activity. However, our samples have not achieved higher photocatalytic activity than reference P25 it is hoped that these new composite materials will have potential application at the field of photocatalysis because of the synergism of the physical and chemical properties of the two components.

T2. The effect of solvent on the preparation of WO_3/MWCNT nanocomposites

T2.1. During the investigation of tungsten containing nanocomposites it was confirmed that among the tested solvents (ethanol, isopropyl alcohol and acetone) and synthesis methods ("simple impregnation" and impregnation combined with precipitation) simple impregnation technique using acetone is the most effective way for the preparation of WO_3/MWCNT nanocomposite materials.

T2.2. From the results of spectroscopic analysis – e.g. new absorption band was appeared – it can be concluded that chemical bond was evolved between WO_3 and oxygen containing functional groups of MWCNTs.

T2.3. X-ray diffraction and Raman microscopy measurements have revealed that during the preparation of WO_3/MWCNT nanocomposites with simple impregnation method using acetone a continuous covering layer of nanoparticles was grown onto the surface of carbon nanotubes (average thickness: 40-70 nm). It was also proved that these nanoparticles consisted of tungsten trioxide of monoclinic phase. Based on the literary data concerning the formation of this phase the effect of calcination temperature was also investigated. The results have shown that a minor change in calcination temperature (400°C ± 50°C) had no significant effect on the surface morphology of composite materials.

T3. The effect of heat treatment on the preparation of In_2O_3/MWCNT nanocomposites

<u>T3.1.</u> The importance of heat treatment was proved by the synthesis of In-containing nanocomposites prepared *via* impregnation using $InCl_3$ as precursor and distilled water as solvent. It was verified that an inorganic covering layer (average thickness 10-12 nm) was evolved on the surface of MWCNTs in case of composite sample heat treated at 300°C. The sample calcined at 350°C has shown drastically different morphology: since a recrystallization process had begun around this temperature both nanoparticles (average size of 10–20 nm) and bigger crystals (approximately 300–400 nm) were arisen among the carbon nanotubes. Significantly new results were produced by the sample heat treated at 400°C (the highest we applied). The previously mentioned recrystallization process has become complete and the composite material have consisted of regular octahedral crystals of different sizes (200–500 nm in average). It was confirmed that MWCNTs were built into these crystals and connected the crystals to each other. I have proved that the covering layer observed at 300°C consists of indium oxychloride, the octahedrons prepared at 400°C are pure indium oxide and at 350°C the recrystallization step InOCl → In_2O_3 is still in progress.

<u>T3.2.</u> I have confirmed that calcination at 400°C is the most ideal to prepare In_2O_3/MWCNT nanocomposites and minimum 1.5 hours or longer calcination is needed to reach the suitable degree of crystallinity.

<u>T3.3.</u> It was also verified that new bands at 485 cm^{-1} and 489 cm^{-1} in FT-IR spectra of composite materials originated from the interaction of the indium atom and the oxygen containing surface functional groups of carbon nanotubes. It can be presumed that the InOCl bounded covalently to MWCNTs at the beginning of the synthesis and transformed into In_2O_3 due to the calcination at higher temperature.

T4. The effect of synthesis method on the preparation of ZrO_2/MWCNT nanocomposites

T4.1. During the preparation of Zr-containing nanocomposites it was verified that all tested synthesis methods provided nanometric sized particles which were attached to the surface of multi-walled carbon nanotubes, however, the thickest zirconia coverage have been prepared *via* solvothermal technique so it can be concluded that this method is the most efficient for the synthesis of ZrO_2/MWCNT nanocomposites.

T4.2. It was proved that in all zirconium-containing nanocomposite samples the tetragonal phase of zirconia was dominant in the crystal structure after heat treatment but the appearance of monoclinic phase was also observable.

T4.3. The spectroscopic investigation of zirconium-containing composites has revealed the existence of a chemical connection between the components of the composite materials.

4. Scientific publications

Hungarian Scientific Bibliography (MTMT) identifier: 10037630

<u>Publications related to the scientific topic of the dissertation:</u>

[1] **Berki P.**, Nemeth Z., Reti B., Berkesi O., Magrez A., Aroutiounian V., Forró L., Hernadi K., *Preparation and characterization of multiwalled carbon nanotube/In_2O_3 composites*; Carbon 60 (2013) p: 266-272.
IF = 6,160

[2] Vass A., **Berki P.**, Nemeth Z., Reti B., Hernadi K., *Preparation and characterization of multiwalled carbon nanotube/WO3 composite materials*; Physica Status Solidi (b) 250 (2013) p: 2554-2558.
IF = 1,605

[3] **Berki P.**, Reti B., Terzi K., Bountas I., Horvath E., Fejes D., Magrez A., Tsakiroglou C., Forró L., Hernadi K., *The effect of titania precursor on the morphology of prepared TiO_2/MWCNT nanocomposite materials*; Physica Status Solidi (b) 251 (2014) p: 2384-2388.
IF = 1,489

[4] Bárdos E., Kovács G., Gyulavári T., Németh K., Kecsenovity E., **Berki P.**, Baia L., Pap Zs., Hernadi K., *Novel synthesis approaches for WO_3-TiO_2/MWCNT composite photocatalysts-problematic issues of photoactivity enhancement factors*; Catalysis Today 288 (2017) p: in Press.
IF = 4,312

ΣIF = 13,566

ΣCitations = 19

<u>Other publications:</u>

[5] Nemeth Z., Reti B., Pallai Z., **Berki P.**, Major J., Horvath E., Magrez A., Forro L., Hernadi K., *Chemical challenges during the synthesis of MWCNT-based inorganic nanocomposite materials*; Physica Status Solidi (b) 251 (2014) p: 2360-2365.
IF = 1,489

[6] Fejes D., Réti B., Németh K., **Berki P.**, Németh Z., Hernádi K., *Többfalú szén nanocsövek előállítása és széleskörű felhasználása az Alkalmazott Nanocső Technológia kutatócsoportban*; Magyar Kémiai Folyóirat 120 (2014) p: 83-88.
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[9] Nemeth Z., Horvath E., Magrez A., Reti B., **Berki P.**, Forro L., Hernadi K., *Preparation of titania covered multi-walled carbon nanotube thin films*; Materials & Design 86 (2015) p: 198-203.
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[10] Magyar M., Rinyu L., Janovics R., **Berki P.**, Hernadi K., Hajdu K., Szabo T., Nagy L., *Real-Time Sensing of Hydrogen Peroxide by ITO/MWCNT/Horseradish Peroxidase Enzyme Electrode*; Journal od Nanomaterials (2016) Paper 2437873., 11 p.
IF = 1,758

[11] Baia L., Orban E., Fodor Sz., Hampel B., Kedves E., Saszet K., Szekely I., Karacsonyi E., Reti B., **Berki P.**, Vulpoi A., Magyari K., Csavdari A., Bolla Cs., Coşoveanu V., Hernadi K., Baia M., Dombi A., Danciu V., Kovacs G., Pap Zs., *Preparation of TiO_2/WO_3 composite photocatalysts by the adjustment of the semiconductors' surface charge*; Materials Science in Semiconductor Processing 42 (2016) p: 66-71.
IF = 2,264

ΣΣIF = 25,912

ΣΣCitations = 31

Conference lectures and posters:

[1] **Berki P.**, *Szervetlen fém-oxid alapú szén nanocső nanokompozitok előállítása és vizsgálata*; MTA SZAB Anyagtudományi Munkabizottsági ülés, 2017. Szeged **[oral presentation]**

[2] A. Kinka, E. Kecsenovity, D. Fejes, **P. Berki**, K. Hernadi, *CCVD preparation of highly uniform carbon microand nanocoil fibers*; 15th International Conference on Nanotechnology (IEEE-NANO), 2015. Rome **[poster]**

[3] **P. Berki**, *Preparation of inorganic metal oxide composite materials based on carbon nanotubes*; Closing Conference of Swiss Contribution SH 7/2/20, 2015. Lausanne **[oral presentation]**

[4] **Berki P.**, *Szervetlen fém-oxid alapú szén nanocső nanokompozitok előállítása*; Nanokompozitok: alapkutatástól az ipari alkalmazásokig, 2014. Szeged **[oral presentation]**

[5] M. Magyar, V. Gombos, T. Szabó, **P. Berki**, K. Hernádi, E. Horváth, A. Magrez, L. Forró, L. Nagy, Limit of detection of hydrogen peroxide determined by carbon nanotube/horseradish peroxidase/ITO enzyme electrode; From Solid State to Biophysics – 7th International Conference, 2014. Dubrovnik **[poster]**

[6] M. Magyar, V. Gombos, T. Szabó, **P. Berki**, K. Hernádi, E. Horváth, A. Magrez, L. Forró, L. Nagy, *Real-time sensing of hydrogen peroxide by carbon nanotube/horseradish peroxidase/ITO enzyme electrode*; Regional Biophysics Conference, 2014. Smolenice **[poster]**

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[8] Z. Nemeth, B. Reti, Z. Pallai, **P. Berki**, J. Major, E. Horvath, A. Magrez, L. Forró, K. Hernádi, *Chemical challenges during the synthesis of MWNT based inorganic nanocomposite materials*; XXVIIIth International Winterschool on Electronic Properties of Novel Materials, 2014. Kirchberg **[poster]**

[9] **P. Berki**, *The effect of heat treatment during the production of In_2O_3-MWCNT nanocomposites*; 21th Annual International Conference on Composites/Nano Engineering (ICCE-21), 2013. Tenerife **[oral presentation]**

[10] **P. Berki**, *Progress in SNSF project in the field of composite materials based on carbon nanotubes*; SNSF Swiss National Science Foundation Valorization Meeting, 2013. Szeged **[oral presentation]**

[11] **P. Berki**, Z. Nemeth B. Reti, K. Hernádi, *The effect of the synthesis method on the morphology of indium-oxide/MWCNT composites*; XXVIIth International Winterschool on Electronic Properties of Novel Materials, 2013. Kirchberg **[poster]**

[12] A. Vass, **P. Berki**, Z. Nemeth B. Reti, K. Hernádi, *Comparative study of tungsten-trioxide/MWCNT composite materials fabricated by various methods*; XXVIIth International Winterschool on Electronic Properties of Novel Materials, 2013. Kirchberg **[poster]**

[13] Z. Nemeth, **P. Berki**, A. Magrez, L. Forró, V. Aroutiounian, K. Hernádi, *Preparation and comparative characterization of MWNT/In_2O_3 nanocomposite materials*; XI International Conference of Nanostructured Materials, 2012. Rhodes **[poster]**

[14] K. Hernadi, A. Magrez, Z. Nemeth, Z. Pallai, **P. Berki**, L. Forro, *Preparation and characterization of MWNT based inorganic nanocomposite materials*; E-MRS Spring Meeting, 2012. Strasbourg **[poster]**

[15] **Berki P.**, Németh Z., Hernádi K., *In_2O_3/MWCNT nanokompozitok előállítása és vizsgálata*; XXXV. Kémiai Előadói Napok, 2012. Szeged **[oral presentation]**